

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

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**The guest authors validated an in-tube solid-phase microextraction device, which was designed for on-line coupling with a capillary gas chromatography system, for the trace analysis of organic contaminants in water. They used a 5 m × 0.53 mm, 1.2 μm *d<sub>f</sub>* 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, because of on-line operation, improved the precision of quantification. The cost per sample was the same as that of classic fibre SPME, and might even be lower in long-term use because of the use of an ordinary switching valve and conventional GC column extractor.**

Belardi and Pawliszyn<sup>1</sup> 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.<sup>2</sup> Among those approaches, SPME has been implemented practically by placing the fibre in a micro-syringe. This approach has been commercialized by Supelco (Bellefonte, Pennsylvania, USA).

To date, this manual SPME syringe device is commonly used for off-line sample preparation.<sup>3–5</sup> 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<sup>6,7</sup> realized the interfacing of fibre 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 fibre SPME syringe–LC approach.<sup>8</sup> In-tube SPME is similar to fibre SPME, but the extraction device has a piece of fused-

silica GC capillary column in place of a fibre. Conceptually, in-tube SPME should preserve the advantages of SPME and could offer improved enrichment efficiency, quantification 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 fibres. 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.<sup>9–11</sup> For the extraction step, the sample solution was pushed or pulled through the capillary extractor at a reasonable flow-rate. The adsorbed analytes were then desorbed with a minimum amount of stripping solvent for off-line collection before chromatographic analysis.<sup>9</sup> 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.<sup>10,11</sup> Using those approaches, researchers obtained promising results and avoided the problems that are observed with fibre SPME such as the bleed from the ultra thick 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,<sup>12</sup> liquid–liquid extraction<sup>13</sup> and solid-phase extraction with small packed cartridges.<sup>14</sup> 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<sup>15</sup> 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 instalment of “Sample Preparation 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.

## Quantification

As shown in Equation 1, it is common for analysts to calculate the theoretical

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recovery or to evaluate quantification based upon equilibrium theory:<sup>16</sup>

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

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 was recently proposed for easier quantification and higher enrichment factors.<sup>17</sup> 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 instance,  $K_D V_s \ll V_0$ , and the absolute amount of extracted analyte can be easily obtained from Equation 2:

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

### Experimental

#### On-line in-tube SPME instrument

**set-up 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 μm  $d_f$  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 μm 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.

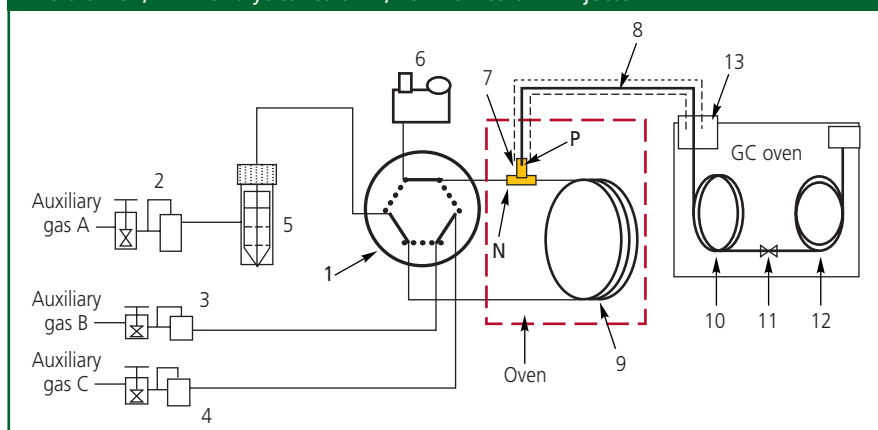
During the extraction period (the solid-line position of the valve in Figure 1), the sample solution was forced through the capillary extractor by the push of auxiliary

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 is always 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 make-up 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. However, 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.<sup>18</sup> 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 analysing 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.

**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 = precolumn, 11 = press-fit or micro union, 12 = analytical column, 13 = on-column injector.



## 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-litre level to evaluate the performance of our apparatus. As Table 1 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 fibre SPME system, which result in drastic increases of the extraction efficiency and enrichment factor.

