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Pervaporation: a useful tool in food analysis

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Abstract

An overview of applications of analytical pervaporation in food analysis is presented. Various designs of both the analytical pervaporation module and the continuous manifolds utilised are discussed in order to show the versatility of this non-chromatographic continuous separation technique for different challenges encountered in the automation of the overall analytical processes. Examples of the on-line analysis of liquid, semi-solid and solid samples in food and beverage industries are detailed. Finally, the potential of pervaporation as an alternative to commonly used gas–liquid separation techniques is also discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Pervaporation; Continuous separation approaches; Food analysis

1. Introduction

It is often the case that samples obtained from biological and environmental sources are too complex, too dilute and/or incompatible with a suitable detection system for the direct determination of the target compounds of interest. Therefore, preliminary operations such as separation of interferents and preconcentration of the analytes are required prior to analysis.

Although sample pretreatment stages are often the weakest link of the entire analytical method and may be considered as bottlenecks as they are usually very time consuming, often unreliable and inefficient in terms of sample/reagent consumption, the importance of these steps is often overlooked. Traditional separation processes are usually tedious and time-consuming, involve multiple steps of careful operation and are the main areas of contamination risks, particularly in trace analysis.

For these reasons, analytical separation techniques play an increasingly important role in analytical chemistry today. In recent years, many research efforts have been focused on the development of efficient non-chromatographic continuous separation techniques which may be characterised by the presence of at least one flow (liquid or gaseous) of one of the phases involved in the mass transfer (Valcarcel & Luque de Castro, 1991). Unlike chromatographic techniques whose chief aim is the separation of individual analytes, non-chromatographic continuous separation techniques are used principally for the separation of components into groups, the removal of interferences and preconcentration.

Continuous separation techniques which are suitable for use in routine laboratories may be considered as those which feature (a) simple continuous configurations, (b) ease of handling, (c) reduced human participation, (d) short start-up time, (e) robustness, and (f) repeatable, reproducible results. Flow injection (FI) has proved to be an effective auxiliary tool for the implementation of non-chromatographic continuous separation techniques (Valcarcel & Luque de Castro, 1987). Various separation techniques (such as solvent extraction, dialysis, precipitation, gas diffusion and ion-exchange) coupled to FI manifolds have been successfully introduced to routine laboratories, so improving analytical procedures (Fang, 1993; Valcarcel & Luque de Castro, 1991).

Continuous gas diffusion is especially useful in the on-line determination of volatile compounds, as it can increase the selectivity of a particular analytical method by avoiding sample matrix effects and can increase sensitivity through preconcentration. However, this technique suffers from two serious drawbacks, namely: potential clogging of the membrane pores by suspended

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particles or components of a high molecular weight and, deterioration of the membrane through contact with the sample. Fortunately, both shortcomings can be overcome by using pervaporation.

Analytical pervaporation can be defined as the integration of continuous evaporation and gas diffusion processes in the one module. It consists of two steps, the first being the evaporation of volatile species from a heated donor liquid or solid phase; once the species are sorbed and diffused through a porous hydrophobic membrane, they are desorbed in a cool acceptor solution on the other side of the membrane, which may be flowing or stationary (Bell, Gerner & Strathmann, 1988; Luque de Castro & Papaefstathiov, 1998). The temperature difference, which results in a vapour pressure difference across the membrane, provides the driving force for the separation process. One important feature of the performance of an analytical pervaporation module is the air gap between the donor phase and the hydrophobic membrane. This prevents any contact with the membrane by the donor stream so avoiding any problems associated with membrane fouling. Since the analytical pervaporation module is easy to adapt to a continuous manifold, this separation technique allows great simplification and miniaturisation of the preliminary operations, facilitating the automation of the overall analytical process.

In recent years, analytical pervaporation has been successfully used for the continuous determination of volatile analytes or volatile reaction products from complex liquid and solid samples in different areas, including environmental (Bryce, Izquierdo & Luque de Castro, 1996, 1997; Papaefstathiou & Luque de Castro, 1995a; 1997b), clinical and pharmaceutical (Canizares & Luque de Castro, 1996, 1997), and food and industrial analysis (Papaefstathiou, Luque de Castro & Valcarcel, 1996; Prinzing, Ugbomo, Lehn & Schmidth, 1990).

