

Short communication

Hyphenated pervaporation–solid-phase preconcentration–gas chromatography for the determination of volatile organic compounds in solid samples

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Abstract

The use of pervaporation as an alternative to headspace is proposed, using as an example the determination of three chlorinated solvents (i.e., chloroform, carbon tetrachloride and trichloroethene) in solid samples. For this purpose, a pervaporation module has been coupled to a gas chromatograph equipped with a ^{63}Ni electron-capture detector. The assembly was provided with a HPLC injection valve, whose location enabled two operation modes to be implemented: with and without preconcentration. When no preconcentration was carried out, the detection limits were 17.4 ng/g for CHCl_3 , 14.0 ng/g for CCl_4 and 182.6 ng/g for C_2HCl_3 , whereas when the analytes were preconcentrated on the sorbent column, the detection limits decreased to 0.98 ng/g, 0.50 ng/g and 4.42 ng/g, respectively. The proposed method was applied to soil matrices with good recovery and precision. © 1997 Elsevier Science B.V.

Keywords: Pervaporation; Sample handling; Membranes; Soil; Volatile organic compounds

1. Introduction

Volatile halogenated hydrocarbons belong to the category of volatile organic compounds (VOCs), frequently used as solvents; therefore their presence in the environment is commonplace. They can also be originated from natural sources and they are easily absorbed by human beings. The methods proposed so far for their determination in water, soil and air usually involve gas chromatography (GC)

coupled to dynamic [1–4] or static [5–7] headspace analysis using selective [3,5,6,8] or non-selective [1,4,9–12] chromatographic columns and different detectors [1–3,9] with a preference towards electron-capture detectors [5,8,10,13].

Various methods have been reported on the determination of VOCs by GC, making use of membrane extraction techniques, followed normally by the preconcentration of the analytes on an adequate trap. Subsequently, desorption is done either by application of an electric pulse or by heating at elevated temperatures [11,14–19].

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In industry, pervaporation has found application to the selective separation of a liquid feed mixture using a non-porous polymeric membrane and it is based on the relative rates of permeation through the membrane [20]. On a laboratory scale, pervaporation has been recently employed for withdrawing volatile compounds from a complex matrix. Volatile substances in a heated donor stream evaporate through a porous hydrophobic membrane and the vapor condenses on the surface of a cool acceptor stream on the other side of the membrane. The most important difference between analytical pervaporation and gas diffusion lies upon the presence of an air gap between the process fluid and the membrane, which avoids any contact between them and, hence, diminishes the problems connected with fouling of the membrane [21–24]. In this sense, pervaporation has been successfully applied to the determination of various analytes in both liquid and solid matrices [25–27].

In the present work, the coupling of a pervaporation module to a gas chromatograph for the determination of chlorinated solvents in solid samples is described. Placing a sorbent minicolumn at the outlet of the acceptor chamber of the pervaporation cell enables the preconcentration of the analytes, thus

improving the sensitivity of the proposed method. The desorption of the retained analytes is achieved by heating at 200°C.

2. Experimental

2.1. Instruments and apparatus

The pervaporation–gas chromatograph assembly with and without solid-phase preconcentration is presented in Fig. 1. It consisted of an HPLC injection valve, the pervaporation unit, the gas chromatograph and the computer used for the acquisition and processing of the experimental data and delivery of the results.

A modification of the gas chromatograph was necessary in order to divert the flow of nitrogen either through the upper part of the pervaporation cell or through the preconcentration column, then drive the analytes to the chromatographic column. This was achieved by placing the HPLC injection valve (Rheodyne 7125) between the inlet of the carrier gas to the split ratio flow controller and the inlet of the carrier gas to the injector. When working

