Anal. Chem. **2002,** *74,* 5688−5692

Fiber Introduction Mass Spectrometry: Fully Direct Coupling of Solid-Phase Microextraction with Mass Spectrometry

Eduardo C. Meurer, Daniela M. Tomazela, Rogerio C. Silva, Fabio Augusto, and Marcos N. Eberlin*

UNICAMP, Institute of Chemistry, State University of Campinas, CP 6154 13083−970 Campinas, SP Brazil

This work describes the first fully direct coupling of solid-phase microextraction (SPME) with mass spectrometry. An inlet system using a septum as the only interface between the ambient and the high-vacuum mass spectrometer was constructed to allow the introduction of the SPME needle directly into the ionization region of a mass spectrometer. The PDMS-coated fiber was then placed and exposed exactly between the two ionization filaments. Uniform heating of the fiber, efficient thermal desorption, and electron ionization of the analytes were achieved. Using this new analytical technique, here termed fiber introduction mass spectrometry (FIMS), we have been able to detect and quantitate several volatile (VOC) and semivolatile (SVOC) organic chemicals (carbon tetrachloride, benzene, toluene, xylenes, γ-terpinene, diisoamyl ether, chlorobenzene, and many PAHs) and two herbicides (Sylvex and its methyl ether) from aqueous solutions at low-ppb to ppt levels using either SPME headspace or solution extraction. FIMS shows high sensitivity (ng/L), good reproducibility, and accuracy, providing therefore a simple and effective approach to rapid analysis of VOC and SVOC in various matrixes.

Solid-phase microextraction (SMPE), an attractive alternative to most of the conventional sampling techniques, has gained widespread acceptance and is advantageously used in many analytical procedures.[1] SPME has become popular in GC and HPLC analyses since it integrates sampling, extraction, concentration, and sample introduction procedures into an easy, rapid, sensitive, and single solvent-free step. SPME uses a small piece of fused-silica fiber on which a stationary liquid phase is coated to absorb or adsorb the analytes and to concentrate them on the fiber. Fibers with a variety of sorbents are available, and poly(dimethylsiloxane) (PDMS) has became a major SPME coating material for volatile organic chemical (VOC) and many semivolatile organic chemical (SVOC) analyses. SPME is normally coupled with GC(/MS), but a simpler coupling of SPME to MS via a short GC transfer line has recently been described to achieve higher sample throughput and to obtain chemical "fingerprint" characterization of complex mixtures.[2]

PDMS membranes are also widely used for direct sample introduction into a mass spectrometer in the analytical technique known as membrane introduction (inlet) mass spectrometry (MIMS).[3] Similarly to SPME, MIMS also integrates easy, rapid, solvent-free, and sensitive VOC and SVOC sampling, extraction, concentration, and introduction all into a single step and has also been applied extensively in many analytical procedures.[4] In MIMS, VOC and many SVOC migrate selectively from the matrix (often aqueous solutions) to the hydrophobic membrane, concentrate in and diffuse through the membrane, and evaporate from the membrane surface directly into the high-vacuum ion source region of a mass spectrometer, in which they are ionized and then detected by mass analysis.

In the derived MIMS technique known as trap-and-release (T&R)-MIMS,[5] and the related single-sided MIMS (SS-MIMS)

* Corresponding author. E-mail: eberlin@iqm.unicamp.br.