The aim of this paper is to outline the characteristics of the pervaporation module, its coupling to continuous manifolds and the scope of application of this non-chromatographic continuous separation technique in food analysis, in order to demonstrate the real analytical capabilities of pervaporation in this field.

2. The pervaporator

The conventional version of the *analytical pervaporator* used by our group (Mattos, Luque de Castro & Valcarcel, 1995) is presented in Fig. 1. It consists of: (a) a lower donor chamber in which the sample is introduced, either by injection or continuous aspiration for liquid samples, or by direct weighing when dealing with solid samples; (b) a thin PTFE membrane support; (c) spacers of varying thickness (between 2 and 10 mm) located below and/or above the membrane support in order to increase the volume of the respective chamber(s); and (d) an upper acceptor chamber with inlet and outlet orifices, through which an appropriate liquid flows and traps the volatile compounds. The whole pervaporation module (membrane support excluded) is made of methacrylate, which allows the operator to see that the module is functioning correctly. Both chambers (donor and acceptor), the membrane support and spacers are aligned by means of four metallic rods, and close contact of the individual parts is achieved by screwing them between two aluminium supports. The temperature of the donor chamber is adjusted by immersing the module in a thermostatted water bath.

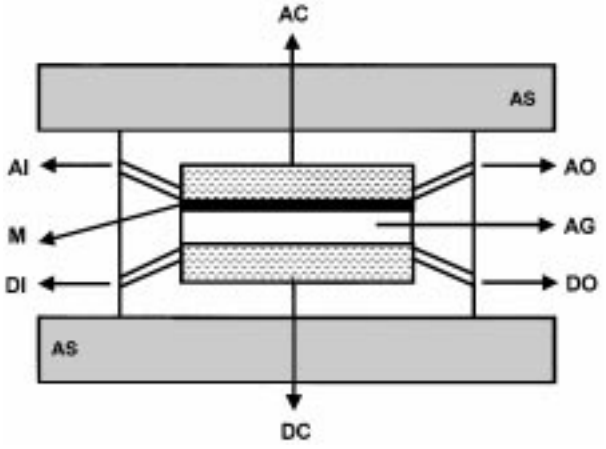

Fig. 1. Conventional pervaporation module: AC, acceptor chamber; AI and AO, acceptor inlet and outlet, respectively; M, membrane; AG, air-gap; DC, donor chamber; DI and DO, donor inlet and outlet, respectively; AS, aluminium support.

Sulistyarti et al. have proposed a hexagonal home-made Perspex pervaporation unit, in which the donor and acceptor chambers have constant depths (5 and 1 mm, respectively); other dimensions are equal for both the donor and the acceptor chambers (length 15 mm and width 10 mm). The membrane is supported on a PTFE membrane support and the temperature is controlled by immersing the donor chamber in the waterbath with a thermoregulator (Sulistyarti, Cardwell, Luque de Castro & Kolev, 1999).

A *microwave-assisted pervaporation* unit, similar to that shown in Fig. 1, has also been proposed (Bryce et al., 1996), constructed in PTFE/methacrylate but without any metal parts for it to function in the presence of microwaves. The whole pervaporation cell has an external diameter of less than 35 mm, in order to fit it inside the chamber of the focused microwave system used to heat the sample.

When the *integration of pervaporation and detection* in the same module is desired, a hole can be drilled in the centre of the upper chamber and the sensor fitted by means of suitable adapters (Papaefstathiou & Luque de Castro, 1995a, 1997b). In this case, the flow of the

acceptor stream is stopped during measurement, and so the kinetics of the mass transfer through the membrane may be monitored.