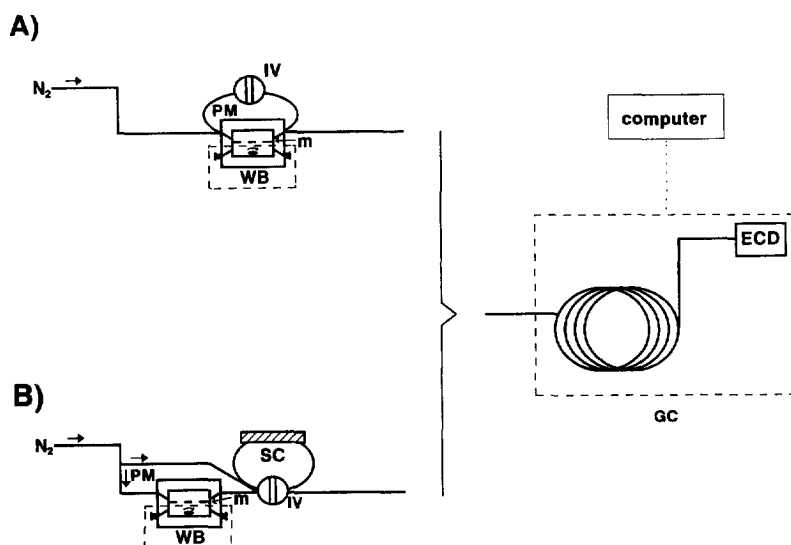


Fig. 1. Pervaporation–GC–ECD assemblies for the determination of VOCs in solid samples. (A) Without preconcentration step. (B) With preconcentration of the analytes on a sorbent minicolumn. N₂, nitrogen (carrier); PM, pervaporation module; m, membrane; WB, water bath (80°C); SC, sorbent minicolumn; IV, high pressure injection valve (HPLC); GC, gas chromatograph; ECD, electron-capture detector.

without solid-phase preconcentration, the upper part of the pervaporation cell was placed in the loop of the injection valve (with the sample inlet and outlets closed), whereas in the preconcentration mode, the Tenax minicolumn (a stainless-steel one) was situated at the loop of the valve (in this case, the outlet of the upper part of the pervaporation unit was connected to the sample inlet of the valve, whose outlets were open). All steel tubes used for the coupling of the injection valve to the chromatograph and for the connection of the preconcentration column in the loop positions of the HPLC valve, had an inner diameter (I.D.) of 0.5 mm. When the pervaporation cell was placed in the loop of the

injection valve, PTFE tubing of 0.7 mm I.D. was used for connection.

The pervaporation cell, designed in our laboratory [23–27] and presented in Fig. 2, consisted of two chambers: a donor chamber (lower part of the pervaporation unit) and an acceptor chamber (upper part of the unit) both fitted with inlet and outlet orifices for connectors of the donor and acceptor streams and a membrane support. The volume of the chambers could be changed by placing spacers between the membrane support and the corresponding chamber. Both chambers and the membrane support were aligned by means of two metallic rods and a closer contact was achieved by screwing