(1) Artur, C. L.; Pawliszyn, J. *Anal. Chem.* **1990**, *62*, 2145. (b) Pawliszyn, J. *Solid-phase Microextraction: Theory and Practice;* Wiley: New York, 1997. (c) Yu, X.; Yuan, H.; Georechi, T.; Pawliszyn, J. *Anal. Chem.* **1999**, *71*, 2998. (d) Zygmunt, B.; Jastrzebska, A.; Namiesnik J. *Crit. Rev. Anal. Chem* **2001**, *31*, 1. (e) Ulrich, S. *J. Chromatogr., A* **2000**, *902*, 167. (f) Snow, N. H. *J. Chromatogr., A* **2000**, *885*, 445. (g) Eisert, R.; Pawliszyn, J. *Crit. Rev. Anal. Chem.* **1997**, *27*, 103. (h) Beltran, J.; Lopez, F. J.; Hernandez, F. *J. Chromatogr., A* **2000**, 885, 389. (i) Valente, A. L. P.; Augusto, F. *Quim. Nova* **2000**, *23*, 523. (j) Augusto, F.; Koziel, J.; Pawliszyn, J. *Anal. Chem.* **2001**, *73*, 481. (k) Zini, C. A.; Augusto, F.; Christensen, E.; Smith, B. P.; Caramao, E. B.; Pawliszyn, J. *Anal. Chem.* **2001**, *73*, 4729. (l) Augusto, F.; Valente, A. L. P.; Tada, E. D.; Rivellino, S. R. *J. Chromatogr., A* **2000**, *873*, 117.

(2) Peres, C.; Viallon, C.; Berdage, J.-L. *Anal. Chem.* **2001**, *73*, 1030.

(3) Kotiaho, T.; Lauritsen, F. R.; Choudhury, T. K.; Cooks, R. G. *Anal. Chem.*, **1991**, 63, 875A. (b) Lauritsen, F. R.; Kotiaho, T. *Rev. Anal. Chem.* **1996**, *15*, 237. (c) Mendes, M. A.; Pimpim, R. S.; Kotiaho, T.; Barone, J. S.; Eberlin, M. N. *Quim. Nova* **1996**, *19*, 480. (d) Srinivasan, N.; Johnson, R. C.; Kasthurikrishnan, N.; Wong, P.; Cooks, R. G. *Anal. Chim. Acta* **1997**, *350*, 257. (e) Johnson, R. C.; Cooks, R. G.; Allen, T. M.; Cisper, M. E.; Hemberger, P. H. *Mass Spectrom. Rev.,* **2000**, *19*, 1. (f) Ketola, R. A.; Kotiaho, T.; Cisper, M. E.; Allen, T. M. *J. Mass Spectrom.* **2002**, *37*, 457.

(4) For recent examples, see: (a) Cisper, M. E.; Garret, A. W.; Cameron, D.; Hemberger, P. H. *Anal. Chem.* **1996**, *68*, 2097. (b) Mendes, M. A.; Pimpim, R. S.; Kotiaho, T.; Eberlin, M. N. *Anal. Chem.* **1996**, *68*, 3502. (c) Creaser, C. S.; Stygall, J. W.; Weston, D. J. *Anal. Commun.* **1998**, *35*, 9H. (d) Kostiainen, R.; Kotiaho, T.; Mattila, I.; Mansikka, T.; Ojala, M.; Ketola, R. A. *Anal. Chem.* **1998**, *70*, 3028. (e) Moraes, L. A. B.; Eberlin, M. N.; Cagnon, J. R., Urbano, L. H. *Analyst* **2000**, *125*, 1529. (f) Mendes, M. A.; Sparrapan, R.; Eberlin, M. N. *Anal. Chem.* **2000**, *9*, 2166. (g) Alberici, R. M.; Zampronio, C. G.; Poppi, R. J.; Eberlin, M. N. *Analyst* **2002**, *127*, 230. (h) Nayar, A.; Liu, R.; Allen, R. J.; McCall, M. J.; Willis, R. R.; Smotkin, E. S. *Anal. Chem.* **2002**, *74*, 1933. (i) Short, R. T.; Fries, D. P.; Kerr, M. L.; Lembke, C. E.; Toler, S. K.; Wenner, P. G.; Byrne, R. H. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 676.

(5) Lauritsen, F. R.; Ketola, R. A. *Anal. Chem.* **1997**, *69*, 4917. (b) Matz, G.; Lennemann, F. *J. Chromatogr., A* **1996**, *750*, 141. (c) Mendes, M. A.; Eberlin, M. N. *Analyst* **1999**, *125*, 21. (d) Haddad, R.; Mendes, M. A.; Hoehr, N. F.; Eberlin, M. N. *Analyst* **2001**, *126*, 1212. (e) Vellasco, A. P.; Haddad, R.; Eberlin, M. N.; Höehr, N. F. *Analyst* **2002**, *127*, 1050.