3. The continuous manifold

It is possible to couple the pervaporation cell to both continuous and discontinuous configurations. A generic FI pervaporation manifold is shown in Fig. 2. The sample is either injected (through a low pressure valve) into the carrier stream or directly aspirated and merged with a reagent (R1), before passing through a mixing coil (RC1). The resulting stream containing the analyte continues to the lower (donor chamber) part of the pervaporation unit, which is thermostatted at a preset temperature. The analyte evaporates, diffuses through the hydrophobic membrane and is collected by the appropriate solution in the upper acceptor chamber. The outlet of the acceptor chamber can be either sent to the detector or mixed with another reagent stream (R2) in order to form a detectable product. By locating the acceptor chamber in the loop of an injection valve, the system can be operated in the stopped-flow mode. When a discontinuous configuration is used, the process cannot be considered as fully automated since the preparation and cleaning of the cell have to be carried out manually.

3.1. Chemical reactions in FI pervaporation manifolds

Undoubtedly, the absence of chemical reactions simplifies enormously the FI configuration; however, there are very few systems where a chemical reaction is not necessary, either to convert the compound of interest into a volatile substance capable of being pervaporated, or to increase the sensitivity and/or selectivity of the determination. When a chemical reaction is developed in any of the subsystems (i.e. before or after the pervaporation cell), additional channels must be connected to the main lines in order to ensure the optimal development of the target reaction(s).

Enzymatic reactions in particular are of special interest in this context. A solid reactor containing the immobilised biocatalyst may be placed between the injection valve and the separation module, allowing the in situ formation of a volatile reaction product before the stream reaches the donor chamber of the pervaporation module (Canizares & Luque de Castro, 1996). Alternatively, an enzyme may be immobilised on a suitable support and be placed in the donor chamber, in order to increase the yield of the catalysed reaction (by displacing the equilibrium to quantitivity), thus avoiding dispersion of the analyte in the carrier solution (Canizares & Luque de Castro, 1997). Similarly, when the enzymatic reaction is used for a post-pervaporation derivatization to obtain a compound suitable for detection, the biocatalyst can be immobilised either in the acceptor chamber (Delgado-Reyes, Papaefstathiou, Fernandez Ramero & Luque de Castro, 1998) or in a reactor placed between the acceptor chamber and the detector (Papaefstathiou, Bilitewski & Luque de Castro, 1996).

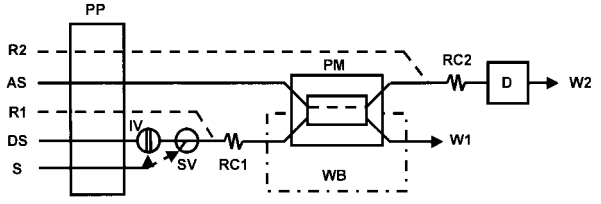

Fig. 2. Generic dynamic manifold-pervaporation assembly: S, sample; DS, donor solution; R, reagent; AS, acceptor solution; PP, peristaltic pump; IV, injection valve; SV, switching valve; RC, reaction coil; PM, pervaporation module; WB, waterbath; D, detector; W, waste.

3.2. Types of samples

The variable volume of the pervaporation module and the air gap inside it has enabled liquid, semisolid and solid samples to be analysed. The introduction of liquid samples to the pervaporation donor chamber may be carried out by means of a peristaltic pump (by continuous aspiration or by injection using a low-pressure injection valve), or by a hypodermic syringe, through a septum located in the inlet orifice of the chamber (Mattos & Luque de Castro, 1994; Papaefstathiou & Luque de Castro, 1995b). The introduction of solid samples is made in a discontinuous manner, weighing the sample directly into the donor chamber and adding the necessary reagents through a septum located at the entrance of the lower chamber (Bryce et al., 1996; Papaefstathiou & Luque de Castro, 1997a). In such cases the pervaporation unit acts as a leaching, derivatization and separation vessel.

