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Review

Pervaporation in chemical analysis

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ABSTRACT

Unlike thermal processes such as distillation, pervaporation relies on the relative rates of solute permeation through a membrane and is a combination of evaporation and gas diffusion. The analytical pervaporation systems consist of a membrane module suitable for liquid sample introduction and a vacuum (or a sweeping gas) on the permeate side. It has been used in a wide range of applications including the analysis of various organic and inorganic compounds, and sample concentration. It has been directly interfaced with gas chromatography, spectrophotometry, capillary electrophoresis, electrochemical detectors, liquid chromatography, and mass spectrometry. A wide range of liquids, slurries, and solids samples has been analyzed using these techniques. This review highlights the basic principles of the pervaporation and the state of its current development as applied to analytical chemistry.

Contents

1. Introduction

Membrane separation is an emerging technology that has undergone rapid development in recent years. Serving as a selective barrier, its primary function is the separation of two bulk phases and controls the mass transfer between them. This allows the enrichment of the species of the interest and their removal from the sample matrix. The movement of the solutes or analytes across a membrane maybe driven by a chemical, pressure, or an electrical potential gradient [1]. The use of the membranes in analytical applications has become a preferred sample preparation option where the membrane can perform multiple functions that range from extraction, concentration, to cleanup prior to the detection by instrument. This is largely due to the fact that they facilitate extraction without the mixing of two phases, thus eliminating problems such as emulsion formation and high solvent usage [2]. Moreover, the sample and the extractant can be continuously brought into contact, thus providing the basis of continuous, real-time process leading to automation and online interfacing to instruments [3]. Some major large scale applications of membrane separation techniques include desalination, dialysis, ultrafiltration, gas separation, dehumidification, osmosis, reverse osmosis, electrodialysis, and pervaporation [4], while analytical applications range from volatile/semi-volatile organics to inorganics and metals.

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Pervaporation is a promising alternative to conventional energy intensive processes such as distillation and evaporation. It is often referred to as "clean technology", especially for the treatment of volatile organic compounds. The separation is not based on relative volatilities as in the case of thermal processes, but rather on the relative rates of permeation through a membrane. It is a combination of evaporation and gas diffusion in a single module [5]. The analytical pervaporation systems consist of a suitable membrane in a module, a delivery system for liquid feed, and a vacuum or a sweeping gas on the permeate side. It has been used in a wide range of applications including the analysis of various organic pollutants [6–9] and inorganic compounds [10–13], and has been directly interfaced with gas chromatography (GC), spectrophotometry, capillary electrophoresis (CE), liquid chromatography (LC), and mass spectrometry (MS) [14–18]. In pharmaceutical and clinical fields, this technique has been reported in a variety of matrices such as tablets, toothpaste, and urine [19–21]. In food analysis, a number of publications have reported the analysis ranging from liquids, slurries, to solids [17,22–25]. In addition, the authors believe that there are many other applications that are yet to be explored. This review highlights the fundamental principles of pervaporation, and the current status of analytical applications.

2. Principles

A membrane is a selective barrier through which different gases, vapors and liquids move at varying rates. The membrane facilitates the contact of two phases without direct mixing. Molecules move through membranes by the process of diffusion and are driven by a concentration (ΔC), pressure (ΔP), or electrical potential (ΔE) gradient. Pervaporation, is an integral operation involving *permeation* and *evaporation*. It is unique among membrane processes because a phase change occurs across the membrane. Removal of the analytes from the sample is accomplished by partial pressure differential created on feed and permeate sides of the membrane. The separation is a function of the rate of permeation of the analytes through the membrane. The sample flows on one side, while the vacuum or sweeping gas is applied on the other side. The process is demonstrated in Fig. 1. The interesting aspect of this technique is that both the donor (feed side) and acceptor (permeate side) can flow continuously leading to the development of real-time monitoring techniques.

Solution-diffusion is generally the accepted mechanism for mass transport through non-porous membranes [26]. Permeation through the membrane consists of the following steps [27], as also shown in Fig. 2:

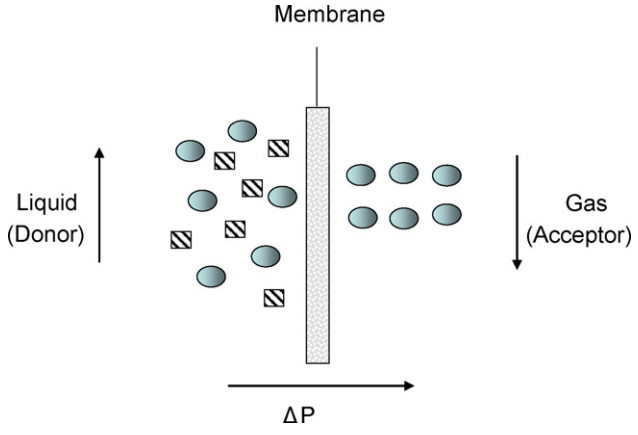

Fig. 1. Pervaporation across a membrane. ΔP is the partial pressure gradient which is the driving force for mass transfer.

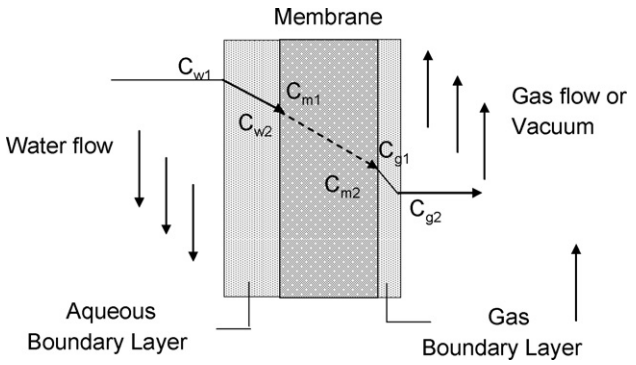

Fig. 2. Concentration profile in a pervaporation process, where C_w, C_m and C_g refer to analyte concentration in aqueous, membrane and the gas phase, respectively.

(1) Diffusion through the liquid boundary-layer on the feed side of the membrane (C_{w1} to C_{w2}).
(2) Selective partitioning of molecules into the membrane (C_{w2} to C_{m1}).
(3) Diffusion across the membrane under a concentration gradient (C_{m1} to C_{m2}).
(4) Desorption into the vapor phase on the permeate side (C_{m2} to C_{g1}).
(5) Diffusion away from the membrane through the boundary layer on the permeate side of the membrane (C_{g1} to C_{g2}).

These mechanisms govern the mass transport across pervaporation membranes. Separation takes place due to the differences in the partitioning coefficient, diffusitivity, and vaporization of the donor components. Flux (J) through a pervaporation membrane can be expressed in term of the partial pressure difference across the two sided of the membrane such that:

$$J_a = P_a^G \frac{P_{ao} - P_{al}}{t} \quad (1)$$

where J_a is the flux for component a, t is the membrane thickness, P_a^G is the gas separation permeability coefficient, P_{ao} is the partial pressure on the donor side, and P_{al} is the partial vapor pressure in acceptor for component a. The chemical potential or vapor pressure difference is generally maintained either by maintaining partial vacuum on the permeate side of the membrane, or by depressing the partial pressure by introducing a sweep gas. The other important parameter is selectivity which is represented by terms such as separation factor (α) and enrichment factor (β). The separation factor of a membrane for species a and b can be defined as:

$$\alpha_{ab} = \frac{(C_a/C_b)^v}{(C_a/C_b)^L} \quad (2)$$

The enrichment factor is used as an indication of the separation selectivity for component a:

$$\beta = \frac{(C_a)^v}{(C_a)^L} \quad (3)$$

where C_a and C_b are the concentration of a and b in vapor (v) and liquid (L) phase, respectively.

