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Hollow fiber membrane concentrator for on-line preconcentration

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Abstract

Solvent removal by membrane permeation is presented as a method for on-line preconcentration. Experiments were carried out to develop a one-step, on-line, concentration process using a microporous composite hydrophobic membrane, or a polar solvent-permeable Nafion membrane depending on the solvent. Both polar and non-polar hollow fiber membranes were found to be effective in concentrating trace analytes. A large increase in analyte enrichment factors was found for both concentrator modules. Enrichment factors as high as 18.9 were observed. Residence time and operating temperature were found to be important parameters. Several different model compounds were preconcentrated. Further, in a Nafion membrane (polar solvent-permeable), analyte interaction with membrane bound sulfonic acid residues resulted in the loss of reactive analytes such as atrazine (ATZ). All analytes were successfully concentrated and detected using a polypropylene–siloxane composite membrane system when hexane was used as the solvent.

Keywords: Hollow fiber membranes; Sample preparation; Pentachlorophenol; Atrazine; Naphthalene; Biphenyl

1. Introduction

Analysis of trace semivolatile compounds usually requires the extraction of analytes from the sample matrix, followed by preconcentration prior to analytical detection [1]. For example, sample preparation for aqueous samples may be accomplished by liquid–liquid extraction (LLE) or solid-phase extraction (SPE) [2]. Both methods dilute the analytes in solvents which contribute to lower sensitivity. In SPE, the analytes are extracted onto a solid sorbent and then eluted with an organic solvent. LLE is the classical extraction method that uses a liquid solvent for extraction. In both cases, an additional concentration step may be necessary to increase the signal intensity [1], and a solvent exchange may be required for good chromatography. The general drawback in many laboratory based analysis methods is the requirement of discreet and often lengthy extraction and concentration procedures.

1.1. Classical concentration techniques

Traditionally, post extraction concentration has been carried out by evaporative techniques. Essentially, it concentrates the sample by selectively reducing the solvent. Evaporation of the volatile solvents is the simplest method of solvent elimination. A common procedure is to blow an inert air stream across the sample–air interface. The more volatile solvents are removed, while the less volatile analytes are retained, thus, concentrating them. The rate of evaporation can be increased simply by heating the sample, thereby, speeding the concentration process. Kuderna–Danish (K–D) concentrators are commercially available, and have been used for many years. Rotary evaporators are also used routinely in laboratories utilizing a water bath as the heat source. These are relatively laborious procedures involving multiple handling steps which can lead to sample loss by mishandling, contamination or labile-sample degradation. Also, solvent evaporation is inherently a slow process.

Recently, there has been a move towards automated, faster and higher throughput analytical methods. While much attention has been focused on analytical instrumentation and

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extraction techniques, faster and more efficient concentration techniques have not been developed. There has also been a push towards totally automated analytical systems. The development of these instruments require the integration of sample preparation and concentration steps along with the analytical instrumention. While some continuous extraction–analysis techniques have been developed, no on-line solvent removal/concentration methods are currently available.

1.2. Alternative concentration technique

A promising alternative to traditional separation procedures is hollow fiber membrane (HFM) extraction. Traditionally, membrane extraction has been used in sample preparation by selective permeation of the analytes of choice [3–9]. Different organic molecules and metals have been extracted by utilizing appropriate membranes and optimum operating conditions [6–8,10,11]. HFM extraction has been used for on-line pervaporative monitoring of volatile organics in water at parts per billion levels [9,12,13]. Pervaporation is an efficient separation method utilizing membrane permeation and evaporation [14,15]. It is characterized by having a liquid stream of two or more components in contact with a membrane barrier, and a vacuum or strip gas on the permeate side. The volatile components are selectively removed through the membrane by maintaining a concentration gradient, which then evaporate into the vapor phase.

In this paper, we present a novel pervaporative concentration technique that utilizes selective solvent permeation with subsequent enrichment of the analytes. The dilute sample flows into the lumen of the HFM and an inert gas circulates in the permeate side. The solvent selectively migrates across the membrane and a concentrated solution emerges at the lumen outlet. This is the opposite of more traditional analytical extraction, where the analytes are selectively extracted across the membrane. The pervaporative concentration eliminates the need of evaporative concentration, thus reducing the analysis time. It is also a "user-friendly", on-line procedure for real-time continuous analysis.

