Solid Phase Microextraction Using Fused Silica Fibers Coated with Graphitized Carbon Black

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Key Words

Gas chromatography
Solid phase micro extraction
Graphitized carbon black
Volatile organic compounds

Summary

This paper presents the results obtained using fused-silica fibers coated with graphitized carbon black (Carbograph-Alltech) for solid-phase microextraction (SPME). The extraction and calibration curves relative to organic micro-pollutants present in gaseous and aqueous samples are reported. Examples of applications of this extraction procedure to GC and GC-MS analysis of organic micro-pollutants in actual samples are also reported.

Introduction

In recent years a new technique of extraction and sample pre-concentration for analyzing organic micro-pollutants in different matrices, e.g. air and water, has been introduced; this technique is called solid-phase microextraction (SPME) [1–3]. SPME is an alternative to traditional extraction procedures, e.g. liquid-liquid extraction, static and dynamic head space, thermal trap desorption, SPE, etc.

This new technique utilizes a thin, fused-silica optical fiber coated with a film of polymeric liquid, like polydimethylsiloxane. When the fiber is introduced into a sample, the analytes present in the sample partition into the polymeric liquid which coats the fiber, and are then thermally desorbed into the injector of a gas chromatograph. The fiber is contained in a syringe needle which protects it during the introduction of the sample into the injector of gas chromatograph.

Because of its simplicity, speed and low cost, this technique won immediate acceptance, as affirmed in recent publications relative to this field [1–12].

This paper discusses studies using a fused-silica fiber coated with graphitized carbon black (GCB) [13]. This adsorbent was chosen due to its particular properties. Carbograph I (Alltech), the graphitized carbon black we used, has the following characteristics: a homogeneous and macroporous surface; an elevated thermal stability; it does not retain water; and, it does not manifest irreversible adsorption phenomena [14]. The graphitized fiber which operates with adsorption mechanisms, is characterized by considerable speed of extraction and good capacity. In light of the above, we have chosen to use this fiber for GC and GC-MS analysis of organic micro-pollutants in air, water and biological fluids. The results obtained are reported in this paper.

Experimental

Sampling Device

The device utilized for SPME was created by modifying a 5 µl Hamilton 7000 syringe [1], placing the fused-silica fiber coated with graphitized carbon black into the needle of this syringe. This device (Figure 1) allows the coated fiber to move in and out of the syringe needle which protects the fiber when the sample is introduced into the GC injector. The fused-silica fiber (Polymicro Technologies, Tucson, AR, USA), which has a diameter of 180 µm and is 15 cm long, is coated for a length of 4 cm with a homogeneous layer of Carbograph 1 (Alltech Associates, Deerfield, IL, USA), through immersion into a slurry and subsequent evaporation of the solvent; the process is repeated three times. For optimum and efficient coating of the fiber, the slurry must be perfectly homogeneous and consisting of submicron particles.

The slurry is prepared by sonicanting a suspension of Carbograph 1 in an *n*-pentane-dichlorornethane mixture (1:1), using the procedure used for the preparation of graphite-layer open-tubular (GLOT) capillary columns [15, 16]. After coating, the fiber is inserted into the suitably modified syringe, and then conditioned for 15 hours at 320 °C in the injector of the gas chromatograph under a low flow of helium.

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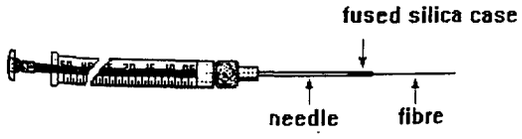

Figure 1
Diagram of the SPME device.

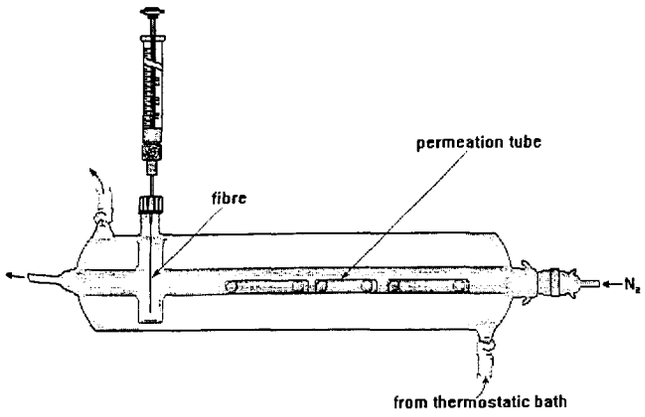

Figure 2
Diagram of the calibration apparatus.