In the experiments, a  $5\text{ m} \times 0.53\text{ mm}$ ,  $1.2\text{ }\mu\text{m}$   $d_f$  poly(dimethylsiloxane) phase capillary extractor provides approximately

$10\text{ }\mu\text{L}$  of solid phase for extraction, which is roughly 10-fold more solid phase than that of an SPME fibre ( $\sim 1\text{ }\mu\text{L}$ ). Figures 2(a) and 2(b) show that the extraction of the same  $15\text{ mL}$  aqueous sample with a  $10\text{ }\mu\text{g/L}$  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 fibre SPME. When the extraction time was limited to 5 min, we were able to extract only few analytes of interest by fibre SPME [see Figure 2(d)]. However, with a 40-min extraction time, the peaks obtained by in-tube SPME are roughly 50-fold higher than that of fibre SPME (extraction for 35 min), even for

components with concentrations as low as  $2\text{ }\mu\text{g/L}$  [Figure 2(c)]. 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 fibre 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 quantification, obtained using a  $5\text{ m} \times 0.53\text{ mm}$ ,  $1.2\text{ }\mu\text{m}$   $d_f$  poly(dimethylsiloxane) capillary, varies from 5% to 15% relative standard deviation (RSD) (for  $n = 6$ ), depending upon the

**Table 1:** Comparison of a typical apolar capillary extractor ( $5\text{ m} \times 0.53\text{ mm}$ ,  $1.2\text{ }\mu\text{m}$   $d_f$ ) and a 100 mm apolar SPME fibre.

Extractor Type	Character of Extractants	Phase Volume ( $\mu\text{L}$ )	Exchanging Surface of Extraction ( $\text{mm}^2$ )	Type of Mixing During Extraction
Capillary extractor	Bonded on the inner wall	$9.9852^*$	$8321^\dagger$	Turbulence of flow convection
100 $\mu\text{m}$ apolar SPME fibre	Coated outside the fibre	$0.9734^\ddagger$	$9.7^\S$	Agitation by stirrer

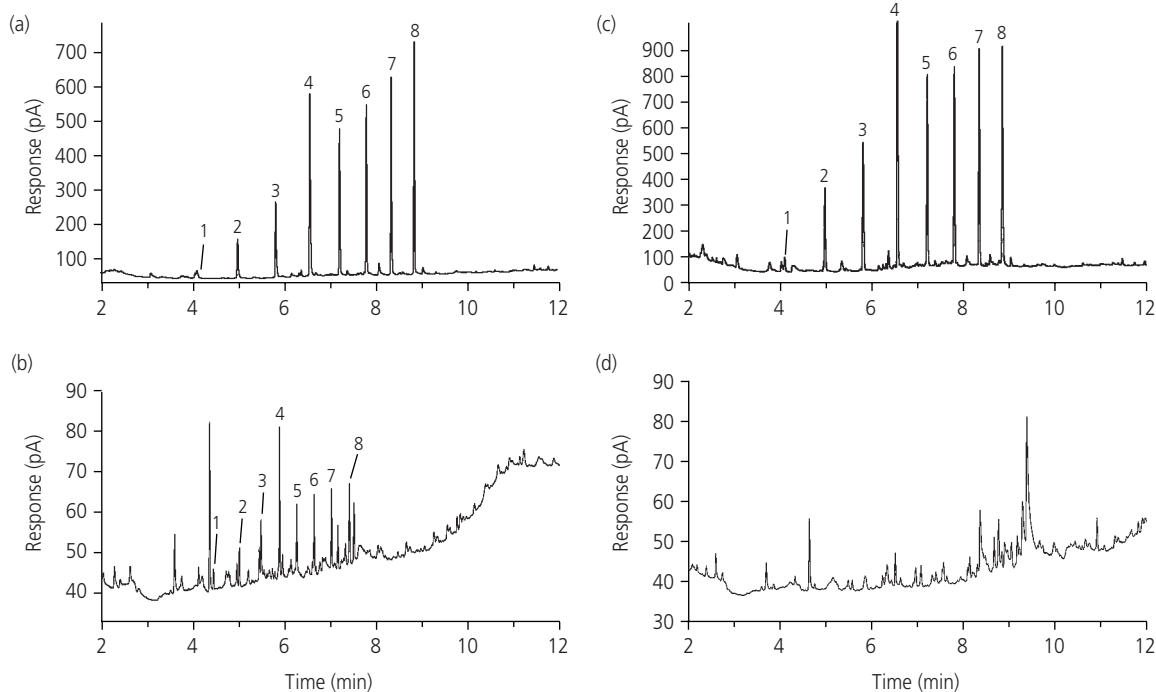
\*  $V = \pi D_i d_f L$ , where  $D_i$  is the inner diameter of capillary tube,  $d_f$  is the film thickness of solid phase and  $L$  is the length of capillary column.