The operational variables are critical for controlling the pervaporation process [28]. For example, a change in the feed concentration directly affects the sorption phenomena at the liquid–membrane interface and also the permeation characteristics dictated by the solution-diffusion principle. Pressure at the feed and permeate sides is also important. Pervaporation operation is carried out by applying vacuum or sweep gas to the permeate side of the membrane, which creates a chemical potential difference. This can be explained by the increase in driving force in the right hand

term of Eq. (1). Temperature affects all of the steps in the analyte transport process mentioned above, and also alters the driving force for mass transfer. Arrhenius-type relationships have been used to describe the effect of temperature on flux as follows [27]:

$$J = J_0 \exp\left(\frac{E_a}{RT}\right) \quad (4)$$

where J_0 is a constant, E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature. On the other hand, the selectivity is strongly dependent on temperature; in most cases a small decrease is observed with increasing temperature.

Among morphological factors, pervaporation membrane shows a mass transfer resistance that is proportional to its thickness. The permeation flux is inversely proportional to the membrane thickness as shown in Eq. (1). However, the thickness can only be decreased to a certain point due to the limitations in manufacturing techniques and mechanical stability as well as the selectivity which is influenced by thickness. Apart from all the other factors mentioned above, the boundary layer which is formed by a thin coat of liquid on the surface is an important consideration because it could be the major contributor to the mass transfer resistance which is less significant in vapor phase boundary due to the gas flow or vacuum on the permeate side. These steps are illustrated in Fig. 2.

2.1. Membrane classification

Pervaporation is strongly dependent upon factors such as morphology, geometry, and structure of the membrane. The membranes may be classified as shown in Fig. 3.

2.1.1. Morphology

The pervaporation membranes can be non-porous or porous membranes (Fig. 4A and B). Membranes that have no pores in their structure are known as non-porous, while those which possess pores are classified as porous. It has been demonstrated that the difference in pore size, shape, and distribution strongly affects the pervaporation efficiency and selectivity [5]. The mechanism of transport strongly depends upon the type of membrane. The permeation in porous membranes is often by size exclusion. Anything that can permeate through the pores migrates across. For example, in pervaporative separation of organic from water, significant amount of the latter also permeates through. As a result, the porous membranes in general provide higher flux but lower selectivity and are excellent for applications such as nanofiltration and dialysis. In non-porous membranes, the molecule must first partition and then diffuse under a concentration gradient through the solid material. Therefore, the separation by non-porous membrane is influenced by partition coefficient as well as diffusivity of the component in the membrane. This type of membrane is mostly used in pervaporation and provides high selectivity [29]. Composite membranes usually consist of a thin dense surface layer coating on top of the microporous support layer (Fig. 4C). The top layer that determines the membrane's selectivity is of a material different from the porous support layer [28]. For example, a one micron silicone layer on top of a porous polypropylene provides high volatile organic compounds (VOCs) flux during pervaporation while preventing large amount of water from permeating through [2]. A more recent development is mixed matrix membrane (MMM), which consists of interpenetrating polymer matrix and solid fillers such as zeolite, carbon molecular sieves, silica, carbon graphite, fullerene, cyclodextrin, and metal oxide [30–36] (Fig. 4D). Typical fabrication process for MMM involves adding the filler material to the polymer solution followed by film casting or spinning [37]. Nanomaterial such as carbon nanotubes (CNTs) have also been applied to filters and membranes used in the extraction and pervaporation [38–40]. For example, a novel MMM was prepared by incorporating the NaY zeolite into chitosan for the separation of isopropanol–water mixture [41]. An increase in zeolite content in the membrane resulted in the simultaneous increase of both permeation flux and selectivity. On the other hand, in the pervaporation of water/ethanol mixture by the incorporation of CNTs into polymeric membrane, the flux increased with the increase in CNTs content, but the selectivity decreased [39]. Scanning electron microscope (SEM) images of different types of membranes are shown in Fig. 5.

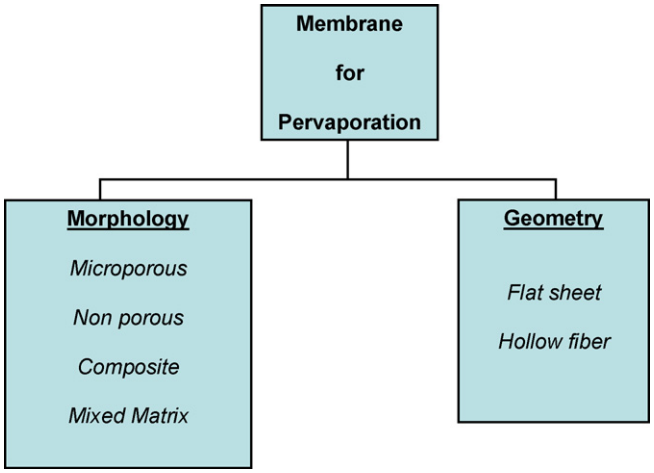

Fig. 3. Classifications of membranes.

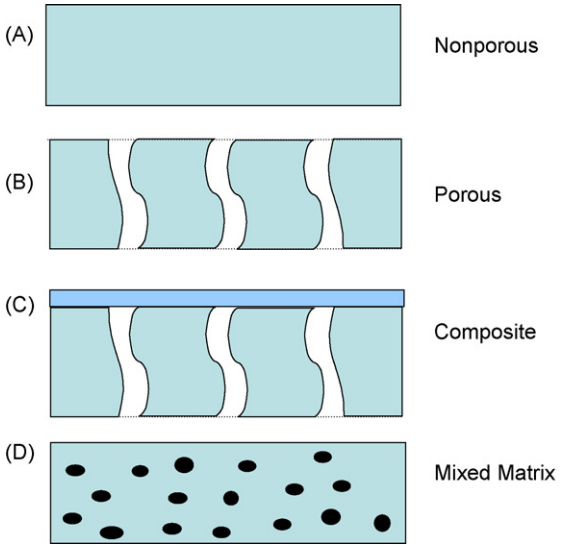

Fig. 4. Schematic representation of four different types of membrane morphology.

2.1.2. Geometry

The membrane geometry refers to the shape of the membrane. There are two common types of commercial membrane, flat and hollow fiber. The latter have a tubular geometry. The membrane module designs (plate-and-frame, spiral-wound, and hollow fiber) are based on the membrane geometry. The flat sheet membranes are used in plate-and-frame and spiral-wound modules while the tubular geometry type is used in the hollow fiber design.