Analysis of Gaseous Samples

In order to study the behavior of the Carbograph coated fiber when used for sampling organic compounds in gaseous matrixes, we used gaseous mixtures of the compounds of interest in ultra pure N_2, prepared using the apparatus illustrated in Figure 2. This apparatus, which utilizes permeation tubes as primary standards for the analytes of interest, has been described in previous papers [17, 18].

For the present study, the apparatus was modified, as illustrated by Figure 2, by equipping it with an opening, sealed with a silicone septum, to permit direct sampling of the organic compounds present in the mixture by simply introducing the coated fiber into the system. The concentration of the analytes in the gaseous mixture, produced by this apparatus, depends on the temperature of the permeation tubes, the nitrogen flow rate, the material of the tubes (Teflon FEP, Dupont, in our case), and the permeation tube dimensions (internal diameter, wall thickness, and length). Using the apparatus shown in Figure 2 and by adjusting these parameters, gaseous mixtures in which the analytes of interest are present in the desired concentrations can be obtained.

During sampling, the coated fiber (4 cm) is kept in contact with the gaseous mixture for the time necessary for the analytes to reach an equilibrium of distribution between the fiber surface and the gaseous matrix. This way an enrichment of the analytes on the surface of the adsorbent which coats the fiber is achieved.

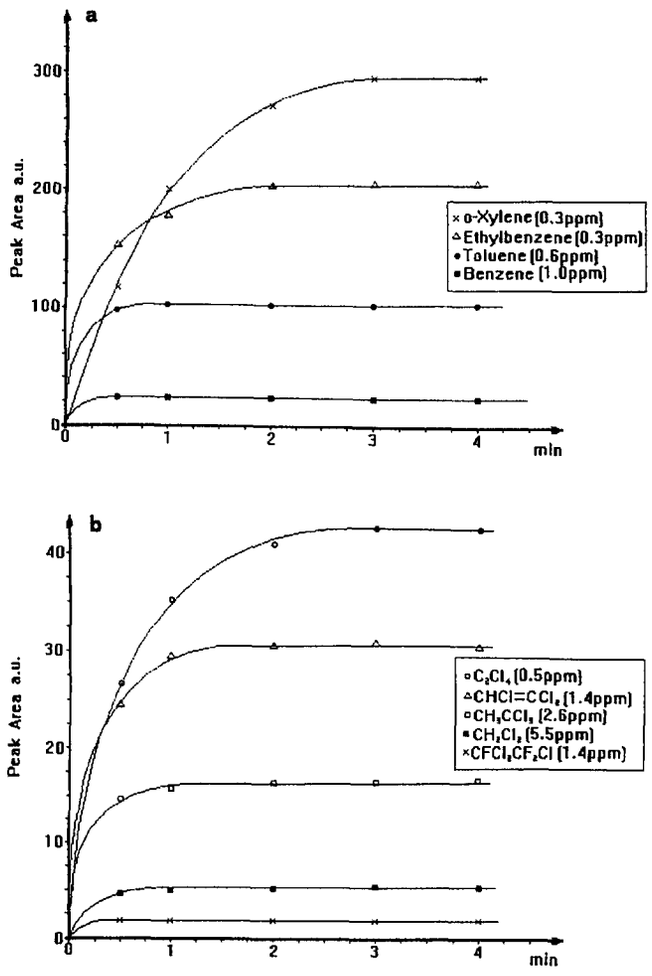

Figure 3
Adsorption-time profile of some volatile organic compounds adsorbed by graphitized fiber from gaseous mixture.

Once sampling is terminated, the fiber is drawn back into the syringe needle and then analyzed by GC by introducing it into a vaporizing injector (240 °C) for one minute; this procedure rapidly desorbs the analytes which, in this way, are introduced into the chromatographic column.

The sampling time is experimentally determined by establishing the extraction curves (Figures 3a–3b) obtained by keeping the fiber in contact with the gaseous mixture for increasingly longer time periods, until a constant adsorption of the analytes is reached. The sampling time is plotted on the abscissa and, the area of the chromatographic peak, which is proportional to the quantity of analyte adsorbed on the GCB-coated fiber surface, is plotted on the ordinate.