2. Experimental

Fig. 1 is a schematic of the HFM system used in the sample concentration studies. The sample was delivered through the lumen of the HFM by a HPLC pump (Hewlett-Packard 1050). The permeate side of the HFM column had a counter-current nitrogen flow which removed the permeated solvent from the feed stream. The concentrate was collected into HPLC vials. Analysis was done by a Hewlett-Packard 1050 HPLC system equipped with a C_{18} reversed-phase analytical column (Waters Nova-Pak, 150 mm × 3.9 mm) utilizing an isocratic mobile phase of 0.01 M K_3PO_4–acetonitrile (45:55) at pH 7. Analyte determination was carried out by an UV detector (254 nm). A MiniChrom V1.61 (SRI Instruments, Torrance, CA, USA) data system was used for data acquisition and analysis.

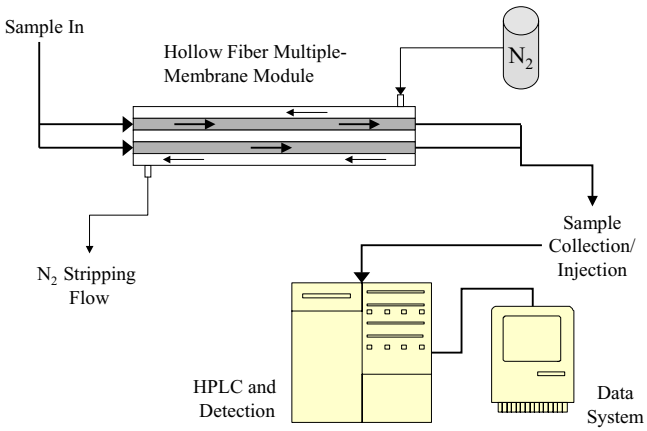

Fig. 1. Schematic diagram of hollow fiber membrane concentrator and analysis.

2.1. Membrane module construction

The membrane module consisted of hollow fiber membranes held within a 50 cm long polypropylene casement. A stainless steel, Swagelok-type, "T" (Components and Controls, Carlstadt, NJ, USA) placed at each end of the column coupled the casement and HFM strands, and were sealed using a fast-drying epoxy resin (A1 with activator E, Armstrong Adhesives, Easton, MA, USA). The sealed "T" unit prevented intermixing of the lumen and permeate contents. It also served as the inlet/outlet for the sample and the permeate stripping N_2 gas.

One membrane module consisted of a five-strand composite hollow fiber membrane (0.260 mm o.d. × 0.206 mm i.d.). It was made of a microporous hydrophobic polypropylene coated with a 1 μm-thick film of homogenous siloxane (Applied Membrane Technology, Minnetonka, MN, USA), and was effective in the pervaporation of non-polar solvents. The other module comprised of one strand of Nafion hollow fiber (0.533 mm o.d. × 0.356 mm i.d.; manufactured by DuPont, Wilmington, DE, USA, and obtained from Perma-Pure, Toms River, NJ, USA). The Nafion membranes are a copolymer of tetrafluoroethylene (Teflon) and perfluoro-3,6-dioxa-4-methyl-7-octene-sulfonic acid, and are permeable to polar solvents [16].

2.2. Reagents and instrumentation

All chemicals and solvents used in the experiments were of analytical grade or better. They were purchased from Supelco, (Supelco Park, PA, USA) and Sigma–Aldrich (Milwaukee, WI, USA). Nitrogen gas was obtained from Matheson (Secaucus, NJ, USA). The nitrogen pressure was measured using a battery-operated digital pressure gauge from TIF Instruments (Miami, FL, USA). A fiber-glass insulated electrical heating tape powered by a variable transformer (Staco

Energy Products, Dayton, OH, USA) was used to heat the membrane modules. The temperature was measured using a digital thermometer and probe from Cole–Palmer (Vernon Hills, IL, USA). The isocratic HPLC assay calibration curves were generated for each analyte in the range of 1–1600 ppm and were found to be linear. The regression coefficients for pentachlorophenol (PCP), atrazine (ATZ), naphthalene (NAP) and biphenyl (BPN) were 0.999, 0.998, 0.998 and 0.996, respectively. The residence times shown in the figures were measured and calculated from the apparent flow rate at the inlet side. Also, it was observed that a continuous flow through the membrane was maintained, at no time were air bubbles or pockets formed during the pervaporation.

