Use of open-tubular trapping columns for on-line extraction-capillary gas chromatography of aqueous samples

ARTICLE *in* JOURNAL OF HIGH RESOLUTION CHROMATOGRAPHY · JULY 1993

DOI: 10.1002/jhrc.1240160706

3 AUTHORS, INCLUDING:

H. G.J. Mol
Wageningen University
79 PUBLICATIONS **1,818** CITATIONS

SEE PROFILE

Hans-Gerd Janssen
University of Amsterdam
152 PUBLICATIONS **3,018** CITATIONS

SEE PROFILE

Use of Open-Tubular Trapping Columns for On-Line Extraction–Capillary Gas Chromatography of Aqueous Samples

Hans G.J. Mol*, **Hans-Gerd Janssen**, and **Carel A. Cramers**
Eindhoven University of Technology, Laboratory of Instrumental Analysis, P.O. box 513, 5600 MB, Eindhoven, The Netherlands

Key Words:

On-line extraction–GC
Phase-switching
Open-tubular traps
Stationary phase swelling
Large volume injection
PTV

Summary

The applicability of open-tubular trapping columns for on-line extraction–capillary GC analysis is evaluated. The extraction step involves sorption of the analytes from water into the stationary phase of an open-tubular column, removal of the water by purging the trap with nitrogen, and desorption of the analytes with an organic solvent. The effect of swelling of the stationary phase with organic solvents on the retention power of the trap is studied. When using pentane or hexane as swelling agent breakthrough volumes of at least 10 ml can easily be obtained for non-polar compounds. For a number of medium polarity compounds breakthrough volumes of 5 ml can be achieved when chloroform is used as the swelling agent. The required drying time is less than 1 minute. Quantitative desorption requires only 75 µl of organic solvent. Solvent elimination prior to transfer to the GC column is carried out using a PTV injector and a multidimensional GC system. The system is applied for the analyses of river water, urine, and serum samples.

1 Introduction

On-line extraction–capillary gas chromatography is an attractive method for the analysis of aqueous samples. As the analytes from the entire sample volume will be quantitatively transferred to the GC column, sample volumes from 1–10 ml are often sufficient to achieve detection limits in the sub-ppb range. Several methods for on-line extraction–GC have been reported in the literature: membrane extraction [1], liquid-liquid extraction in a segmented flow [2], and solid-phase extraction with small packed cartridges [3,4]. In these methods the compounds are transferred from the aqueous solvent to an organic solvent which is introduced into the GC system. This procedure is often referred to as phase-switching. In membrane extraction an extraction cell containing a short length of silicon tubing is used. Analytes are extracted from the water phase through the silicon wall into the organic solvent which flows through the tubing. Liquid-liquid extraction in a segmented flow appears to be especially useful when on-line derivatization is desired [5,6]. Solid-phase extraction (SPE), a technique that has gained wide spread acceptance in off-line sample preparation [7], has been reported to be a useful alternative to the previously mentioned techniques.

An important step in on-line extraction-GC is the removal of water, as water can adversely affect the performance of the combined system. When water is immiscible with the desorption solvent, water remaining in the SPE-cartridge after sampling can result in reduced desorption efficiencies. On the other hand, if water is (partially) miscible with the desorption solvent it will be transferred to the GC-system deteriorating the system performance [8]. Therefore, a rigorous drying step is necessary between sorption and desorption. Packed cartridges are generally dried by purging with nitrogen. Drying times depend on the dimensions of the cartridge and the packing density and may alter after prolonged usage. Typical drying times are 15–30 min. In case of long drying times losses of more volatile analytes can occur. Due to channel formation in the packing, complete water elimination can sometimes be difficult to obtain. A major improvement in this respect is the use of particle loaded membranes (membrane disks) [9] which are a very promising alternative to SPE with small cartridges filled with sorbent particles [10,11]. Typical drying times for extraction disks are 10–20 minutes. Owing to the rigid structure of the membrane matrix, however, channel formation is highly unlikely. In contrast to the situation in packed SPE-cartridges, complete removal of water can easily be achieved by using open-tubular traps. In previous work we have described the use of open-tubular trapping columns in on-line coupled reversed-phase LC-GC [12]. In that work it was demonstrated that the water containing eluent could be efficiently removed by purging the trap with a low flow of nitrogen. Complete water elimination was achieved in only 1 minute.