A simple flat sheet module, shown in Fig. 6A, could comprise a cell with a single flat sheet dividing the acceptor and donor [2]. A more complicated structure is the one referred to as the plate-and-frame design. It essentially consists of flat sheets stacked on top of each other with an interspersed support material. A generic design

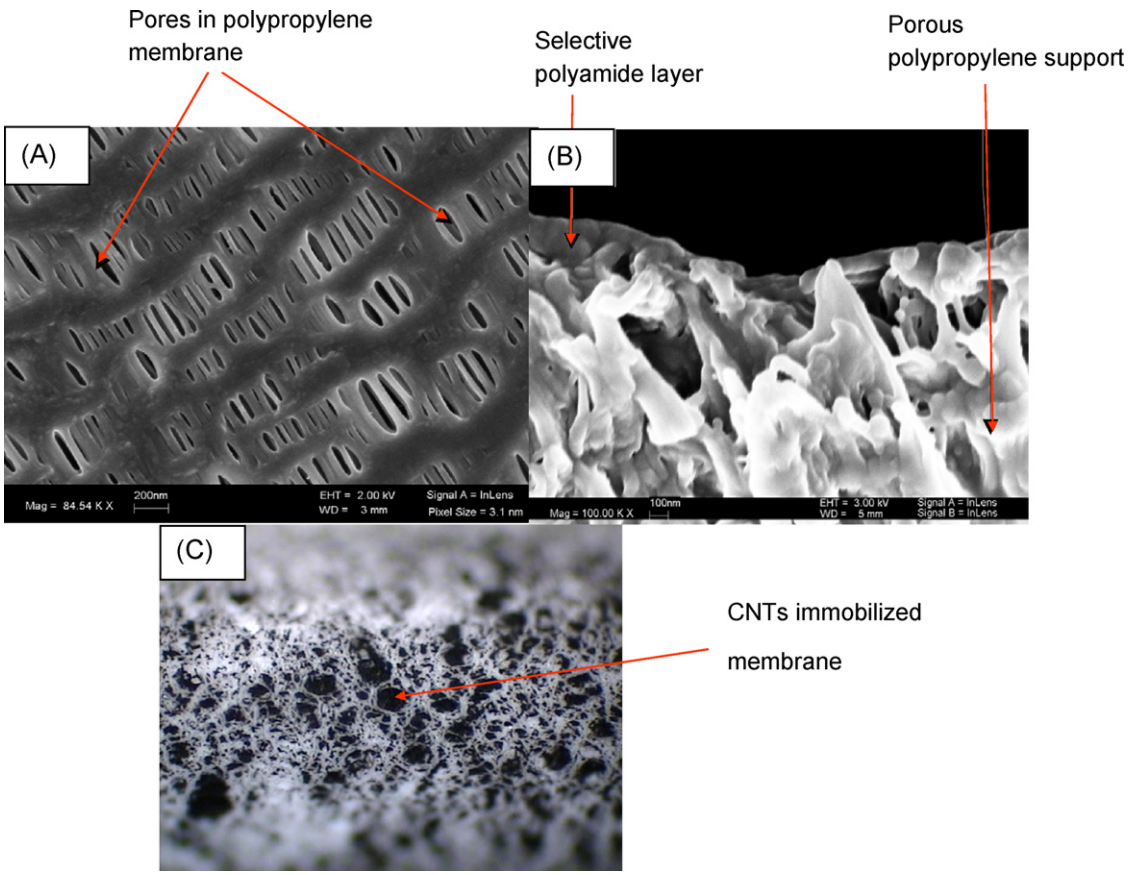

Fig. 5. SEM images (A) microporous polypropylene, (B) thin film composite (polyamide surface layer supported by polypropylene) [2]; and (C) Confocal Raman image of CNTs immobilized membrane [40].

is shown in Fig. 6(B). The spiral-wound module which is like a plate-and-frame module rolled into a cylinder with liquid flow entering along the end of the cylinder and leaving at the other end [27] (Fig. 6C) [42]. Fundamentally, two or more membrane sheets that are glued together along the edges are wound around a centrally located permeate collecting tube.

A hollow fiber module consists of a cylindrical shell with a bundle of individual fibers (Fig. 7). Multiple parallel fibers are encased in a large tubing to provide high packing density. It can be configured for liquid flow either on the shell side (outside the fiber) or on the lumen side (inside the hollow fibers) of the hollow fibers. The permeate is collected at the end of the fibers and hence the parallel flow can be concurrent or countercurrent depending on the direction of permeate flow with respect to the feed [28]. Typical hollow fibers are 100–500 μm in diameter. As a result, these modules offer the advantage of being able to accommodate a much higher surface area per unit volume compared to their flat counterparts.

3. Applications of analytical pervaporation

3.1. Analysis of organic compounds

One of the most interesting application of pervaporation is the extraction of VOCs from either liquid or solid matrix followed by direct interfacing with an analytical instrument such as gas chromatography (GC) [7,8,22,23,43–47], mass spectrometry [48–50], capillary electrophoresis (CE) [24], spectrophotometry [6,51–53], gas-phase absorptiometry [54]. In fact, when a pervaporator is coupled to a GC or GC/MS it is equivalent to a static or dynamic headspace (purge and trap) sampling, with the added advantage that very short analysis time is required and the process can be easily automated [55]. An important advantage over purge and trap is the fact that there is no need for a water condenser because the hydrophobic membrane prevents the passage of much of the water.

Use of pervaporation in the VOCs analysis has been reported in various fields. In environmental field [6–8], the extraction of toluene from wastewater by using polydimethylsiloxane (PDMS) membrane filled with carbon black showed higher selectivity and enrichment factors compared to the original PDMS membrane [7]. In addition, VOCs have been extracted from a variety of food and beverages samples such as wine, orange juice, fruit, etc. by using either composite membrane, e.g. POMS-PEI or homogeneous membrane, e.g. polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PDVF), cellulose, styrene-butadiene-co-styrene (SBS) [22–24,43–47,52,53,56,57]. The pervaporation coupling with analytical instruments usually shows very low limit of detection. For example, Gómez-Ariza et al. presented the detection limit of 54 pg for the analysis of 2,4,6-trichloroanisole in wine by pervaporation and on-line GC–MS. Moreover, pervaporation has been used in the study of ammonia in fertilizers [54], as well as ethanol in industrial fermentations [51].

The analysis of semi-volatile organic compound (SVOC) in air and water samples have also been reported [9]. An in-line system for trace analysis of 4,4′-Dichlorodiphenyl trichloroethane (4,4′-DDT) by pervaporation technique connected with a high-resolution GC was developed [9]. The detection limit was as low as 90 μg/L for 4,4′-DDT analysis by using this technique.