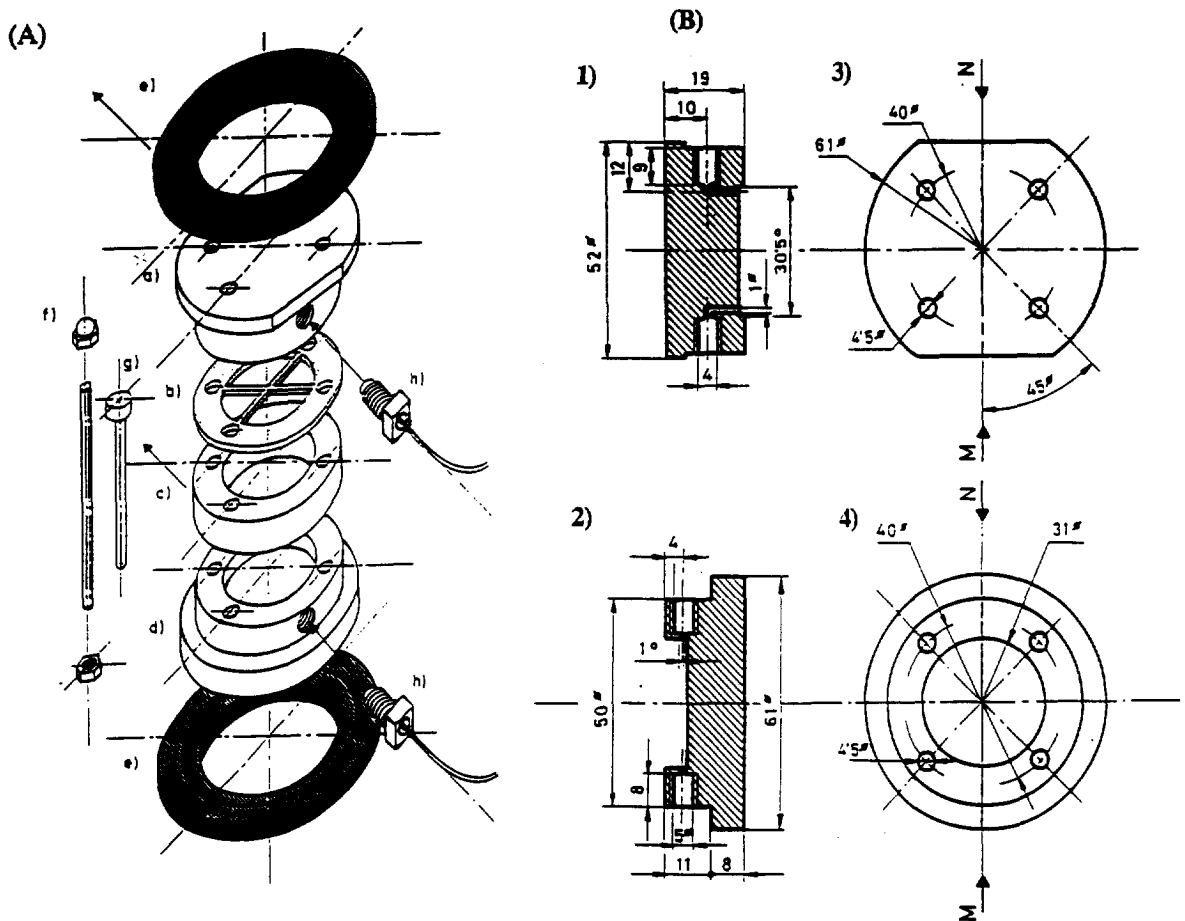


Fig. 2. (A) Parts of the pervaporation module. (a) Receptor chamber, (b) membrane support, (c) spacers, (d) donor/sample chamber, (e) aluminium supports, (f) and (g) rods for screwing and aligning the module, (h) connectors. (B) Cross-sectional (1 and 2) and plane views (3 and 4) of the acceptor and sample chambers, respectively.

them with four screws between two aluminium supports.

A Varian Star 3400 CX gas chromatograph equipped with an electron-capture detection (^{63}Ni ECD) system and connected to a computer was used in the experiments. A 30 m \times 0.32 mm I.D. fused-silica capillary column coated with a 0.25 μm film thickness of methylsilicone TRB-1 (supplied by Tecnochroma) was used to separate the compounds. The temperature ramp started at 33°C (hold for 2 min) and then increased at intervals of 2°C/min. Both the injector and the detector were heated at 220°C. The injector was operated in the split mode with a split ratio of 1:10. The carrier gas (nitrogen) flow-rate was 2.3 ml/min.

A Heron HD-150 muffle oven was used for the desorption of the analytes from the preconcentration minicolumn.

2.2. Reagents

Standard 0.2% (v/v) solutions of the three analytes were prepared by adding the appropriate volumes of the pure compounds, namely: chloroform (Scharlau, HPLC grade); carbon tetrachloride [Sigma–Aldrich, neat standard for US Environmental Protection Agency (EPA) methods]; trichloroethene (Sigma–Aldrich, neat standard for EPA methods) in *n*-pentane (Scharlau, for pesticide residue analysis) and kept in the refrigerator. Bromotrichloromethane (Merck, for synthesis) was used as an internal standard and a 10 $\mu\text{g}/\text{ml}$ solution of it was also prepared in *n*-pentane. All working solutions, containing 500 ng/ml of the internal standard, were prepared by dilution of the standard solutions in *n*-pentane immediately before use.

Tenax TA (Supelco, 60–80 mesh) was used as the solid-phase, where the analytes were preconcentrated. The separation membranes were purchased from Millipore and Trace (Braunschweig, Germany). The nitrogen gas used (Nitrógeno C-50, minimum purity >99.999%) was supplied by Carburros Metálicos (Barcelona, Spain).

2.3. Procedure

Initially, two types of experiments were carried out: the first, using diatomaceous earth spiked with the analytes and allowing the organic solvent evapo-

rate at room temperature and the second, spiking the matrix just before subjecting it to the experiment. The results obtained were similar and, finally the second working mode was adopted.

Ca. 1 g of the inert support (diatomaceous earth) was accurately weighed in the lower chamber of the pervaporation module and a spacer was located between this chamber and the membrane support, in order to increase its volume and maintain the free volume between the sample surface and the membrane constant. The appropriate volume of water required for analytes leaching from the support was added, a magnetic minibar was also located and the cell was shut after placing the membrane and the acceptor chamber. The analytes were then injected into this chamber by a syringe equipped with a hypodermic needle through a septum. Finally, the pervaporation module was located in a magnetic stirrer thermostatted at 80°C.

