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Development of membrane extraction with a sorbent interface–micro gas chromatography system for field analysis

Alina Segal[a], Tadeusz Górecki[a], Phillippe Mussche[b], Jurgen Lips[b], Janusz Pawliszyn[a,*]

[a]*Department of Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1 Canada*

[b]*Chrompack, Herculesweg 8, P.O. Box 8033, 4330 EA Middelburg, The Netherlands*

Abstract

The commercially available portable gas chromatographs have a rather limited scope of applications, typically allowing analysis of gaseous samples only, and having relatively poor sensitivity. Combination of those instruments with modern sampling/sample preparation techniques can remedy these problems. A Chrompack micro-GC system equipped with a thermal conductivity detector has been coupled to membrane extraction with a sorbent interface (MESI). The sorbent trap has replaced the GC injector. The design of the trap was also modified in order to enhance the preconcentration of analytes. The use of a thin flat sheet membrane reduces the response time, and decreases the memory effect of the system. Rapid separation times were achieved, and the sensitivity was significantly improved. MESI enables semi-continuous monitoring of both gaseous and aqueous samples, owing to the selectivity of the membrane material. The system does not use moving parts, therefore being reliable. The sensitivity of the micro-GC system was increased by a factor of more than 100 by the addition of the MESI system, even with a preconcentration time as short as 1 min. Chloroform, having a concentration lower than 1 ppb, was detected in tap water. A cup system was used to allow headspace sampling of volatile organic compounds from aqueous matrices, keeping the membrane away from interfering species that could be present in water, and improving the mass transfer. A linear calibration line was obtained, and the estimated limit of detection was 60 ppt. This represents a great improvement for the sensitivity of the micro-GC system.

Keywords: Membrane extraction with a sorbent interface; Membranes; Extraction methods; Benzene; Toluene; Ethylbenzene; Xylenes

1. Introduction

An increased interest is devoted to the development of field portable instrumentation. Gas chromatography (GC) is a very powerful technique for environmental monitoring. As the analysis time is an important issue especially when multiple analyses or continuous monitoring are to be done, the design of a small field portable gas chromatograph, capable of performing high-speed separations, is very important. Most often, short capillary columns operated at high carrier gas velocities are used in high-speed GC analyses. Also, a very narrow injection band is required in order for a good separation to be achieved. The width of the injection band has to be small compared to the contributions to band broadening due to diffusion, interfaces, detector volume and electronics [1].

A few important aspects must be taken into consideration when a field-portable gas chromatograph is used. Most of the commercially available ones have limited applications, being almost exclusively designed for gaseous samples and isothermal separations. The inconvenience of transporting addi-

*Corresponding author.

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tional gas tanks into the field makes the choice of detectors quite narrow. Thermal conductivity detectors and photoionization detectors are typically used. Even though the micro-thermal conductivity detectors are much more sensitive than the regular ones, they do not reach the sensitivity of a flame ionization detector, and the response of a photoionization detector is limited to the volatile compounds that undergo photoionization. However, the sensitivity can be very much improved by sample preconcentration. Most often cold trapping followed by thermal desorption is used, but this requires additional complicated instrumentation.

A very simple and efficient sample introduction technique that has been successfully used for fast field analysis is solid-phase microextraction (SPME) [2]. The use of a small-diameter fuse-silica fiber coated with a polymeric stationary phase makes the technique very suitable for field applications. The trapped analytes can be liberated by thermal desorption, directly in the injector of the gas chromatograph [3–9]. Even though SPME presents all the advantages of a simple sample introduction technique that very much contributes to the improvement of sensitivity, it can not be used for semicontinuous monitoring without additional instrumentation (like a modified autosampler). However, additional mechanical equipment is not desired in the field.

A promising alternative to SPME is membrane extraction with a sorbent interface (MESI). MESI is a single step sample preparation technique that was developed to allow rapid routine analysis and long-term semicontinuous monitoring of volatile organic compounds. It uses a membrane module, a sorbent interface, a capillary gas chromatograph and a data acquisition system [10–13]. The membrane acts as a selective barrier and is usually nonpolar, thus keeping water from entering the system. It also acts as a selective element, since permeation rates of different molecules vary with membrane material. The membrane can have different forms. Most often, hollow fiber membranes are used, presenting the advantages of being self-supported and easy to connect to the carrier gas line. However, their relatively thick walls (over 100 μm) give long response times and long-lasting memory effect. On the other hand, very thin flat sheet membranes are available, but since they are not self-supported they cannot be connected to the gas lines without the use of special holders [10–13].

Once the analytes cross the membrane, the carrier gas stream carries them away to the sorbent interface, where concentration occurs. The sorbent interface includes a sorbent trap, a heating coil and a power supply. A piece of a chromatographic column or a SPME fiber immobilized into deactivated fused-silica tubing can be used as sorbent traps. A suitable polymeric phase controls the selectivity of the trap. The efficiency of the trap can be increased by placing it on a small Peltier cooler that is capable of significantly decreasing the temperature of the sorbent material. The trap is periodically heated to desorb the analytes. For this purpose, a heating coil is placed around the sorbent trap and short electrical pulses are applied from an external power supply, to obtain temperatures of about 220–250°C. Usually, the concentration time is controlled by the computer or by an external timer. The analytes are than introduced into the gas chromatograph where they are being separated.

Such a technique can be used without modifying or redesigning the gas chromatograph, and can be successfully applied for trace analysis, since it provides sample preconcentration. The purpose of this work was to couple MESI with a Chrompack 2002 micro-GC system and create a field portable system capable of performing high-speed trace analysis of real aqueous and gaseous samples. The sorbent interface was redesigned to increase the sorbent capacity and make it optimal for field transportation. A water trap was introduced into the system, to eliminate moisture that passes through the membrane, especially when analyzing aqueous samples.

2. Experimental

The analyses were performed using a Chrompack 2002 micro-GC system, equipped with two gas chromatographic modules. Each module consists of an injector, two heated columns (an analytical column and a reference for the thermal conductivity detector) and a micromachined thermal conductivity detector (Fig. 1). The injector is etched in a glass wafer and has very low dead volume. It contains pneumatically actuated valves, a micro sampling loop, and flow restrictors for the two columns. Experiments were performed using an unmodified

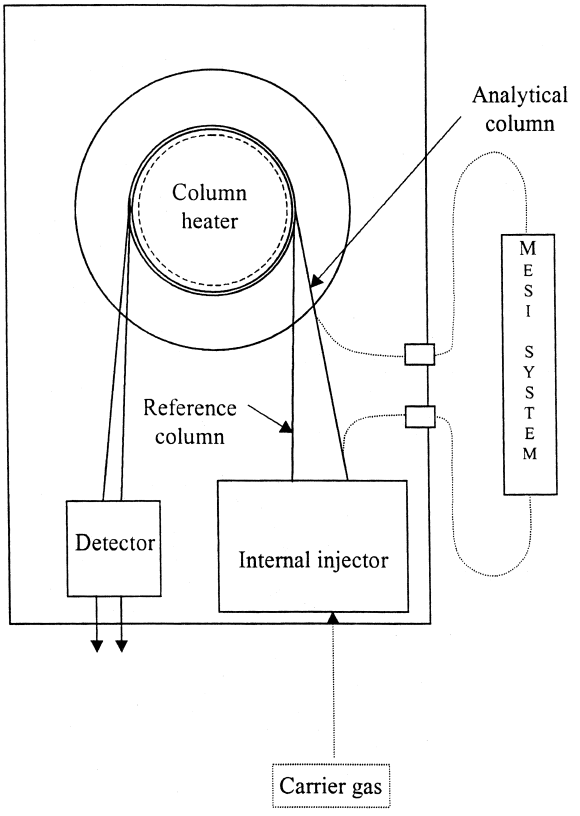

Fig. 1. Schematic of a micro-GC module. Dotted lines represent gas flow path in the custom-made module.

module (4 m×0.15 mm, 0.2 μm CP Sil 5 CB column) and a custom-made module containing a 4 m×0.25 mm, 0.25 μm CP Sil 8 CB column. In the custom-made module, two additional connectors allowed the hook-up of the MESI system after the built-in injector.