In this work the applicability of wall coated open-tubular traps in on-line extraction of organic compounds from water is studied. The effect of swelling the stationary phase with organic solvents prior to water sampling is evaluated. A test mixture containing priority pollutants with varying polarities is used for system evaluation. The applicability of the system is demonstrated by a number of real-life samples including river water, urine and serum samples.

2 Experimental

2.1 Instrumentation

The phase switching device was built around two 10-port valves (Valco, Houston, TX, USA). It is schematically depicted in **Figure 1**. The system consisted of a sampling pump (P1) (Phoenix 20, Carlo Erba, Milan, Italy) and a pump used for desorption (P2) (Digisampler, Gerstel, Mülheim a/d Ruhr, Germany). A fraction loop of 0.5 or 2.25

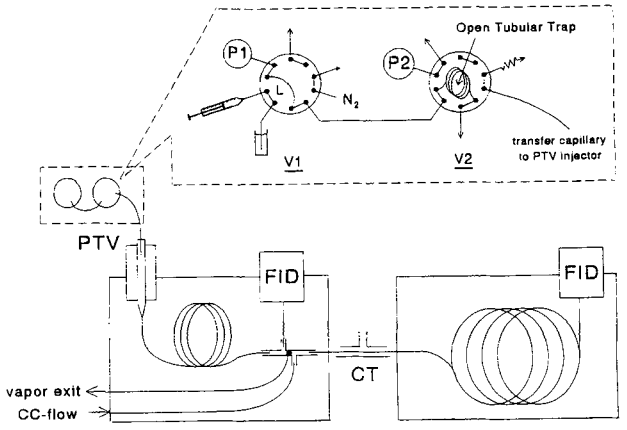

Figure 1
Equipment used for on-line extraction–GC. V1, V2 = valves; P1, P2 = syringe pumps, L = sample loop, CC-flow = counter current flow, CT = cold trap.

ml was connected between two ports of valve 1. The open-tubular traps were connected between two ports of valve 2. Traps of 2 m × 0.32 mm i.d., coated with 5 μm CP-Sil-5-CB (Chrompack, Bergen op Zoom, The Netherlands) or 1.2 μm Carbowax (Chrompack) were used.

For large volume introduction/GC analysis a Gerstel-MCS gas chromatographic system was used (Fig. 1). The MCS-GC system consisted of two gas chromatographs (HP 5890A and HP 5890A Series II, Hewlett-Packard, Avondale, PA, USA), a programmed temperature injection system (CIS-3, Gerstel), a dual column switching module (DCS, Gerstel), and a cryotrap system (CTS-1, Gerstel) in between the ovens. Each of the gas chromatographs was equipped with an FID. The MCS system was operated using the MCS software. For data acquisition a Varian Star integration system (Varian, Walnut Creek, CA, USA) was used.

2.2 Determination of Swelling

The use of an organic desorption fluid in open-tubular traps results in a significant swelling of the stationary phase, which in turn results in increased retention of the compounds in the trapping column [12, 13]. In this study the degree of swelling that occurred for the various desorption fluids was quantified by measuring the difference in void volume of the trap before and after swelling. The void volume was determined by pumping a liquid through the trap at a known flow rate. The dead time could be observed visually by injecting a short plug of nitrogen.

2.3 On-Line Extraction–GC

The test mixture used to evaluate the performance of the system contained the following 14 compounds: toluene, ethylbenzene, methoxybenzene, *p*-dichlorobenzene, 2,6-dimethylphenol, 2,6-dimethylaniline, *p*-chloroaniline, indole, 2,6-dichlorobenzonitrile, 2,4,5-trichlorophenol, *p*-dinitrobenzene, trifluralin, atrazine, and phenanthrene. All solvents were freshly distilled before use. River water was filtered through a glass filter before sampling. Urine and serum were analyzed without pretreatment.