3.2. Membrane interfaces for mass spectrometry and gas chromatography

Membrane introduction mass spectrometry (MIMS) is a technique in which pervaporation is used to selectively transport organic compounds into a mass spectrometer for analysis. In this

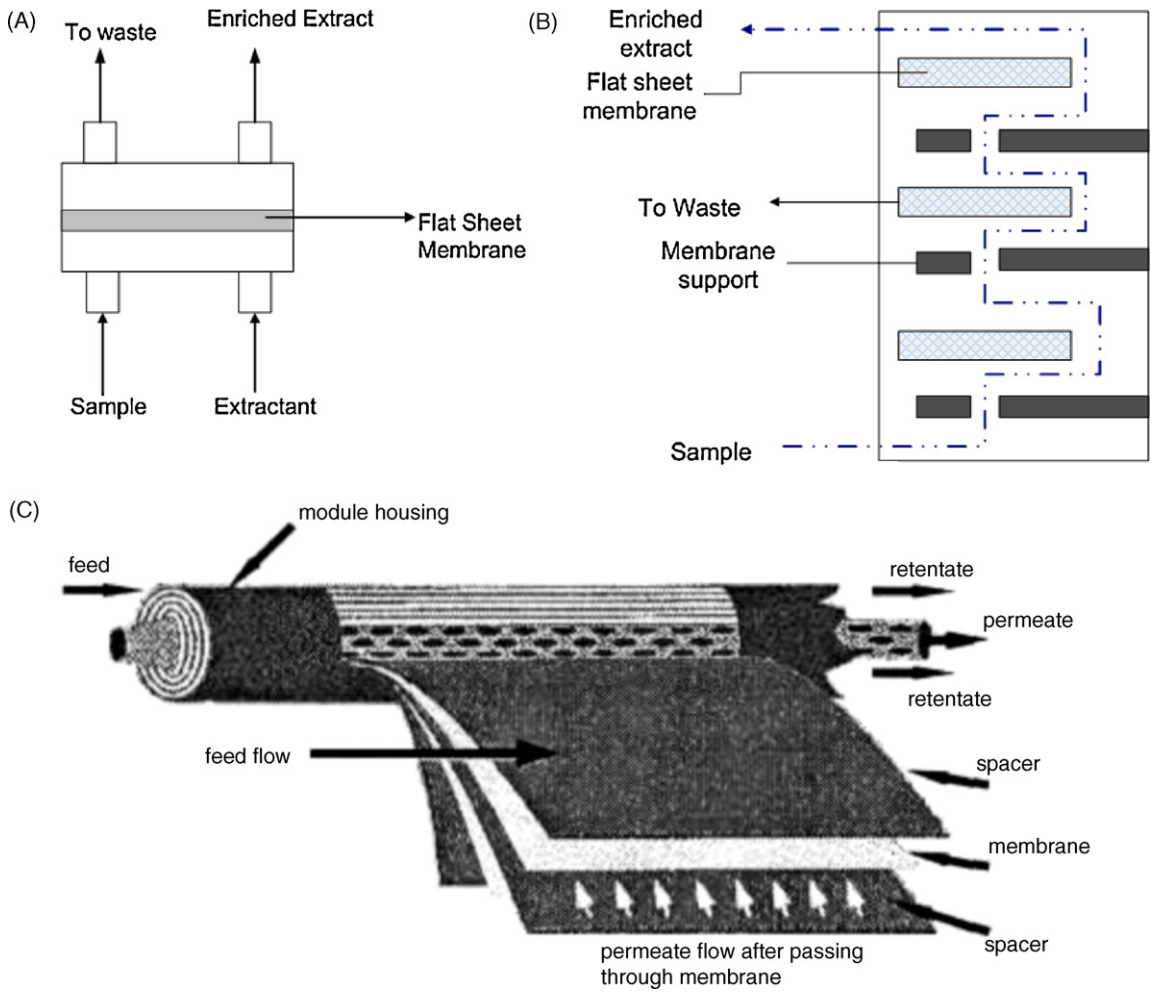

Fig. 6. (A) Simple flat sheet membrane module; (B) schematic of plate and frame design [2]; and (C) spiral-wound module [42].

configuration, the general diagram is shown in Fig. 8(A). The experimental set up is shown in Fig. 8(B). The sample is constantly introduced to the membrane and the permeate is pulled by vacuum into the ion source [58]. MIMS is rapid and has been used to carry out on-line measurements and provide capabilities that fit the requirements for analysis of VOCs and SVOCs in environmental samples [48–50,58–63]. This technique has also been used in the food industry for real-time monitoring of the fermentation of glucose [64] and bio-reductions by baker's yeast [65]. The vacuum in the membrane provides a high partial pressure gradient, consequently a membrane interface is an efficient sample introduction

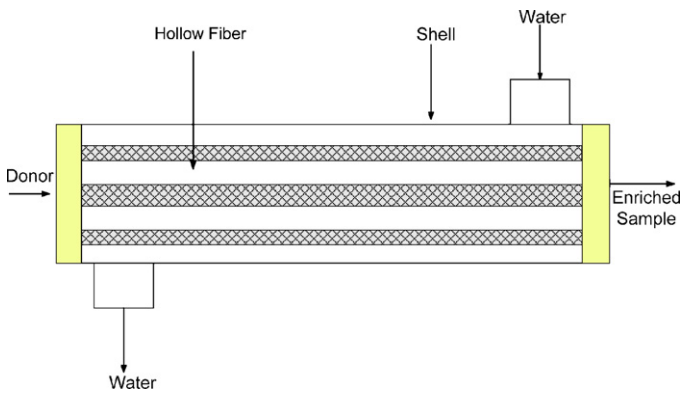

Fig. 7. Hollow fiber membrane module [2].

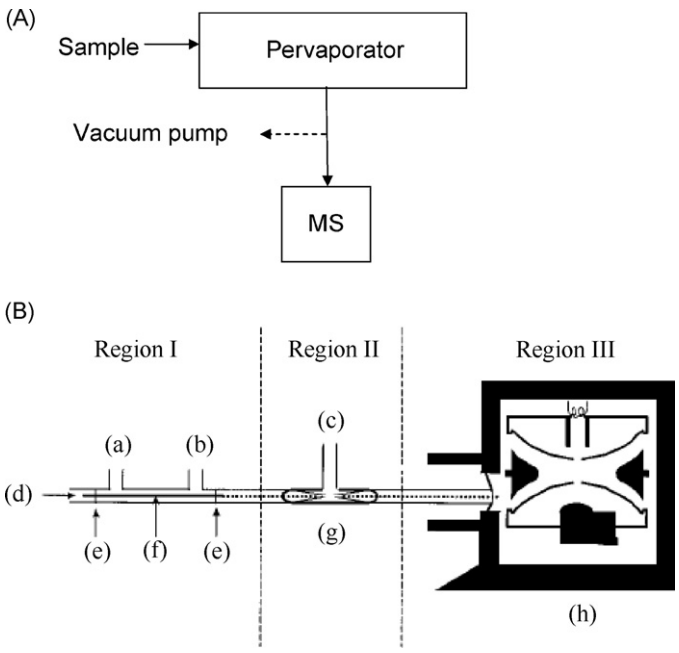

Fig. 8. (A) Schematic representation of the MIMS system, (B) experimental system: (a) sample exit, (b) sample entrance, (c) vacuum pump, (d) input for helium carrier/buffer gas, (e) expoxy seal, (f) hollow fiber membrane, (g) jet separator, and (h) ion trap mass spectrometer [58].

system without the break time in between sample transportation to MS.

A GC interface for a membrane extractor is significantly more difficult because a positive pressure needs to be maintained on the permeate side to facilitate the flow of the carrier gas (Fig. 9A. The development of on-line pervaporation with a sorbent trap interface to a GC has been presented for continuous monitoring of organics in water and air [66]. Water or air sample continuously flowed into membrane module and nitrogen flowed countercurrent at the permeate side to strip the organic compounds into vapor phase. The organics were transported to, and concentrated into a microtrap. Then, the concentrated organics were injected onto GC column by rapid thermal desorption. An alternative approach to continuous on-line pervaporation referred to as pulse introduction membrane extraction (PIME) has been reported [67–69]. Here a pulse of sample is injected into the membrane for pervaporation. Thus, the system does not need to reach steady state as the first version and the errors associated with steady state requirement are eliminated. However, another important issue still remained. That is the boundary layer effect of the analyte in the aqueous stream, which broadens the input pulse to the membrane.