10.1021/ac025880+ CCC: $22.00
Published on Web 10/08/2002

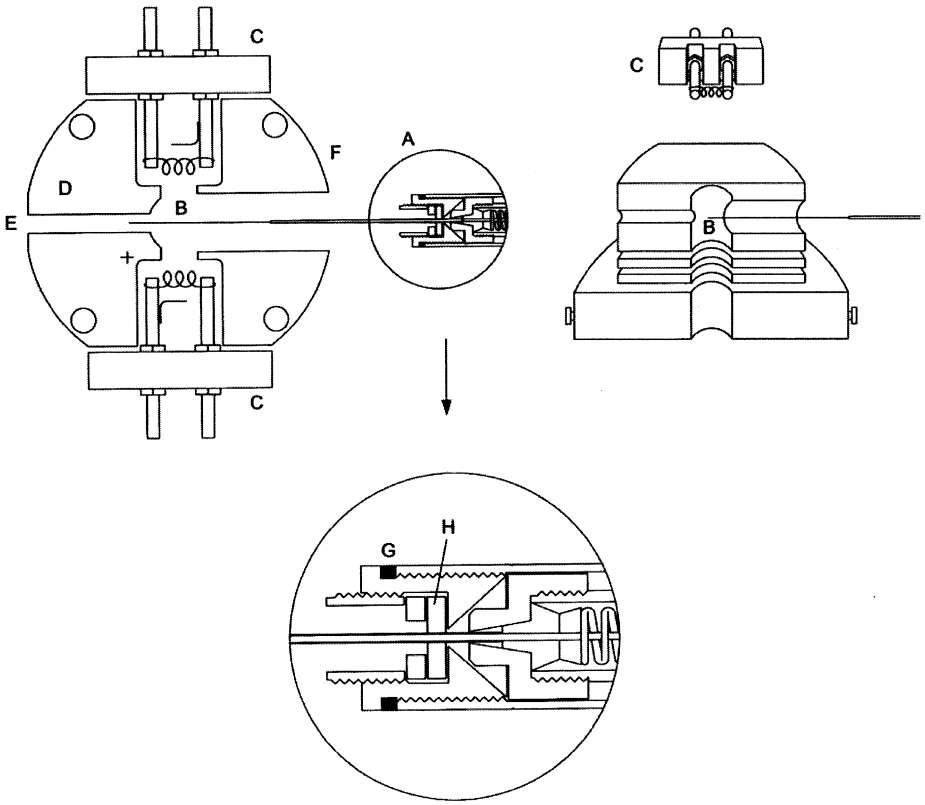

Figure 1. Different views and cross sections of the FIMS system: (A) partial cross section of the head of the FIMS probe; (B) PDMS coating of the SPME fiber in place for analyte thermal desorption and ionization; (C) the two standard EI ionization (and heating) filaments; (D) standard Extrel MS ion source block; (E) gas entrance line for alternative chemical ionization; (F) gas entrance enlarged to $^1/_4$ in. to allow for proper fiber introduction, (G) O-ring for sealing of the FIMS probe; (H) standard GC septum for vacuum sealing during fiber introduction.

technique,[6] more polar SVOC can also be analyzed with high sensitivity owing to preconcentration inside the membrane followed by fast and efficient "single-sided" thermal desorption of the trapped SVOC to the gas phase. In these techniques, the membrane side-to-side diffusion step is eliminated and therefore an ultrathin membranelike performance[7] is attained: the analytes are adsorbed in and desorbed from the same side of a tubular PDMS membrane.

In this paper, we report the first fully direct coupling of SPME to MS, via a new technique termed fiber introduction mass spectrometry (FIMS).[8] A SPME fiber with PDMS coating is used for efficient extraction and analyte (VOC and SVOC) introduction and thermal desorption directly into the ionization region of a mass spectrometer. FIMS combines, therefore, the selectivity of PDMS analyte adsorption with the sensitivity of PDMS analyte preconcentration and single-sided desorption and the versatility of SPME for sampling, extraction, and analyte introduction and thermal desorption—now occurring directly in the ionization region of a mass spectrometer for maximum ionization yield. FIMS allows combined high-throughput VOC and SVOC analyses at trace levels from various matrixes with analysis times being determined mainly by the SPME extraction step (although several fibers can be simultaneously used). As occurs for T&R-MIMS, FIMS also benefits from the heat radiation of the (two[5c]) MS filaments to promote uniform fiber heating and efficient single-sided in situ desorption of the analytes from the PDMS coating directly into the ionization region of a mass spectrometer, for maximum sensitivity.