The position of the valves at the start of an extraction cycle is shown in Figure 1. The content of the sample loop is transferred to the open-tubular trap by pump 1 and the trap is flushed with an additional 150 μl of water. After this valve 1 is switched. The nitrogen flow now slowly pushes the remaining water out of the trap. The total drying time used is only 1 min. Meanwhile pump 2 (containing an organic solvent) is started. When valve 2 is switched the analytes are desorbed from the trap and introduced directly into the PTV injector. Half a minute before the next extraction step, valve 2 is switched back again to remove the organic solvent (remaining in the trap after desorption) by a flow of nitrogen. Meanwhile the sample loop is filled again after which the next extraction can take place.

2.4 Large Volume Introduction into the PTV–MCS System

For elimination of the organic solvent prior to introduction of the compounds into the analytical column a two-dimensional gas chromatographic system equipped with a PTV injector is used. In this approach for the introduction of large volumes in capillary GC the solvent is vaporized in the PTV injector [14]. The solvent vapors are discharged *via* a short, wide-bore thick film GC precolumn, located in the first oven. In this precolumn the solvent is separated from the analytes and vented through a vapor exit. After venting the solvent the vapor exit is closed and the PTV and the first oven are heated rapidly. The compounds are then refocused in the cold trap mounted between the two ovens. The analytical column is located in the second oven. With this system losses of volatiles during solvent elimination can be greatly reduced.

In the first oven a 5 m × 0.53 mm column with a 5 μm CP-Sil-5-CB film (Chrompack) was installed. In the second oven a 50 m × 0.31 mm column with a 0.17 μm HP-Ultra-1 stationary phase (Hewlett-Packard) was mounted. Helium was used as the carrier gas. The system was operated in the constant flow mode at a flow rate of 4.5 ml/min. During solvent elimination the vapor exit was open and the gas flow rate was increased to facilitate solvent evaporation. The conditions for large volume injection were as follows. For pentane, dichloromethane and isopropyl chloride the total helium flow rate during introduction was 15 ml/min, the counter current flow rate 20 ml/min, the PTV initial temperature 50 °C, and the initial temperature of the first oven 35 °C. For chloroform these values were 25 ml/min, 30 ml/min, 50 °C, and 50 °C, respectively. For trichloroethene the values were 75 ml/min, 30 ml/min, 80 °C, and 50 °C, respectively. The initial temperature of the cold trap was set to −160 °C. After elimination of the solvent had reached completion, as was monitored from the signal of the monitor FID on the first oven, the run of the MCS was started. The start of the MCS system involved reduction of the carrier gas flow rate to 4.5 ml/min, switching off the counter current flow, closing of the vapor exit and starting of the temperature programs of the injector, cryotrap, and the two ovens. The temperature programs were as follows: PTV injector: from initial temperature to 275 °C (100 s) at 2 °/s. First oven: from initial temperature to 240 °C (5 min) at 30 °/min. Cryotrap: held at its initial temperature for 4 min and then heated to 250 °C at 5 °/s (10 min) followed by heating at 1 °/s to 270 °C. Second oven: from 60 °C to 230 °C (1 min) at 15 °/min. In case of the real-life samples the final temperatures of both the PTV and the second oven were 300 °C.

3 Results and Discussion

The maximum volume of sample that can be passed through an adsorption column is determined by the breakthrough volume of the solute (V_b), defined as V_r- 2.326σ_v. Here V_r is the retention volume and σ_v the standard deviation of the Gaussian peak eluting from the trapping column. The breakthrough volume of a compound in a trapping column is given by equation (1) [15]:

Table 1
Properties and experimental data for possible swelling agents.