3.3. Multideterminations

Multideterminations using pervaporation can be carried out by making some small alterations of some parameters affecting the overall process. The sequential formation of volatile compounds is a common approach for the determination of two analytes in the same sample, illustrated by the determination of ammonium and urea in biological fluids by means of distinct derivatization reactions (Canizares & Luque de Casteo, 1996). Programmed temperature changes during pervaporation assisted by a focused microwave device has been proposed for the speciation of mercury in solid samples (Bryce et al., 1996). The use of two detectors in parallel (potentiometer and spectrophotometer) in the same manifold has been suggested

for the determination of the chemical oxygen demand (COD, expressed as permanganate value) and inorganic carbon (expressed as carbonate) (Papaefstathiou & Luque de Castro, 1997b); in addition, two detectors in series (also potentiometric and photometric) have been reported for the simultaneous determination of SO_2 and CO_2 in wines (Mataix & Luque de Castro, in press). However, for the simultaneous determination of several volatile compounds the use of a highly discriminating separation techniques such as gas chromatography is recommended in conjunction with the FI pervaporation manifold (Papaefstathiou & Luque de Castro, 1997a).

3.4. Pervaporation instead of headspace sampling

One of the most promising uses of pervaporation is as an alternative to headspace methods; with this in mind, the manifolds proposed for mercury speciation (Bryce et al., 1997) and for VOCs (Papaefstathiou & Luque de Castro, 1997a) in solid samples are of special interest. Once the solid sample has been placed in the donor chamber of the pervaporation cell and this has been closed, the cell is thermostatted either in a waterbath or a focused microwave device and connected to a Tenax minicolumn, positioned in the loop of an injection valve. During pervaporation, the volatile compounds are desorbed from the membrane by an argon acceptor stream and preconcentrated on the Tenax minicolumn. The flow of argon is then interrupted, the valve loop is shut off and the minicolumn is placed in a microwave device or a muffle oven, depending of the polar or non-polar nature of the target compounds. The valve is switched to the "inject" position and a helium stream passes through the minicolumn in order to carry the desorbed species to the gas chromatograph. A pyrolysis unit and an atomic fluorescence detector are used for the detection of mercury species, while an electron capture detector is used for VOCs.

4. Scope of application

Owing to the versatility of the design of the analytical pervaporator, it has been successfully used in the analysis of samples with different aggregation state coming from food and beverage industries; the distinct physical properties of the sample matrices require different mechanisms for their introduction and/or treatment in the corresponding analytical manifolds.

4.1. Liquid samples

Fermentation processes obviously play a major role in the beverage industry, where the strict control of the growth and cultivation conditions for microorganisms is mandatory. With this in mind, efforts have been focussed on carrying out real-time bioprocess monitoring with the aid of on-line determination of volatile compounds using different FI-pervaporation assemblies, which avoid the need for any preliminary clean-up or separation steps.

The first such publication was by Prinzing et al. who proposed for the first time the use of an FI-pervaporation arrangement in conjunction with a biosensor for the on-line determination of ethanol and diacetyl during a fermentation process in beer production (Prinzing et al., 1990). For the determination of ethanol, the donor stream was a solution containing yeast extract, peptone and ethanol, while a phosphate buffer was used as the acceptor stream; after the injection of NAD+ into the acceptor solution, the enzymatic reaction, catalysed by alcohol dehydrogenase, yielded NADH as a product, which was monitored fluorimetrically. For the determination of diacetyl, an acetate buffer solution was used as both the donor and acceptor streams; small volumes of NADH were injected into the acceptor solution and, after reaching constant signals for NADH, the donor stream was replaced by a diacetyl standard. The decrease of NADH consumed during the enzymatic reaction catalysed by diacetyl reductase was then measured. In both cases, the pervaporation process avoided inhibition and/or deactivation of the immobilised enzymes by macromolecules, impurities and inhibiting substances in the complex cultivation liquid.