The variety of the commercially available flat sheet membranes is considerably bigger then that of the hollow fiber membranes. This fact, as well as the faster response time and shorter memory effect was the reasons why flat sheet membranes were used in the research described herein. A membrane module had to be designed for this purpose, and a schematic diagram of it is presented in Fig. 2. Carrier gas was supplied to the module through a small diameter PTFE tube, fitting tightly into the PTFE washer. The pressure of the carrier gas lifted the membrane, allowing free passage of the gas to the outlet tube. A fine stainless steel mesh, mounted in a stainless steel ring, supported the membrane. The ring was screwed to the bottom plate of the module with three bolts. The membrane used in this research was a 0.25 μm silicone polycarbonate one.

A 10 cm long, poly(metahacrylate) tube having an inner diameter of 3.5 cm was used to build the water trap. Two rubber stoppers were placed at the ends of the plastic tube, to ensure the sealing. A piece of Nafion tubing, having a length of 70 cm was placed inside, and connected to the carrier gas line using two Valco connectors and vespel ferrules. Holes were drilled in the rubber stoppers in order to accommodate the connectors. The cylinder was then filled with 70 g of activated molecular sieve, to surround the Nafion tube.

BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds of 99+% purity were purchased from Aldrich. Stock solution was prepared by dissolving 1.7 ml of each individual compound in 100 ml methanol. Appropriate amounts of this stock solution were spiked into 150 ml water, to give different concentrations of BTEX. Standard gas mixture of benzene, toluene and *o,m,p*-xylenes was obtained in the dynamic mode, using a standard gas generator and permeation tubes (Kn-Tek Labs., Texas City, TX, USA). For the last set of experiments, an aqueous solution of BTE was used. The individual components were dissolved in water, in order to obtain a concentrated stock solution. Appropriate amounts of this stock solution were then spiked into 150 ml of water to obtain the desired concentrations.

Flat-sheet silicone polycarbonate membrane (SSP-M213), of 0.25 μm thickness was purchased from Membrane Components (Ballston Spa, NY, USA). For the construction of the MESI trap, deactivated stainless-steel tubing (MXT guard column) was obtained from Chromatographic Specialties (Brockville, Canada). Four different trapping materials were used: XAD-2 resin, Tenax-TA, Carboxene-100 (Supelco, Oakville, Canada) and polydimethylsiloxane. The last sorbent material was obtained by grinding a Polydimethylsiloxane hollow fiber membrane (Baxter Health Corp., IL, USA) under liquid nitrogen. For the water trap, Nafion tubing from Perma Pure (Toms River, NJ, USA) and 4A-type molecular sieve (BDH, Toronto, Canada) were used. A custom-made capacitive discharge (CD) power supply, containing a single computer-grade 16 000 μF/50 V capacitor was used to heat the MESI trap.

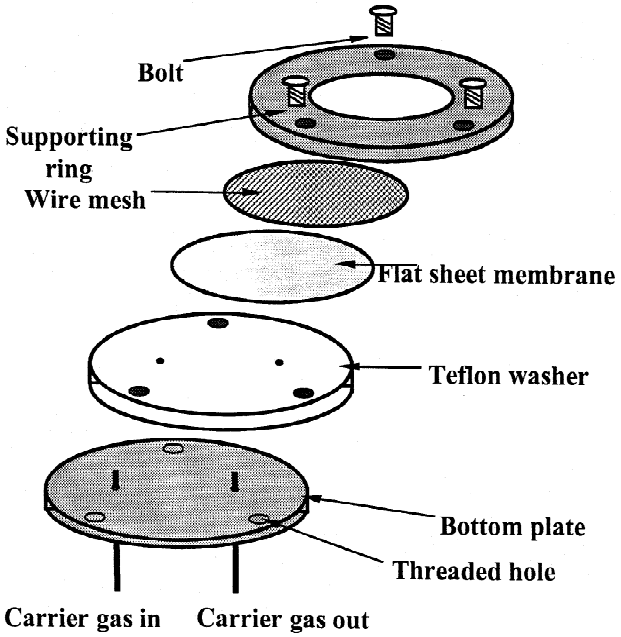

Fig. 2. Design of the MESI membrane module.

An external H3CR-F timer (Omron, Kyoto, Japan) controlled the concentration time.

A concentrated chloroform solution was prepared in water, by spiking 1 μl chloroform in 100 ml deionized water. The chloroform was purchased from Supelco. The solution was used to determine the retention time of chloroform in the system, and compare it with that of the presumed chloroform peak in tap water.

Tap water from one of the sinks in the laboratory was analyzed. For the quantification of chloroform in tap water, 50 ml standard solution was prepared by using 21.0 μl of chloroform, and methanol as solvent. Standard addition method was performed by SPME, using a 100 μm polydimethylsiloxane fiber (Supelco). The samples were prepared as follows: 6 vials having a volume of 40 ml were used, and 25 ml of tap water were pipetted in each of them. In three of the vials, 1, 2 and respectively 3 μl of the stock chloroform solution were spiked, to give an additional concentration of 25, 50 and respectively 75 ppb (w/w) chloroform in the tap water. SPME extraction was performed from each vial, using a concentration time of 6 min. A Varian Star 3400 (Varian, Sunnyvale, CA, USA) gas chromatograph coupled with a Varian Saturn II ion trap MS system were used to detect and quantify chloroform.

The solutions were stirred using a 2.5 cm stir bar and a digital stirrer to favor the transport of analytes from the solution into the headspace. The stirring rate was set to 500 rpm.

3. Results and discussion

The purpose of this research was to couple MESI with a Chrompack 2002 micro-GC system. In order to create a system suitable for field applications, the sorbent interface was redesigned and a water trap was introduced to eliminate the moisture. Fig. 3 presents a diagram of the MESI system used for this research.

One of the goals was to increase the sorbent capacity of the MESI trap, without using a Peltier cooler, which requires additional power supply and would be unsuitable for transportation in the field. For this purpose, a 6 cm long deactivated stainless steel tubing (having an outer diameter of 0.75 mm) was packed with about 0.0019 g of XAD-2 resin. The packing was about 1.3 cm long. Using stainless

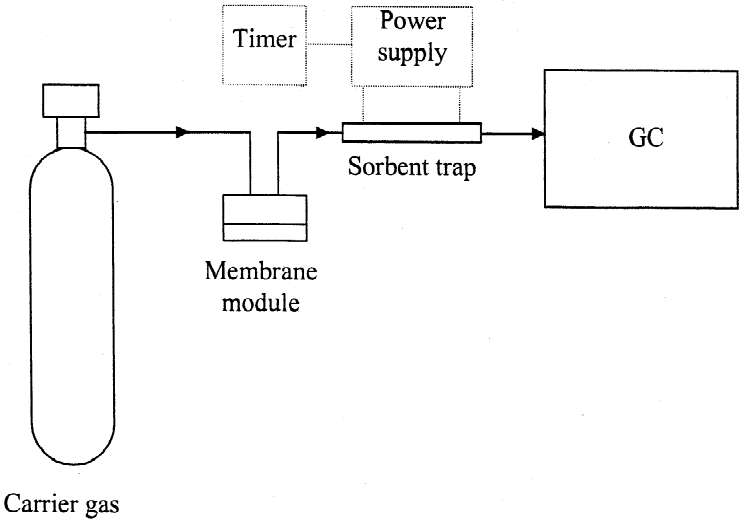

Fig. 3. Schematic of MESI system.

steel tubing instead of deactivated fused-silica tubing, the need of a heating coil was eliminated. Also, the amount of the sorbing material in this configuration is much higher than in the one that uses SPME fibers, thus increasing the sorbent capacity of the trap. The packing material was immobilized in the middle of the stainless steel tube, by placing glass wool and squeezing the tube at the ends of the packing (Fig. 4).

