PERVAPORATION: A TECHNIQUE WITH A PROMISING FUTURE IN ENVIRONMENTAL ANALYSIS

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ABSTRACT

An overview of the potential of analytical pervaporation in environmental analysis is hereby presented. A classification of the methods proposed so far is done according to the aspects of the separation modules and the energy favouring the process, the samples used, the analytes determined, the derivatization reactions used, the detectors employed and the techniques to which the pervaporation unit is coupled; all possibilities discussed verify the usefulness of pervaporation in the study and monitoring of parameters in environmental samples.

Keywords: Pervaporation; environmental analysis; separation technique

INTRODUCTION

Non-chromatographic continuous separation techniques are promising alternatives to chromatographic ones as they permit overcoming various analytical problems associated with preliminary operations, are easily coupled on-line with many instruments and increase sampling frequency with low sample and reagent consumption and acquisition and maintenance costs. Moreover, they can improve both the sensitivity of an analytical method by including preconcentration steps and its selectivity, as they avoid matrix effects and eliminate interfering species. Membrane-based non-chromatographic continuous separation techniques are especially useful for improving selectivity and, sometimes, sensitivity /1/.

Pervaporation, a separation technique based on the use of membranes, has been for long used in the industry and recently proposed for analytical purposes /2,3/. Analytical pervaporation can be defined as the integration of an evaporation and a gas diffusion step in the same module. The volatile analyte (or its volatile reaction product) present in a heated donor phase evaporates through a porous membrane and the vapour condenses in contact with a cool acceptor stream on the other side of the membrane. The temperature difference, which results in a vapour pressure difference across the membrane, is the driving force for the separation. A pervaporation module designed for analytical purposes (Fig. 1) consists of the following parts: an upper, acceptor chamber fitted with inlet and outlet orifices through which the acceptor stream (liquid or gas) is circulated and in which the pervaporated analyte (or its volatile reaction product) is collected; a lower, donor chamber where the feed stream is circulating; a membrane support of small thickness and spacers of varying thickness which can be placed below or above the membrane support so as to increase the volume of the corresponding chambers. The module is normally made of methacrylate, a transparent material that allows continuous checking of the performance of the unit (i.e. checking the liquid level in the donor chamber and the appearance of the membrane). The different parts of the pervaporation module are aligned by inserting metallic rods in the drilled orifices and a closer contact is achieved by screwing them together with four screws between two aluminium supports. The temperature enhancing the process is adjusted by immersing the lower part of the module in a thermostated waterbath /4,6,10,11/. An important characteristic of analytical pervaporation is the presence of an air gap between the sample in the donor chamber and the membrane, thus avoiding any contact between them and diminishing the problems associated with membrane fouling.

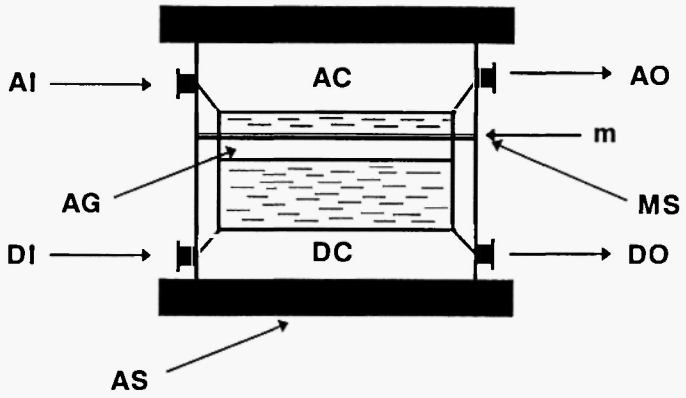

Fig. 1: Conventional pervaporation module. AC: acceptor chamber, DC: donor chamber, MS: membrane support, m: membrane, AG: air gap, AS: aluminium supports, AI/AO: acceptor inlet/outlet, DI/DO: donor inlet/outlet.

The present article is aimed at the presentation of the already existing information referring to the determination of various analytes in samples of environmental origin in order to show the unexploited potential of the technique in this field.