Swelling agent	Boiling point °C	S^v/v%[a] O in W	S^v/v%[b] W in O	Swelling factor[c]	Phase ratio[c]	d_f[c] (µm)	F_{evap}[d] µl/min
Pentane	36	0.0061	0.0075	4.7	1.9	30.8	190
Hexane	69	0.0014	0.0049	4.5	2.0	29.6	72
Heptane	98	0.0005	0.0057	4.2	2.1	28.0	28
Cyclohexane	81	0.0071	0.0079	4.4	2.0	29.1	40
Ethyl acetate	77	9.7	2.7	2.4	3.7	17.8	38
Ethyl ether	35	9.0	1.1	4.8	1.8	31.6	180
Isopropyl ether	68	1.7	0.43	4.7	1.8	31.3	76
Isopropyl chloride	36	0.35	-	4.2	2.1	27.8	155
Dichloromethane	40	0.99	0.27	3.2	2.9	22.1	94
Chloroform	61	0.55	0.11	4.4	2.0	29.0	56
Trichloroethene	87	0.074	0.046	2.2	4.1	16.4	26
1,1,1-Trichloroethane	74	0.098	0.045	1.3	6.0	11.9	-

[a] Solubility of the organic solvent in water [16,17].
[b] Solubility of water in the organic solvent [16,17].
[c] After swelling the stationary phase (5 µm CP-Sil-5-CB) with the organic solvent.
[d] Evaporation rate according to equation 4 [18] at conditions given in text.

$$V_b = V_0(1+k)\left(1 - \frac{2.326}{\sqrt{N}}\right) \quad (1)$$

where V_0 is the void volume of the trapping column, k the capacity factor of the solute in the trap and N the plate number of the trapping column (with $N > 5.4$). Assuming a high capacity factor, equation (1) can be simplified to [12]:

$$V_b = K V_s \left(1 - 0.9\sqrt{\frac{F}{D_m L}}\right) \quad (2)$$

Here K is the partition coefficient, V_s the volume of the stationary phase, F the sampling flow rate, D_m the diffusion coefficient of the compound in water and, L the length of the trapping column. From equation (2) it can be seen that the sampling flow rate should not exceed a certain maximum value. This has been verified experimentally [12]. For trapping capillaries of 2 m, as used in this study, flow rates not exceeding 100 µl/min were used in order to prevent immediate breakthrough.

In practice the most important way to enhance the breakthrough volume of open-tubular traps is through maximizing K and V_s. For trapping compounds from water this means that, apart from length and diameter of the trapping column, the use of a thick film and a selective stationary phase is essential.

An alternative way to increase both K and V_s is to swell the stationary phase with an organic solvent. For the extraction with open traps this means that the stationary phase (preferably a thick film) should be swollen before sampling the water. After sampling and water removal desorption is carried out with the same organic solvent as was used for swelling. In this way desorption and renewed phase swelling for the next extraction is achieved in one step.

The swelling agent in the situation described above is also the desorption solvent and the solvent to be introduced into the GC system. Therefore a suitable swelling agent should meet the following requirements: i) the organic solvent should swell the stationary phase significantly; ii) the swelling agent should have a low solubility in water because otherwise the swelling agent is rapidly stripped from the stationary phase during water sampling; iii) the swelling agent should have favorable evaporation characteristics; iv) water should not be soluble in the swelling agent (this is because water dissolved in the organic solvent will be transferred to the GC); v) the analytes should have a high affinity for the swelling agent.

In this study two types of stationary phases were evaluated, *i.e.* a dimethylsiloxane (d_f = 5 µm) and a Carbowax (d_f = 1.2 µm) stationary phase. However, preliminary results with the Carbowax trap were, even after swelling, not very promising. Experiments were therefore continued only with the dimethylsiloxane trap.

