



Sample Prep

Perspectives

Guest Authors

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The guest authors validated an in-tube solid-phase microextraction (SPME) device, which was designed for on-line coupling with a capillary gas chromatography (GC) system, for the trace analysis of organic contaminants in water. They used a 5 m × 0.53 mm, 1.2- μ m d_f poly(dimethylsiloxane) phase capillary column as the in-tube extractor. The dynamic extraction technique used a high sampling flow rate, thermal desorption, and valve switching in a novel system design. Compared with classic SPME, the on-line in-tube SPME system increased enrichment factors dramatically, and, due to on-line operation, improved the precision of quantitation. The cost per sample was the same as that of classic fiber SPME, and might be even lower in long-term use because of the use of an ordinary switching valve and conventional GC column extractor.

Ronald E. Majors

Sample Prep Perspectives Editor

In-Tube Solid-Phase Microextraction and On-Line Coupling with High-Resolution GC

Belardi and Pawliszyn (1) first described the concept of solid-phase microextraction (SPME) based upon the principle of partitioning of analytes between the extracting phase and the matrix (air, water, and so forth). Many have developed modifications of this extractive approach and associated devices to improve the availability and application of this sample preparation technique (2). Among those approaches, SPME has been implemented practically by placing the fiber in a micro-syringe. This approach has been commercialized by Supelco (Bellefonte, Pennsylvania). To date, this manual SPME syringe device is used commonly for off-line sample preparation (3–5). However, sample preparation techniques that cannot be automated are used less often for routine analysis, even if they offer other attractive features such as high selectivity or sensitivity. Thus, by modifying a commercial gas chromatography (GC) autosampler, R. Eisert and colleagues (6,7) realized the interfacing of fiber SPME–GC in a quasi-automated mode.

In-tube SPME has been used in HPLC as an efficient and simple preparation method, and it offers several advantages over the fiber SPME syringe–LC approach (8). In-tube SPME is similar to fiber SPME, but the extraction device has a piece of fused-silica GC capillary column in place of a fiber. Conceptually, in-tube SPME should preserve the advantages of SPME and could offer improved enrichment efficiency, quantitation, and automation through the on-line coupling with a chromatograph. By using a piece of bonded-phase capillary GC column for sorption, a larger amount of stationary phase and a more robust film are obtained, relative to outside-coated films of conventional SPME fibers. These differences result in higher enrichment factors and longer extractor life.

Because many capillary GC stationary phases are commercially available, in-tube SPME enables easy changing of the extraction-phase polarity, which extends the application range of the method. The analysis of aqueous samples using in-tube SPME–GC has been reported in the literature (9–11). For the extraction step, the sample solution was pushed or pulled through the capillary extractor at a reasonable flow rate. The adsorbed analytes next were desorbed with a minimum amount of stripping solvent for off-line collection before chromatographic analysis (9). In addition, the capillary extractor could be assembled manually in front of the GC analytical column with a press-fit connector and a piece of precolumn. A temperature-programmed GC run completed the procedure of both thermal desorption and analysis (10,11). Using those approaches, researchers obtained promising results and avoided the problems that are observed with fiber SPME such as the bleed from the ultrathick film and the appearance of ghost peaks.

On-line extraction-capillary GC is an attractive method for the analysis of aqueous samples. Several methods for on-line extraction GC have been reported in the literature, including membrane extraction (12), liquid–liquid extraction (13), and solid-phase extraction with small packed cartridges (14). In contrast to these conventional methods, the complete removal of water can be achieved easily by using an open-tubular capillary. Mol and co-workers (15) developed a method using open-tubular trapping columns for on-line extraction–capillary GC in the analysis of aqueous samples. In that study, they used two switching valves and organic solvent for desorption.

In this installment of “Sample Prep Perspectives,” we will present a novel device

for coupling on-line in-tube SPME with capillary GC. We will demonstrate this method's application for the analysis of contaminants in water.

Quantitation

As shown in equation 1, it is common for analysts to calculate the theoretical recovery or to evaluate quantitation based upon equilibrium theory (16):

$$n = C_0 \left[\frac{K_D V_s}{1 + (K_D V_s / V_0)} \right] \quad [1]$$

where n is the amount of extracted analyte, C_0 the initial concentration of the analyte in the matrix, K_D the distribution constant of the analyte, V_s the volume of the stationary phase, and V_0 the volume of sample.