For the analysis of actual samples, e.g. environmental air, the fiber is simply exposed to the air for a period of time slightly longer than necessary for reaching equilibrium, as indicated by the extraction curves of the analytes. If GC analysis is not conducted immediately following the sampling, the device is conserved at a low temperature, after having capped the syringe needle

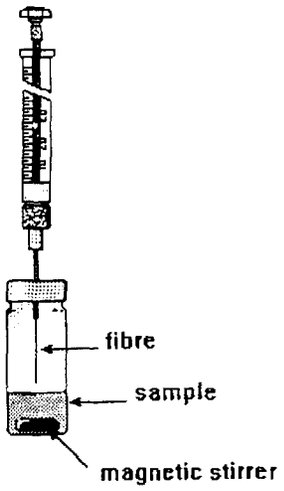

Figure 4
Diagram of the device for head space-SPME sampling.

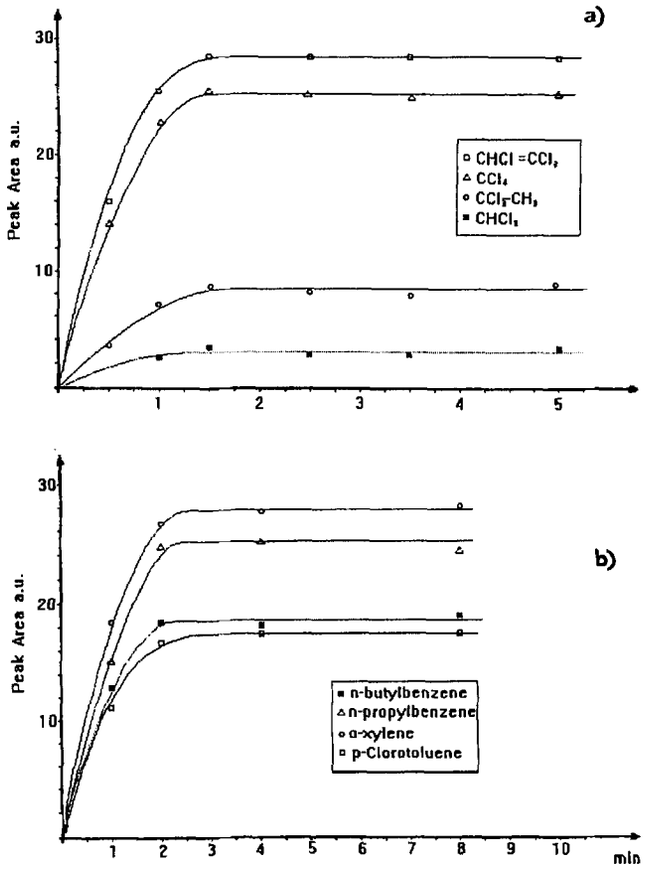

Figure 5
Adsorption-time profile of some VOCs adsorbed by GBC coated fiber from aqueous solutions; a) Analyte concentrations = 1 ng mL^{-1}; b) Analyte concentrations = 0.05 ng ml^{-1}.

with a previously purged green septum. After one hour of storage at 5 °C, no significant leakage was noted, not even in the case of the more volatile compounds.

Analysis of Aqueous Samples

From 2 ml to 4 ml of the aqueous sample to be analyzed are introduced into a carefully cleaned 20 ml vial which is then sealed with a teflon-coated silicone septum. A magnetic stirrer is kept in the vial to agitate the sample.

To sample organic compounds contained in the aqueous solution, the coated fiber is introduced into the vial (Figure 4) and exposed to the head space for a period of time sufficient for reaching equilibrium, which, as has been described for gaseous compounds, is determined through the extraction curves of the individual compounds (Figures 5a, 5b).

As a result of this operation the analytes are enriched on the surface of the adsorbent which coats the fiber.

The solutions of a known concentration of the various analytes in water or in other aqueous matrixes were prepared by spiking the clean matrix with a small volume of a standard solution of the analytes in methanol to obtain the desired concentrations. Water purified with "Milli-Q Plus" (Millipore Corp., Bedford, MA) was used to prepare the solutions.

The procedure used for the analysis of halogenated hydrocarbons in human blood was the following:
0. 5 ml of whole blood was diluted with 2 ml of water and left to incubate in the sampling vial at 25 °C for 25 minutes. After incubation, sampling was performed as previously described. The urine samples were diluted with water in a proportion of 1:1 prior to analysis.

Instrumentation

The gas chromatographic analysis was performed using a DANI 8500 gas chromatograph with a PTV (programmed temperature vaporization) injector and a FID detector.