Twelve organic solvents, among which the most commonly used extraction solvents, were tested with respect to the degree of swelling of the siloxane phase in the trap and the rate of stripping of the organic solvent from the trap by water. Some relevant properties of these possible swelling agents are given in **Table 1** [16,17]. The uptake of organic solvent in the stationary phase of a 2 m × 0.32 mm i.d., 5 µm CP-Sil-5-CB trap was determined by measuring the

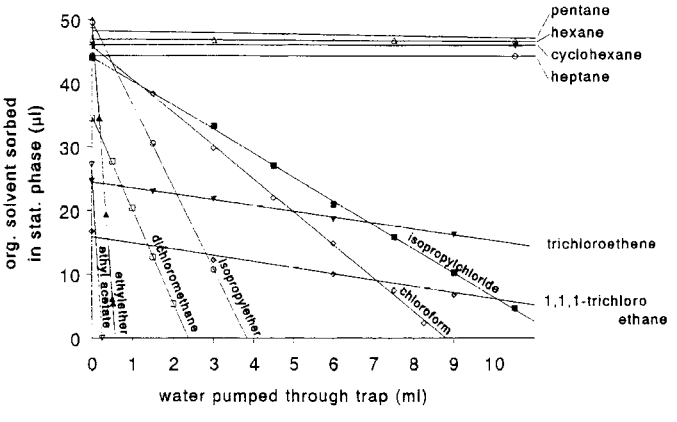

Figure 2
Removal of organic solvent from the trap by water after swelling. Trap: 2 m×0.32 mm i.d., 5 µm CP-Sil-5-CB.

void volume of the trap before and after rinsing with the organic solvent. As can be seen from **Figure 2**, the uptake varied from 17 to 50 µl. From the total stationary phase volume the swelling factor (equation (3) [13]) as well as the apparent film thickness and the phase ratio can be calculated. The values for the twelve organic solvents tested are given in Table 1.

$$S_V = \frac{\text{volume of swollen phase} - \text{volume of original phase}}{\text{volume of original phase}} \quad (3)$$

After swelling water was pumped through the trap and the void volume was measured at distinct intervals. From this the decrease of the volume of organic solvent in the trap could be calculated. The volume of swelling agent left in the trap as a function of the volume of water pumped through the trap is shown in Figure 2. As can be seen from this figure, most organic solvents tested swell the stationary phase considerably. The stripping rate of the swelling agent from the trap by water is, as expected, high for the relatively polar ethyl acetate and diethyl ether. In fact, the stripping rate (in µl/ml water) approximately resembles the solubility of the organic solvent in water. From Figure 2 it can be concluded that ethyl acetate and diethyl ether are not suited as swelling agents because they are removed from the trap by only half a milliliter of water. Also 1,1,1-trichloroethane is not suited because phase swelling is less pronounced for this solvent.

Another important aspect to consider in selecting a desorption/swelling agent is the speed with which it can be introduced in the PTV injector. Information about the evaporation characteristics can be obtained from calculations of the evaporation rate. The evaporation rates can be calculated from [18]:

$$F_{evap} = \frac{M p_j}{\rho R T_0} \frac{p_0}{p_i} F_{t,0} \quad (4)$$

where F_{evap} is the evaporation rate, M, ρ, and p_j are the molecular weight, the density and the vapor pressure of the swelling agent, respectively, R is the gas constant, $F_{t,0}$ the helium flow at outlet conditions (T_0, p_0) and p_i the inlet pressure of the liner. Evaporation rates for a PTV initial temperature of 50 °C, p_0/p_i=1 and $F_{t,0}$= 25 ml/min are given in Table 1. As the introduction speed in the PTV should not exceed the evaporation rate of the liquid sample, only low introduction flow rates can be applied for solvents which have a low F_{evap} value. Evaporation rates can be increased by increasing the initial temperature of the PTV and the helium flow rate, but this can result in losses for volatile compounds. From this point of view, heptane, cyclohexane, and trichloroethene are less suited as desorption/swelling agents when volatile analytes are concerned.