†  $A = \pi D_i L$ .

‡  $V = \pi D_o d_f L$ , where  $D_o$  is the outer diameter of fibre core ( $\sim 110\text{ }\mu\text{m}$ ),  $d_f$  is the coating film thickness of solid phase and  $L$  is the length of fibre (normally 10 mm).

§  $A = \pi D_o L$ .

**Figure 2:** Comparison of chromatograms of spiked aqueous samples by in-tube SPME and fibre SPME: (a) extraction of 15 mL samples within 2.5 min with alkanes of  $10\text{ }\mu\text{g/L}$  level by on-line in-tube SPME; (b) extraction of 15 mL samples within 35 min with alkanes of  $10\text{ }\mu\text{g/L}$  level by fibre SPME; (c) extraction of 300 mL samples within 40 min with alkanes of  $2\text{ }\mu\text{g/L}$  level by on-line in-tube SPME; (d) extraction of 15 mL samples within 3 min with alkanes of  $10\text{ }\mu\text{g/L}$  level by fibre SPME. Column:  $30\text{ m} \times 0.53\text{ mm}$ ,  $0.6\text{ }\mu\text{m}$   $d_f$  MXT-1 (Restek Corp., Bellefonte, Pennsylvania, USA) with a 5 m retention gap; carrier gas: hydrogen at 8 mL/min; oven programme:  $30\text{ }^\circ\text{C}$  for 0.5 min,  $30$ – $110\text{ }^\circ\text{C}$  at  $40\text{ }^\circ\text{C/min}$ ,  $110\text{ }^\circ\text{C}$  for 1 min,  $110$ – $250\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C/min}$ ,  $250\text{ }^\circ\text{C}$  for 10 min; fibre 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 =  $n\text{-C}_{19}$ .



alkanes and concentration of samples studied. Table 2 shows the precision and linearity for all compounds investigated under different concentration conditions. The average RSD was 8.0% for the 0.5 µg/L

concentration level and 5.3% for the 20 µg/L concentration level.

We determined linearity by extracting spiked aqueous samples with concentrations ranging from 0.1 µg/L to

100 µg/L. The method was linear throughout at least three orders of magnitude. The coefficient of correlation achieved was better than 0.99 (Table 2). 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<sup>19</sup> and stir-bar sorptive extraction<sup>20</sup> have recently 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-litre or sub-microgram-per-litre concentrations. We applied two types of clean water as the sample matrices: Wahaha purified drinking water (Wahaha Corp., Hangzhou, China) [Figure 3(a)] and tap water from the laboratory faucet [Figure 3(b)]. 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 mg/L, much lower than that estimated by the fibre 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 fibre 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-**

**Table 2:** Precision, linearity and sensitivity of on-line in-tube SPME–high-resolution GC.

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

\* *n* = 6.

† Concentration range from 0.1 µg/L to 100 µg/L/L.

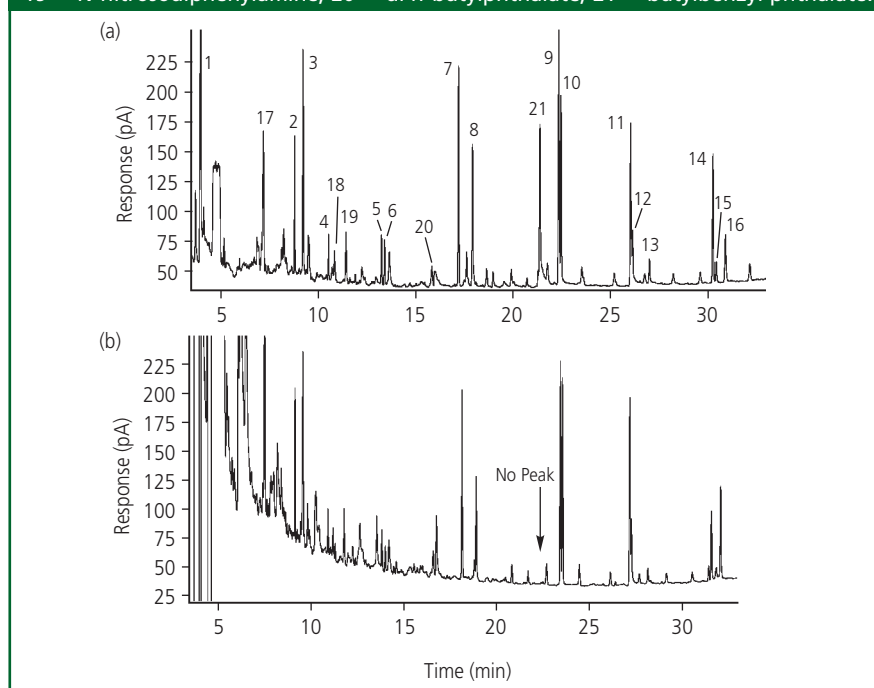
‡ Extraction flowrate: 10 mL/min for 300 mL samples of the lowest concentration of 0.1 µg/L.