3. Results and discussion

The recovery (R) in the membrane concentration procedure is defined as:

$$\%R = \frac{C_o V_o}{C_i V_i} \times 100$$

where C_o is outlet analyte concentration, V_o is outlet sample volume, C_i is inlet concentration and V_i is inlet volume.

The enrichment factor (EF) is defined as:

$$\mathrm{EF} = \frac{C_o}{C_i}$$

Residence time (t_R) in the membrane is defined as:

$$t_R = \frac{V}{F}$$

where V is the internal (lumen) volume of the hollow fiber and F is the flow rate.

The rate of permeation through the membrane is a function of the size and the chemical nature of the permeating molecule. In pervaporation, the sample solution is in direct contact with the membrane and the permeated molecules are removed as vapor. The steady-state membrane permeation flux is described by Fick's first law:

$$J = D\left(\frac{\delta c}{\delta x}\right) \quad (1)$$

where D is the diffusion coefficient of the penetrant and ($\delta c/\delta x$) is the concentration gradient across the membrane. At steady state, the sample is introduced continuously, and the analyte permeation is allowed to reach equilibrium.

Fick's first law defines the permeation flux, and for a hollow fiber membrane, it is reduced to:

$$\frac{\delta c}{\delta x} = \frac{C_P - KC_M}{L} \quad (2)$$

where C_P is the concentration of the permeant on the permeate side, C_M is the concentration of the permeant on the lumen side, K is the partition coefficient between the membrane and permeant and L is the membrane thickness. The downstream strip gas removes essentially all of the permeate, consequently, C_P approaches zero. The upstream concentration of the sample permeant is described by KC_M in Eq. (2). Simplifying Eqs. (1) and (2) yields:

$$J = \frac{DKC_M}{L} \quad (3)$$

Diffusion coefficient of methanol in Nafion membranes has been published in the literature [17,18]. Nafion hollow fibers were used for the permeability of polar solvents, whereas the hydrophobic membranes were used for non-polar ones [19].

3.1. Removal of polar solvents

To determine if Nafion could be used for the concentration of a methanol extract, NAP, BPN, PCP and ATZ were used as model analytes. Fig. 2 shows the typical pervaporation of methanol as a function of flow rate (residence time) using NAP as the analyte. Experimental conditions were the initial volume of 2 mL and initial concentration of NAP at 5 ppm. The membrane module was at ambient temperature and the N_2 strip gas on the permeate side was maintained at 10 psi. (1 psi = 6894.76 Pa) As the solvent permeated through the membrane, the volume of the solution decreased, thus increasing the enrichment factor. Sample flow rate had a significant impact on the EF, which increased with the sample residence time in the membrane (Fig. 2). A lower flow rate resulted in a longer residence time, allowing more time for solvent permeation. An increase in analyte concentration in the remaining solution was observed. At low flow rates (t_R of 0.492 min) almost all the solvent was lost, consequently, no analyte was recovered. At optimum conditions, the solvent volume was reduced by more than 90%, and the EF were 5.7, 6.6 and 7.0 for NAP, BPN and PCP, respectively. EF was directly related with solvent loss and is seen in Fig. 3. As the flow rate decreased, nominally lower recovery was observed. For all practical purposes, recovery appeared to be independent of the flow rate. This implied that the analytes had limited permeability through the membrane.

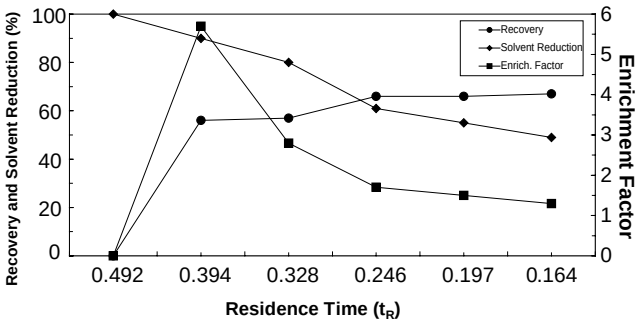

Fig. 2. Preconcentration of naphthalene from a methanol extract. Recovery, solvent reduction and enrichment factor are plotted as a function of residence time. A Nafion membrane was used in these experiments. Calculated residence times are based on inlet flow rate. Experimental conditions were: initial volume, 2 mL; initial concentration, 5 ppm; counter-current N_2 flow, 10 psi and ambient temperature.