EXPERIMENTAL SECTION

Equipment. The experiments were performed using an Extrel (Pittsburgh, PA) mass spectrometer fitted with a high-transmission $^3/_4$-in. quadrupole. As Figure 1 shows, the standard Extrel ion source (D) was used with a minor modification: the inner diameter of one (F) of the two gas entrance lines (E and F) was enlarged to $^1/_4$ in. to allow proper introduction of the SPME needle. A direct fiber inlet system was designed (Figure 1): a FIMS probe (A) was built using $^1/_2$-in. stainless steal tubing with a septum properly supported at the probe head (H). Proper septum and needle sealing was attained by applying an adjustable tension to the septum using a washer−nut pair. A standard SPME holder was used to slide the 100-μm PDMS fiber (Supelco, Bellefonte, PA) through the septum, in and out of the high-vacuum mass spectrometer, to place the fiber inside the ion source (D), and then to expose its coating (B) to the heat radiation from the two MS filaments (C). The PDMS coating was placed right between the two parallel MS filaments for uniform heating, efficient desorption, and 70-eV electron ionization of the analytes.

SPME Extraction. The aqueous solutions were prepared using Milli-Q water by serial dilution of 1 mg/mL methanol solutions. The analyte solutions (5 mL) were placed in proper headspace vials (10 mL) sealed with septum caps, and SPME

(6) Riter, L. S.; Takats, Z.; Cooks, R. G. *Analyst* **2001**, *126*, 1980.
(7) Alberici, R.; Sparrapan, R.; Eberlin, M. N.; Windmoller, D.; Augusti, R. *Anal. Commun.* **1999**, *36*, 221.
(8) Eberlin, M. N.; Meurer,E. C.; Tomazela, D. M.; Silva, R. C.; Augusto, F. Presented at the 50th ASMS conference on Mass Spectrometry and Allied Topics, Orlando, FL, June 2002.

extraction was performed at room temperature (23 ± 1 °C) with constant stirring: 700 rpm for solution extraction and 1200 rpm for static headspace extraction. In all cases, quantitation was performed using desorption MS selected-ion monitoring peak areas.

RESULTS AND DISCUSSION

FIMS Inlet System. In SPME-GC analysis, the thermal desorption of the analytes from the fiber coating is performed at the injector of the gas chromatograph.[1] Even in the case where gas chromatographic separation was not employed and SPME was directly coupled with MS,[2] thermal desorption was also carried in a GC injector with the transport of the analytes to the mass spectrometer being performed through a heated silica capillary column interface. In the GC injector, a septum is used for proper sealing between the ambient and the pressurized gas carrier line and the injector is heated at temperatures normally in the range of 100−300 °C.

A simple and efficient FIMS direct inlet system (Figure 1) was therefore designed to perform fully direct coupling of SPME to MS. A common GC septum (H) was used as the only interface between the ambient and the high-vacuum mass spectrometer, thus allowing proper introduction of the SPME needle directly into the MS ion source. To ensure no substantial air leak into the mass spectrometer, proper septum and needle sealing was attained by slightly pressing the septum with a adjustable washer−nut pair. The FIMS probe with the septum firmly adjusted at its front (A) was then assembled to locate the septum interface close enough to the MS ion source (D) and to place the fiber and its PDMS coating (B) exactly between the two tungsten MS filaments (C). The analytes are therefore thermally desorbed rapidly and efficiently into the gas phase exactly in the MS ionization region, where the two filaments also provide uniform thermal radiation, for desorption, as well as 70-eV electrons for efficient ionization of the analytes.