CLASSIFICATION OF APPLICATIONS OF ANALYTICAL PERVAPORATION

Various aspects of analytical pervaporation can be taken into account when it comes to the classification of the methods described in the literature, employing this separation technique. This can be done according to the nature of the samples referring to liquid or solid ones, to the type and number of analytes to be determined, to the derivatization reactions employed either for the formation of the volatile species or for the determination of the reaction product, to the modules and corresponding energy types, to the configurations used, to the coupling of the technique with gas chromatography or to the detectors employed. In the following sections, the above mentioned aspects of the pervaporation separation technique are discussed.

Sample Types

The versatility of the design of the analytical pervaporator, attributed to its changeable donor volume and the air-gap present above the sample, has permitted its use with both liquid /4,6,7/ and solid samples /5,8-11/. The configuration used in these cases is shown in Fig. 2.

The introduction of liquid samples to the lower, donor chamber of the pervaporation cell can be done either 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 at the entrance of the chamber. The former sample introduction mode is employed when the sample is available in relatively large quantities, whereas the latter is used when this is scarce; in this case, the configuration used is a hybrid between a continuous and a discontinuous manifold.

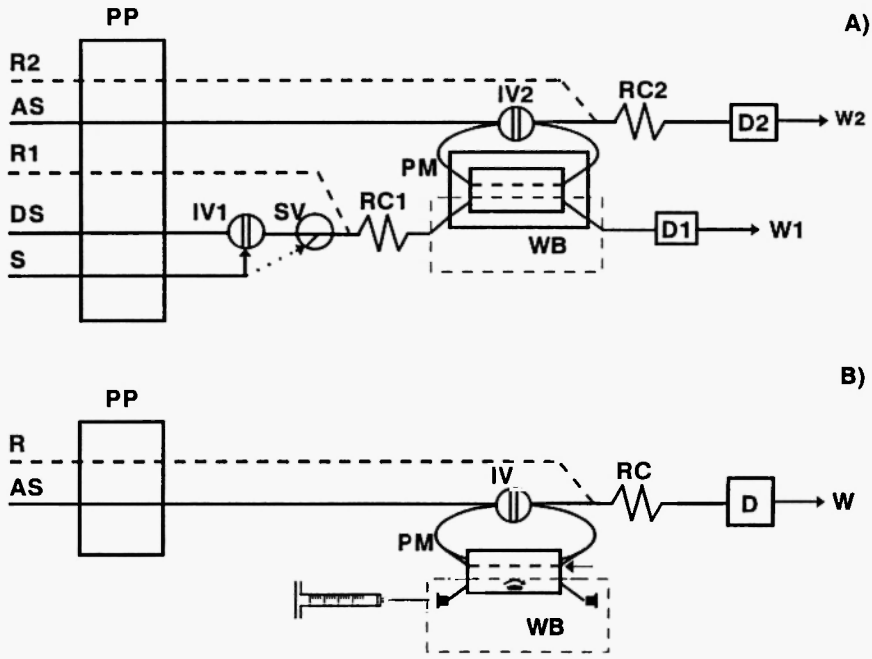

Fig. 2: Dynamic configuration-pervaporation assemblies A) for liquid samples and B) for solid samples. PP: peristaltic pump, IV: injection valve, SV: selection valve, RC: reaction coil, PM: pervaporation module, WB: water bath, D: detector, w: waste, S: sample, DS: donor stream, AC: acceptor stream, R: derivatization reagent.

The most interesting application of pervaporation is that referring to the direct introduction and treatment of solid samples in the separation unit /5,8-11/. The relatively big volume of the donor chamber, which can be further increased by the location of spacers of adequate thickness, permits direct weighing of the solid, as well as addition of the reagents necessary for analyte leaching and its possible derivatization by injection through a septum located at the entrance of the lower chamber, after the separation cell is tightly closed. The analytical pervaporator hence works simultaneously as a leaching, derivatization and separation vessel; excessive sample manipulation is avoided and therefore no losses of analyte occur. The analytical configuration is similar to that used for scarce liquid samples, that is a combined continuous/discontinuous manifold.