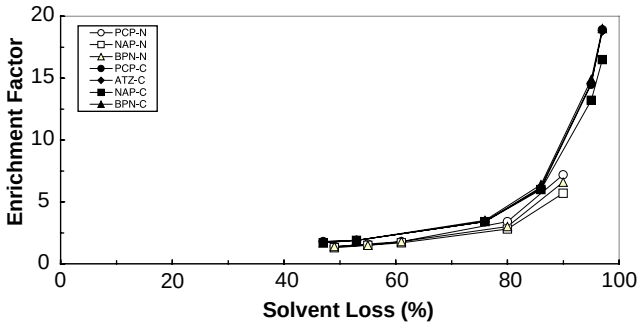

Fig. 3. Enrichment factor as a function of solvent loss during analyte preconcentration. PCP, ATZ, NAP and BPN were the analytes. The composite membrane (denoted as –C) and Nafion (denoted as –N) were used for hexane and methanol, respectively.

Shown in Table 1 is the recovery and EF of several analytes through Nafion using methanol as the solvent. Experimental parameters for Nafion–methanol work were an initial volume of 5 mL, an inlet sample flow rate of 0.25 mL/min, a counter-current N_2 flow of 10 psi, and the membrane module maintained at a temperature of 55 °C. The composite-hexane experimental conditions were an initial volume of 5 mL, an inlet sample flow rate of 0.75 mL/min, a counter-current N_2 flow of 0.4 psi and module temperature of 55 °C. Due to the low permeability of the analyte and the high permeability of the solvent, most compounds showed high EF. However, ATZ appeared to diffuse through the membrane along with the methanol. The analysis for ATZ showed recovery between 0.3% and 0.9%, and EF of 0.03–0.08. ATZ (an amine) readily partitioned into the membrane. The Nafion polytetrafluoroethylene backbone contained flurocarbon sidechains terminating in sulfonic acid residues [16]. The sulfonic acid groups are immobilized within the flurocarbon matrix as residue "clusters" forming ionic pores through the membrane matrix [16]. These bind with primary and secondary amines, resulting in the loss of atrazine.

Variation in N_2 pressures (1–25 psi) of the strip gas was also investigated. It did not appear to effect either solvent reduction or EF in the Nafion–methanol system for PCP, NAP and BPN. In comparison, small changes in N_2 pressure had a large impact on EF and solvent reduction in the hexane-composite membrane system described in the next section.

To test the selectivity of the Nafion towards non-polar solvents, an experiment was designed using PCP as the analyte in hexane. The non-polar solvent was expected to be retained by the Nafion, while the polar PCP was expected to have a relatively high permeation through the membrane. The results are presented in Table 1. It was observed that hexane did not permeate through the Nafion and 97% of it was retained. However, only 78% of starting PCP was detected yielding a low EF of 0.8. This indicated that in spite of being significantly less volatile, the higher molecular weight PCP was more permeable than hexane in Nafion.

It has been reported that conditions leading to higher recovery can lead to lower enrichment, or vice versa [20,21]. For example, high residence time which leads to high enrichment factors may result in decreased extraction efficiency. Higher enrichment via solvent loss can also be accomplished by utilizing higher surface area modules (more HF membrane strands) and/or longer columns. Another approach may be to use larger sample volumes at lower flow rates to yield higher detection sensitivity simply because of the increased amount of analyte. The trade off is that larger sample volumes would require longer time for concentration.