When an electrical pulse is applied to the trap, the gas inside expands very fast and the analytes could be pushed back towards the carrier gas lines instead of going directly into the column (which is placed at the other end of the sorbent trap). The injection band would be broadened in this case, and the separation would be worsened. The trap was designed to minimize this phenomenon. Two centimeters from the beginning of the trap, the stainless steel tubing was squeezed. Glass wool was than packed into the tubing. A large particle of the sorbent (having the diameter only slightly smaller than the inner diameter of the tubing) was placed at the beginning of the sorbent bed. By squeezing the tubing and placing the large particle at the beginning of the trap, the gas flow towards the membrane module was restricted during the heating pulse. The trap was further packed with small size particles for about 1.3 cm. Glass wool was than placed at the end of the sorbent bed. Than the stainless steel tubing was squeezed a bit, to help immobilize the packing material (the tubing was

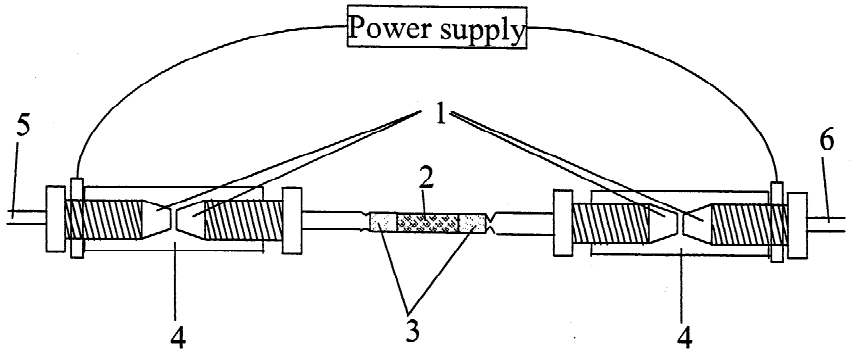

Fig. 4. The sorbent trap. 1=ferrules; 2=packing material; 3=glass wool; 4=internal reducing union; 5=column; 6=PTFE gas line.

squeezed much more at the beginning of the trap than at the end). With this configuration, when a heating pulse was applied, the carrier gas, following the less restricted path, would mainly flow towards the column, pushing the analytes in this direction.

For the desorbing pulses, a temperature of approximately 220°C was obtained by passing electrical current through the stainless steel tubing. The capacitive discharge power supply provided the required voltage, and an external timer controlled the concentration time, acting as a switch. Very high heating rates were achieved with the capacitive discharge power supply, and thus very narrow injection bands were produced, even though the direction of the carrier gas flow was the same during the desorption and the concentration cycles. This proved to be very advantageous since there was no need of introducing moving parts into the system. Usually the inversion of the direction of the flow during desorption (typically applied in such circumstances), requires the use of multiport valves, which can be trouble-prone.

Two Valco zero volume fittings (having a 0.75 mm bore) connected the trap into the system. The electrical contact between the trap and the connectors was obtained by placing the stainless steel tubing about 1.5 mm deep into the connectors' bore and ensuring a tight fit. Vespel ferrules were used to seal the trap. Two wires placed at the opposite ends of the connectors provided the electrical connection to the power supply.

Perfect sealing of the two ends of the trap is very important in order to prevent moisture and oxygen from entering the system. Graphite ferrules could be used for both sealing and providing the electrical contact for the trap. However, each time an electrical pulse is applied, the trap bends, and because of the softness of the graphite, the trap would not be sealed well anymore.

The sorbent trap was placed in a holder made of Teflon, and mounted on the sidewall of the GC module. A hole was drilled in the same wall, to allow the column to be connected to the trap.

Fig. 5 presents a set of 5 chromatograms obtained with the previously described MESI system [14], using progressively longer trapping times (30, 60, 90, 120 and 180 s), for a dynamically generated standard gas mixture, in which the concentration of benzene was approximately 2 ppm (v/v), while those of the xylenes were approximately 1 ppm (v/v). The bottom trace corresponds to a trapping time of 1 min, while the top trace to 3 min. The desorption pulses are visible on the chromatograms as small, negative dips preceding the groups of peaks. The first peak in each group corresponds to water and air, which also permeate through the membrane and are trapped to some extent by the sorbent. The remaining four peaks in each group correspond to benzene, toluene, *m,p*-xylene and *o*-xylene (from left to right). It is clear from Fig. 5 that within the time frame examined, the response of the system was proportional to the trapping time. For example, the benzene peak height for 1 min trapping time was ~0.5 V, while for 3 min trapping time it was 1.5 V. This proves that no breakthrough of analytes occurred in the trap. Each individual separation was completed in ~25 s, and the peak shapes were satisfactory. The width of the benzene peak at half height was ~250 ms, which was very good taking into account that the desorption of the analytes was carried out without reversing the direction of the carrier gas flow through the sorbent trap. This proves that the MESI system in the configuration examined can be successfully used for semi-continuous monitoring of trace levels of volatile analytes.

The most important aspect of MESI is its ability to selectively concentrate volatile analytes on-line, before fast separation. This can result in dramatically improved sensitivity, as illustrated in Fig. 6. The lower trace in this figure is a MESI chromatogram obtained for a statically generated standard BTEX mixture [~4 ppm (v/v) each compound] prepared in a SUMMA canister. The trapping time was 1 min. The scale for this chromatogram is presented on the left *y*-axis. The upper trace is a chromatogram obtained for the same mixture with a regular microsampling loop injection, using the second GC module in the same instrument. This chromatogram is presented in a 100 times larger scale (see right *y*-axis). It is clear from this Figure that even with preconcentration time of only 1 min, the sensitivity of MESI was higher by more than two orders of magnitude compared to direct injection of a gas sample. The conditions used for direct injection (with the detector sensitivity set on high and a maximum injection time of 225 ms) corresponded to the maximum sensitivity of the instrument.