Types of Analytes

Analytical pervaporation can be used for determination of a single analyte or of number of them, being of both inorganic /4-9/, organic /7,10/ and organometallic nature /3,11/. The most common methods are referring to the determination of a single analyte and those reported up to now are concerned with the determination of fluoride in wastewater and orange tree leaves /4,5/ and of sulphide in Kraft liquors /6/.

Multideterminations can be achieved by manipulation of parameters affecting the pervaporation process (for instance, by varying the pervaporation temperature). These can be carried out in a simultaneous manner, either by using two detectors /7/ or by coupling the separation unit to a highly discriminating separation device /10,11/, or sequentially /8,9/. The speciation of nitrogen (as ammonium and urea) in soil samples constitutes an example of sequential formation of volatile compounds /8/. The sample is directly weighed in the lower chamber of the pervaporation cell, which is shut after locating the membrane and the acceptor chamber together with the ammonium selective electrode. The baseline is obtained upon propelling the acceptor solution through the upper chamber. NaOH is injected to the sample for conversion of ammonium into volatile ammonia, separated by pervaporation at a preset temperature; the flow of the acceptor solution is stopped and the signal is recorded. The flow is then restored, the sample is neutralized and its pH is regulated by addition of a certain buffer volume. Finally, a given volume of urease is added catalyzing the conversion of urea to the volatile ammonia. The detection is done in the same way as for ammonium.

Two detectors have been simultaneously used for the determination of chemical oxygen demand (COD, expressed as permanganate value) and inorganic carbon (expressed as carbonate) /7/. The sample is injected into a stream of sulphuric acid and it is finally mixed with a potassium permanganate solution (prepared in the same concentration of sulphuric acid), while passing through a 100 cm reaction coil. The product of the chemical reaction is led to the lower chamber of the pervaporation cell thermostated at the required temperature, from where the carbon dioxide formed evaporates and diffuses through a hydrophobic PTFE membrane to be accepted by a static CO_3^{2-}/HCO_3^- buffer. The change of the pH of this stream is measured by the pH-electrode located on top of the acceptor chamber of the separation unit. At the same time, the outlet of the donor chamber is led to a spectrophotometer, where the fading of the colour of the permanganate solution is measured at 525 nm. After the necessary time of stopping the flow at the upper chamber, this is restored so as to remove the carbon dioxide that was accumulated in the static acceptor solution. All variables affecting the performance of the system (including chemical parameters, hydrodynamic and pervaporation ones) were studied and calibration curves were run for both the spectrophotometric and potentiometric determination of COD and for the potentiometric determination of inorganic carbon with respective limits of detection of 0.13 mg O_2 l^{-1}, 0.45 mg O_2 l^{-1} and 48.6 mg CO_3^{2-} l^{-1}. The carbonate content and the chemical oxygen demand were determined in bleaching liquors, as well as in water samples of different origin and the proposed method was validated by studying recoveries at different concentration levels. The latter were varying between 91.8 and 107.9 %, with precision (expressed as r.s.d.) varying between 0.18 and 1.73 % (for n=3).

Types of Derivatization Reactions

As previously mentioned, pervaporation is employed for the separation of volatile analytes present in a given matrix or of the volatile derivatives of the analytes to be determined. The formation of the latter is done by the addition of the appropriate reagent to the sample either continuously /4,6,7/ or by direct injection to the matrix /8,9/. A derivatization reaction is often required for the formation of the species to be finally detected. These possibilities are clearly demonstrated in Fig. 2 and have been employed for the determination of fluoride in samples of complex matrix /4,5/, of sulphide in white and green bleaching liquors used in paper industry /6/, for the simultaneous determination of chemical oxygen demand

(expressed as permanganate value)/inorganic carbon /7/, for the sequential determination of ammonium and urea in soil samples /8/, as well as for the determination of inorganic and organic mercury compounds in a sewage sludge CRM /9/.