3.2. Removal of non-polar solvents

Nafion membranes were useful for polar solvents, but had limited utility when used in conjunction with non-polar solvents such as hexane. Many chemical entities are readily extracted in non-polar solvents (e.g. hexane), consequently, a non-polar permeable composite membrane was used to investigate hollow fiber concentration. Samples of PCP, BPN, NAP and ATZ in hexane were passed through the composite HF at a constant downstream N_2 pressure of 0.5 psi. The results for PCP are shown in Fig. 4. Experimental conditions were an initial volume of 5 mL with a PCP concentration at 5 ppm. The membrane module had a counter-current N_2 flow of 0.5 psi and was held at ambient temperature. The Fig. 4 results indicate that recovery varied by approximately 20%, with the lowest recovery correlating with the highest EF. Volume reductions of 95%–97% were routinely observed and

Table 1
Extraction efficiency, enrichment factors and solvent volume reduction for different analytes using the two membranes

Analyte	log $K_{O/W}$	Solvent	Membrane type	Solvent reduction (%)	Recovery (%)	Enrichment factor
Biphenyl	4.09	Methanol	Nafion	88	65	6.6
Naphthalene	3.29	Methanol	Nafion	88	66	5.8
PCP	5.01	Methanol	Nafion	88	81	6.8
Atrazine	2.34	Methanol	Nafion	88	1.3	0.1
PCP	5.01	Hexane	Nafion	3	78	0.8
Biphenyl	4.09	Hexane	Composite	97	80	19.0
Naphthalene	3.29	Hexane	Composite	97	70	16.5
PCP	5.01	Hexane	Composite	97	81	18.9
Atrazine	2.34	Hexane	Composite	97	80	18.8

$K_{O/W}$: octanol–water partition coefficient. Nafion–methanol experimental conditions were: initial volume, 5 mL; inlet sample flow rate, 0.25 mL/min; counter-current N_2 flow, 10 psi and temperature 55 °C. Composite-hexane experimental conditions were: initial volume, 5 mL; inlet sample flow rate, 0.75 mL/min; counter-current N_2 flow, 0.4 psi and temperature, 55 °C.

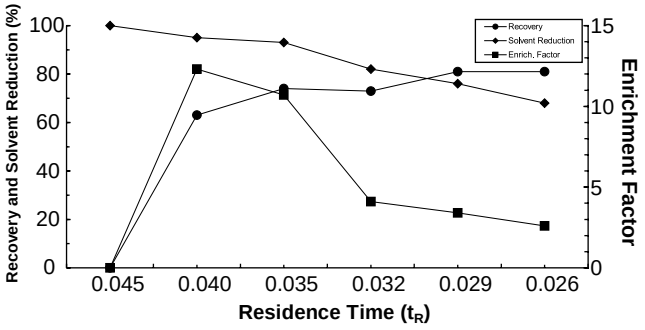

Fig. 4. Concentration of pentachlorophenol from a hexane extract. Recovery, solvent reduction and enrichment factor are plotted as a function of residence time. A composite membrane was used in these experiments. Calculated residence times are based on inlet flow rate. Experimental conditions were: initial volume, 5 mL; initial concentration, 5 ppm; counter-current N_2 flow, 0.5 psi and ambient temperature.

high EF's were achieved. As with the Nafion, it was noted that lower sample flow rate allowed a longer sample residence time, which resulted in increased solvent removal. Here also, EFs increased with solvent loss and this can be seen in Fig. 3. Permeability of the membrane was more selective towards the solvent, thus, relatively less analyte was lost resulting in higher EFs.

It was observed that a small change to N_2 flow on the permeate side had a large impact on the amount of solvent removed. Fig. 5 shows the results of experimental conditions using a constant PCP–hexane flow rate of 0.5 mL/min, while the "stripping" N_2 gas pressure was varied. An initial volume of 5 mL, initial concentration of PCP at 5 ppm, and ambient temperature was used to generate the results. Increasing the N_2 gas flow by as little as 1 psi, the EF increased 7.3-fold. A small decreased recovery was also observed. The large increase in EF and the moderate decrease in recovery may be attributed to limited analyte permeation into the membrane. The higher strip gas flow rate also eliminated the boundry layer, thus facilitating increased solvent flow. Similar results