When the acceptor chamber was inserted in the loop of the injection valve (Fig. 1A), the latter was turned to the inject position as soon as the cell was placed in the magnetic stirrer. In this way, the nitrogen stream passed through the upper chamber and the evaporated analytes were directly carried to the chromatographic column.

In the procedure with the preconcentration step (Fig. 1B), the flow of nitrogen from the gas cylinder was divided into two streams, one stream entering the injection valve as the carrier stream and passing through the GC column and the other passing through the upper chamber of the pervaporation cell. When the injection valve was in the filling position, the nitrogen flowing through the acceptor chamber of the cell carried the evaporated analytes to the preconcentration column, which was kept in an ice-bath (0°C). After a preset preconcentration time, the valve was switched to the inject position and the analytes were desorbed from the minicolumn (placed in the muffle oven) and led to the chromatographic column by the carrier gas.

3. Results and discussion

3.1. Optimization of variables

All variables affecting the system were studied carefully, in order to obtain the optimal conditions

Table 1
Optimization study

Parameter	Range studied	Optimum value
Temperature (°C)	40–80	80
Preconcentration time (min) ^a	0–3	0
Injection time (min)	0.17–0.5	0.25
Nitrogen (acceptor) flow-rate (ml/min)	4–36	4
Preconcentration time (min) ^b	1–10	10
Desorption temperature (°C)	100–300	200
Desorption time (min)	3–10	5

^a The acceptor (upper) chamber of the pervaporation module located at the loop of the injection valve.

^b The sorbent column located at the loop of the injection valve.

for the chromatographic separation/determination of the three analytes (Table 1).

At first, the separation unit was coupled to the system as shown in Fig. 1A and the temperature applied during the pervaporation process was studied. This had a positive effect on the analytical signal (i.e., the area of the peaks), since an increase of it favoured both the evaporation of the analytes and their permeability through the membrane. 80°C was finally chosen as the optimum temperature, as the peak area obtained was approximately 38% higher than that at 70°C. Higher values were not assayed, in order to avoid the destruction of the methacrylate module.

A variable related to the separation module was the type of membrane and its pore size. Both hydrophobic (namely, PTFE with pore sizes of 5.0 and 10.0 µm from Millipore and PTFE with a thickness of 1.5 mm from Trace; polyvinylidene fluoride, PVDF, with a pore size of 5.0 µm from Millipore) and hydrophilic (i.e., cellulose with pore sizes of 5.0 and 8.0 µm from Millipore) membranes were tested. The PTFE membranes provided the greatest peak area, but that with the pore size of 10.0 µm was rejected because it was thin and destroyed very quickly. PVDF provided smaller signals whereas the hydrophilic membranes permitted the passage of water vapors through them, which, as a result, were led to the GC column. A PTFE membrane of 1.5 mm thickness was used for subsequent experiments, as it provided a good sensitivity and a high thermal stability.

The time necessary for preconcentration of the analytes in the static gas (nitrogen) at the upper part of the pervaporation cell was also optimized. A signal was obtained even without preconcentration,

attributed to the high volatility of the analytes. Increased preconcentration times resulted in an increase of the analytical signal, but at the same time a part of the pervaporated material was lost during the filling of the upper chamber with the carrier gas. For this reason, eventually no preconcentration was carried out. Nevertheless, the valve was maintained in the assembly mainly for two reasons: firstly, to keep the carrier gas flowing uninterrupted to the GC column, and secondly, to permit the introduction of a controlled volume of gas containing the pervaporated analytes to the column by controlling the injection time. Peak overlapping was thus avoided.

A parameter influencing the volume of gases entering the chromatographic column was the injection time. Long injection times gave rise to very wide and overlapped peaks. Shorter injection times resulted in better defined chromatographic peaks but, at the same time, the area values were smaller, as too much of the analytes were going to the waste. Finally, an injection time of 15 s was chosen as a compromise.

Moderate stirring was adopted (ca. 700 rpm), as excessive agitation could lead to splashing of the membrane with solid particles and to consequent blockage of its pores. On the other hand, low stirring leads to a lack of homogeneity and, therefore, to irreproducible results.

The variables concerned with the adsorption and desorption of the analytes from the sorbent packed in the preconcentration minicolumn were studied using the configuration shown in Fig. 1B.