Fiber Background. Fiber conditioning is normally performed in SPME extractions. For PDMS fibers, conditioning occurs normally at 250 °C for 4 h under a helium flux in a GC injector. After this conditioning, the SPME fiber was introduced via the FIMS inlet system and its coating exposed to the filaments up to 3 min. No detectable chemical noise for the PDMS coating was observed, which greatly aids analyte identification and limit of quantitation of the FIMS technique. Similar fiber conditioning was also performed at the FIMS inlet system using repeated exposures for 3 min of the PDMS coating to filament radiation.

Memory Effects and Repetitive Use of the PDMS Fiber. In SPME, thermal desorption in GC injectors is quantitative, and normally no substantial memory (carry over) effects are observed.[1] PDMS fibers are also normally heated to 260 °C and used repeatedly for extraction. To test for memory effects in FIMS, fiber extraction from aqueous solutions of all the analytes used in this study were performed, and the fiber was exposed to the filament radiation and ionization for repeated 3-min periods of heating (it is estimated from T&R-MIMS measurements[5] that the PDMS coating is heated to 250−300 °C). Negligible memory effects were observed for the variety of analytes tested (Table 1). A single SPME fiber was also used repeatedly throughout this work with no signs of coating fatigue.

Table 1. FIMS Parameters and Performance for the Analysis of Several VOC and SVOC

analyte	exposure time (min)	characteristic ion (*m*/*z*)	LOD (ng/L, ppt)	R
benzene	5	78	100	0.997
toluene	5	92	100	0.998
xylene	5	106	100	0.995
γ-terpinene	5	71	50	0.999
diisoamyl ether	5	93	200	0.995
chlorobenzene	5	112	200	0.998
carbon tetrachloride	5	117	100	0.995
Sylvex	30	282	200	0.996
PAHs	20−60	various	50−200	0.994−0.996

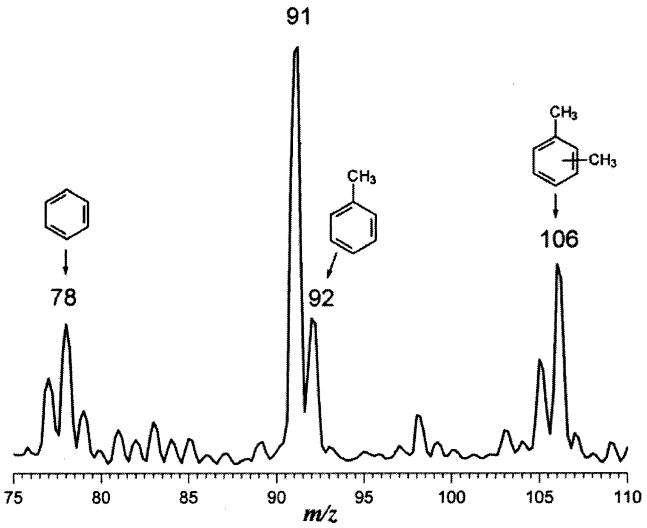

Figure 2. Partial 70-eV EI mass spectrum for a 100 ppb BTX aqueous solution acquired during the nearly 1-min desorption period of FIMS headspace analysis. Note the characteristic ions of *m*/*z* 78 (benzene), 92 (toluene) and 106 (xylenes) and the considerably higher signal-to-noise ratio for full-scan single spectrum acquisition.

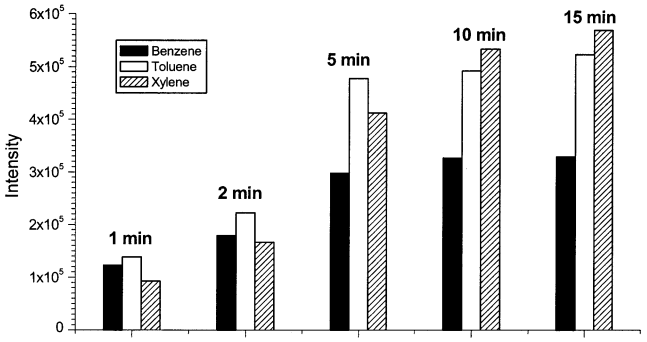

Figure 3. FIMS-SIM signal intensities for a 200 ppb BTX aqueous solution (*m*/*z* 78 for benzene, *m*/*z* 92 for toluene, and *m*/*z* 106 for xylene) as a function of headspace fiber exposition time. Note that, on average, adsorption equilibrium is attained by 10 min.