A concept of *negligible depletion* extraction recently was proposed for easier quantitation and higher enrichment factors (17). For in-tube SPME, the extraction process will not influence the free concentration of the analyte in the matrix when a sufficient amount of sample solution (quasi-infinite relative to extracting phase volume) passes through the extractor. In this case, $K_D V_s \ll V_0$, and the absolute amount of extracted analyte can be obtained easily from equation 2:

$$n = K_D V_s C_0 \quad [2]$$

Experimental

On-line in-tube SPME instrument setup and procedure:

Figure 1 is a schematic of the on-line in-tube SPME device developed in our study. The system consists of a six-port valve and three gas flow controllers (both from Fuli Corp., Wenling, China), a homemade stainless steel micro tee piece, a homemade 5 m × 0.53 mm, 1.2- μ m d_f conventional cross-linked OV-1 (poly-[dimethylsiloxane]) capillary column used as extractor, and a mini water-circulating pump (Tengda Corp., Tianjing, China). A homemade oven capable of heating at a rate of 290 °C/min to temperatures greater than 320 °C provided fast and uniform heating for the capillary extractor. A deactivated 1 m × 100 μ m fused-silica capillary (Ruifeng, Yongnian, China) in close contact with a piece of heating resistor wire was used as the analyte transfer line from the in-tube SPME system to the GC system. An adiabatic sleeve covered the transfer line to maintain heat.

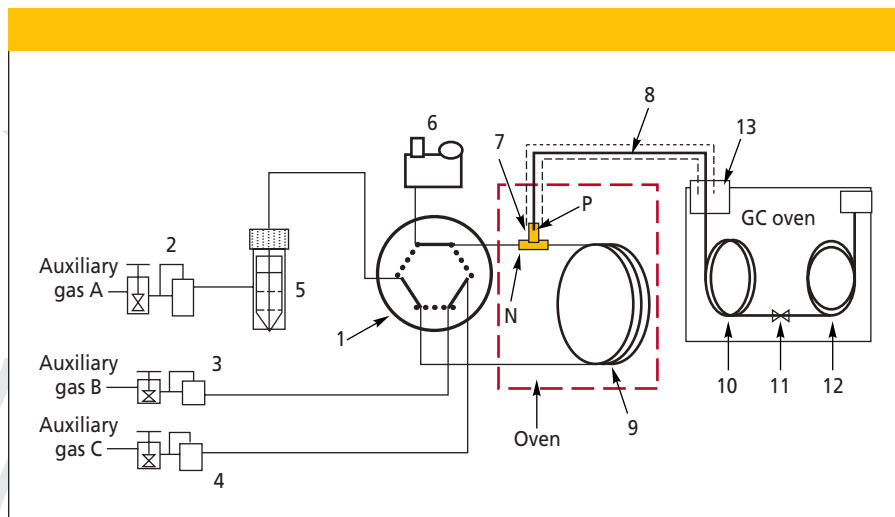


Figure 1: Schematic diagram of the on-line in-tube SPME system coupled with the high-resolution GC system. 1 = six-port valve, 2 = flow controller for sampling, 3 = flow controller for desorption gas, 4 = flow controller for auxiliary gas, 5 = sample vial, 6 = mini water-circulating pump, 7 = micro tee piece, 8 = capillary transfer, 9 = capillary extractor, 10 = pre-column, 11 = press-fit or micro union, 12 = analytical column, 13 = on-column injector.

During the extraction period (the solid-line position of the valve in Figure 1), the sample solution was forced through the capillary extractor by the push of auxiliary gas and the suction force of the mini water-circulating pump. A negative pressure at the N point of the tee piece was generated because of the suction of the mini water-circulating pump. The head pressure of the GC column forced the carrier gas through the transfer line to the tee piece (as shown on the Figure 1). Because the pressure at point P always is higher than that at point N, we avoided the problem of direct influx of the aqueous solution into the GC system during the extraction process.

After the aqueous sample was drained completely from the extractor, the six-port valve was switched to the dotted-line position for desorption. To achieve lower detection limits in high-resolution GC and to obtain a sharp desorption band, the extractor should heat up as fast as possible (at a rate as high as 290 °C/min). The desorption of analytes from the capillary extractor occurs very fast because they are purged by the auxiliary gas through the capillary. The thermal desorption time is approximately 2–6 min for the 5 m × 0.53 mm capillary column under a 6-mL/min purge-gas flow. Another path of auxiliary gas at a flow rate of approximately 1–2 mL/min is used as makeup gas through the tee piece to prevent any back diffusion of analytes. It must be noted that the desorbed analytes are introduced directly to the high-resolution GC system *after* the switching valve, instead of through the valve, to eliminate

the possibility of any carryover or dead volume along the sample transfer line. On the other hand, using the high-temperature switching valve is unnecessary in this system design. The more expensive valve is not required for this system design, which makes the device less expensive.

Finally, the desorbed analytes were transferred to the homemade cold retention gap in the model 6890N gas chromatograph (Agilent Technologies, Beijing, China), with an initial oven temperature of 30 °C, through the hot capillary transfer line and were refocused on the head of the analytical column by the retention gap (18). We used a sequential temperature-programmed high-resolution GC run to accomplish the separation and detection of analytes of interest. Thus, the total process of analyzing organic compounds in aqueous samples, including the on-line extraction, thermal desorption, and sampling to high-resolution GC, was automated using the above-mentioned in-tube SPME device.