An example of the use of derivatization reactions for the formation of both the volatile compound and the product finally detected is given in the method employed for the determination of sulphide in Kraft liquors /6/. The sample is injected or directly aspirated into a buffer stream solution of pH 1.16 and mixed with it, forming the volatile product hydrogen sulphide, which is led to the lower chamber of the pervaporation cell thermostated at the required temperature. From there, it evaporates and diffuses through a hydrophobic PTFE membrane to be finally accepted by a p-dimethylaminoaniline stream, prepared in acidic medium. The outlet of the upper chamber is consequently merged with an oxidant solution to yield the coloured product, which is finally monitored at 670 nm. The calibration curves obtained for injection and continuous aspiration of the sample were linear in the range between 1-15 mg l^{-1} and 1-10 mg l^{-1}, respectively and with detection limits of 0.68 mg l^{-1} and 0.42 mg l^{-1}. The method was applied to the determination of the analyte in both green and white bleaching liquors and the results were compared to those obtained by the conventional photometric method of methylene blue. The recoveries varied between 87.3 and 104.6% with a good precision (r.s.d., %), varying between 0.7 and 5.8%.

Types of Pervaporation Modules-Energy Types

The pervaporator used for analytical purposes in its conventional version corresponds to the one already described in the "Introduction" section.

When separation and detection of the volatile species occur simultaneously, the design of the pervaporation unit, which consists of the same parts as the conventional module, is slightly modificated. The separation module is provided with a hole drilled at the centre of the acceptor chamber top, permitting the accomodation of the sensor by suitable adaptors. During measurement, the flow of the acceptor stream is stopped so as to enable accumulation of the analyte and therefore increase the sensitivity of the method /5,7,8/. The determination of fluoride in both liquid and solid samples has been thus achieved. The method is based on integration of pervaporation and potentiometric detection /5/. In the configuration used for liquid samples, the volatile trimethylfluorosilane formed

after mixing the sample with the derivatizing reagent in acidic medium is either injected or continuously aspirated and consequently led to the donor chamber of the pervaporation cell, from where it pervaporates through a PTFE membrane to be accepted by a static buffer stream. The fluoride formed by hydrolysis of the volatile product is simultaneously monitored by the fluoride-selective electrode located on top of the acceptor chamber. When solid samples are employed, a certain amount of them is directly weighed in the lower chamber of the cell, which is then tightly closed. The acceptor buffer stream is circulated through the upper chamber, its flow is then halted and the baseline obtained. The appropriate volumes of the reagents necessary for the extraction of fluoride from the solid matrix and its conversion into the volatile derivative are added through a septum located at the inlet of the donor chamber and the pervaporation/potentiometric detection module is located in a thermostated magnetic stirrer. The extraction of the analyte, its reaction with the derivatizing reagent, the evaporation of the volatile product, its transfer through the membrane to the acceptor buffer solution and continuous monitoring of the fluoride released take place simultaneously. After optimizing the variables affecting the determination in both types of samples, calibration curves were run with linear ranges between 2.5 -100 mg l^{-1} and 100-500 mg l^{-1} for liquid samples and 2.5-100 mg kg^{-1} for solid samples. The method was applied to liquid samples including wastewaters and dissolved fertilizers with good recoveries and precision (varying between 88.9 and 113.6 %, with r.s.d. varying between 2.7 and 4.5 %). The applicability of the proposed method to solid samples was evaluated by determining the analyte in orange tree leaves. The recoveries in this case ranged from 92.9 to 103.3 % at two analyte concentrations with r.s.d. ranging between 0.8 and 3.7 %.

Microwaves can be used as an energy source for pervaporation of polar analytes that have relatively high boiling points and cannot be efficiently removed from the matrix by conventional heating. The module designed for this purpose is similar to the conventional pervaporation unit but its dimensions are smaller, so that it can be located inside the microwave vessel. The cell is entirely constructed from PTFE/methacrylate (including screws and outer supports), as no metallic parts can be inserted in the microwave vessel /9/. This type of module has been employed for the speciation of mercury in solid samples using atomic fluorescence detection. The sample is weighed in the donor chamber of the cell, which is closed and connected to the loop of an injection valve, acting as a selection valve. In this way, the baseline is obtained, as the carrier stream is continuously flowing to the