§ Concentration range from 1 µg/L to 100 µg/L/L.

\ Detection with the lowest concentration of 1 µg/L/L.

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

**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 × 0.53 mm, 0.6 µm *d*<sub>f</sub> DB-1 (Agilent Technologies, Wilmington, Delaware, USA) with a 5 m retention gap; carrier gas: hydrogen at 8 mL/min; oven programme: 30 °C for 0.5 min, 30–110 °C at 40 °C/min, 110 °C for 1 min, 110–300 °C at 8 °C/min, 300 °C for 10 min. Peaks: 1 = naphthalene (2 µg/L), 2 = acenaphthylene (2 µg/L), 3 = acenaphthene (2 µg/L), 4 = fluorine (0.2 µg/L), 5 = phenanthrene (0.2 µg/L), 6 = anthracene (0.2 µg/L), 7 = fluoranthene (0.2 µg/L), 8 = pyrene (0.2 µg/L), 9 = benzo[*a*]anthracene (0.2 µg/L), 10 = chrysene (0.2 µg/L), 11 = benzo[*b*]fluoranthene (0.2 µg/L), 12 = benzo[*k*]fluoranthene (0.2 µg/L), 13 = benzo[*a*]pyrene (0.2 µg/L), 14 = indeno[1,2,3-*cd*]pyrene (0.2 µg/L), 15 = dibenzo[*a,h*]anthracene (0.2 µg/L), 16 = benzo[*ghi*]perylene (0.2 µg/L), 17 = hexachlorocyclopentadiene, 18 = diethyl phthalate, 19 = *N*-nitrosodiphenylamine, 20 = di-*n*-butylphthalate, 21 = butylbenzyl phthalate.



**capture detection:** To determine chlorinated pesticides in aqueous samples, we coupled our in-tube SPME device on-line with a model 3800 capillary gas chromatograph (Varian Inc., Palo Alto, California, USA), 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 into a silex vial at the 0.25 µg/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'-dichlorodiphenyltrichloro-ethane (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-litre 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-flamephotometric detection:**

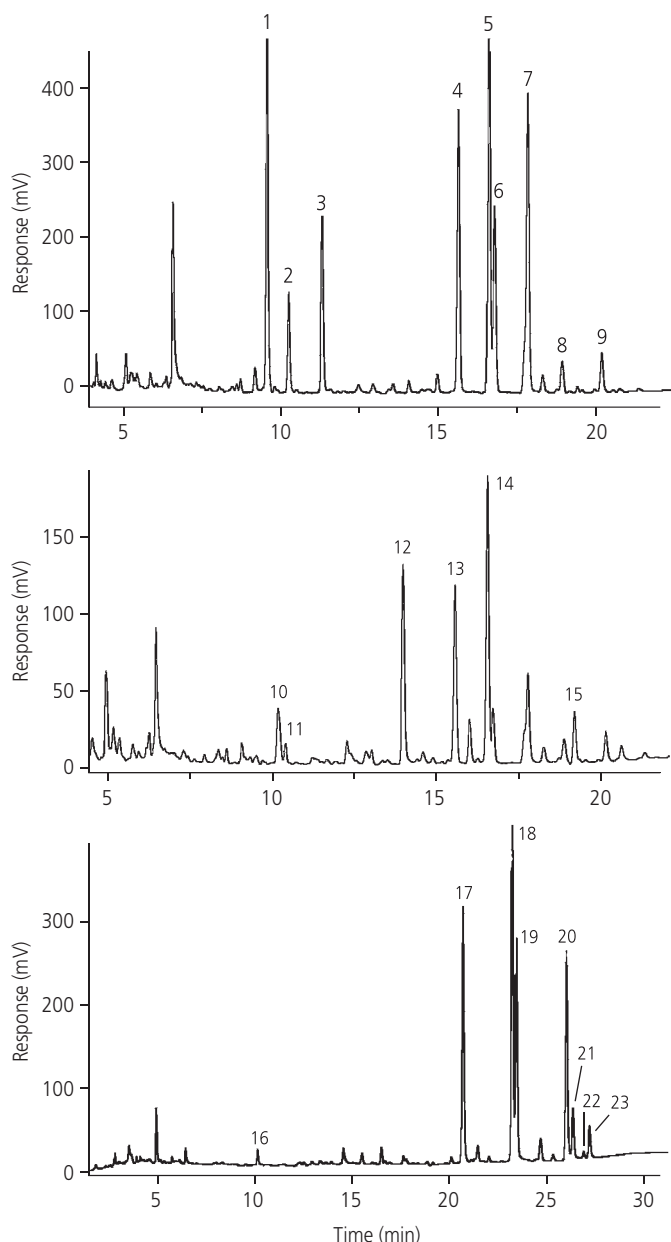
We coupled the same apparatus on-line with the capillary gas chromatograph, this time equipped with a pulsed-flame photometric detector (operated in the phosphorus mode) to determine the phosphorus-containing pesticides. We spiked 16 standard pesticides at 0.5 µg/L each in a 30 mL aqueous sample before 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 µg/L for most of the analytes with an extraction time of only 5 min.