Results and Discussions

Evaluation of on-line in-tube SPME coupled with high-resolution GC:

We used aqueous samples containing a series of alkanes (C_{10} – C_{19}) at the microgram-per-liter level to evaluate the performance of our apparatus. As Table I shows, the in-tube SPME capillary extractor has an increased amount of solid stationary phase and a much larger exchanging surface, when compared with the fiber SPME system, which result in drastic increases of the extraction efficiency and enrichment factor.

In the experiments, a 5 m × 0.53 mm, 1.2- μm d_f poly(dimethylsiloxane) phase capillary extractor provides approximately 10 μL of solid phase for extraction, which is roughly 10-fold more solid phase than that of an SPME fiber (~ 1 μL). Figures 2a and 2b show that the extraction of the same 15-mL aqueous sample with a 10- $\mu\text{g/L}$ concentration of each alkane to obtain an approximately 30-fold concentration of the analytes of interest requires 2.5 min for in-tube SPME versus 35 min for fiber SPME. When the extraction time was limited to 5 min, we were able to extract only few analytes of interest by fiber SPME (see Figure 2d). On the other hand,

with a 40-min extraction time, the peaks obtained by in-tube SPME are roughly 50-fold higher than that of fiber SPME (extraction for 35 min), even for components with concentrations as low as 2 $\mu\text{g/L}$ (Figure 2c). In addition, the baselines of chromatograms from in-tube SPME are very smooth because the capillary extractors have thinner and stronger film of bonded phase, and ghost peaks normally appear with fiber SPME.

We performed six replicate experiments of on-line extraction, desorption, and detection for each concentration of samples to examine the method's reproducibility. The precision of quantitation, obtained

using a 5 m × 0.53 mm, 1.2- μm d_f poly(dimethylsiloxane) capillary, varies from 5% to 15% relative standard deviation (RSD) (for $n = 6$), depending upon the alkanes and concentration of samples studied. Table II shows the precision and linearity for all compounds investigated under different concentration conditions. The average RSD was 8.0% for the 0.5- $\mu\text{g/L}$ concentration level and 5.3% for the 20- $\mu\text{g/L}$ concentration level.

We determined linearity by extracting spiked aqueous samples with concentrations ranging from 0.1 $\mu\text{g/L}$ to 100 $\mu\text{g/L}$. The method was linear throughout at least three orders of magnitude. The coefficient

Table I: Comparison of a typical apolar capillary extractor (5 m × 0.53 mm, 1.2- μm d_f) and a 100- μm apolar SPME fiber

Extractor Type	Character of Extractants	Phase Volume (μL)	Exchanging Surface of Extraction (mm^2)	Type of Mixing During Extraction
Capillary extractor	Bonded on the inner wall	9.9852*	8321 \dagger	Turbulence of flow convection
100- μm apolar SPME fiber	Coated outside the fiber	0.9734 \ddagger	9.7 \S	Agitation by stirrer

* $V = \pi D_i d_f L$, where D_i is the inner diameter of capillary tube, d_f is the film thickness of solid phase, and L is the length of capillary column.
 $\dagger A = \pi D_i L$.
 $\ddagger V = \pi D_o d_f L$, where D_o is the outer diameter of fiber core (~ 110 μm), d_f is the coating film thickness of solid phase, and L is the length of fiber (normally 10 mm).
 $\S A = \pi D_o L$.