3.2.1. Boundary layer effect

As explained before, the aqueous boundary layer formed on the membrane provides the major source of resistance to mass transfer. Thus, the permeation may take a relatively long time to reach steady state, resulting in the errors in any measurement during the transitional period. The time taken to complete the permeation process can be the limiting factor in analysis. Consequently it was realized that the best approach may be a non-steady state one. A pulse introduction process based on pervaporation using a flow injection type sample introduction was developed thus eliminating the boundary layer and reducing the need for the system to equilibrate [68]. This showed the way to significantly quicken instrument response.

The boundary layer issue was addressed by gas injection of liquid samples [70]. This system is referred to as gas injection membrane extraction (GIME) as shown the configuration in Fig. 9(B). GIME involves the introduction of an aqueous sample continuously or as a pulse by a N_2 stream which injects the sample into the lumen side of the hollow fiber membranes. On the permeate side, a countercurrent gas stream strips the organics and transports them to a microtrap. The VOCs are trapped and concentrated by a microtrap in front of the GC column. The retained VOCs are desorbed from the microtrap by an electrically generated temperature pulse. Rapid heating generates a concentration pulse that serves as an injection for chromatographic separation. Continuous monitoring is achieved by making a series of pulses (or injections) and corresponding to each pulse a chromatogram is obtained. The system shown in Fig. 9 can be used for the analysis of individual samples by discrete injections or for continuous on-line monitoring by sequentially injecting a series of samples.

No pump is needed for the delivery of the aqueous sample in GIME. The gas cleans the membrane and reduces the formation of

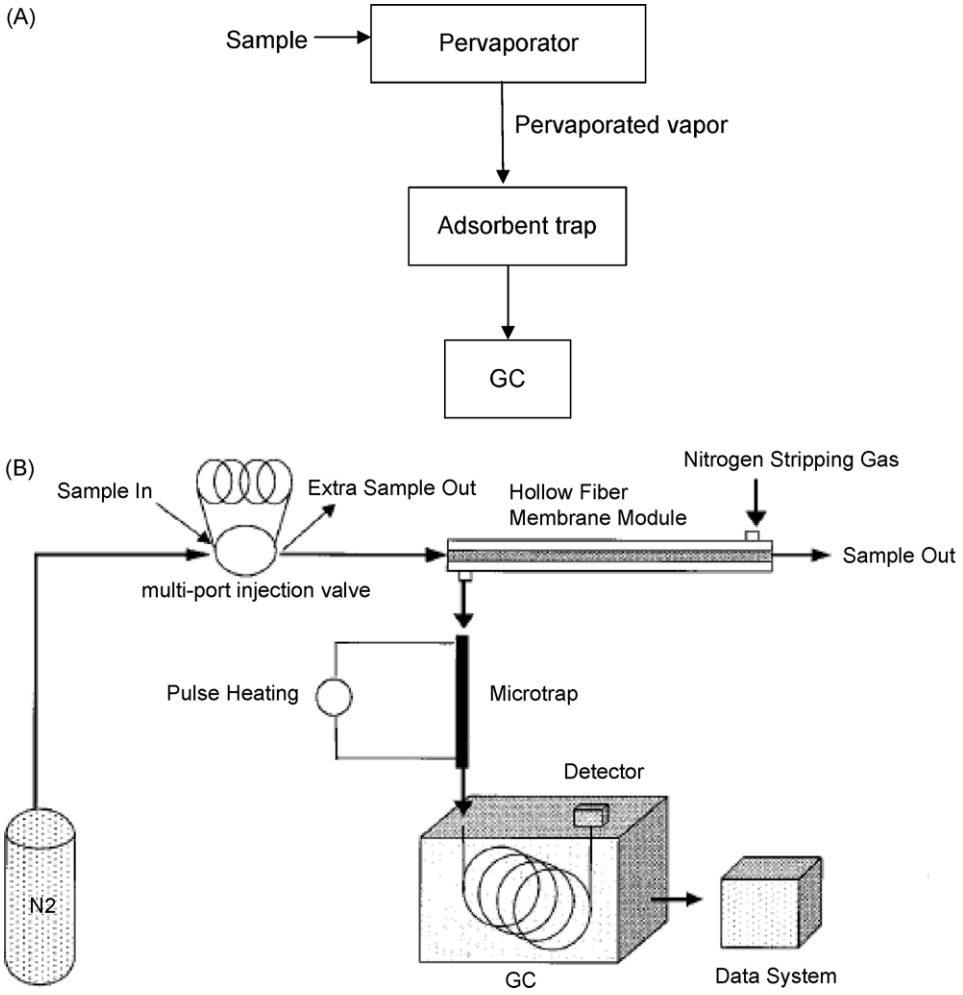

Fig. 9. (A) Schematic representation of membrane interfaces for gas chromatography. (B) Gas injection membrane extraction (GIME) for on-line VOCs monitoring [70]. Nitrogen flows countercurrent to the sample stream and removes VOCs, carrying them to the microtrap.

boundary layer on its surface. The response time decreased dramatically and tailing in permeation profiles was eliminated. The overall analysis of benzene was found to be completed in 2 min by gas injection compared to 8 min by liquid. This method is also simpler in terms of instrumentation and operational procedures [70]. Detection limits of VOCs in aqueous samples were at ppb levels using only 2 mL sample. An added advantage was that individual samples could be analyzed by discrete injections, and continuous monitoring could be carried out by sequential injections.

The membrane selection is an important issue in pervaporation with MS and GC interfaces. The most commonly used membranes are hydrophobic, non-porous, such as, silicone, polydimethylsiloxane (PDMS), latex, polyurethane, polyimide, polyethylene, and nitrile [14,48,62,71]. These membranes have excellent permeability for VOCs present in environmental samples and low permeability for sample matrix. Microporous membranes such as polypropylene, polytetrafluoroethylene (PTFE) have also been used in MIMS [72,73]. In spite of the lack of selectivity in these membranes, their fast response times allow specialized applications, for example, in the determination of polar organic compounds in hydrocarbon matrices, where the hydrocarbons were used as the chemical ionization reagent in the subsequent MS analysis. Both types of membranes provided detection limits in the parts per trillion (ppt) to part per billion (ppb) range for some VOCs [73]. In addition, the composite membranes such as PDMS, ally alcohol (AA), or siloxane coating on polypropylene support have also been used in pervaporation both in MS and GC interfaces to achieve chemical selectivity and sensitivity either for non-polar or polar analytes [58,70]. For example, the use of AA membrane led to nearly 25 times sensitivity enhancement compared to PDMS [58].

3.3. On-line preconcentration via pervaporation

A conventional extraction is usually followed by a concentration step. Traditionally, this is carried out off-line using a rotary evaporator, gas purging and Kuderna-Danish apparatus. These are relatively laborious procedures involving multiple handling steps that can lead to sample loss, contamination and the degradation of labile sample [74]. While there has been much attention placed on on-line extraction techniques, a concurrent development in concentration procedures has not occurred. With the push to develop totally automated systems, concentration procedures also need to be integrated on-line.