BTX Analyses. The first testing of the FIMS system was performed with a 100 ppb aqueous solution of benzene, toluene, and xylene (BTX). The PDMS fiber was exposed to the headspace of a 100 ppb BTX aqueous solution for 5 min with constant 1200 rpm solution stirring and then directly introduced into the ion source of the mass spectrometer using the FIMS inlet system. Figure 2 shows a single (no spectra accumulation) 70 EI mass spectrum in the *m*/*z* 70−110 range acquired with a scan speed of

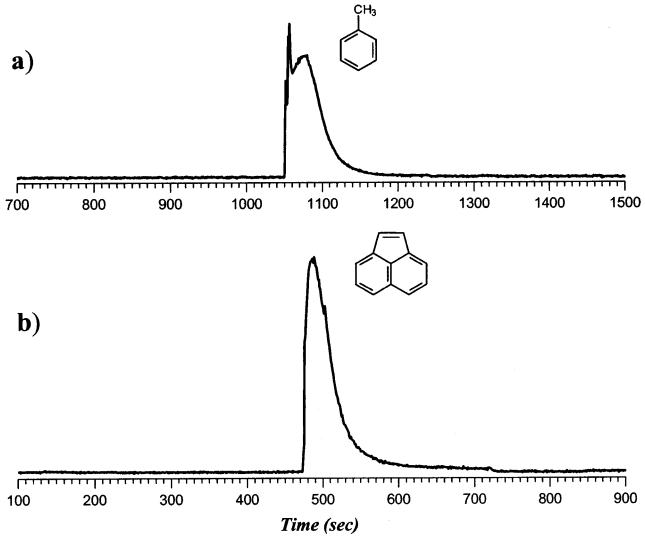

Figure 4. FIMS-SIM signal profile for aqueous solutions of (a) toluene (50 ppb) and (b) acenaphethylene (1 ppb) after 5 min of static headspace fiber exposure time for toluene and 30 min for acenaphethylene. Note the relatively narrow (nearly 1 min) and well-defined desorption peaks and the high signal-to-noise ratios.

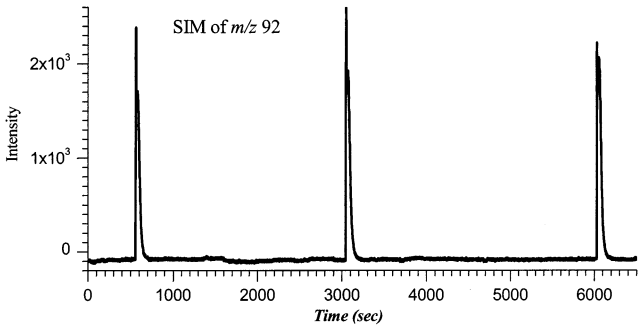

Figure 5. Headspace exposure FIMS profile for triplicate analysis (SIM of *m*/*z* 92) of a 200 ppb toluene aqueous solution.

10 u/s along the thermal desorption period of ~1 min. It is clear that all three analytes, benzene (*m*/*z* 78), toluene (*m*/*z* 91), and xylene (*m*/*z* 106), are easily detected with great sensitivity by the characteristic ions normally used in BTX direct MS detection and quantitation.[3]

Fiber Exposure Time. For maximum sensitivity in SPME analysis, fiber exposure time should be tested until absorption equilibrium is achieved, although nonequilibrium absorption conditions can also be employed with acceptable reproducibility and sensitivity.[1] Figure 3 compares the signal intensity for FIMS analysis with SIM of a 200 ppb BTX aqueous solution using variable PDMS static headspace fiber exposure times within the 1−15-min range. The signal increases from 1 to 10 min, when it starts to level off likely owing to absorption equilibrium. The near 10 min of headspace fiber exposure time for equilibrium BTX extraction from aqueous solutions using FIMS is comparable to that observed for SPME-GC(MS) analysis.[1]