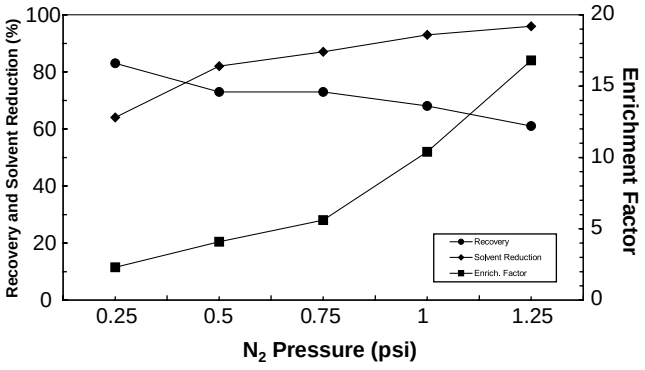

Fig. 5. Pentachlorophenol extraction from hexane. Recovery, solvent reduction and enrichment factor are plotted as a function of nitrogen pervaporation flow pressure. A composite membrane was used in these experiments. Experimental conditions were: initial volume, 5 mL; initial concentration, 5 ppm; inlet sample flow rate, 0.5 mL/min and ambient temperature.

were obtained for all four of the analytes (PCP, ATZ, NAP and BPN). The dependence of strip gas conditions in the hexane-composite membrane system implied that the process was limited by the rate of solvent removal on the permeate side, rather than the rate of diffusion of solvent through the membrane. The opposite was true in the methanol–Nafion system, where the strip gas flow rate did not affect solvent removal, as the overall process was limited by the rate of diffusion through the membrane itself.

Presented in Table 1 are typical results from the concentration of ATZ, NAP, BPN and PCP in hexane using the composite HF membranes. Samples were run using the optimum flow rate and N_2 pressure.

3.3. Effect of temperature

Temperature has been shown to play an important role in the overall pervaporation process by affecting the flux and selectivity [17]. In the pervaporation process, first the analyte dissolves or partitions into the membrane and then diffuses through it under a concentration gradient [22,23]. Diffusion through a membrane is an activation process and follows an Arrhenius type equation:

$$E_a = -\frac{R\mathrm{d}\ \ln\ D}{\mathrm{d}(1/T)} \tag{4}$$

where E_a is the activation energy, R is the gas constant, D is the diffusion coefficient and T is the temperature. As the diffusion coefficient increases with temperature, an Arrhenius-type relationship exists where:

$$D = D_0\ \exp\left(\frac{-E_a}{RT}\right) \tag{5}$$

where D_0 is the reference temperature diffusion coefficient. On the whole, the rate of diffusion increases with temperature.

According to Eq. (3), partition coefficient (K) also plays an important role in determining the total flux through the membrane. In most cases, partition coefficient decreases with increasing temperature. The overall effect of decreased K and increased D with temperature is that as temperature is increased, first the overall flux increases and then decreases. The initial increase is attributed to the increasing D whereas the final decrease is due to the drop in K. On the whole, there is an optimum temperature at which solvent flux is maximum [13,15,17].

Fig. 6 shows recovery, solvent loss and EF for NAP in methanol using the Nafion membrane as a function of temperature. Experimental conditions were initial volume of 2 mL, initial NAP concentration of 5 ppm, an inlet sample flow rate of 0.2 mL/min and a counter-current N_2 flow of 10 psi. Sample flow rate and N_2 permeate pressure were kept constant while the temperature was varied. It was observed that increasing the temperature reduced recovery and increased EF. The reduction in recovery implies that the permeability of the analyte increased with temperature, and more of it was lost.

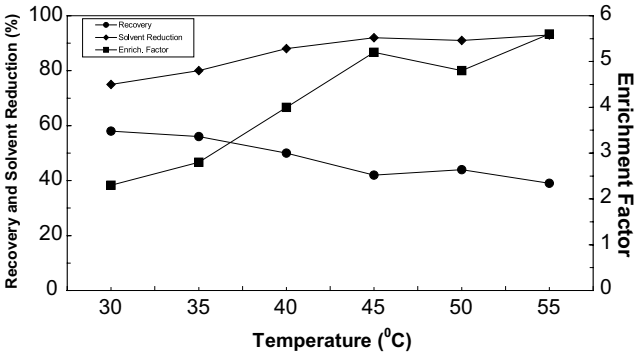

Fig. 6. Concentration of napthalene from a methanol extract. Recovery, solvent reduction and enrichment factor are plotted as a function of temperature. A Nafion membrane was used in these experiments. Experimental conditions were: initial volume, 2 mL; initial concentration, 5 ppm; inlet sample flow rate, 0.2 mL/min and counter-current N_2 flow, 10 psi.