Recently, the on-line concentration technique based on pervaporation has been reported and shown in Fig. 10 [74]. Instead of the selective permeation of the solute (as mentioned before), selective solvent permeation leads to increase the analyte concentration. In this method, the dilute solution is injected into a hollow fiber module, and an inert gas such as nitrogen flows on the permeate side. The membrane preferentially allows the migration of solvents across it, and a concentrated solution is observed. The process was demonstrated using both polar and non-polar membranes for analytes such as, atrazine, pentachlorophenol, naphthalene and biphenyl. The instrumentation is simple and can be automated to concentrate either multiple samples or interfaced with chromatography.

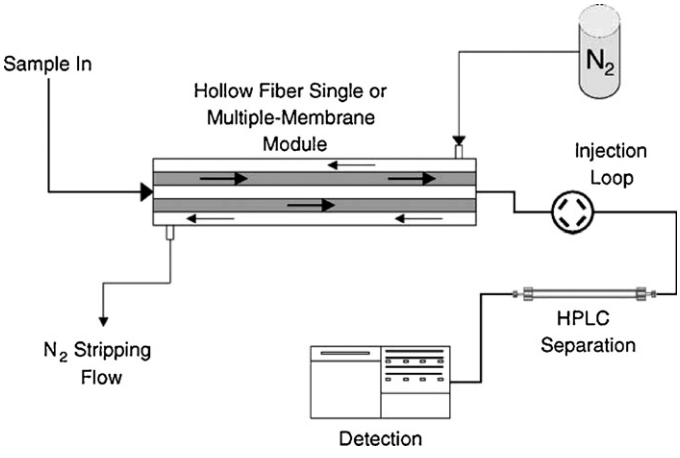

Fig. 10. Hollow fiber membrane concentrator. It can be interfaced with HPLC for on-line analysis [75].

The choice of membrane depended on the solvent. The combination of hexane and a non-polar composite membrane (polypropylene with a thin layer of siloxane), and polar solvents with Nafion™ membrane led to high enrichment factors in less than 30 s. Equivalent concentration using a rotary evaporator would take hours. This technique demonstrated the feasibility of solvent pervaporation as a rapid method for preconcentrating the analytes contained in a sample. Pervaporation has also been used as a method for on-line concentration and monitoring of trace level pharmaceuticals in process streams [75]. A polar solvent permeable Nafion™ hollow fiber membrane was used for monitoring 2,6-dichlorophenylacetic acid (DCPA), naphthylacetonitrile (NA), 4-chloro-3-nitrobenzophenone (CNBP), 1,2-diphenylhydrazine (DPH) and 2-chloro-3,4-dihydroxyacetophenone (CDHAP) in methanol. The concentrated stream was monitored using HPLC with UV/vis detection. The results showed solvent reduction greater than 90% and enrichment factors in excess of 7.9. Once again the process can be used with discrete samples for off-line analysis, and can also be carried out on-line for continuous monitoring.

3.4. Development of total analysis system based on membrane extraction and pervaporation

The theory of a total analytical system (TAS) requires the hyphenation of extraction and concentration, followed by analytical detection so that continuous, on-line analysis can be carried out without manual intervention. The interfacing of continuous membrane extraction, pervaporation, and on-line HPLC-UV detection has been reported [18]. Figure 11 shows the coupling of two membrane modules. In this study, two hollow fiber membrane modules were used in series. First, the analytes are extracted into an organic solvent by liquid–liquid membrane extraction. Second, they are concentrated via pervaporation, which was followed by on-line HPLC detection. The enrichment factors were as high as 192 and the method detection limits were at low ng/mL levels. Conceptually speaking this combination could be used with a variety analytes in diversity matrices.

3.5. Pervaporation in flow injection analysis

Flow injection analysis (FIA) is a powerful flow through technique for on-line detection. It has been used to fabricate portable, semi-automated and automated chemical analyzers [76] using a variety of detection schemes including spectroscopic and electrochemical devices. While FIA does not normally include high-resolution separation like chromatography, the sample is injected into a carrier stream where it may undergo reaction with a reagent to additionally produce chemical species that can be sensed by a flow through detector. Often some preconcentration/clean up may be necessary for real-world samples that have complex matrices. Pervaporation has been used to separate the analytes from such matrices [77,78]. In addition, it can improve the sensitivity via preconcentration and selectivity by eliminating interfering species.

The applications of pervaporation in flow injection analysis can be divided into direct vaporization of a volatile analyte (Fig.

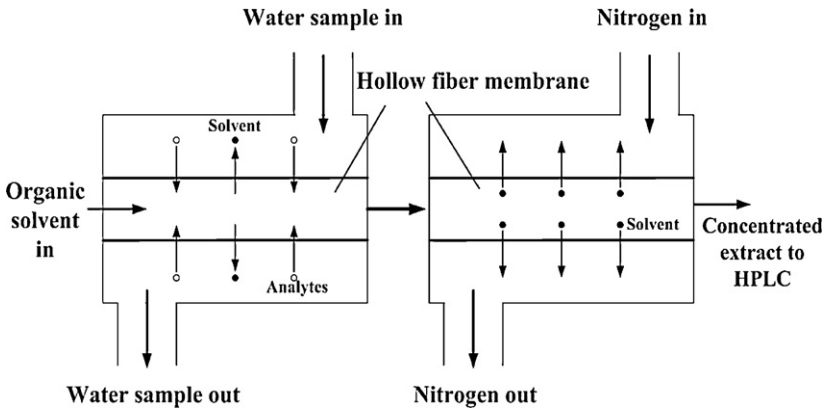

Fig. 11. Interfacing of membrane extraction to pervaporative concentration shows the total analysis system [18].

12A), and indirect methods where the analyte is first derivatized to form a volatile specie suitable for pervaporation (Fig. 12B). In both cases, complexation with a colorimetric reagent may be carried out for spectrophotometric identification. Examples of direct pervaporation include the determination of ethanol in beverages [79,80], diacetal in beer [16], acetaldehyde in food [81], formaldehyde in pharmaceuticals and cosmetics [82]. In the analysis of organic acids in wine, the sequential injection of two sample aliquots, one for total and the other for volatile acids were made into two separate channels [83]. One passed through the pervaporator and was a measure of volatile acids while the other went directly into the photometric detector after merging with an indicator stream. The detection limits were at low mg/L levels [83]. The pervaporation-flow injection method has also been used for the analysis of ammonia in the presence of surfactants [78]. The permeated ammonia was collected in an acceptor solution containing mixed acid-base indicators, cresol red and thymol blue. The color change was monitored photometrically. The sampling rate and detection limits for the ammonia analysis were 11 per hour and 0.1 mg/L respectively. This technique was effective for industrial effluents containing ammonia in the presence of surfactants and other suspended solids [78]. A system for the continuous removal of ammonia from cigarettes with ultrasound assisted extraction has also been coupled to pervaporation-flow injection for direct analysis [84].