FIMS Signal Profile in SIM. Figure 4 shows the FIMS signal profile for aqueous solutions of two aromatic compounds using SIM: (a) toluene (50 ppb) and (b) acenaphethene (1 ppb). A static headspace fiber exposure time of 5 min was used for the more volatile (and more PDMS soluble) toluene, while for acenaphethene, the fiber was dipped into the aqueous solution for 30 min. Relatively narrow (near 1 min) and well-defined desorption peaks were observed whereas the high signal-to-noise ratios show the high sensitivity of the FIMS technique for BTX and PAH analyses.

Reproducibility. Figure 5 shows a representative headspace FIMS profile for triplicate analysis (SIM of *m*/*z* 92) of a 200 ppb toluene aqueous solution. Reproducibility is acceptable as signal deviation (precision) was near 10% (deviations near 10% were also observed for multiple repetitions), a typical value observed in most SPME-GC(MS) analysis.

Linearity. As listed in Table 1, good correlation coefficients for FIMS quantitation were obtained for all the analytes tested with concentrations varying from that of the detection limit up to typically 100 μg/L (ppb). These results demonstrate, therefore, the good linearity of FIMS for VOC and SVOC quantitation in aqueous solutions.

PAHs. A 1 ppb aqueous solution of a 17-component PAH mixture (diluted from a AccuStandard PAH mixture 2.0 mg/mL in dichloromethane/benzene 1:1, Lot B0090027) was also tested. Figure 6 displays a collection of 70-eV mass spectra acquired over narrow *m*/*z* ranges after variable fiber exposition times to the aqueous solution. Most of the PAH components were detected by their relatively intense 70-eV EI molecular ions although by eliminating chromatographic separation this relatively complex multicomponent mixture shows that some isomeric PAHs are not distinguished by mass spectrometric analysis alone.

Herbicides. SPME is known to be an efficient and sensitive method for many chemicals of environmental, chemical, photochemical, and clinical relevance.[1] For instance, SPME has been

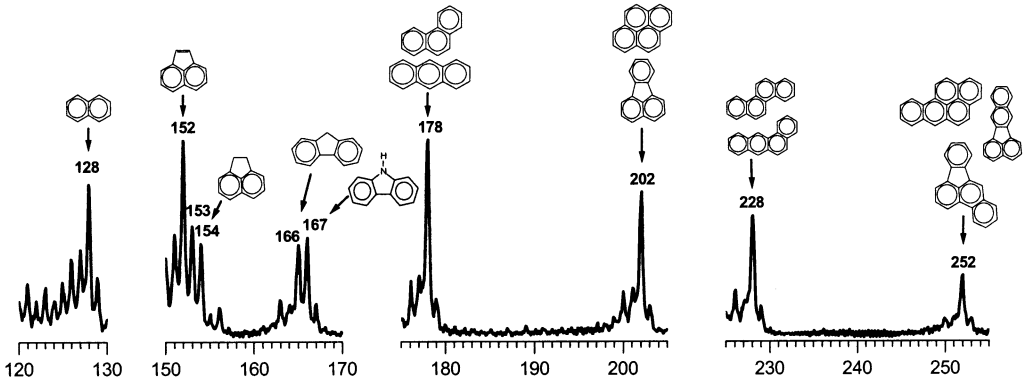

Figure 6. Collection of FIMS 70-eV EI mass spectra in the molecular ion region for a 1 ppb aqueous solution of a PAH mixture after variable fiber exposition times (5−30 min). Note that some isomeric PAHs are not distinguished by the mass spectrometric analysis.