**Conclusion**

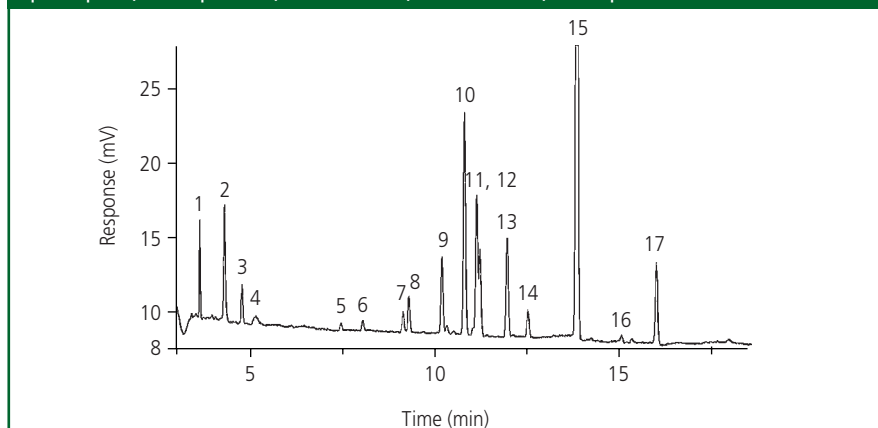
We performed in-tube SPME on-line coupling with high-resolution GC by using a simple device for the trace analysis of organic compounds in aqueous samples. The in-tube SPME-high-resolution GC methods demonstrated in our study successfully performed the on-line extraction, desorption and sampling of various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

- It enables much higher enrichment factors than those of fibre SPME because of its 10-fold greater volume of extracting phase compared with fibre SPME. In our experiments, the enrichment factors by means of in-tube SPME were at least 50-fold that of fibre 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 fibre SPME because of the drastically larger exchanging surface.
- It is performed as a fully on-line operation; therefore, it provides high-

**Figure 4:** On-line in-tube SPME-GC-ECD chromatograms of aqueous samples spiked with chlorinated pesticides. Column: 30 m × 0.53 mm, 0.6 µm *d<sub>f</sub>* DB-5 (Agilent Technologies) with a 5 m retention gap; carrier gas: nitrogen at 8 mL/min; oven programme: 30 °C for 0.5 min, 30–150 °C at 40 °C/min, 150 °C for 1 min, 150–280 °C at 7 °C/min, 280 °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.



**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 × 0.53 mm, 0.6 μm *d*<sub>f</sub> DB-5 (Agilent Technologies) with a 5 m retention gap; carrier gas: nitrogen at 8 mL/min; oven programme: 30 °C for 0.5 min, 30–150 °C at 40 °C/min, 150 °C for 5 min, 150–280 °C at 7 °C/min, 280 °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.



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. Levens, *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 et al., *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 et al., *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, *LC•GC Eur.*, **16**(7), 410–417 (2003).
17. L. Nardi, *J. Chromatogr. A*, **985**, 85–91 (2003).
18. E. Baltussen et al., *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 et al., *J. Microcol. Sep.*, **11**, 737–747 (1999).

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