detector. A certain volume of $SnCl_2$ is injected to the solid sample for the determination of inorganic mercury. The cell is placed inside the microwave vessel and the device is switched on for a pre-set time. The carrier is then diverted by means of the selection valve through the acceptor chamber of the pervaporation cell, driving the elemental mercury formed first to the gas-liquid separator and then to the detector. After obtaining the signal, the selection valve is turned to its initial position isolating the pervaporation cell and preparing the system for the next measurement. Then, a given volume of an oxidising solution containing $Br^-/BrO_3^-/HCl$ followed by the addition of $SnCl_2$ for phenyl mercury acetate determination is injected to the sample and the elemental mercury formed is separated and determined as before. The calibration curve obtained was linear in the concentration range of 10-500 $\mu g\ kg^{-1}$ with a precision of 1.8%, expressed as r.s.d. The method was then applied to the determination of both inorganic and organic mercury in a sewage sludge CRM and the total content in mercury found was compared to the certified value. A recovery of 84.5% was obtained.

The use of ultrasounds for degassing solutions as well as for extraction of analytes from solid matrices has led to the conclusion that this energy form could be employed in order to favour the pervaporation process. However, some experiments done have not resulted in an enhancement of the efficiency of the process as analyte losses were observed, due to the removal of the silicone paste used to seal the cell.

Types of Continuous Manifolds

The pervaporator can be coupled to both continuous and discontinuous configurations, as shown in Fig. 2. The sample is either injected into the carrier stream or directly aspirated and mixed (or not) with a reagent while passing through a mixing coil. The mixture is led to the lower chamber of the pervaporation unit, thermostated at the required temperature. From there, the volatile analyte or its volatile reaction product evaporates and diffuses through the membrane and is accepted by an appropriate stream of a liquid solution (with which it may react or not) or of a gas. The location of an injection valve with its loop positions connected to the inlet and outlet of the acceptor chamber permits operating in the stopped-flow mode. When this valve is in the "load" position, the pervaporated analyte is collected at the static acceptor solution at the upper part of the module, whereas the flow to the detector remains uninterrupted and the baseline is hence

obtained. By switching the valve to the "inject" position, the preconcentrated analyte is driven to the detector for quantification. The non- volatile species present in the donor chamber may be led to another detector directly or after a derivatization reaction. The outlet of the acceptor chamber of the cell may be directly driven to the detector or may be mixed with an additional stream of reagent in order to give the product finally detected. This configuration has been used for the determination of fluoride in samples of complex matrix /4/. The analyte is converted to the volatile trimethylfluorosilane by reaction with hexamethyl-disilaxane (HMDSA); this evaporates and diffuses through a PTFE membrane to be accepted by a NaOH solution. The outlet of the pervaporation cell is then merged with an acetic acid/KCl stream and led to the potentiometric detector. When working in the continuous mode, the mixture sample-HMDSA is injected into a sulphuric acid stream and led to the pervaporation cell whereas when working in the stopped-flow mode the mixture sample-HMDSA is continuously led to the lower chamber of the cell and the volatile product is accumulated in the static NaOH solution. After the necessary preconcentration time, the injection valve, at the loop positions of which the acceptor chamber of the cell is connected, is turned to the "inject" position and the basic stream containing the fluoride is merged with the acetic acid/KCl solution and driven to the potentiometric cell for monitoring. The method showed good linearity for both operation modes with good precision (r.s.d. 2.6% for injection of the mixture and 3.6% for continuous aspiration of it) and it was applied to the determination of the analyte in water samples, dissolved fertilizers and wastewater samples. The recoveries obtained at two concentration levels ranged between 87.2 and 106.1 %.

When a discontinuous configuration is used, the process cannot be fully automated since the preparation of the cell as well as its cleaning have to be done manually. The upper part of the configuration is in principle similar to the one described in the previous paragraph; in the case of employing a sensor located on top of the pervaporation cell, the flow of the acceptor stream is stopped so as to accumulate the pervaporated analyte and simultaneously measure it.