Breakthrough volumes of 14 test compounds were determined first using the plain, unswollen, trap by sampling 0.5 ml of a solution of the compounds in water followed by flushing with different volumes of water. After water elimination, desorption/introduction, and GC analysis the recoveries were calculated relative to a splitless injections of 1 µl of a concentrated standard solution. Breakthrough volumes were again determined by applying phase swelling prior to sorption. The results are given in **Table 2**. For the plain trap only trifluralin and phenanthrene are well retained. Even non-polar compounds like ethylbenzene and dichlorobenzene showed only little retention. The more polar compounds were not trapped at all. Swelling the stationary phase with one of the *n*-alkanes resulted in breakthrough volumes higher than 10 ml for the non-polar compounds while immediate breakthrough occurred for most of the polar analytes. To trap these compounds more polar organic swelling agents have to be used. Dichloromethane is a commonly used solvent in liquid-liquid extraction. It also has favorable swelling characteristics and evaporation properties. When water samples with a volume lower than 1.5 ml are sampled through the trap after swelling the stationary phase with dichloromethane, quantitative recoveries are found for all 14 test compounds (**Figure 3a**). At volumes beyond 1.5 ml, however, the more polar sample constituents show recoveries below 100%. This is mainly due to stripping of the dichloromethane from the trap by water (see Figure 2). As an example, in **Figure 3b** all but the non-polar compounds are completely lost when 3 ml of water was sampled through the trap. When using chloroform as the swelling agent higher breakthrough volumes were found because of the lower solubility of this solvent in water and because of the high affinity of most of the components for the chloroform-swollen phase. Two other solvents were also tested. Trichloroethene, because it is more polar than the alkanes and still has a low solubility in water, and isopropyl chloride because of its high solvent elimination rate in the PTV–GC system. However, except for toluene, ethylbenzene, dichlorobenzene, and dichlo-

Table 2
Breakthrough volumes for a 2 m × 0.32 mm i.d., 5 µm trap without or with swelling.

	Breakthrough volume (ml)						
Swelling agent:	None	Pentane	Dichloro-methane	Chloroform	Trichloro ethene	Isopropyl chloride	Dichloromethane-pentane (1:1)
Toluene	0.5	>10	2	5	-	>10	>10
Ethylbenzene	1	>10	2.5	5	-	>10	>10
Methoxybenzene	<0.5	2.5	1.5	5	1	5	1.5
Dichlorobenzene	<0.5	>10	2.5	5	>10	>10	>10
Dimethylphenol	<0.5	<0.5	1	2.5	1	1	1
Dimethylaniline	<0.5	<0.5	1.5	5	2.5	1.5	1
Chloroaniline	<0.5	<0.5	1	2.5	1	1	0.5
Indole	<0.5	<0.5	1.5	2.5	1	1.5	1
Dichlorobenzonitrile	<0.5	2.5	1.5	5	>10	10	1.5
Trichlorophenol	<0.5	1	1.5	5	5	5	1.5
Dinitrobenzene	<0.5	<0.5	1.5	5	2.5	2.5	1.5
Trifluralin	>10	>10	>10	>10	>10	>10	>10
Atrazine	<0.5	<0.5	2	5	2.5	1.5	1
Phenanthrene	>10	>10	>10	>10	>10	>10	>10