Following this, Ogbomo et al. proposed the continuous determination of ethanol in beer and bakers' yeast culture, based on the separation of ethanol by pervaporation through a porous hydrophobic membrane (Ogbomo, Steffl, Schuhmann, Prinzing & Schmidt, 1993). In this work, the analyte diffusion into the acceptor stream was controlled by an electrical control device situated in the pervaporation module. For its determination, ethanol was enzymatically oxidised either with alcohol oxidase or alcohol dehydrogenase, and the reaction products monitored electrochemically or fluorimetrically, respectively. The use of alcohol dehydrogenase was preferred to alcohol oxidase as it gave the lowest detection limits and greatest stability of the immobilised enzyme. The results showed good reproducibility and satisfactory agreement with those of a common commercial enzymatic test kit. Recently a new automatic-spectrofluorimetric method for monitoring ethanol during wine fermentation has been suggested (Delgado-Reyes et al., 1998). A two-step derivatization reaction involving alcohol oxidase and horseradish peroxidase with fluorimetric detection of the dimer formed was used in order to increase the selectivity and sensitivity of the method. The efficiency of the derivatization reaction was tested using different flow injection approaches, with the biocatalyst both in solution and immobilised, resulting in the use of the first pervaporation module with the enzyme immobilised on the upper

acceptor chamber of the pervaporator. A linear determination range of 0.001–0.002% v/v for ethanol, with a relative standard deviation of 3.9% and a sampling frequency of 5 h^{-1} was obtained.

High diacetyl levels during beer fermentation lead to an unpleasant taste in the final product, prompting Izquierdo et al. to develop an on-line FI-pervaporation system for the determination of this α-diketone (Izquierdo-Ferrero, Fernandez-Romero & Luque de Castro, 1997). The method was based on the condensation of diacetyl using an excess of α-naphtol and creatine in basic medium to form a reaction product which was then monitored spectrophotometrically. The donor stream of the pervaporator was an aqueous solution into which the beer sample was injected, while a solution containing α-naphtol, creatine and sodium hydroxide was used as the acceptor stream. Under optimum experimental conditions, a wide linear range of 10–2000 ng ml^{-1} of diacetyl was obtained, with a relative standard deviation less than 3% and a sampling frequency of 8 h^{-1}. The limits of as detection and determination were found to be 5 and 10 ng ml^{-1}, respectively. The method was applied to the determination of diacetyl in beer from bottled and medium-process samples and showed good agreement with results obtained using the conventional method. Papaefstathiou et al. have also reported an enzymatic method for the determination of acetaldehyde which may also be used for the on-line monitoring of this analyte in fermentors (Papaefstathiou, Bilitewski et al., 1996). The sample was injected into a stream of water flowing through the donor chamber of the pervaporator module thermostated at a preset temperature. Once the analyte evaporated and diffused through the hydrophobic membrane, it came into contact with an acceptor solution containing NAD^+, KCl, and 2-mercaptoethanol dissolved in phosphate buffer. The NADH formed in the enzymatic reaction was monitored spectrophotometrically at 340 nm. Maintaining the pervaporation module at different temperatures allowed a wide determination range between 1 and 100 μg ml^{-1} to be obtained, with relative standard deviations less than 3.5% in all instances. The proposed method was successfully applied to the determination of acetaldehyde in spiked fermentation media.

The development of simple, rapid and low-cost methods for the determination of volatile compounds in fermentation media is one of the principal challenges for routine analysts in the beverage industry. The use of hyphenated FI-pervaporation techniques in conjunction with biosensors offers interesting alternatives for the analysis in this type of complex matrix, as can be seen from the above. Nevertheless, there are other commercial drink samples where the presence of suspended particles could cause severe problems in the on-line determination of volatile compounds; for this reason, the incorporation of a pervaporator could improve the efficiency of the FI manifolds proposed, without the need for clean-up or additional filtration steps. This is the case of the FI-pervaporation manifold proposed for the continuos determination of acetaldehyde in fruit juice samples (Papaefstathiou, Bilitewski & Luque de Castro, 1997). A derivatization Schiff reaction with fuchsin–sodium sulphite in acidic medium was selected for the spectrophotometric determination of the aldehyde at 582 nm. The spiked sample was injected into the aqueous donor stream of the analytical pervaporator; once the compound of interest evaporated and diffused through the polymeric membrane, it was dissolved in a fuchsin ethanolic solution used as acceptor stream and finally merged with a sodium sulphite solution to yield the chromophore compound. In this case, some leakage problems were reported owing to the presence of ethanol used for dissolving fuchsin, which destroyed the PTFE membranes employed. The study suggested the use of hydrophobic membranes with an adequate thickness and pore size in conjunction with the lowest concentration of ethanol required. For these liquid samples, a linear determination range up to 1000 μg ml^{-1} was reported. The method was satisfactorily applied to the determination of acetaldehyde in spiked fruit juice samples of different flavours.