Types of Coupled Techniques

Pervaporation has been already coupled to a gas chromatograph /10,11/, constituting in this way an alternative to headspace sampling techniques having substantial advantages with respect to both static and dynamic headspace modes,

such as speed (equilibrium conditions are rapidly reached), increased separation efficiency (through displacement of the mass transfer equilibrium, since the volatilized analytes are continuously separated), ease of automation of the whole process (dynamic regime) and simplification (absence of the condenser necessary in dynamic headspace for removing water vapours, because the presence of the hydrophobic membrane in pervaporation prevents their passage to the chromatographic column). The two methods proposed refer to mercury speciation and to the determination of volatile organic compounds (VOCs) in solid samples, using an atomic fluorescence detector and an electron-capture detector, respectively. Both use the same experimental assembly shown in Fig. 3, by which the analytical process takes place in the following steps:

Pervaporation of the Analytes:

An adequate amount of the solid sample is placed in the donor chamber of the pervaporation cell, which is closed after locating the membrane support, the membrane and the acceptor chamber. The separation unit is then connected to the system and placed in a waterbath at the required temperature. The analytes evaporate into the gas layer above the sample and then diffuse through the membrane to be accepted by the gaseous acceptor stream.

Preconcentration/Desorption of the Pervaporated Analytes:

This is made possible by the location of a low-pressure injection valve for mercury speciation and a high-pressure one for VOCs) connected to the chromatographic injector through a hypodermic needle or located between the carrier gas entrance to the gas chromatographic column and the split ratio flow controller, respectively. The flow of the gas stream leaving the cylinder is divided in two streams, one of them passing through the upper chamber of the pervaporation unit and entering the injection valve through the sample entrance position while the other is connected to the carrier entrance position. In this way, when the injection valve is in the "load" position, the pervaporated analytes crossing the membrane are preconcentrated in the Tenax minicolumn, connected at the loop positions of the valve and situated in an ice bath; meanwhile, the flow of the carrier gas to the chromatographic column is uniterrupted. For desorption of the retained analytes, the Tenax minicolumn is removed from the ice bath and