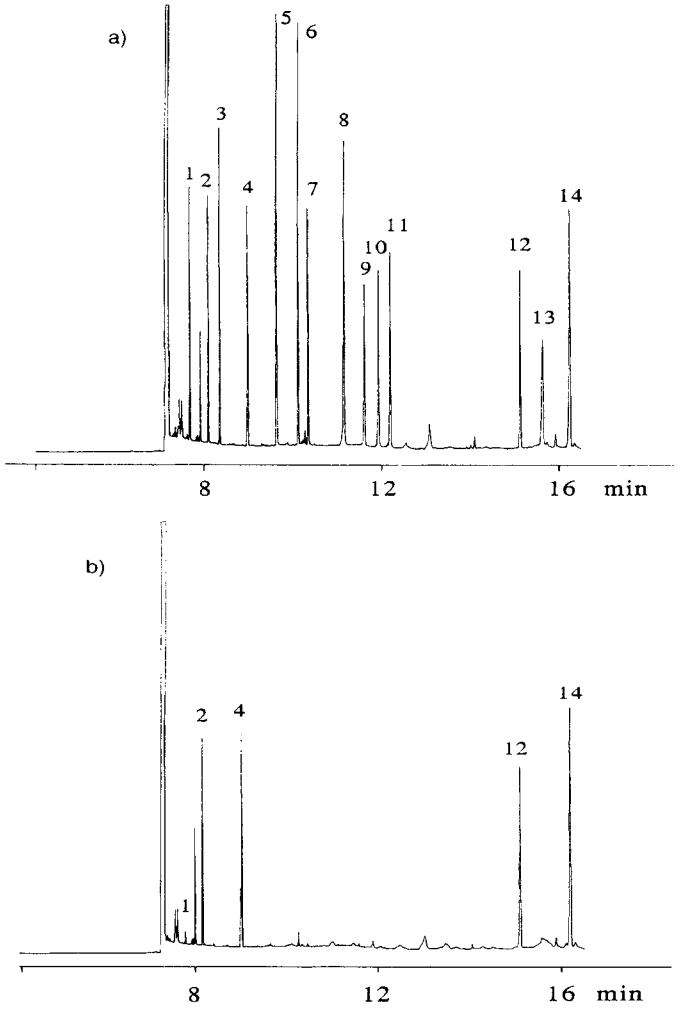

Figure 3
Chromatograms obtained after sampling 1 ml (a) and 3 ml (b) of water through a 2 m×0.32 mm i.d. trap with a 5 μm stationary phase swollen with dichloromethane. Sampling flow rate 100 μl/min, desorption with 75 μl dichloromethane. Compounds: 1) toluene, 2) ethylbenzene, 3) methoxybenzene, 4) *p*-dichlorobenzene, 5) dimethylphenol, 6) dimethylaniline, 7) chloroaniline, 8) indole, 9) dichlorobenzonitrile, 10) trichlorophenol, 11) dinitrobenzene, 12) trifluralin, 13) atrazine, and 14) phenanthrene (*ca.* 40 ng/compound).

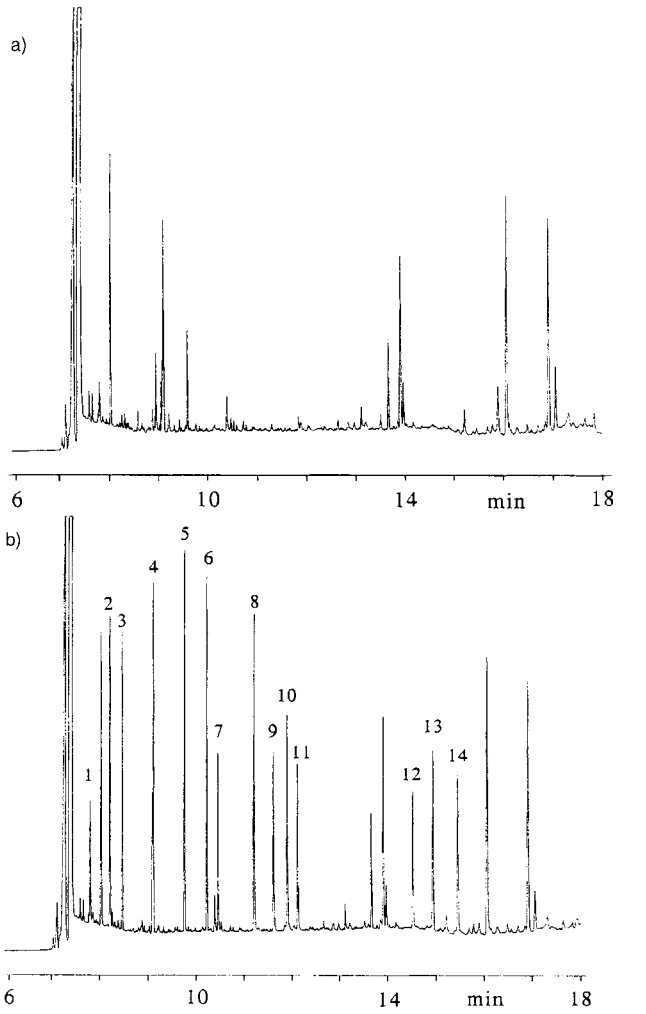

Figure 4
On-line extraction–GC of water from river Dommel. (a) 2.25 ml river water, (b) 2.25 ml river water spiked at a 5 ppb level with the compounds given in Fig. 3. Swelling agent: chloroform, other conditions: see Fig. 3.