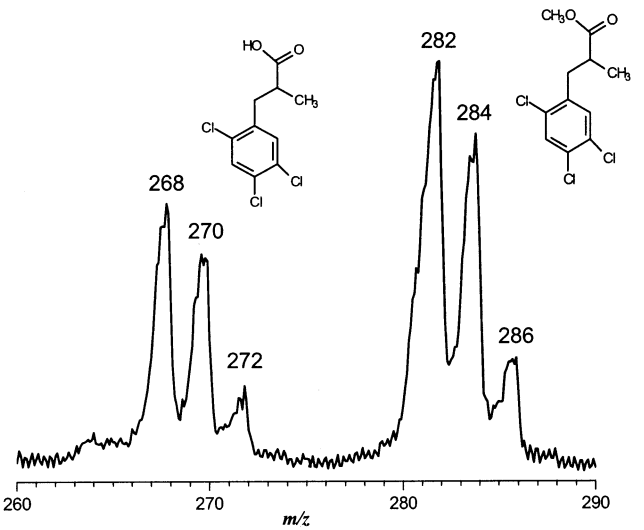

Figure 7. Partial FIMS 70-eV EI mass spectrum of a 100 ppb aqueous solution of (a) the Sylvex herbicide and (b) its methyl ester after 30 min of fiber exposure to the solution. Note the secure analyte identification owing to the characteristic Cl_3 isotopic distribution of the molecular ions.

applied with high efficiency to pesticide and herbicide analysis in aqueous samples using PDMS and other coating materials such as polyacrylates.[1h] Figure 7 provides an example of efficient FIMS detection of an important herbicide, Sylvex, as well as its methyl ester. The fiber was exposed to a 100 ppb aqueous solution of both chemicals for 30 min and directly analyzed using FIMS. Note the better sensitivity for the less polar methyl ester derivative (as expected for a PDMS fiber) and that a mass spectrum in the molecular ion region of both analytes could be easily acquired during the relatively short FIMS desorption period. Secure analyte identification can be therefore made based on the characteristic Cl_3 isotopic distribution of the molecular ions. Unequivocal identification and quantitation (at trace levels; see Table 1) of these (and others herbicides and pesticides) using the characteristic chlorine isotopomeric ions either by full scan or SIM can therefore be performed by FIMS.

Other VOC and SVOC. SPME is know for its versatility and capability to efficiently extract a large variety of organics from different matrixes. Three other VOC were tested: chlorobenzene (a common pollutant), γ-terpinene (a natural product), and disoamyl ether (a common solvent), and detection was achieved with high sensitivity and linearity (Table 1).

Limits of Detection and Linearity. Table 1 displays all the analytes tested by FIMS, their limits of detection using SIM of characteristic ions, and the linearity observed for quantitation over the dynamic range tested (typically from low ppt to 100 ppb unless for the less water soluble analytes). These results demonstrate the high sensibility and reproducibility of FIMS analysis for a variety of VOC and SVOC.

CONCLUSION

The first fully direct coupling of SPME to MS has been performed. This new technique, termed here fiber introduction mass spectrometry, allows the introduction of SPME fibers directly into the ionization region of a mass spectrometer, thus using the MS filaments for both uniform and efficient thermal desorption and maximum ionization yield of the analytes. Compared to other (less) direct SMPE-MS couplings, FIMS is advantageous since it eliminates the memory effects associated with transfer lines and shows enhanced sensitivity. FIMS desorption is very fast (nearly 1 min); hence, FIMS analysis times are mainly determined by the SPME extraction time (several fibers can be simultaneously used). As no chromatographic separation is performed, FIMS allows simpler and higher throughput analysis with similar detection limits as compared to conventional SPME-GC(MS) analyses. A disadvantage of eliminating the separation step is that FIMS mixture quantitation based on characteristic 70-eV EI ions from each analyte becomes less likely as the complexity of the mixture increases. This limitation can be minimized by increasing selectivity by the use of softer ionization techniques such as CI (which may produce a single ion, the protonated molecule, from each analyte) and MS/MS. We are currently evaluating the use of different fibers and the efficacy of FIMS in several analyses of environmental, chemical, and clinical relevance. FIMS has been shown to be a potentially simple and effective approach to rapid VOC and SVOC quantitation from various matrixes.

ACKNOWLEDGMENT

This work has been supported by the Research Support Foundation of the State of São Paulo (FAPESP) and the Brazilian National Research Council (CNPq).

Received for review June 21, 2002. Revised manuscript received August 5, 2002. Accepted August 30, 2002.

AC025880+