This decrease was relatively small and did not impact detectability. However, the solvent flux increased significantly, thus increasing EF. The benefits of an increase in membrane temperature is that higher flux at higher temperature allows higher flow rate, thus increasing the speed of analysis. This is particularly true when the concentration process is to be carried out in an on-line analysis procedure. It should be noted that the maximum temperature of the modules is limited by the boiling points of the solvents, and the stability of the membrane.

Extraction temperature played an important role during pervaporation in the composite membrane, which corroborated the data obtained for the Nafion. Fig. 7 shows the effect of varying temperature on solvent extraction from hexane–NAP samples at a constant sample flow rate of 0.7 mL/min and N_2 pressure of 0.3 psi. An initial volume of 5 mL with a NAP concentration of 5 ppm was used. Only NAP results are shown here for brevity, other analytes showed comparable results. Both sample loss and EF were significantly increased at higher temperatures. Recovery showed the same moderate downward trend as exhibited by the Nafion–methanol system (Fig. 6). On the whole, these results show that the effects of temperature was similar for both membranes.

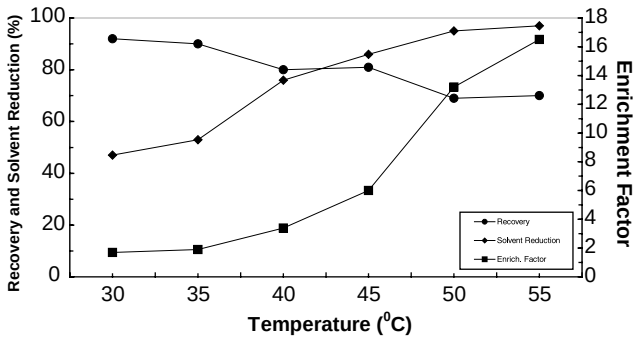

Fig. 7. Concentration of napthalene from a hexane extract. Recovery, solvent reduction and enrichment factor are plotted as a function of temperature. A composite membrane was used in these experiments. Experimental conditions were: initial volume, 5 mL; initial concentration, 5 ppm; inlet sample flow rate, 0.7 mL/min and counter-current N_2 flow, 0.3 psi.

3.4. Membrane carryover

Sample carryover from the concentration was quantified by passing pure methanol through the Nafion HFM, as a wash solution. This removed residual analyte from the boundary layer on the membrane and those that partially permeated into the membrane. Aliquots of 0.5 mL of pure methanol wash solvent were passed through the lumen and collected. Faster methanol flow and lower N_2 pressure were used to prevent excessive permeation of residual analyte during the washing. The total analyte recovered was 12% of the original sample. Overall mass-balance showed that 68% of the analyte (NAP) was found in the concentrate. About 20% of the analyte was unaccounted for and had probably permeated through the membrane during the preconcentration. A similar experiment was carried out using BPN, which showed that 12% of the total analyte had carried over and 77% was recovered. Further experiments have shown that these results were reproducible and indicate that the amount of analyte, approximately one-fifth of the total, was lost through the membrane during the concentration. It was observed that approximately 1.5 mL of pure wash solvent was required to clean the membrane surface of any remaining analyte that had not been eluted, or fully permeated through the membrane.

The relative standard deviations (RSD) of four replicate preconcentrations was used as a measure of analytical performance on the composite membrane column. Triplicate measurement of EFs using 5 mL, 5 ppm solutions, an inlet sample flow rate of 0.7 mL/min, a counter-current N_2 flow of 0.3 psi, and an operating temperature of 50 °C of PCP and ATZ yielded relative standard deviations of 3.3% and 2.9%, respectively. This demonstrated high precision of the preconcentration process.

4. Conclusions

Pervaporation through hollow fiber membranes were used to investigate pre-analysis concentration of analytes. This paper demonstrated the feasibility of solvent pervaporation as a rapid method for preconcentrating the analytes contained in a sample. Depending on the solvent used, both polar and non-polar permeable membrane systems have been demonstrated to be effective for concentrating analytes. A large increase in analyte EFs was seen for both, although more so in the hexane-composite membrane system. Further, in the Nafion membrane, analyte that attached to the sulfonic acid residue chemistry could not be recovered. All analytes were successfully concentrated and detected using the hexane-composite membrane system.

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