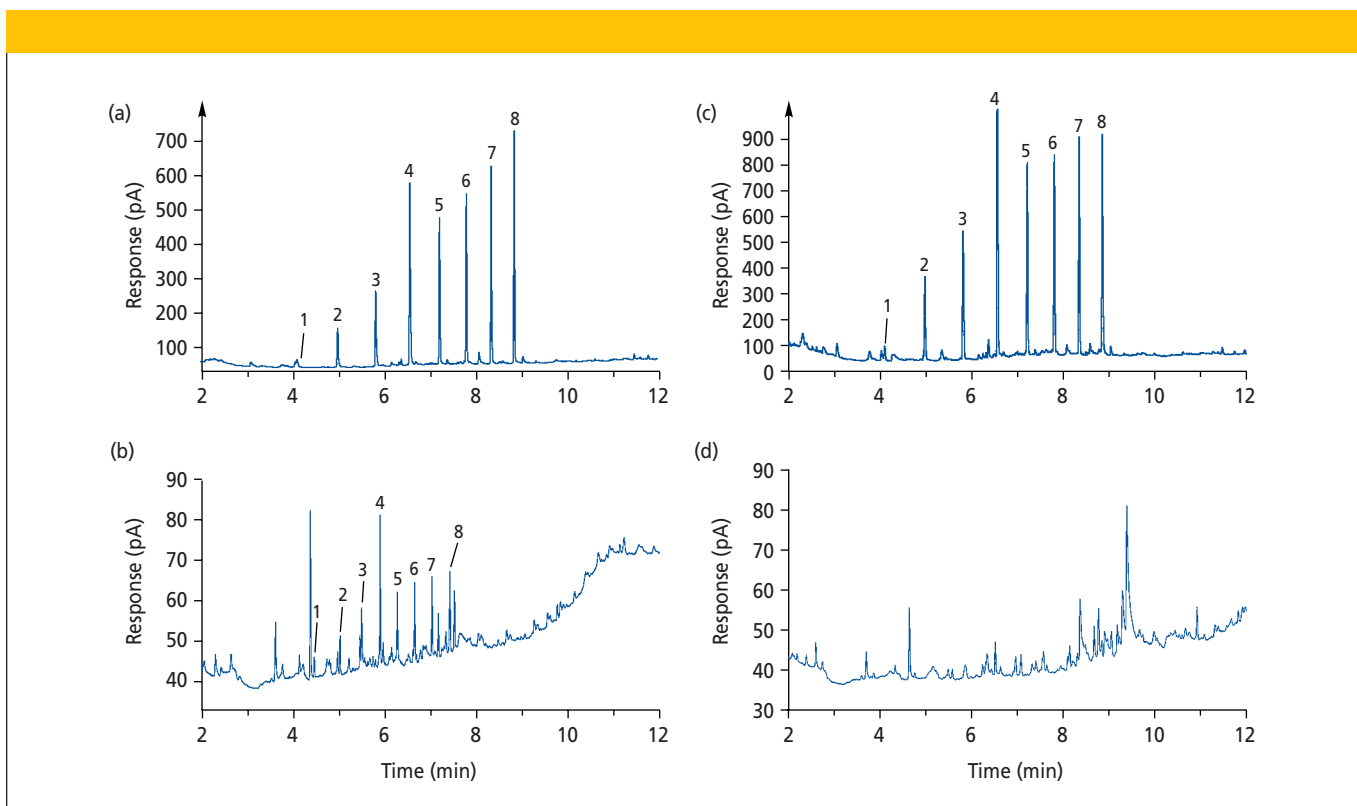


Figure 2: Comparison of chromatograms of spiked aqueous samples by in-tube SPME and fiber SPME: (a) extraction of 15-mL samples within 2.5 min with alkanes of 10- $\mu\text{g/L}$ level by on-line in-tube SPME; (b) extraction of 15-mL samples within 35 min with alkanes of 10- $\mu\text{g/L}$ level by fiber SPME; (c) extraction of 300-mL samples within 40 min with alkanes of 2- $\mu\text{g/L}$ level by on-line in-tube SPME; (d) extraction of 15-mL samples within 3 min with alkanes of 10- $\mu\text{g/L}$ level by fiber SPME. Column: 30 m × 0.53 mm, 0.6 μm d_f MXT-1 (Restek Corp., Bellefonte, Pennsylvania) with a 5-m retention gap; carrier gas: hydrogen at 8 mL/min; oven program: 30 $^{\circ}\text{C}$ for 0.5 min, 30–110 $^{\circ}\text{C}$ at 40 $^{\circ}\text{C}/\text{min}$, 110 $^{\circ}\text{C}$ for 1 min, 110–250 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$, 250 $^{\circ}\text{C}$ for 10 min; fiber desorption time in (b): 4 min. Peaks: 1 = $n\text{-C}_{12}$, 2 = $n\text{-C}_{13}$, 3 = $n\text{-C}_{14}$, 4 = $n\text{-C}_{15}$, 5 = $n\text{-C}_{16}$, 6 = $n\text{-C}_{17}$, 7 = $n\text{-C}_{18}$, 8 = $n\text{-C}_{19}$.

of correlation achieved was better than 0.99 (Table II). In addition, we found no carryover or memory effects with this on-line coupled in-tube SPME–high-resolution GC system.

Applications of On-Line In-Tube SPME Coupled with High-Resolution GC

Determination of PAHs with on-line in-tube SPME, high-resolution GC, and flame ionization detection:

Polycyclic aromatic hydrocarbons (PAHs) are an important class of environmental pollutants that represent a risk for living organisms and human health. Among various techniques of PAH determination, SPME (19) and stir-bar sorptive extraction (20) recently have gained wide acceptance. For sub-parts-per-billion level measurement, the SPME device has a limited enrichment factor; however, the stir-bar sorptive extraction device, which has a two-orders-higher enrichment factor than the SPME system, needs several hours to reach extraction equilibrium, especially for four-ring and larger polynuclear compounds. In addition, a number of manual steps are necessary to successfully use the stir-bar sorptive extraction technique.

In our experiment, we examined 16 PAH standards spiked in water at microgram-per-liter or sub-microgram-per-liter concentrations. We applied two types of clean water as the sample matrices: Wahaha purified drinking water (Wahaha Corp., Hangzhou, China) (Figure 3a) and tap water from the laboratory faucet (Figure 3b). The resulting chromatogram (Figure 3) shows that the 16 PAHs were well separated without any tailing peaks. The lowest detection limit for most PAHs was estimated to be less than 0.01 $\mu\text{g/L}$, much lower than that estimated by the fiber SPME technique. In addition, the overall extraction time was within 40 min for sample volume of 400 mL, quite short compared with stir-bar sorptive extraction or fiber SPME. It was interesting to note that trace amounts of plasticizers were found in the purified water, but no peak of butylbenzyl phthalate was found in the tap water (Figure 3). However, many more volatile compounds were in the tap water, which we suspected were halogenated hydrocarbons that resulted from the chlorination process.