A critical parameter was the flow-rate of the nitrogen passing through the upper part of the pervaporation cell, collecting the pervaporated analytes and leading them to the injection loop and

therefore to the sorbent column situated in it. Different flow-rates were achieved by changing the length and the diameter of the tube placed after the division of the total flow of nitrogen from the gas cylinder. High flow-rates resulted in small signals, whereas low flow-rates resulted in higher peak areas, as the contact time between the analytes and the sorbent material was longer and therefore better adsorption occurred. A flow-rate of 4 ml/min was chosen for further experiments, as lower values could not possibly permit the fast removal of the analytes to the sorbent column and the enrichment of the gas phase with a fresh portion of the pervaporated analytes.

Long preconcentration times meant also higher amounts of pervaporated analytes by displacement of the mass transfer equilibrium, and therefore higher concentrations in the sorbent material. This variable was studied in the range between 1 and 10 min with the latter one chosen as optimum, because it gave a signal almost 8 times higher than that for 5 min and 16 times higher than that for 3 min. Longer preconcentration times were not assayed in order to

adopt a compromise between sensitivity and sampling frequency.

Two other variables that had to be optimized were the duration and temperature of the desorption step. Temperature was studied in the range between 100 and 300°C and the signal for the three analytes was constant in this interval. Finally, 200°C was used as working temperature. The duration of the desorption step was varied between 3 and 10 min and the signals obtained for the three analytes were similar within this interval thus confirming the fast kinetics of the desorption step. A 5 min desorption time was employed for subsequent experiments.

The volume of water added to the solid sample in the pervaporation cell was the one required so as to avoid the formation of a mud, that would hinder stirring. Therefore, 3 ml of Milli-Q extra pure water were added to 1.0000 g of the solid sample, followed by the addition of spacers between the donor chamber and the membrane support, so as to keep the air volume between both constant.

A well-resolved chromatogram obtained with the optimal values of the variables is shown in Fig. 3.

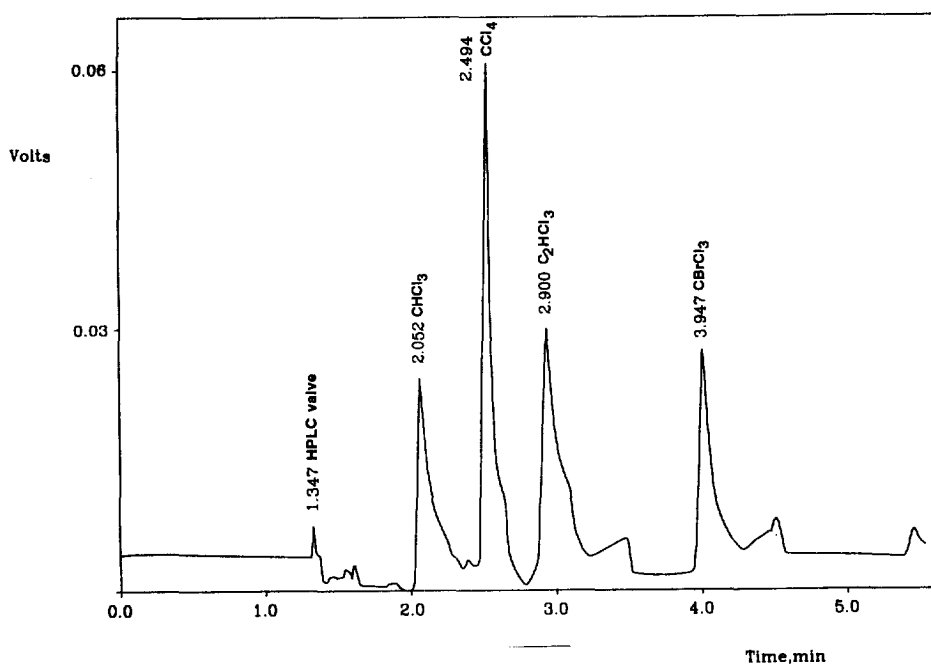


Fig. 3. Chromatogram obtained under the optimal working conditions (preconcentration mode). Concentration of each analyte: 17 ng/g. In order of appearance the peaks correspond to switching of the HPLC valve, chloroform, carbon tetrachloride, trichloroethene and internal standard (bromotrichloromethane).