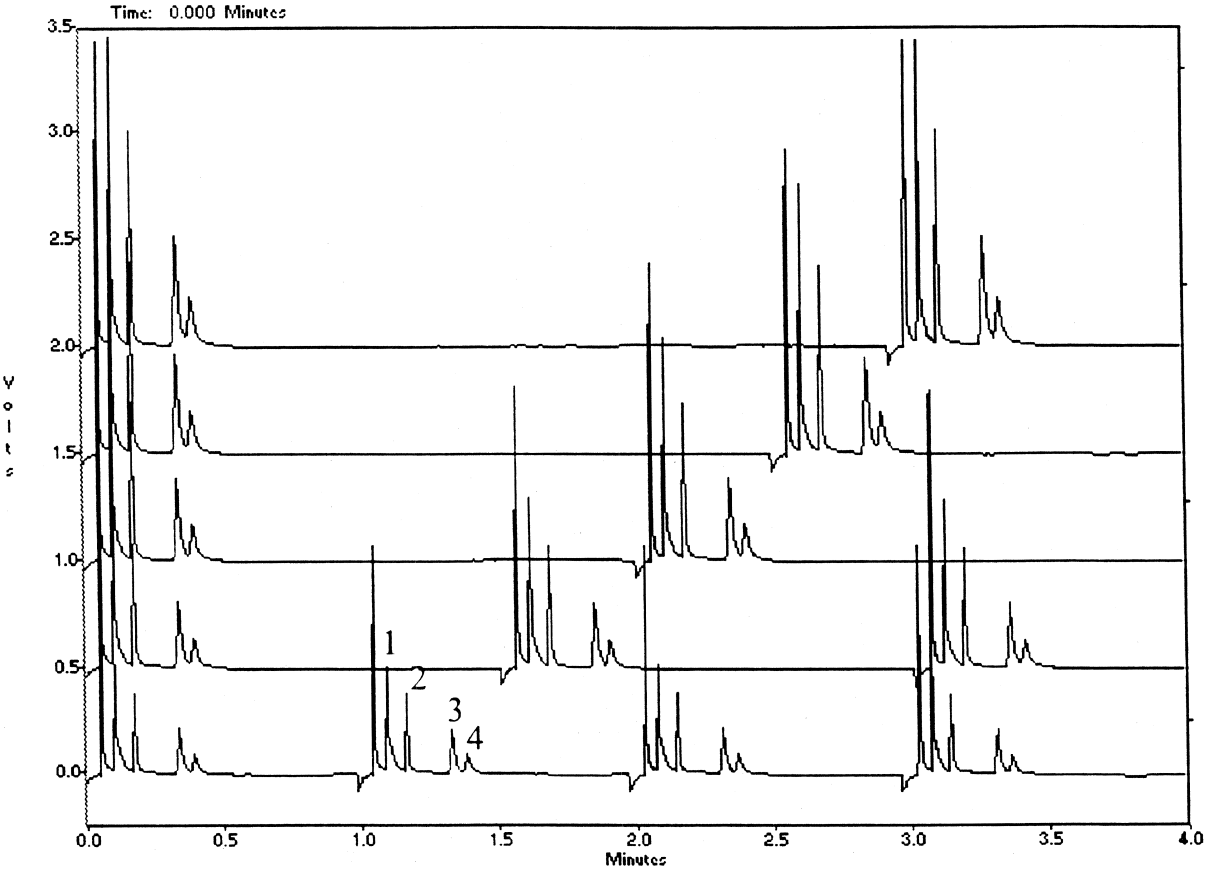

Fig. 5. Chromatogram obtained with the MESI system with progressively longer trapping time (30 s increments). The bottom trace corresponds to a trapping time of 1 min, whereas the top trace corresponds to 3 min. Peaks: 1=benzene; 2=toluene; 3=*m, p*-xylenes; 4=*o*-xylene.

As proven by the presented experiments, MESI can increase the sensitivity by concentrating the sample for just 1 min. However, the improvement of the sensitivity crucially depends on the design of the trap. It is very challenging to construct a sorbent trap that is selective for the compounds of interest and has the optimum amount of sorbent in order to reach a very good concentration and not having the analytes breaking through the trap after a short period of time. On the other hand, a too strong sorbent material can cause problems for desorption, or a too long trapping path can produce wide injection bands.

The sorbent trap used in the research presented herein allows the use of reasonably long concentration times, but as the heights of the peaks corresponding to the analytes of interest increase with the trapping time, so does the peak of water and air (which are usually not separated in two peaks). This can be a very big inconvenience for those analytes that elute very close to the water peak and are present in the matrix at very low concentrations. Their peaks can be lost in the tail of the water peak. Water also breaks through the trap very fast, and the baseline drift can also cover the previously mentioned peaks.

In order to eliminate the inconvenience of concentrating water on the sorbent trap, a water trap was placed in the system between the membrane module and the sorbent interface (Fig. 7). As the whole system was designed for field applications, the water trap also had to meet the requirements of a portable

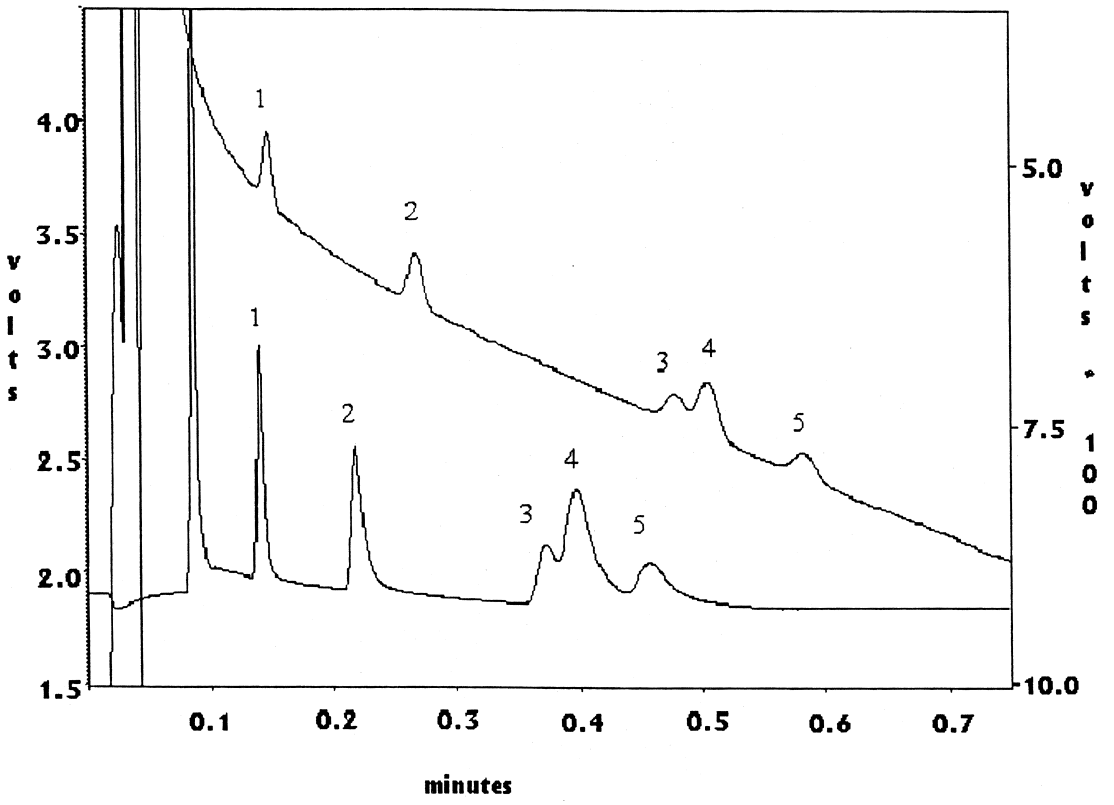

Fig. 6. Comparison of results obtained using the MESI system with those obtained using regular gas-phase injection through the built-in injector. The lower chromatogram (left *y*-axis) has been obtained using the MESI system; the upper trace (right *y*-axis) is a chromatogram for direct gas injection. BTEX concentration ~ 4 ppm (v/v) of each compound. Peaks: 1=benzene; 2=toluene; 3=ethylbenzene; 4=*m,p*-xylenes; 5=*o*-xylene.