Determination of chlorinated pesticides with on-line in-tube SPME, high-resolution GC, and electron-capture detection: To determine chlorinated pesti-

Table II: Precision, linearity, and sensitivity of on-line in-tube SPME–high-resolution GC

Alkanes	Repeatability RSD* (%) for 0.5 $\mu\text{g/L}$	Repeatability RSD* (%) for 20 $\mu\text{g/L}$	Correlation Coefficient†	Detection Limit‡ (S/N = 3, $\mu\text{g/L}$)
<i>n</i> -C ₁₂	14.8	11.3	0.996§	0.3
<i>n</i> -C ₁₃	9.2	6.4	0.99	0.07
<i>n</i> -C ₁₄	7.2	5.3	0.996	0.05
<i>n</i> -C ₁₅	7.4	5.2	0.996	0.030
<i>n</i> -C ₁₆	6.6	4.3	0.998	0.024
<i>n</i> -C ₁₇	6.2	5.5	0.996	0.017
<i>n</i> -C ₁₈	7.0	5.2	0.998	0.012/3#
<i>n</i> -C ₁₉	5.8	4.7	0.993	0.01

* $n = 6$.

† Concentration range from 0.1 $\mu\text{g/L}$ to 100 $\mu\text{g/L/L}$.

‡ Extraction flow rate: 10 mL/min for 300-mL samples of the lowest concentration of 0.1 $\mu\text{g/L}$.

§ Concentration range from 1 $\mu\text{g/L}$ to 100 $\mu\text{g/L/L}$.

|| Detection with the lowest concentration of 1 $\mu\text{g/L/L}$.

#The lowest detection limit with the use of 100- μm poly(dimethylsiloxane) fiber.