A VG 70-70 H magnetic sector mass spectrometer coupled to a 3800 gas chromatograph equipped with a PTV injector and an HP 5970 quadrupole mass spectrometer coupled to an HP 5870 gas chromatograph equipped with a split/splitless injector were used for the GC-MS analysis.

The initial and final temperatures of the PTV injector were, respectively, 40 °C and 240 °C. The temperature of the split/splitless injector was 240 °C.

For desorption, the fiber was kept in the injector at 240 °C for one minute, with the split valve closed.

The gas chromatograph with an FID detector was equipped with a Carbograph 1 capillary column, i.d. 0.25 mm, 30 m long (Alltech) and the gas chromatographs coupled to the mass spectrometers were equipped with a Carbograph VOC capillary column, i.d. 0.25 mm, 30 m long (Alltech).

The Carbograph 1 slurry was prepared using a Branson Mod. 450 Sonicator (Branson, Danbury, CT, USA). Pure standards purchased from Alltech were used both for the preparation of the permeation tubes and the preparation of stock solutions of the studied compounds.

The permeation tubes were made "in house" [17] using two types of Teflon FEP (Dupont) tubing: the first with an internal diameter of 5 mm and a wall thickness of 0.3 mm and the second with an internal diameter of 6.5 mm and a wall thickness of 1.4 mm. The permeation tubes which we constructed were between 4 and 6 cm in length.

The Carbograph 1 (surface area = 100 $m^2 g^{-1}$) was purchased from Alltech.

Results and Discussion

Figure 3(a) shows the extraction-time profiles of several aromatic hydrocarbons obtained by sampling a gaseous mixture in which the investigated analytes were present at ppm level, for time intervals between 30 seconds and 4 minutes, followed by GC-FID analysis.

Figure 3(b) shows the extraction-time profiles of several halogenated hydrocarbons obtained through the same procedure used for the aromatic hydrocarbons, but followed by GC-MS-SCAN analyses using the quadrupole mass spectrometer.

As can be seen, for each compound, there exists a time after which the quantity of analyte adsorbed on the GBC-coated fiber surface remains constant even if the sampling time is increased. This indicates that distribution equilibrium of the analytes between the gaseous phase and the fiber surface was reached.

Due to the rapidity with which this equilibrium is reached, the sampling times are very brief (max. 3 min), even in the case of the less volatile aromatic and halogenated hydrocarbons. This experiment was repeated with 10 times less diluted samples and with 10 times more concentrated samples and the results obtained were similar to those shown in the Figures 3a and 3b.

Figures 6(a) and 6(b) show the calibration curves obtained by using GC-FID to analyze several gaseous mixtures of hydrocarbons in nitrogen prepared with the apparatus in Figure 2, and sampled using the SPME procedure. The calibration curves show that for all of the investigated compounds, a linear dependence exists between the quantity of each analyte adsorbed on the coated fiber surface and the concentration of the same analyte in the gaseous mixture. These curves can be used for the quantitative determination of the analytes present in actual samples.

Figure 7 shows a FID chromatogram obtained by analyzing a standard mixture of hydrocarbons in nitrogen, sampled with SPME procedure.

Table I shows the concentrations and standard deviations obtained by analyzing the same gaseous sample containing aliphatic and aromatic hydrocarbons 8 times, using GC-FID. The low relative standard deviation values are an indication of the good reproducibility of this sampling procedure.