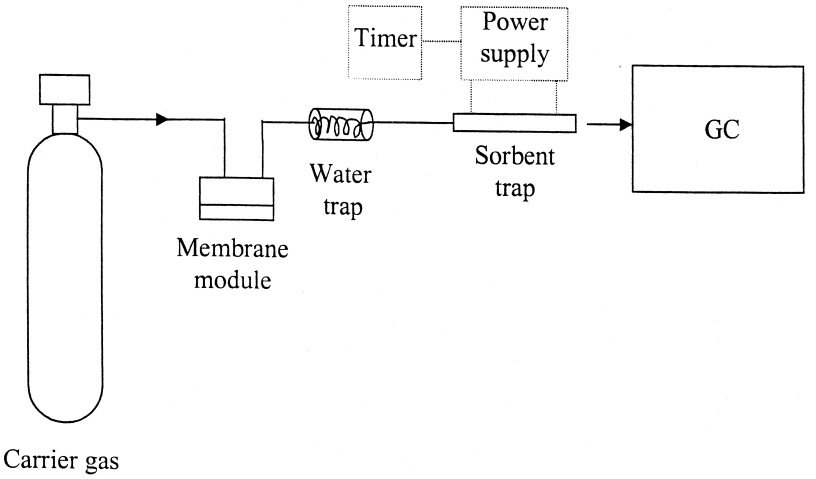

Fig. 7. Schematic of MESI system, with water trap.

device. This also includes the elimination of an extra gas cylinder for flashing the trap. For this purpose Nafion tubing was used. The analytes and moisture were passed through the Nafion tubing. Because water can penetrate the walls of the Nafion tubing, the molecular sieve that was placed on the outside part of the tubing retained it. To some extent, polar analytes can be lost in the water trap too, but because they are concentrated after the water trap, the amount lost is insignificant. The dimensions of the trap can vary depending on the space available in the GC system to mount it, and on the time that the trap is required to function without being replaced. The trap in this configuration could be successfully used for five months, without changing the molecular sieve. A significantly smaller one could be used for a few weeks.

Before the water trap was introduced in the system, aqueous sample analysis was difficult to perform. So, a good way of trying the efficiency of the trap is to do headspace analysis. For this purpose, headspace analysis of BTEX (in this case benzene, toluene, ethylbenzene and *m*-xylene) solution was performed. 150 ml deionized water were placed in a 225 ml jar, and the membrane was placed in the headspace of the water. Appropriate amounts of the standard BTEX solution in methanol were spiked into the water, to give different concentrations of BTEX. The solution was stirred and left to equilibrate with the headspace and the membrane for 1 min before the analysis.

A 20 ppb (w/w) solution was obtained by spiking 0.2 μl of the concentrated BTEX standard solution into 150 ml water. The chromatogram obtained after a 4 min concentration time is presented in Fig. 8. The temperature of the column was 50°C and the flow rate was 5 ml/min. The first peak in the chromatogram is the air peak, followed by the peak

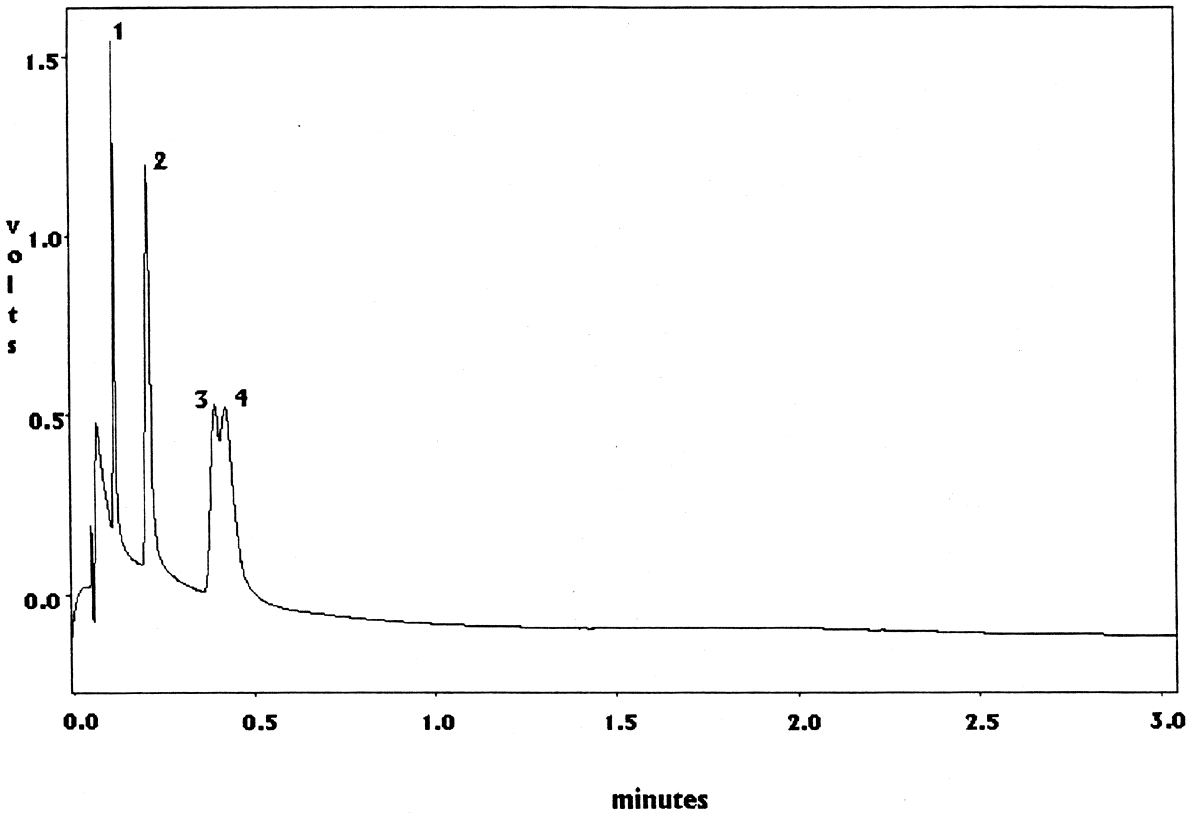

Fig. 8. Chromatogram of BTEX, obtained after the introduction of the water trap. Peaks: 1=benzene; 2=toluene; 3=ethylbenzene; 4=*o*-xylene.

of water and methanol. The next four peaks are as follows: 1=benzene, 2=toluene, 3=ethylbenzene and 4=*o*-xylene. It can be seen that in this chromatogram obtained with the new system, the peak of water (and methanol) is as small as 0.5 V after a 4 min concentration time. In the experiments performed without the water trap and having the membrane exposed to a standard gas mixture containing very little moisture, the water peak was 1.5 V high after 3 min concentration time. Water from one of the sinks in the laboratory was analyzed, using the same stirring rate. When the water sample was taken from the sink, it was actually exposed to the air for about 1 min before the analysis was performed. The analytes were concentrated for 6 min. The flow rate was 4 ml/min, and the temperature of the column was 50°C. The lower trace from Fig. 9 presents the chromatogram obtained in this way. The first peak in the chromatogram corresponded to air and water, and the second one was suspected to be chloroform.

The experiment was repeated, and the goal was to see an increase in the peak height, when standard chloroform solution was added to tap water. For this, a concentrated chloroform solution was prepared by spiking 1 μl of pure chloroform in 100 ml deionized water. The tap water was reanalyzed, using the same concentration time. After the first 6 min, 20 μl of the concentrated chloroform solution were added to the tap water, and the solution was again analyzed after a 6 min concentration time. The amount of the additionally introduced chloroform was about 1 ppb (w/w). The peak suspected to be chloroform increased significantly, as it can be seen in the upper trace of Fig. 9. The experiment was repeated several times, using different amounts of the chloroform solution and the peak of interest increased proportionally each time. Thus, it was concluded that the unknown peak was probably chloroform. It can be seen in Fig. 9 that the increase in the height of the peak produced by an increase in concentration with about 2 ppb (w/w) is much bigger than the height of the original peak in the tap water. This fact leads to the conclusion that the original concentration of chloroform in water (at the time when the analysis was done) was in the sub-ppb range.