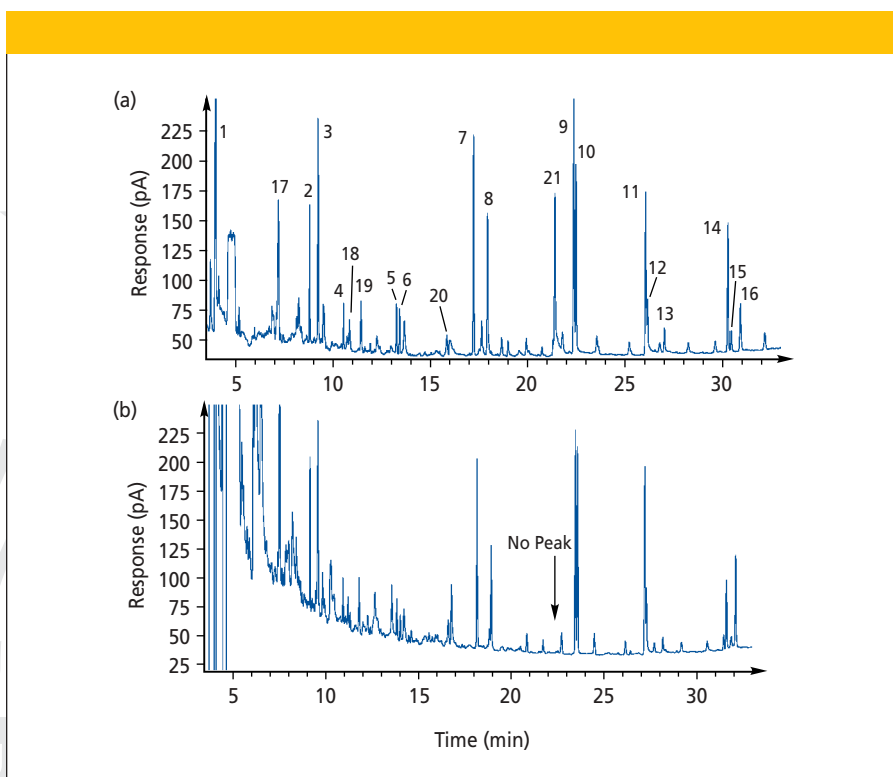


Figure 3: On-line in-tube SPME–GC–flame ionization detection chromatogram of (a) Wahaha purified water and (b) tap water spiked with polyaromatic hydrocarbons. Column: 30 m \times 0.53 mm, 0.6- μm d_f DB-1 (Agilent Technologies, Wilmington, Delaware) with a 5-m retention gap; carrier gas: hydrogen at 8 mL/min; oven program: 30 $^{\circ}\text{C}$ for 0.5 min, 30–110 $^{\circ}\text{C}$ at 40 $^{\circ}\text{C}/\text{min}$, 110 $^{\circ}\text{C}$ for 1 min, 110–300 $^{\circ}\text{C}$ at 8 $^{\circ}\text{C}/\text{min}$, 300 $^{\circ}\text{C}$ for 10 min. Peaks: 1 = naphthalene (2 $\mu\text{g/L}$), 2 = acenaphthylene (2 $\mu\text{g/L}$), 3 = acenaphthene (2 $\mu\text{g/L}$), 4 = fluorine (0.2 $\mu\text{g/L}$), 5 = phenathrene (0.2 $\mu\text{g/L}$), 6 = anthracene (0.2 $\mu\text{g/L}$), 7 = fluoranthene (0.2 $\mu\text{g/L}$), 8 = pyrene (0.2 $\mu\text{g/L}$), 9 = benzo[a]anthracene (0.2 $\mu\text{g/L}$), 10 = chrysene (0.2 $\mu\text{g/L}$), 11 = benzo[b]fluoranthene (0.2 $\mu\text{g/L}$), 12 = benzo[k]fluoranthene (0.2 $\mu\text{g/L}$), 13 = benzo[a]pyrene (0.2 $\mu\text{g/L}$), 14 = indeno[1,2,3-*cd*]pyrene (0.2 $\mu\text{g/L}$), 15 = dibenzo[a,h]anthracene (0.2 $\mu\text{g/L}$), 16 = benzo[ghi]perylene (0.2 $\mu\text{g/L}$), 17 = hexachlorocyclopentadiene, 18 = diethyl phthalate, 19 = *N*-nitrosodiphenylamine, 20 = di-*n*-butylphthalate, 21 = butylbenzyl phthalate.

cides in aqueous samples, we coupled our in-tube SPME device on-line with a model 3800 capillary gas chromatograph (Varian Inc., Palo Alto, California), which was

equipped with an electron-capture detector. We divided standard mixtures of 26 total pesticides into three groups, and each pesticide compound was spiked directly