Mataix and Luque de Castro proposed the use of analytical pervaporation for the on-line determination of total and free sulfur dioxide in wine in order to remove SO_2 from the matrix, so avoiding clogging the hydrophobic membrane caused by the presence of suspended particulates principally found in red wines (Mataix & Luque de Castro, 1998). In this case, free SO_2 was determined by injecting the sample solution into donor stream (0.2 M H_2SO_4) in the reactor located before the pervaporator module, for quantitative conversion of HSO_3^- into volatile SO_2; once in the pervaporator module, the analyte evaporated and diffused through the PTFE membrane to be finally accepted by a solution of *p*-rosaniline and formaldehyde, the reaction product being monitored spectrophotometrically at 578 nm. For the determination of total SO_2, the sample solution was injected into a previous reactor, where the basic medium enabled the hydrolysis of SO_2 bound to carbonyl or unsaturated compounds and/or phenol derivatives, and the same procedure as for free SO_2 was followed. The concentration of bound-SO_2 was obtained by difference. A detection limit of 1.2 μg ml^{-1} was reported. The proposed method showed a series of advantages over that recommended by the EU, based on titration with iodine. The same authors have also suggested a FI-pervaporation approach for the sequential determination of total and volatile acidity in wines, in order to both automate the determination of the two acid-related parameters of wine and avoid shortcomings arising from the separation of the volatile species (Mataix & Luque de Castro, 1999). For these purposes,

two sample aliquots were simultaneously injected into the FI manifold through distinct injection valves; using bromothymol blue as indicator in an aqueous acceptor solution, one of the samples was merged and transported to the spectrophotometer in order to monitor the total acidity. Meanwhile, the second sample passed through the pervaporation module to facilitate the separation of the volatile acidic species, which were entrapped in a static acceptor solution of the same indicator. This allowed preconcentration and subsequent determination. Using this procedure the overall analysis was carried out in 12 min. Under the optimum experimental conditions, determination limits of 10 and 20 μg ml^{-1} for total and volatile acidity were obtained, as well as linear ranges which were adequate for their monitoring during wine production.

Potentiometric and photometric detectors have been used in series for the determination of CO_2 and SO_2 in wine after pervaporation. The method was based on monitoring the pH-change of the acceptor solution caused by the two volatile analytes and subsequent individual photometric determination of SO_2 by the coloured product it forms with *p*-rosaniline and formaldehyde. The results obtained are in excellent agreement with those provided by the official methods for these analytes (Mataix & Luque de Castro, in press).

4.2. Semi-solid samples

For the analysis of highly viscous samples, weight instead of volume is preferable for reproducible sampling; therefore the discontinuous introduction of the sample and use of a continuous analytical procedure is recommended. This is the case with the semiautomatic spectrophotometric determination of acetaldehyde in semi-solid food samples after pervaporation and derivatization steps (Papaefstathiou, Bilitewski et al., 1997). The FI-pervaporation manifold was similar to that used for the determination of acetaldehyde in liquid samples, but some changes were necessary for the introduction of sample and reagents. First, a portion of the semi-solid sample was accurately weighed into the lower chamber of the pervaporator before the module was closed. Appropriate volumes of a citric acid solution and water were injected into the lower chamber by syringe and hypodermic needle through a septum located in its inlet, while a screw closed the outlet; the pervaporator with magnetic stirrer was immersed in a thermostatted waterbath. A few minutes were allowed for the preconcentration in the acceptor stream, allowing the signal corresponding to the acetaldehyde concentration to be measured. The proposed method was satisfactorily applied to the determination of the analyte in yoghurt samples, where acetaldehyde is obtained as a byproduct during lactic fermentation and is mainly responsible for its taste.