The results obtained with the MESI system were compared with results obtained by SPME. Tap water was analyzed using SPME and a mass spectrometer. Chloroform was detected in water, and its concentration (which varies from day to day) was determined in several different days, using SPME and the standard addition method. The concentration of chloroform determined this way in the tap water fluctuated between 2 and 4 ppb (w/w). This fact proved the high sensitivity of the MESI system, even when the detector used was a thermal conductivity detection. However, when the tap water was analyzed by MESI, a considerable amount of chloroform was lost during the exposure of the sample to air, and this is the reason why the height of the chloroform peak was so small.

By coupling MESI to a micro-GC system, a very powerful system for field analysis can be obtained. In order to create a sampling device for volatile organic compounds (VOCs) that would be free from interference of semivolatile organic compounds, and to improve the mass transfer, a ''cup'' membrane system was designed in our laboratory. Fig. 10 presents a schematic diagram of this sampling device. The membrane is placed inside a cup, and a Teflon piece makes a tight seal around the cup. The designed system can be placed on the top of a water stream, and headspace can be created in this way. The membrane is kept away from the interfering species present in the water, and mass transfer is improved by sampling VOCs from the headspace.

Even though this sampling system was successfully used, a ''hump'' was observed to appear in many chromatograms, after the water peak. It was the same hump that the chloroform peak was observed to have eluted on (Fig. 9). This hump appeared to be dependent on the amount of sorbent packed in the trap, and its presence was conditioned by the presence of the membrane module in the system. The hump was not present in any of the chromatograms that were recorded while the membrane module was bypassed. This fact led us to the conclusion that the presence of the hump might be related to the increased amount of oxygen in the system permeating through the membrane. Fig. 11 presents two overlaid chromatograms obtained with (lower trace), and without (upper trace), the membrane module in the system. It can be seen that in the upper chromatogram, in which the membrane was bypassed, no hump appears after the water and oxygen peak. Fig. 12 presents the overlaid chromatograms obtained

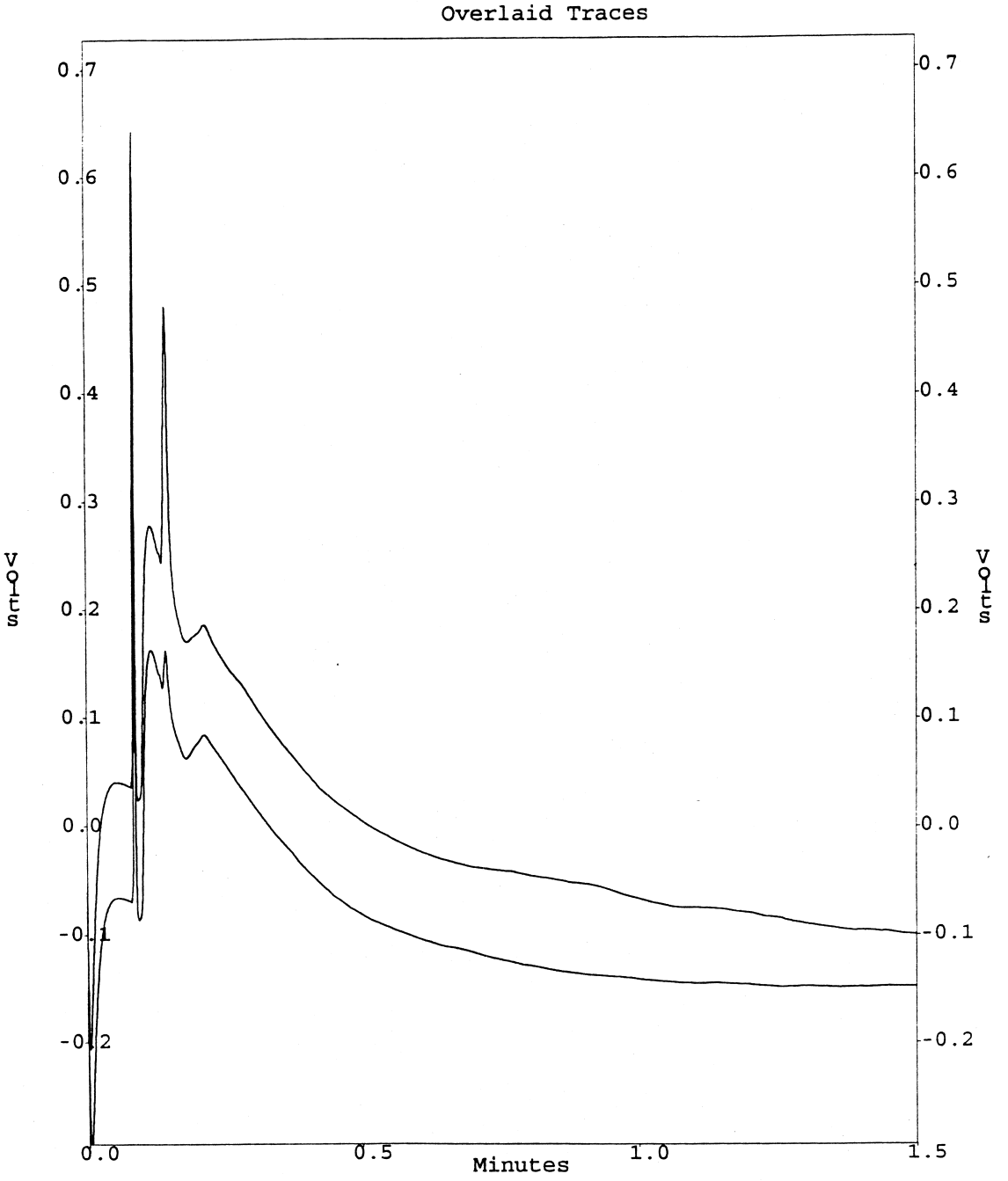

Fig. 9. Chromatogram of tap water. The lower trace has been obtained by analyzing chloroform in tap water. The upper trace corresponds to the standard addition of 2 ppb of chloroform in the same tap water.

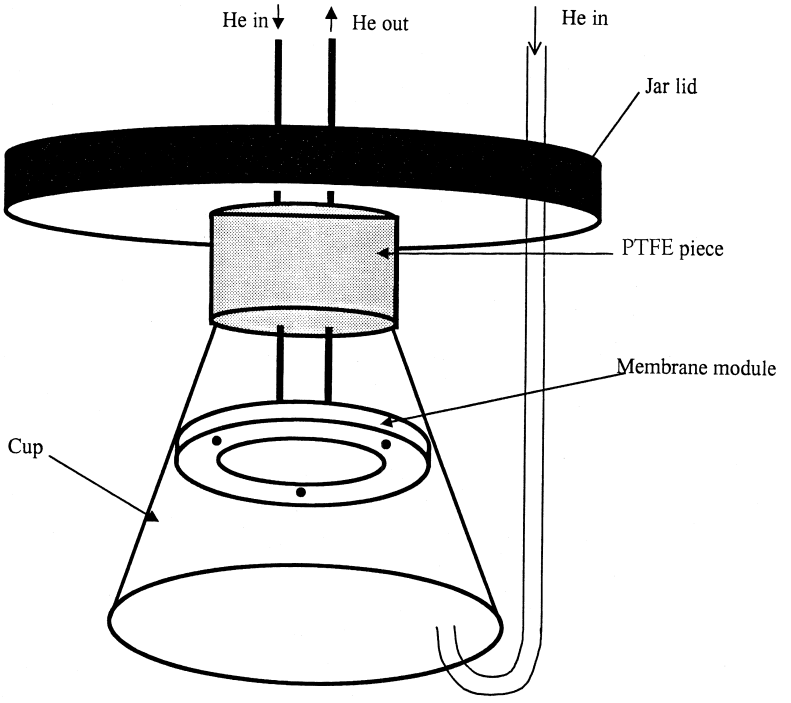

Fig. 10. Design of the cup-sampling device.