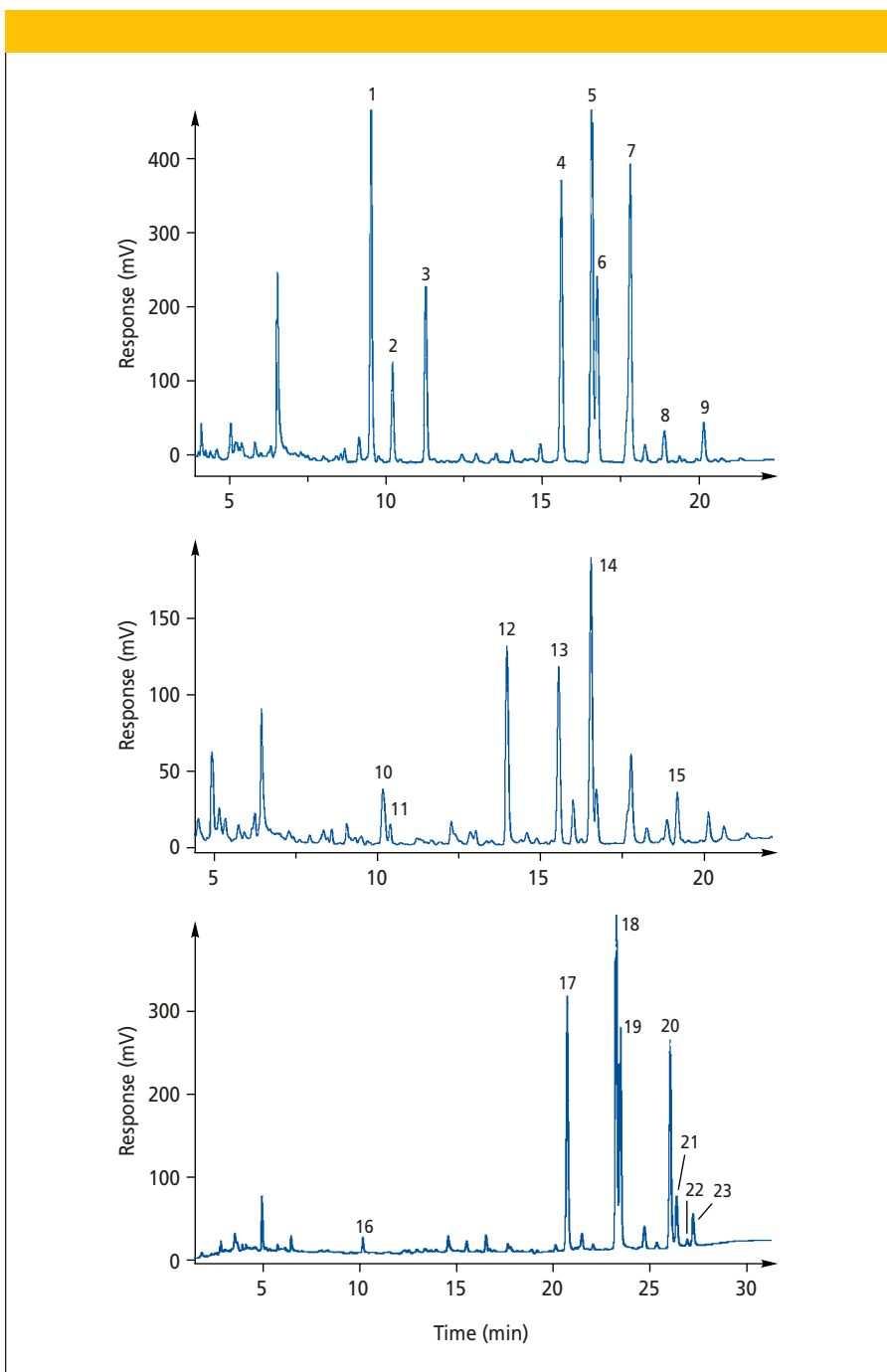


Figure 4: On-line in-tube SPME-GC-ECD chromatograms of aqueous samples spiked with chlorinated pesticides. Column: 30 m \times 0.53 mm, 0.6- μ m d_f DB-5 (Agilent Technologies) with a 5-m retention gap; carrier gas: nitrogen at 8 mL/min; oven program: 30 $^{\circ}$ C for 0.5 min, 30–150 $^{\circ}$ C at 40 $^{\circ}$ C/min, 150–280 $^{\circ}$ C at 7 $^{\circ}$ C/min, 280 $^{\circ}$ C for 10 min; detection: electron capture. Peaks: 1 = α -BHC, 2 = β -BHC, 3 = δ -BHC, 4 = *op*-DDE, 5 = *pp'*-DDE, 6 = *op*-DDD, 7 = *pp'*-DDD, 8 = *pp'*-DDT, 9 = iprodione, 10 = lidane, 11 = pentachloronitrobenzene, 12 = vinclozolin, 13 = keithane, 14 = *op*-DDT, 15 = cyhalothrin lambda, 16 = dicloran, 17 = fenpropathrin, 18 = *cis*-permethrin, 19 = *trans*-permethrin, 20 = *cis*-fenvalerate, 21 = *trans*-fenvalerate, 22 = *cis*-deltamethrin, 23 = *trans*-deltamethrin.

into a silex vial at the 0.25- μ g/L level using a microsyringe. Figure 4 depicts the resulting chromatogram. It is noteworthy to point out that the detectability of the peaks of *pp'*-dichlorodiphenyltrichloroethane (*pp'*-DDT) and iprodione, which are barely detectable using GC systems that

display poor inertness, was rather good. The lowest detection limits of some components such as benzene hexachloride (BHC) were estimated at the sub-nanogram-per-liter level, which was obtained in only 5 min with extraction of a 30-mL aqueous sample. Actually, lower

detection limits could be reached by using a larger sample volume.

Determination of phosphorus-containing pesticides with on-line in-tube SPME, high-resolution GC, and pulsed-flame photometric detection:

We coupled the same apparatus on-line with the capillary gas chromatograph, this time equipped with a pulsed-flame photometric detector (operated in the phosphorus mode) to determine the phosphorus-containing pesticides. We spiked 16 standard pesticides at 0.5 $\mu\text{g/L}$ each in a 30-mL aqueous sample before extraction, and the dilution of compounds was performed in a silex vial using a microsyringe. The chromatogram obtained is illustrated in Figure 5. The lowest detection limit observed was 0.05 $\mu\text{g/L}$ for most of the analytes with an extraction time of only 5 min.

Conclusion

We performed in-tube SPME on-line coupling with high-resolution GC by using a simple device for the trace analysis of organic compounds in aqueous samples. The in-tube SPME–high-resolution GC methods demonstrated in our study successfully performed the on-line extraction, desorption, and sampling of various contaminants in water, followed by analysis of high-resolution GC with different detectors. The novel in-tube SPME–high-resolution GC device presents the follow-

ing advantages over manual fiber SPME–high-resolution GC:

- It enables much higher enrichment factors than those of fiber SPME because of its 10-fold greater volume of extracting phase compared with fiber SPME. In our experiments, the enrichment factors by means of in-tube SPME were at least 50-fold that of fiber SPME, if both experiments were performed under optimum conditions, even though the ratio of extracting phase volume was approximately 10.
- It provides faster extractions than those of fiber SPME because of the drastically larger exchanging surface.
- It is performed as a fully on-line operation; therefore, it provides high-precision reproducibility.
- The technique's cost is relatively low because it uses conventional capillary columns and an ordinary switching valve.

References

- (1) C. Arthur and J. Pawliszyn, *Anal. Chem.* **62**, 2145–2148 (1990).
- (2) H. Lord and J. Pawliszyn, *J. Chromatogr. A* **885**, 153–193 (2000).
- (3) D. Louch, S. Motlagh, and J. Pawliszyn, *J. Anal. Chem.* **64**, 1187–1199 (1992).
- (4) K.D. Buchholz and J. Pawliszyn, *J. Anal. Chem.* **66**, 160–167 (1994).
- (5) J. Chen and J. Pawliszyn, *Anal. Chem.* **67**, 2520–2533 (1995).
- (6) R. Eisert and K. Levsen, *J. Chromatogr. A* **737**, 59–65 (1996).