Fig. 12(B) shows the indirect method involving the pervaporation-analysis of volatile reaction products. An example is the determination of biogenic amines in food, where trichloroacetic acid solution was used as the leaching solution and reaction with sodium hydroxide was used to convert the leached amine into volatile species [17]. The latter pervaporated through the membrane was collected in an acceptor solution and analyzed by capillary electrophoresis. This approach has been used to quantify biogenic amines in fish, meat, and sausage at detection limits between 0.2 and 0.6 μg/mL. The analysis frequency was higher than 3 per hour and sample sizes were of the order of 100 mg. A similar method was used for the determination of trimethylamine for both liquid tissue extracts and the direct analysis of solid samples [25]. Other examples of derivatization-pervaporation include the conversion of urea into ammonia by urease catalysis [85] and phenols to phenyl acetate [86]. Fig. 12(C) shows the system for the latter analysis. On-line derivatization of phenol containing

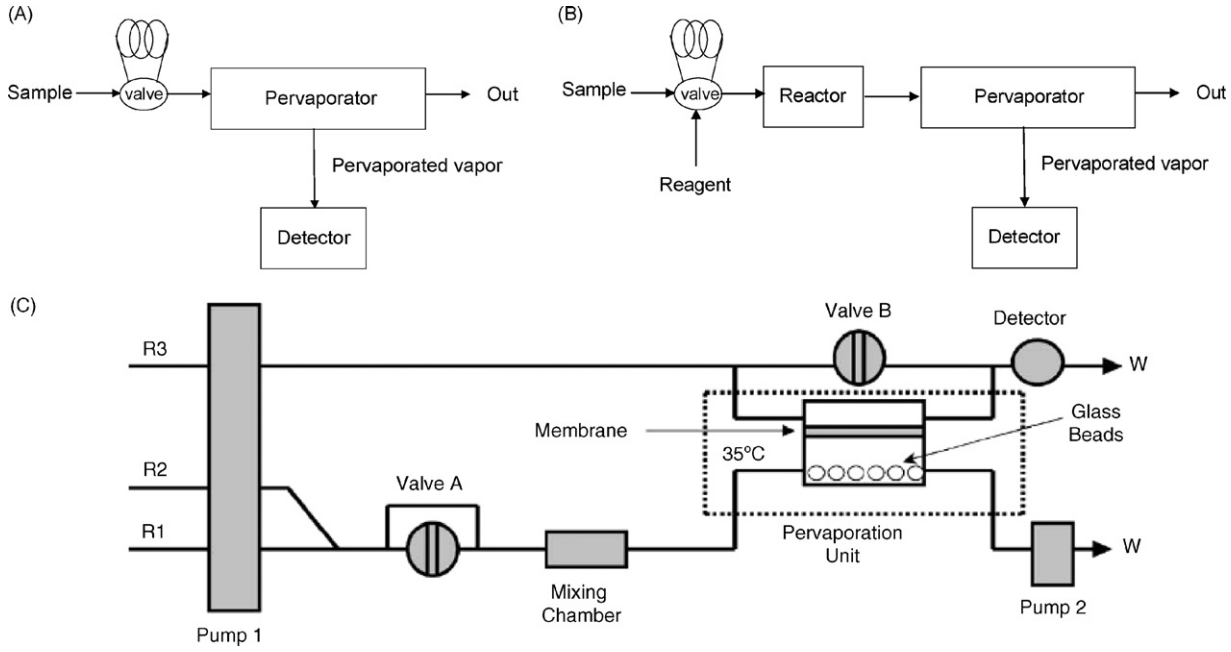

Fig. 12. Schematic representation of flow injection analysis system (A) direct method, (B) indirect method, and (C) experimental set up for the pervaporation in flow injection on-line derivatization analysis of phenol: R1, phenol solution; R2, NaOH/NaCl solution; R3, NaOH/KNO_3 electrolyte; valve A, 20 μL loop; Detector, amperometric with glassy carbon working electrode [86].

sample (R1) was performed using acetic anhydride (valve A) and alkaline sodium chloride stream (R2). The resulting phenyl acetate diffused through the membrane into an alkaline solution (R3) in the acceptor chamber and was detected electrochemically. The detection limit was 25 μg/L and 4 samples could be analyzed per hour.

3.6. Analysis of inorganic species and metal speciation

Analytical pervaporation has also been used in the analysis of a wide variety of inorganic species that ranged from ions to volatile metals. Complex environmental, food, and pharmaceutical matrices have been successfully analyzed using pervaporation as a separation/sample preparation step. Different detection schemes including atomic absorption [87], atomic fluorescence [13,15,88,89], UV–vis spectrophotometry [12,20,90], and electrochemistry [10,11,21,91–93] have been used for detection.

Analytical pervaporation has been used as an auxiliary device in metal speciation in liquid and solid samples [94]. The isolation of volatile metals such as arsenic [12,13,89,90], mercury [88], and cadmium [87] has been carried out using flow injection analysis-pervaporation followed by detection using photometric or atomic fluorescence method. A pervaporator has been used for the speciation of organomercury compounds in soil samples [15], where it functioned in a manner similar to a headspace device. The pervaporated compounds were preconcentrated on a Tenax cartridge, thermally desorbed and the speciation of mercury as Me_2Hg, Et_2Hg and MeHgCl were carried out in a GC column without any derivatization of the analytes. The detector was a combination of an on-line pyrolyzer with an atomic fluorescence spectrometer. Recoveries were of the order of 95–107% and detection limits were as low as sub ng/g of soil.

The volatile hydrides species have been generated and removed from a sample matrix by permeation and diffusion through the membrane [12,13,87–90]. The experimental set up is shown in Fig. 13. In this method, the removal of arsenic in soil was achieved with the help of a microwave digester [89]. The samples were introduced as slurry prepared by mixing the soil with hydrochloric acid solution. A slurry plug was injected into a carrier stream of hydrochloric acid and transported to the microwave reactor. Then, it was reacted with $NaBH_4$ under acidic conditions to generate arsine that was volatile and could be separated by pervaporation. Finally, the analysis was carried out with atomic fluorescence spectrometry. The detection limits were around 1 ng/mL, and the sampling frequency was 4 per hour. The results obtained from the certified reference materials, sediments, and soil demonstrated the reliability of the method. The relative standard deviation for within-laboratory reproducibility was 4.5% [89]. The analysis of arsenic in aqueous samples including suspensions have be carried out directly [12,13] by injecting into a hydrochloric acid stream and mixed with $NaBH_4$. This method has been applied to aqueous samples with solid particles in suspension, and provided a sampling frequency of 12 per hour [13]. Flow injection-pervaporation has also been described for the continuous derivatization and determination of cadmium in leaves [87]. The samples were extracted using a mixture of hydrochloric and peroxide solution with the help of an ultrasonic probe. Then the solution was injected into the system to react with $NaBH_4$ and the volatile hydride was analyzed using an atomic absorption spectrometer. Another application has been that of organotins in wastewater using on-line HPLC/pervaporation/surface-induced luminescence flame photometric detector (QSIL-FPD) [95]. Methyltins, monomethyltin, dimethyltin, and trimethyltin, were separated by HPLC, then reacted on-line with potassium borohydride (KBH_4) to generate volatile hydride products. The volatile compounds were separated from the matrix by pervaporation and further introduced into QSIL-FPD for detection. This method showed the detection limit at ng/mL levels and was used for the determination of methyltin compounds in seawater, wastewater and the process streams from the chemical factory.