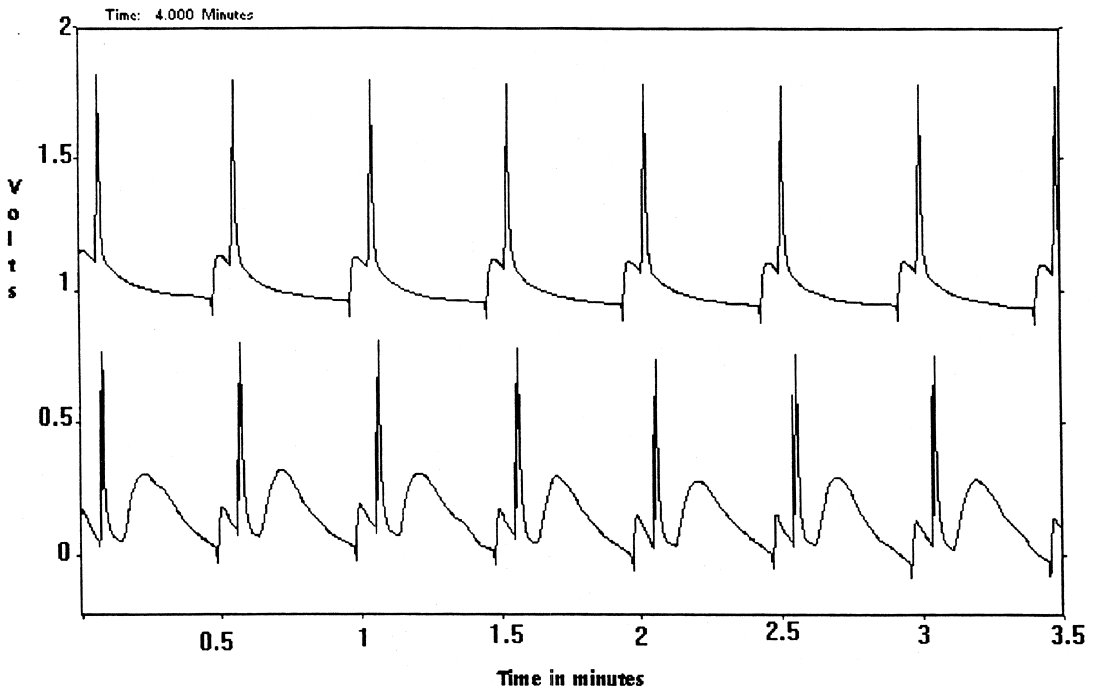

Fig. 11. Overlaid chromatograms obtained with (lower trace), and without (upper trace) the membrane module in the system.

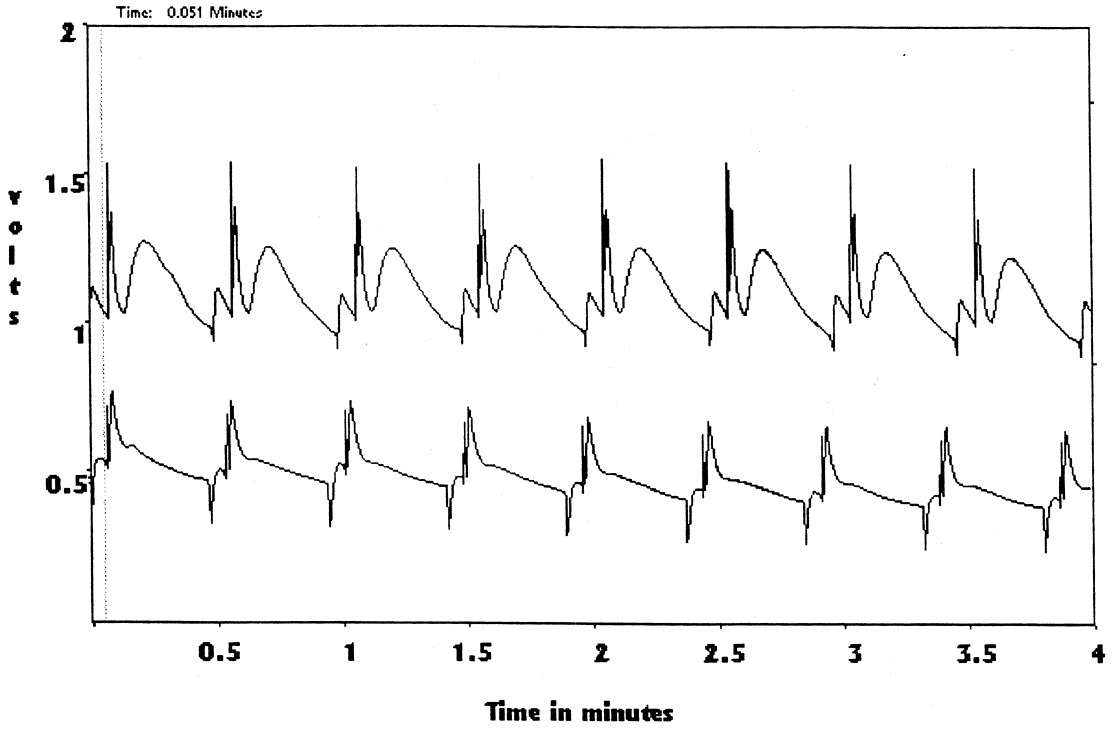

Fig. 12. Overlaid chromatograms obtained using traps containing different amount of sorbent material: for the upper trace the trap contained very high amount of sorbent, and for the lower trace, the trap contained very little sorbent.

with the membrane module connected in the system, and two different traps containing the same sorbent but in different amounts. The upper chromatogram was recorded using a trap that contains a very high amount of sorbent, whereas the trap used when recording the lower chromatogram contained very little sorbent.

Four different sorbent materials (PDMS, dibenylbenzene, Tenax-TA and Carboxene-1000) were used, and their performance was compared. The hump was present in all chromatograms, regardless of the sorbent used in the traps.

Because of the obtained results, preliminary experiments were performed to verify if the oxidation products of the trapping material produce the hump. A first experiment checked the effect of water on the system: the membrane module was immersed in water, and the system was left running for several minutes. The hump disappeared from the chromatogram. A second experiment was conducted having the membrane module placed in an inert gas atmosphere. The membrane was placed in an empty jar, and the jar was flushed with He, at a flow rate of about 100 ml/min. The hump became smaller, but did not disappear completely. However, this has been suspected to be caused by the traces of air that remained in the jar (the air was not completely displaced by He).

In order to create a completely inert atmosphere around the membrane, the cup-system was slightly modified: a piece of Teflon tubing was attached to the cup, and He was purged through it. Because of the lower density of He in comparison to air, He would displace the air from the top of the cup, and would remain trapped in it for as long as the cup is not lifted or turned upside down. In this way oxygen would be prevented from entering the system, and the mass transfer would be even more improved (faster diffusion through He).