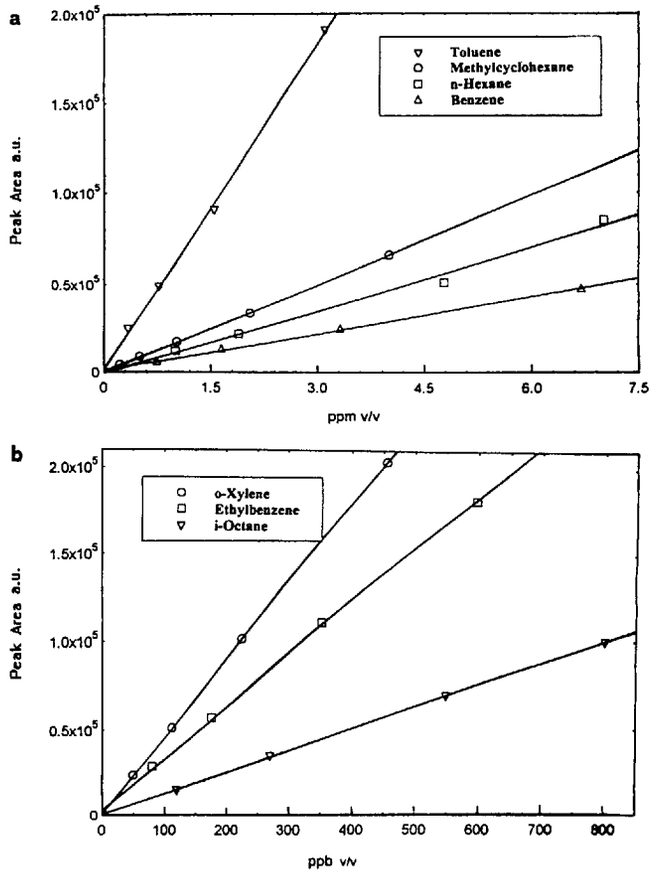

Figure 6
Calibration curves of some hydrocarbons adsobed by GBC coated fiber from gaseous mixture.

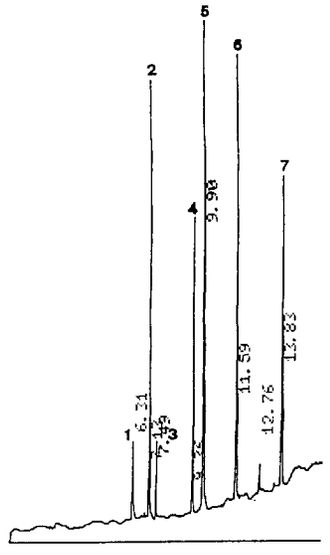

Figure 7
Chromatogram of a gaseous mixture of hydrocarbons sampled with the SPME procedure: **1** = Benzene 0.7 ppm (vol/vol); **2** = *n*-Hexane 1,5 ppm (vol/vol); **3** = Methylcyclohexane 0.2 ppm (vol/vol); **4** = *i*-Octane 0.1 ppm (vol/vol); **5** = Toluene 0.3 ppm (vol/vol); **6** = Ethylbenzene 80 ppb (vol/vol); **7** = *o*-Xylene 50 ppb (vol/vol). Column: 30 m × 0.25 mm i.d. Carbograph 1 (Alltech). Chromatographic conditions: Carrier gas = He; linear gas velocity = 30 cm s^{-1}. Oven temperature = 2 min at 40 °C, then programmed at 15 °C min^{-1} to 200 °C. Detector = FID (210 °C).

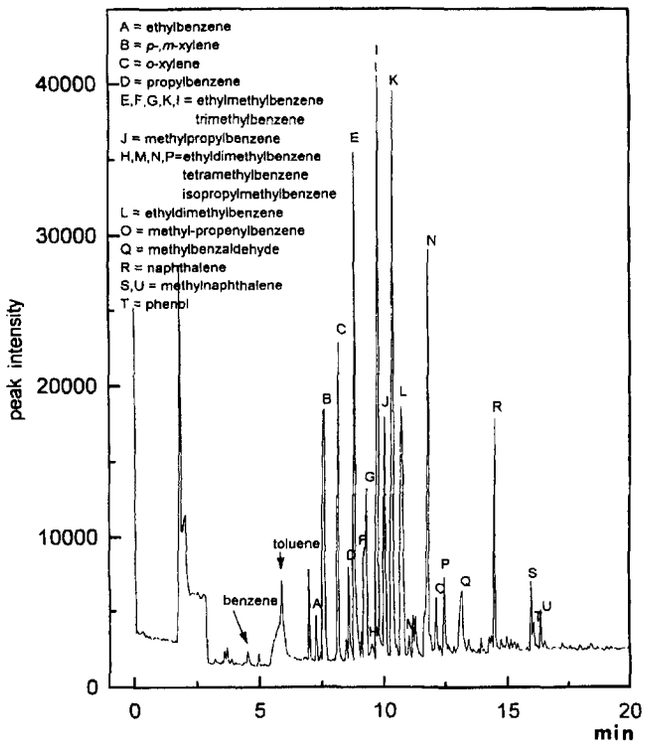

Figure 8

Chromatogram of an air sample taken from an underground parking lot sampled with the SPME procedure. Column: 30 m × 0.25 mm. i.d. Carbograph VOC (Alltech). Chromatographic conditions: Carrier gas = He; linear gas velocity = 30 cm s^{-1}. Oven temperature = 2 min at 30 °C then programmed at 13 °C min^{-1} to 200 °C. Detector: magnetic sector MS in the SCAN mode from m/z 30 to m/z 250. MS resolution = 1000.