The determination of ionic species such as cyanide [91,92], sulfide [10], fluoride [11,21,93], and iodide [20] has been reported using pervaporation coupled to flow injection using the electrochemistry and chemiluminescence as the detection methods. Cyanide in water was converted into hydrogen cyanide by a flow injection system, separated from the matrix by pervaporation, and detected by electrochemical methods [91,92]. The detection limit for cyanide analysis was 0.01 μg/L and sample throughput of the system was 40 per hour [91]. The determination of sulfide in liquid and solid samples was based on the integration of hydrogen sulfide pervaporation and potentiometric detection has been reported [10]. Aqueous samples were injected into acid medium by a flow injection system to form hydrogen sulfide. This diffused through the membrane and was trapped into the acceptor stream for detection. Fluoride has been continuously converted into volatile trimethylfluorosilane by reaction with hexamethyldisilazane, pervaporation, and potentiometric detection

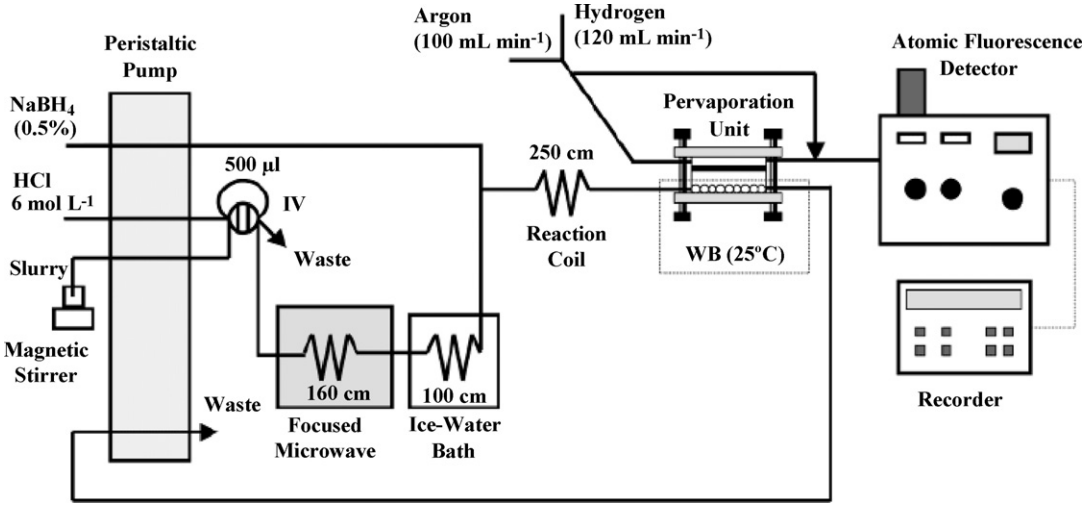

Fig. 13. Determination of arsenic from environmental samples based on microwave-assisted leaching, flow injection, pervaporation, and atomic fluorescence detection. IV is injection valve; WB is water bath [89].

Table 1
Overview of analytical pervaporation applications.

Analyte	Membrane used	Interface	Compounds extracted	Reference
Organic compounds analysis	• Flat sheet, e.g. PTFE (polytetrafluoroethylene), silicone, POMS-PEI (polyoctylmethylsiloxane/polyetherimide) composite, PDMS (polydimethylsiloxane), AA (allyl alcohol), latex (polyisoprene), PVC (polyvinyl chloride), Teflon (copolymer of tetrafluoroethylene and hexafluoropropylene), polyurethane, polyimide, polyethylene, nitrile, PDVF (polyvinylidene fluoride), cellulose, styrene-butadiene-co-styrene (SBS)	GC, GC–MS, FIA-GC, CE-DAD, gas-phase absorptiometry, MS (MIMS), Laser desorption-MS, HPLC-UV	• VOCs in environmental matrices, e.g. tetrachloride, trichloroethene, chloroform, toluene, diclovos, acetone, aldehydes compounds, benzene and derivatives	[6–9,14,18,22–24,43,46–48,52,54,57,58,61,62,64,70,74,75,96]
	Hollow fiber, e.g. polypropylene coated homogenous siloxane, silicone, Nafion™ [copolymer of tetrafluoroethylene and perfluoro-3,6-dioxa-4-methyl-7-octene-sulfonic acid]		• VOCs in food matrices, e.g. ammonia, methanol, ethanol, ethyl acetate, isoamyl acetate and alcohol, anisoles and haloanisoles, ethyl butanoate, limonene, linalool, α-pinene, geranial, neral, α-terpineol • VOCs in fermentors, e.g. acetaldehyde, ethanol • SVOCs in environmental sample, e.g. 4,4′-DDT, PAHs, terbutryne, butylated hydroxyl toluene, naphthalene • SVOCs in pharmaceuticals, e.g. pethidine, benzophenone, cocaine • Atrazine, biphenyl, pentachlorophenol, 2,6-dichlorophenylacetic acid, naphthylacetonitrile, 4-chloro-3-nitrobenzophenone, 1,2-diphenylhydrazine, and 2-chloro-3,4-dihydroxyacetophenone	
Inorganic compounds analysis	• Flat sheet PTFE	Electrochemical detectors, FIA, atomic fluorescence, spectrophotometry	• Metal analysis, e.g. Cd, Hg, As, Sn • Ionic analysis, e.g. iodide, fluoride, cyanide, sulfide	[10,20,21,87–89,92,95]

[11,21,93]. The method was used for the determination of fluoride in pharmaceuticals such as capsules, toothpastes, mouthwash, and nutritional supplement [21], in natural and industrial wastewater [11,93], and in orange tree leaves [11]. Pharmaceuticals and consumer products were prepared by dissolving in water, and ethanol was added in order to avoid foam formation in samples such as toothpaste. Then the sample was injected into a flow injection system. The analyte in solid samples were first extracted by acid and reacted with reagent to form volatile compound. The detection limits were 1.1, 1.5, and 1.3 μg/mL in pharmaceutical, liquid, and solid samples, respectively. Iodides were analyzed by oxidizing with potassium dichromate under acidic conditions to form iodine, which permeated through a membrane. The detection was based on its catalytic effect on the redox reaction of Ce(IV)-As(III), with the decrease in Ce(IV) concentration being monitored spectrophotometrically [20]. This method was applied to analyze iodide in multivitamin tablets. The sample was first dissolved in deionized water, filtered, and processed into anion exchange to remove the interferences before being injected into flow injection-pervaporation system. The detection limit was 0.5 mg/L and the sample throughput was determined as 30 injections per hour (Table 1).

4. Conclusion

Recent developments in pervaporation have been reviewed, and important issues related to these techniques have been emphasized. The application may be classified under broad categories of extraction, concentration and automation. Different approaches that have facilitated direct interfacing with diverse analytical instrumentation including chromatography, MS, spectroscopy and electrochemical devices have been highlighted. The continued development of new membrane structures that provide higher selectivity and extraction efficiency and novel methods for handling for complex matrices will provide new opportunities for membrane pervaporation both in the laboratory research and in commercial products. Novel membrane interfaces for different instrumentation are of great potential that will lead to the development of the next generation of analytical devices including those fabricated on microfluidic platforms.

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