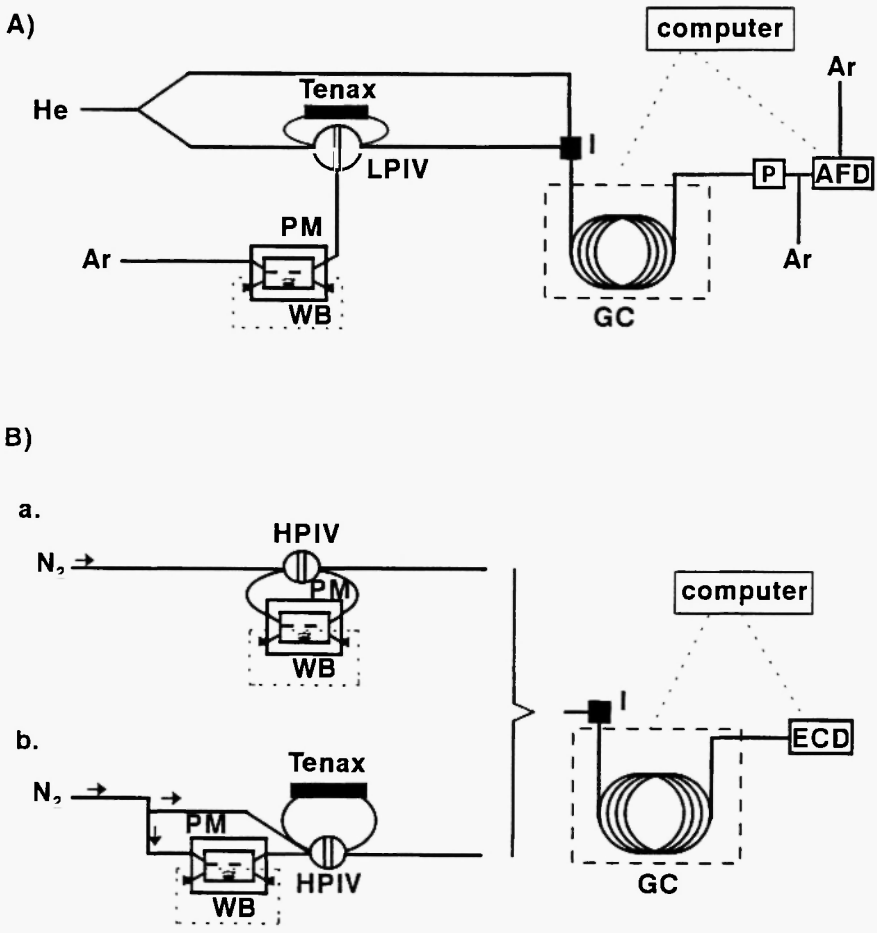

Fig. 3: Gas chromatography-pervaporation coupling for determinations in solid samples. A) Mercury speciation and B) VOCs determination a. without and b. with preconcentration. LPIV: low pressure injection valve, HPIV: high pressure injection valve, I: injector (gas chromatograph), GC: gas chromatograph, P: pyrolysis unit, AFD: atomic fluorescence detector, ECD: electron capture detector. Other abbreviations as in Fig. 2.

placed in a muffle oven at the necessary temperature. The valve is then changed to the "inject" position and the desorbed analytes are driven to the chromatographic column.

Chromatographic separation:

The carrier stream containing the desorbed compounds enters the injector in a continuous mode either through the septum of the injector inlet (when a low pressure valve is used) or directly to the injector liner (in the case of employing the high pressure valve). The chromatograph oven is programmed as required and the species are separated.

Detection of the separated species:

In the case of mercury speciation, the species emerging from the column are passed through a pyrolysis unit set at a high temperature in order to break the compounds down to elemental mercury. This stream is consequently mixed with a make-up gas on its way to the detector. A second stream of the same gas is used as sheath gas, increasing the reproducibility as the gas flow is maintained in the beam of the atomic fluorescence detector. VOCs do not require any pyrolysis unit and therefore the analytes after their separation in the chromatographic column are directly driven to the electron-capture detector for quantification.

The determination ranges obtained for mercury species were 0.595-5.95 μg kg^{-1} for Me_2Hg, 1.61-50.52 μg kg^{-1} for Et_2Hg and 518-25910 μg kg^{-1} for MeHgCl with respective limits of detection of 0.25, 0.41 and 255 μg kg^{-1}. The proposed method was successfully applied to the determination of the first two analytes in added soil and sewage sludge CRM providing recoveries which vary between 94.7 and 107.8%. The calibration curves run for VOCs determination were linear between 1-50 μg kg^{-1} for $CHCl_3$ and CCl_4 and between 5-50 μg kg^{-1} for C_2HCl_3, having detection limits of 0.98, 0.57 and 4.42 μg kg^{-1} respectively. The application of the proposed methodology to spiked soil samples of different composition confirmed the characteristics of the method (recoveries varying between 83.3 and 116.5%).

Detector Types

Both molecular and atomic detectors can be coupled to a pervaporation unit through an adequate interface, such as a transport tube, a minicolumn packed with an adsorptive or ion-exchange material, a gas-liquid separator etc. The acceptor stream can be either a liquid or a gas, depending on the characteristics of the detector. The detectors that have been used in conjunction with a pervaporator are

spectroscopic, including both atomic (atomic fluorescence detector) /9/ and molecular (spectrophotometric and spectrofluorimetric detectors) ones /6,7/, electroanalytical (potentiometric detectors) /4,5,7,8/ and detectors used in gas chromatography (electron-capture detector) /10/.

CONCLUSIONS

The versatility of the above mentioned separation technique has already permitted its use with a variety of samples including both liquid and solid ones. The air gap between the sample in the donor chamber and the membrane could make possible the use of pervaporation for monitoring parameters during, for instance, the aerobic or anaerobic biodegradation of wastewater or for continuous monitoring of evolving systems, as well as for the determination of various analytes in slurries not subjected to any previous treatment; the only requirement in the latter case would be the use of PTFE tubing and of inlet and outlet channels of the donor chamber of a larger internal diameter, so as to avoid their possible clogging. The possibility of employing derivatization reactions prior to or after the separation step broadens the application field of the technique to a variety of analytes and, at the same time, permits the coupling of the unit to several types of detectors. The use of pervaporation instead of headspace sampling in gas chromatography constitutes one of the most attractive applications of the technique to environmental samples, as it offers an alternative to the existing EPA methods for the determination of volatile organic compounds in solid samples and can be used for speciation studies.

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