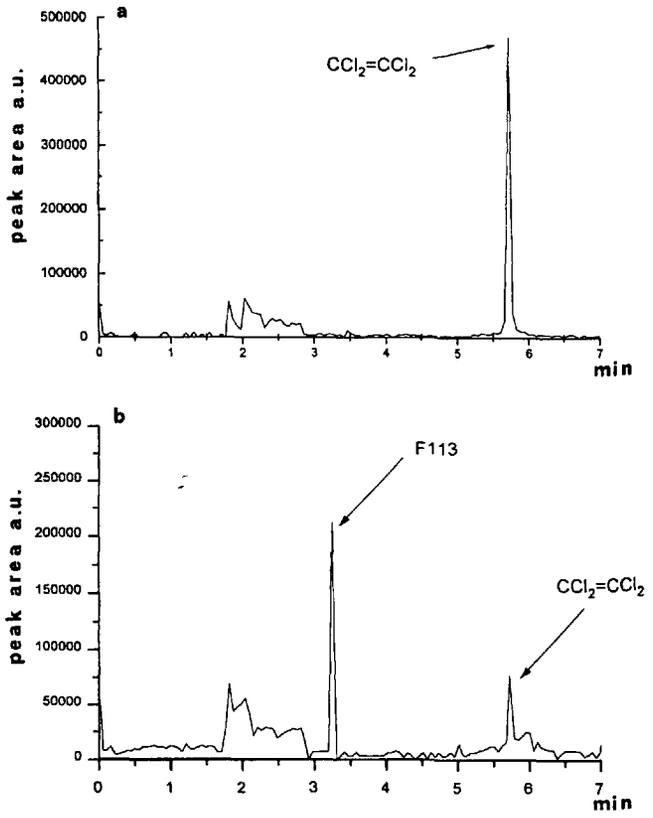

Figure 9

Chromatograms of air samples taken from dry-cleaning establishments: a) Dry-cleaner uses $Cl_2C=CCl_2$; b) Dry-Cleaner uses a mixture of CFC 113 and $Cl_2C=CCl_2$. Same column and chromatographic conditions as in Figure 7. Detector: magnetic sector MS in the SIM mode.

Table I. Mean concentration values and relative standard deviations (calculated on 8 analyses) of a gaseous hydrocarbon mixture sampled with the SPME procedure. Detector: FID.

	ppm (vol/vol)	R.S.D %
Benzene	1.0	0.9
n-Hexane	1.9	0.5
Methylcyclohexane	0.2	1.0
i-Octane	0.1	1.0
Toluene	0.3	0.9
Ethylbenzene	0.08	1.4
o-xylene	0.04	1.5

Table II. Analysis of the same environmental air, sampled using two different procedures.

Compound	SPME ppb (vol/vol)	TRAP ppb (vol/vol)
Benzene	33	37
n-Hexane	357	348
i-Octane	8	5
Toluene	18	15
Ethylbenzene	6	3
o-Xylene	4	n.d.

The detection limits of this sampling procedure, using MS-SIM detection, range from ppt (vol/vol) to ppb (vol/vol).

The air in the proximity of the exit area of the effluent from the apparatus containing the permeation tubes was analyzed for the comparison of SPME procedure with that using traps containing Carbograph 1 [19].

For this purpose, while the graphitized fiber was exposed to this air for 4 minutes, at the same time 100 ml of this air were sampled by means of a trap containing Carbograph 1, and then analyzed by means of thermal desorption. Table II compares the results obtained using the two different sampling procedure; the two sets of results are in good accord. It should be noted that *o*-xylene, given its low concentration (4 ppb), was not detected by the method which utilizes the trap. The SPME method is rapid and simple, while the method which uses the trap requires dedicated instruments and is time-consuming.

Analyses were also conducted on actual samples, such as the air in an underground parking garage and in work environments.