- (7) R. Eisert and J. Pawliszyn, *Crit. Rev. Anal. Chem.* **27**, 103–135 (1997).
- (8) R. Eisert and J. Pawliszyn, *Anal. Chem.* **69**, 3140–3147 (1997).
- (9) B.C. Dennis, J. Philip, H.K. Lee, and P.D. Morrison, *Analyst* **124**, 651–655 (1999).
- (10) L. Nardi, "In-Tube SPME System for Trace Determination of Organic Compounds in Water by HRGC," paper presented at the 23rd International Symposium on Capillary Chromatography, Riva del Garda, Italy, 5–10 June 2000.
- (11) L. Nardi, *Am. Lab.* **34**(1), 30–37 (2002).
- (12) R.G. Melcher and P.L. Morabito, *Anal. Chem.* **62**, 2183–2188, (1990).
- (13) E.C. Goosens, R.G. Bunschoten, V. Engelen, and J.H.M. van den Berg, *J. High Resolut. Chromatogr.* **13**, 438–442 (1990).
- (14) J.J. Vreuls, W.J.G.M. Cuppen, and U.A.Th. Brinkman, *J. High Resolut. Chromatogr.* **13**, 157–161, (1990).
- (15) H.G.J. Mol, H.-G. Janssen, and C.A. Cramers, *J. High Resolut. Chromatogr.* **16**, 413–418 (1993).
- (16) F. David, B. Tienpont, and P. Sandra, *LCGC* **21**(1), 1–7 (2003).
- (17) L. Nardi, *J. Chromatogr. A* **985**, 85–91 (2003).
- (18) E. Baltussen, P. Sandra, F. David, and C. Cramers, *J. Microcol. Sep.* **11**, 737–747 (1999).
- (19) J.J. Langenfeld, S.B. Hawthorne, and D.J. Miller, *Anal. Chem.* **68**, 144–148 (1996).
- (20) E. Baltussen, P. Sandra, F. David, and C. Cramers, *J. Microcol. Sep.* **11**, 737–747 (1999).

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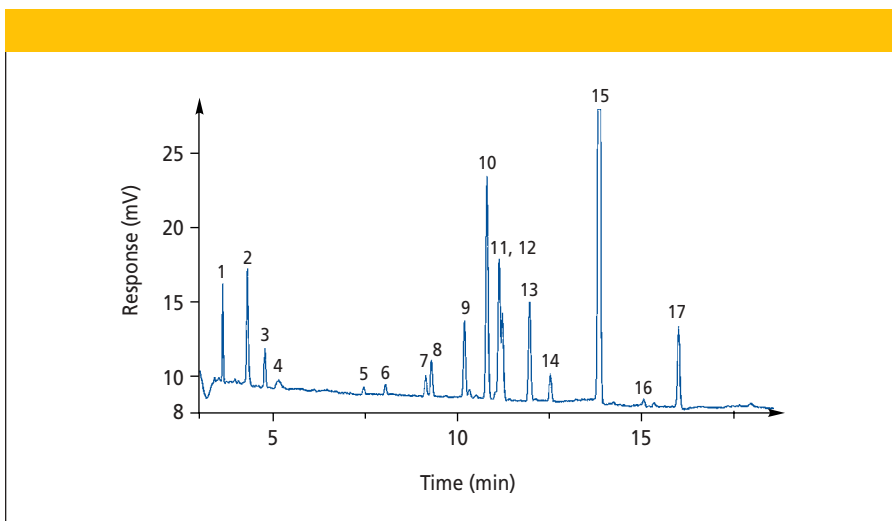


Figure 5: On-line in-tube SPME–GC–pulsed-flame photometric detection chromatogram of an aqueous sample spiked with phosphorus-containing chlorinated pesticides. Column: 30 m \times 0.53 mm, 0.6- μm d_f DB-5 (Agilent Technologies) with a 5-m retention gap; carrier gas: nitrogen at 8 mL/min; oven program: 30 $^{\circ}\text{C}$ for 0.5 min, 30–150 $^{\circ}\text{C}$ at 40 $^{\circ}\text{C}/\text{min}$, 150 $^{\circ}\text{C}$ for 5 min, 150–280 $^{\circ}\text{C}$ at 7 $^{\circ}\text{C}/\text{min}$, 280 $^{\circ}\text{C}$ for 10 min. Peaks: 1 = methamidaphos, 2 = dichlorvos and trichlorfon(dylox), 3 = unknown peak, 4 = omethoate, 5 = dimethoate, 6 = propetamphos, 7 = diazinon, 8 = parathion methyl, 9 = chlorpyrifos methyl and paraoxon, 10 = pirimiphos methyl and malathion, 11 = parathion ethyl, 12 = chlorpyrifos, 13 = isofenphos and quinalphos, 14 = phoxim, 15 = ethion, 16 = imidan, 17 = phosalone.