4.3. Solid samples

The analytical pretreatment of solid samples is one of the main shortcomings in many routine analyses developed in food industry. For this reason, the reduction in the sample manipulation that non-chromatographic separation techniques such as pervaporation offer is of great interest.

Garcia-Garrido and Luque de Castro (1997) have reported a FI pervaporation approach for the determination of trimethylamine in fish samples, an important parameter in the evaluation the freshness of fish. In this method the solid sample was accurately weighed into the donor chamber, and several reagents injected through septa located in the inlet and outlet orifices of this chamber: trichloroacetic acid for leaching the analyte, formaldehyde for masking other amines and sodium hydroxide for the formation of the volatile form of the analyte. After a preset interval to allow the pervaporation of the volatile species and the preconcentration in the acceptor solution of bromothymol blue, the pH change was determined photometrically. The method showed linearity between 2 and 30 μg ml^{-1} of trimethylamine, with precision of 4.7% and a sample throughput of 8 samples h^{-1}.

Papaefstathiou, Bilitewski et al. (1997) have determined acetaldehyde in grated bread samples, using pervaporation for the removal the target analyte from its matrix. A derivatization reaction between acetaldehyde and fuchsin in acidic medium was developed for the formation of an alkylsulphonic acid chromophore, determined spectrophotometrically. Satisfactory recoveries were obtained.

5. Potential of pervaporation

As a non-chromatographic continuous separation technique, pervaporation offers the following advantages: (a) it is easily coupled to automatic analysers, (b) it reduces manual handling of toxic reagents and solvents, (c) it improves the precision by reducing human errors, (d) substantially increases sample throughput, (e) reduces sample and reagent consumption, and (f) lowers analytical costs. However, additional advantages offered by pervaporation over some other common separation techniques should also be mentioned at this point.

5.1. As an alternative to gas diffusion

The on-line monitoring of evolving systems (e.g. fermentation processes), the routine analysis of liquid samples with solid particles in suspension or the direct analysis of solid samples are all cases in which pervaporation offers considerable advantages over gas diffusion.

These advantages are due to the presence of the air gap in the pervaporation module which avoids contact between the sample and the membrane, thereby avoiding the clogging of the membrane pores by suspended particles or components of high molecular weight, while increasing the lifetime of the membrane in routine analysis. Since the sample does not come into contact with the separation membrane, higher temperatures can be applied in the separation process than in gas diffusion, hence improving the mass transfer efficiency.

5.2. As an alternative to distillation

Continuous microdistillation modules coupled to FI manifolds are of great complexity, involving a large number of channels, propulsion modules and connectors. In addition, long start-up times are required, the sample is continuously aspirated into the system and so unusually large sample volumes are handled.

Taking into account the characteristics of continuous microdistillation, it is easy to understand its convenient substitution by pervaporation, which is characterized by simplicity, ease of automation and possibilities for miniaturisation.

5.3. As an alternative to headspace sampling

The use of a pervaporation module instead of a headspace sampling device in gas chromatography offers advantages such as: (a) low equilibration times, owing to the presence of the constant-volume air gap chamber which requires very small amounts of the analytes to establish equilibrium conditions; (b) the favourable displacement of the mass-transfer equilibrium produced by the continuous removal of the target compounds through the membrane; (c) easy automation of the overall analytical procedure by means of its coupling to a FI manifold; and (d) protection of the chromatographic column from water, due to the use of a hydrophobic membrane in the pervaporator. Thus, pervaporation can be considered as an interesting alternative to the existing headspace methods for the determination of volatile organic compounds such as aliphatic aldehydes or the trimethylsilyl derivatives of aliphatic and aromatic carboxylic acids, to mention only a few.

The determination of aroma compounds in wine, smoke or fruits, methyl isothiocyanate in wine, organochlorine pesticides in water, volatile dairy products, flavours in food products, and for the identification of frauds in spices and food aroma are examples of the wide variety of cases in which the use of pervaporation in the automation of complex analyses in the food and beverage field can be implemented.

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