Figure 8 illustrates the GC-MS-SCAN chromatogram (from m/z 50 to m/z 250 using magnetic sector MS) ob-

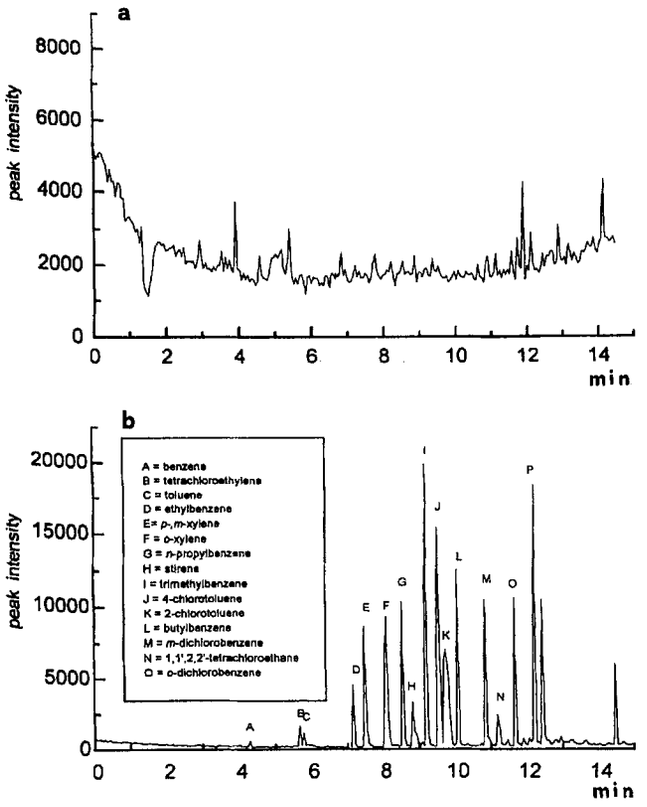

Figure 10
Sampling comparison of 0.2 ng mL^{-1} solutions of some VOCs. Chromatogram a) headspace procedure; chromatogram b) headspace-SPME procedure. Detector: magnetic sector MS in SCAN mode from m/z 30 to m/z 250. Same column and chromatographic conditions as in Figure 7.

Table III. Detection Limits (DL) of some VOCs in water sampled using Head SpaceSPME procedure. Detector: magnetic sector MS in the SIM mode. Sample amount: 4 mL.

Compound	m/z	DL (pg mL^{-1})
Bromodicbloromethane	83	6
Toluene	91	4
Benzene	78	10
Carbontetrachloride	117	5
Chlorobenzene	112	1
Cblorofo rm	83	10
2-Chlorotoluene	91	2
Etbylbenzene	91	1
Tetrachloroethylene	166	2
1,1,1-Tricbloroetbane	97	3
o-Xylene	91	1

tained by analyzing the air in an underground parking lot in Urbino after 10 minutes of sampling using the present method. Different aromatic compounds, an aldehyde and phenol were identified at ppb (vol/vol) levels.

The air in two dry-cleaning establishments was also analyzed; the air was sampled for 5 minutes using the SPME procedure. Figure 9 illustrates the GC-MS-SIM chromatograms relative to these samples; they were obtained by selecting m/z 83 for tetrachloroethylene and m/z 101 for CFC 113 (Cl_2FC-$CClF_2$): chromatogram a) refers to a dry-cleaner which uses the solvent tetrachloroethylene, while chromatogram b) refers to a dry-cleaner which uses the solvents CFC 113 and tetrachloroethylene. The concentrations detected were 3 ppm (vol/vol) for tetrachloroethylene in the first dry-cleaner, and 4 ppm (vol/vol) for CFC 113 and 0.4 ppm (vol/vol) for tetrachloroethylene in the second. The analysis of these actual samples were performed with the magnetic sector mass spectrometer coupled to the gas chromatograph equipped with a PTV injector.

As shown in Figure 4, the determination of the organic compounds in the aqueous samples was performed by using the Carbograph I coated fused-silica fiber to sample the head space inside a 20 ml vial containing from 2 to 4 ml of the sample. This is an alternative procedure to that in which the fiber is immersed into the liquid sample. This alternative also permits the analysis of those samples which, like whole blood, may damage the surface of the fiber when they come into contact with it.

Using this procedure, significant enrichment of the analytes on the fiber surface is reached. This is evidenced by Figure 10 which illustrates the chromatograms obtained by GC-MS-SCAN (to m/z 50 from m/z 250) analysis of a sample of purified water spiked with a solution of aromatic hydrocarbons and halogenated hydrocarbons in methanol. The sample was opportunely diluted so that the final concentration of each analyte in water was 0.2 ng ml^{-1}. 2 ml of this solution were introduced into two different vials so that two types of sampling procedures could be performed.