Fig. 13 presents two chromatograms obtained using the cup-system. The upper trace was obtained for the analysis of a mixture of benzene and ethyl-

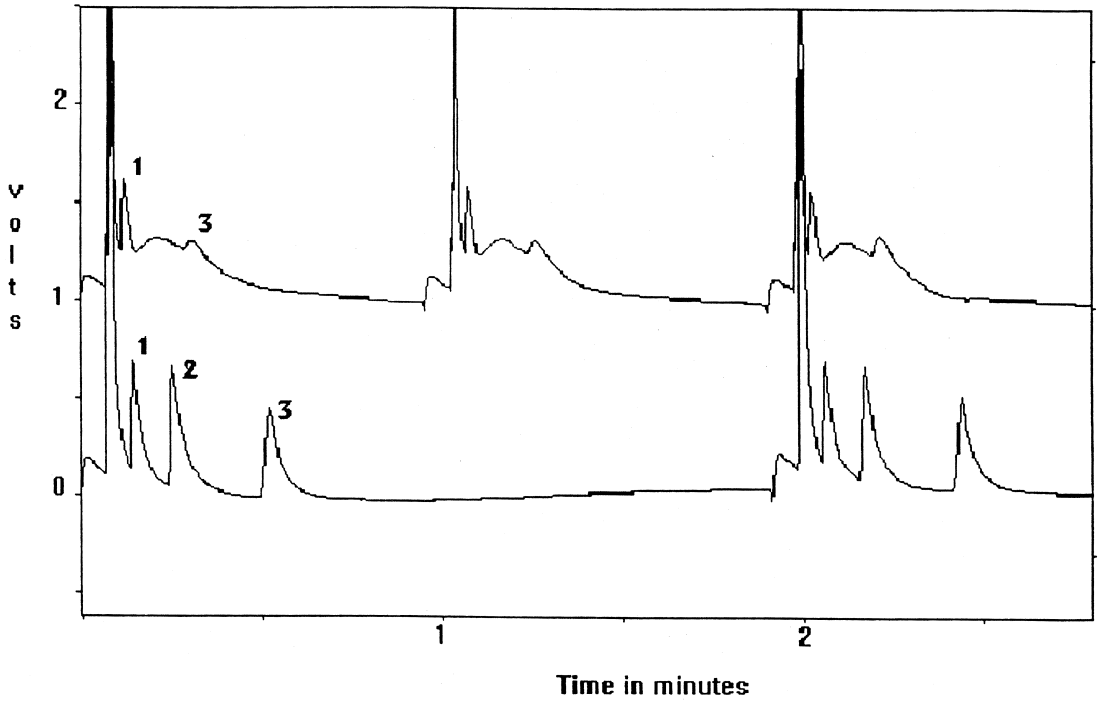

Fig. 13. Comparison of chromatograms obtained before (upper trace), and after (lower trace) the elimination of oxygen from the system. Peaks: 1=benzene; 2=toluene; 3=ethylbenzene.

benzene, with the membrane exposed to the headspace of the aqueous sample. The second trace was obtained for a mixture of benzene, toluene and ethylbenzene, with the cup being purged by He. It can be seen that the hump is not present in the lower chromatogram.

Having solved the problem of the hump, a calibration curve was obtained for toluene. The concentrations used were 1, 3, 10, 30 and 100 ppb (w/w). As it can be seen in Fig. 14, the calibration curve was linear. The estimated limit of detection was 60 ppt (w/w).

4. Conclusions

Membrane extraction with a sorbent interface proved to be a very useful sample introduction technique for fast analysis of volatile organic compounds. Semi-continuous monitoring of both, gaseous and aqueous samples can be done. Elimination of laborious sample preparation steps shortens the analysis time. Sensitivity is very much improved by preconcentrating the sample. Analysis of complex samples can be performed by headspace extraction, combined with the use of selective membranes and detectors.

The preliminary research presented in this paper demonstrates that the scope of field GC analysis with existing instrumentation can be dramatically improved without completely redesigning the instruments, by coupling them with modern sampling/sample preparation techniques. Future research will try to combine the water trap with an oxygen trap, and have the moisture and the oxygen removed from the system without the use of the purging inert gas. However, the use of the cup-system will still be considered because of the other advantages mentioned before.

Acknowledgements

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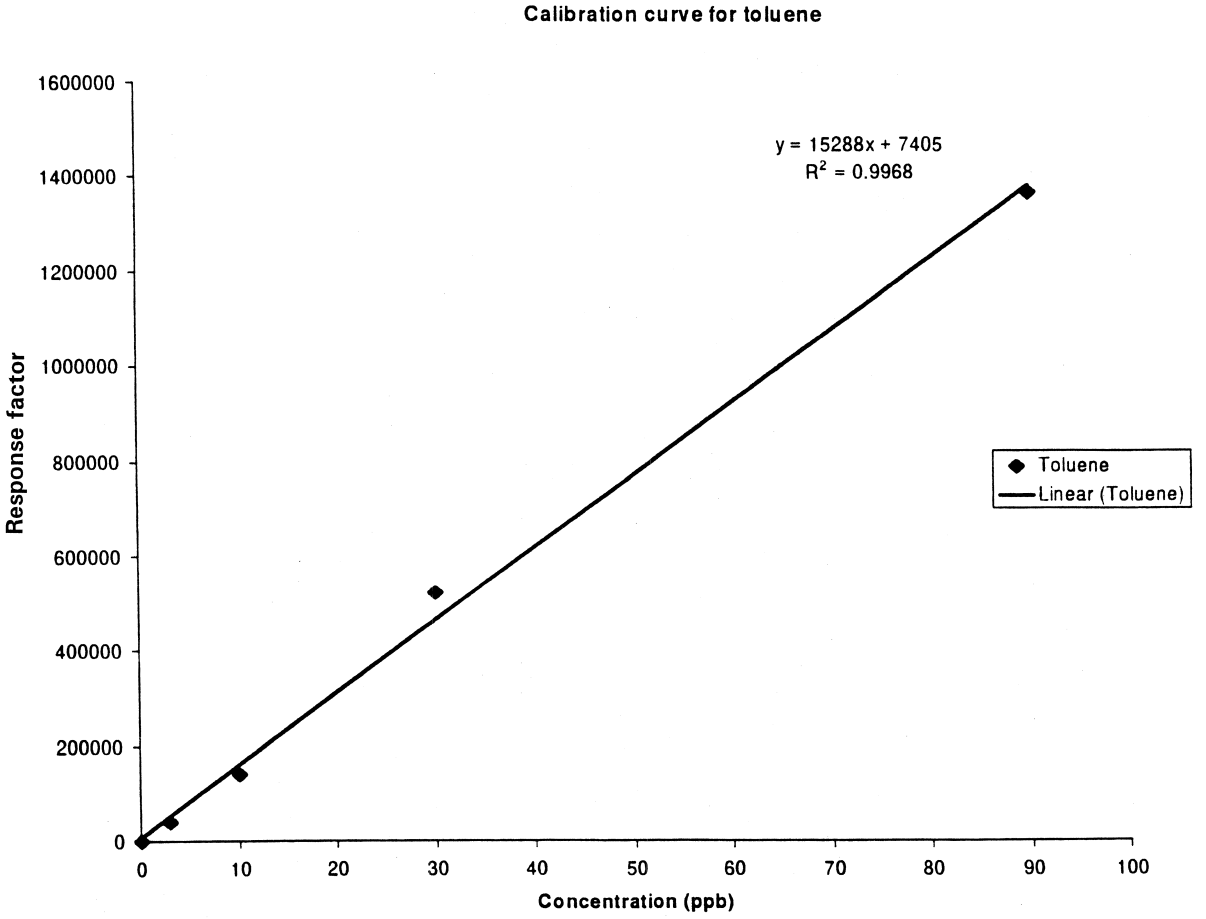

Fig. 14. Calibration curve for toluene.

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