Table 2
Features of the method

Analyte	Linear range (ng/g)	Equation	<i>r</i>	Limit of detection (ng/g)	R.S.D. (%) (<i>n</i> =9)
<i>(A) The pervaporation module located at the loop of the injection valve</i>					
Chloroform	25–2000	$y=0.3276+1.86 \cdot 10^{-4}x$	0.9962	17.4	8.14
Carbon tetrachloride	25–2000	$y=0.0238+5 \cdot 10^{-3}x$	0.9999	14	6.42
Trichloroethene	250–2000	$y=-0.0375+5.75 \cdot 10^{-4}x$	0.9994	182.6	5.65
<i>(B) The sorbent column located at the loop of the injection valve</i>					
Chloroform	1–50	$y=0.0317+0.5086x$	0.9968	0.98	3.72
Carbon tetrachloride	1–50	$y=0.1083+0.0506x$	0.9983	0.57	5.87
Trichloroethene	5–50	$y=-0.0299+0.01715x$	0.9940	4.42	4.44

x: Analyte concentration in ng/g.

y: Relative analyte area (i.e., analyte area-to-internal standard area ratio).

3.2. Features of the method

Two calibration curves for each analyte were run, corresponding to the two operation modes (with and without preconcentration). In the first case, the calibration graph for chloroform and carbon tetrachloride was linear between 25 and 2000 ng/g, whereas for trichloroethene the linearity encompassed 250–2000 ng/g. When the pervaporated analytes were preconcentrated, chloroform and carbon tetrachloride could be determined in the range between 1 and 50 ng/g and trichloroethene in the range between 5 and 50 ng/g. The equations obtained after the regression analysis of the obtained data, the correlation coefficients, the detection limits and repeatability (expressed as relative standard deviation; R.S.D.) are shown in Table 2.

3.3. Application of the method

As there is a lack of available Certified Reference Materials with information on the content of VOCs

[11], the proposed method could only be validated by studying recoveries from spiked samples. Three matrices were chosen as representative of environmental samples: a sandy soil, a humic soil and a mixture of these. The results for the three analytes including the concentration found, recovery and R.S.D. (*n*=3) are shown in Table 3. The recoveries, which varied for the three analytes and for the matrices between 83 and 116%, are significantly better than those reported by Voice and Kolb [3] for chloroform and trichloroethene.

4. Conclusions

The method proposed here has as main advantages when compared with both dynamic and static headspace modes that it can be easily automated with minimal acquisition and maintenance costs, and provides both better repeatability and recovery.

Concerning the static mode the analysis time is

Table 3
Application of the method to spiked samples

Sample	Chloroform			Carbon tetrachloride			Trichloroethene		
	Added (ng/g)	Found (ng/g)	Recovery (%) (R.S.D., %, <i>n</i> =3)	Added (ng/g)	Found (ng/g)	Recovery (%) (R.S.D., %, <i>n</i> =3)	Added (ng/g)	Found (ng/g)	Recovery (%) (R.S.D., %, <i>n</i> =3)
Sandy soil 1	8.0	7.4	92.5 (1.9)	8.0	7.1	88.8 (0.8)	8.0	8.2	102.5 (6.7)
Sandy soil 2	12.0	10.0	83.3 (2.6)	12.0	11.2	93.3 (1.9)	12.0	11.6	96.7 (1.5)
Humic soil 1	10.0	10.8	108.0 (1.0)	10.0	9.6	96.0 (2.8)	10.0	9.8	98.0 (2.1)
Humic soil 2	21.0	20.4	97.1 (2.4)	21.0	22.9	109.0 (3.9)	21.0	20.3	96.7 (3.4)
Mixed soil 1	17.0	15.4	90.6 (1.1)	17.0	19.8	116.5 (2.4)	17.0	15.5	91.2 (3.0)
Mixed soil 2	28.0	25.1	89.6 (3.3)	28.0	28.1	100.4 (2.6)	28.0	28.3	101.1 (3.3)

shortened, since no equilibrium conditions have to be reached.

The use of the hydrophobic membrane is supported by the fact that the analytes are swept off in a continuous way and removed from the separation system, thus enhancing the displacement of the equilibrium and favouring the mass transfer process. Moreover, there is no need for a water vapour condenser, as in the case of purge and trap mode [28], or a hydrophobic adsorbent, since no water-crossing through the hydrophobic membrane occurs.

With respect to the purge and trap mode, except for the fact that the condenser is avoided, as mentioned before, another advantage of the proposed methodology is the automatic introduction of the sample into the separation module achieved either continuously or by injection.

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