Chromatogram in Figure 10 (a) refers to the injection of 100 µl of headspace taken from the first vial (60 °C) with a gas syringe, while chromatogram in Figure 10(b) refers to a 5 minute sampling of the head space in the second vial (25 °C) using the SPME technique. The enrichment of the sample obtained using the second procedure is evident.

Table III shows the "detection limits" (signal/background noise = 2) of several volatile organic compounds present in water(4 ml) which were sampled using the headspace-SPME method. The analyses were conducted using GC-MS-SIM, monitoring the more abundant ion fragment of each compound. The magnetic sector mass-spectrometer was operated at a resolution of 1000. The low DL (detection limits) values, from 1 to 10 pg ml^{-1}, evidence the sensitivity of this method.

Figures 5(a) and 5(b) report the extraction-time profile of several halogenated hydrocarbons and several aromatic hydrocarbons present in water. The concentration of the halogenated hydrocarbons was 1 ng/ml, while that of the aromatics was 50 pg ml^{-1}. The two figures show that the times necessary to reach distribution equilibrium are less than 5 minutes, even in the case of the less volatile compounds.

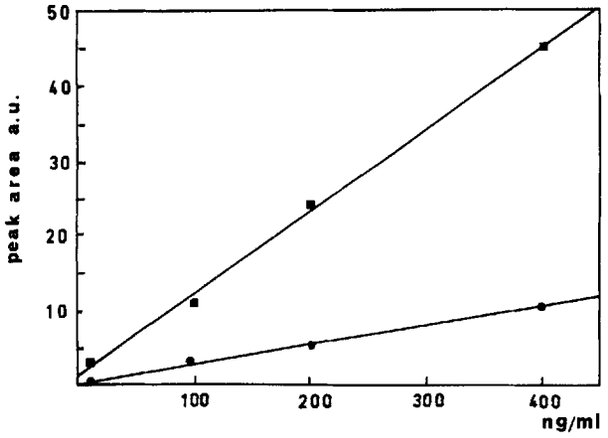

Figure 11
Calibration curves of $Cl_2C=CCl_2$ (■) and CFC 113 (●) in human blood-water 1:5. Detector: magnetic sector MS in SIM mode.

Table IV. CFC 113 and $Cl_2C=CCl_2$ levels (ng mL^{-1}) in blood and urine of dry cleaner employees. Drycleaner A and B use $Cl_2C=CCl_2$, drycleaner C uses CFC 113 and $Cl_2C=CCl_2$.

	CFC 113	$Cl_2C=CCl_2$	
	Whole blood	Whole blood	Urine
Employee of dry cleaner A	–	1203	424
Employee of dry cleaner B	–	825	290
Employee of dry cleaner C	772	710	210

When the concentrations of the analytes in the aqueous samples analyzed are at the level of several ppb, the relative standard deviations of this method are comprised between 4 % and 7 %.

We utilized the headspace-SPME procedure for the determination of tetrachloroethylene and of CFC 113 in blood and in urine samples of the employees working at the dry-cleaning establishments. For this study, blood and urine samples were taken from the employees, immediately following the dry-cleaning cycle, in three different dry-cleaning establishments. These samples were then analyzed by GC-MS SIM, using the previously described procedure. For the quantitative determination, the calibration curves of tetrachloroethylene and CFC 113, both in blood and urine, were constructed using clean blood spiked with these two compounds. Figure 11 shows the calibration curves for tetrachloroethylene and CFC 113 in human blood used to calculate the concentrations of the two analytes in the actual samples. Table IV shows the results of the analysis of the biological fluids of the employees in the three different dry-cleaning establishments (A, B, C).

In conclusion the results reported in this paper demonstrate that the device, which utilizes a fused-silica fiber coated with Carbograph 1, can be used for sampling volatile organic compounds from water, air and biological samples, prior to GC or GC-MS analysis.

The SPME method, which combines sampling and preconcentration of the analytes into one step, is simple, sensitive, rapid and inexpensive. The GBG-coated fiber can be used for an elevated number of samplings without losing its initial characteristics.

Using permeation tubes as primary standards allows gaseous mixtures of the analytes of interest at known concentrations to be obtained with good accuracy.

Acknowledgment

The authors would like to express their gratitude to L. Lattanzi for his help in the preparation of the GCB slurry.

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Received: Aug 18, 1995
Accepted: Sep 21, 1995