robenzonitrile, the breakthrough volumes observed for these two solvents were equal to or lower than those obtained for chloroform. Finally, the use of a mixed swelling agent was tested, *i.e.* pentane/dichloromethane 1:1, in order to create a swollen phase which is more polar than pentane and that would have a better resistance towards stripping by water than a dichloromethane swollen phase. For most of the polar compounds, however, the results were not better than those of neat dichloromethane, indicating that the mixed phase was not sufficiently polar or that dichloromethane was rapidly stripped from the siloxane/pentane layer.

In the experiments described above a 2 m trapping column was used. If larger breakthrough volumes are required, longer traps (*e.g.* 5 m) can be used. This also allows the use of higher sampling flow rates [12] which results in acceptable sampling times when analyzing sample volumes larger than 1 to 2 ml.

After the sorption step, water is completely removed from the trap by a 1 min drying step with a nitrogen purge flow of 1 ml/min. Next the compounds are desorbed from the trap with the desorption/swelling agent. For all solutes the volume needed for desorption was found to be 75 μl, irrespective of which solvent was used for desorption. The maximum allowable desorption/introduction flow rate into the PTV–GC system is determined by the volatility of the analytes, the properties of the solvent and the PTV–GC conditions. For pentane, dichloromethane, and isopropyl chloride a flow rate of 75 μl/min was used. For chloroform and trichloroethene a desorption flow rate of 25 μl/min was applied.

For elimination of the organic solvent prior to introduction of the compounds into the analytical column a two-dimensional gas chromatographic system equipped with a PTV injector is used. Important parameters affecting the solvent elimination process in the PTV–MCS system are the PTV initial temperature, the temperature of the first oven, carrier gas flow rate through the GC-precolumn, introduction flow rate, sample volume, and the physico-chemical properties of the solvent [14]. Here, for large volume introduction, all compounds in the test mixture could be quantitatively transferred to the analytical column when pentane, dichloromethane or isopropyl chloride were used as solvent. In case of chloroform, toluene was partially lost due to the small difference in boiling points between the solvent and this test compound. For the same reason both toluene and ethylbenzene were partially lost when trichloroethene was used as the solvent.

To evaluate the applicability of on-line extraction–GC using open-tubular traps for real-life samples, river water was spiked with the

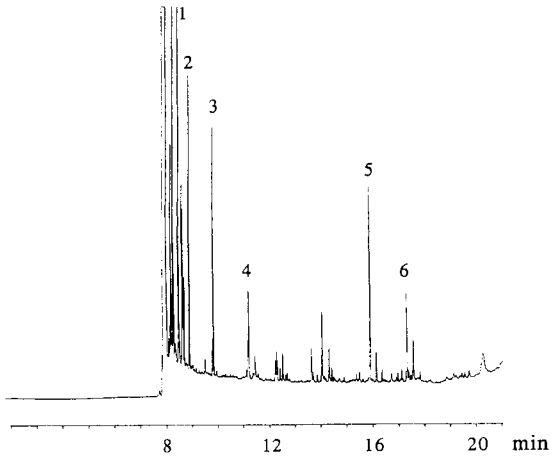

Figure 5
On-line extraction–GC of 0.5 ml of urine spiked at a 20–40 ppb level. 1) toluene, 2) ethylbenzene, 3) *p*-dichlorobenzene, 4) 1,2,4-trichlorobenzene, 5) lindane, 6) heptachlor. Sorption flow rate, 100 µl/min; swelling agent, dichloromethane; desorption volume. 75 µl.

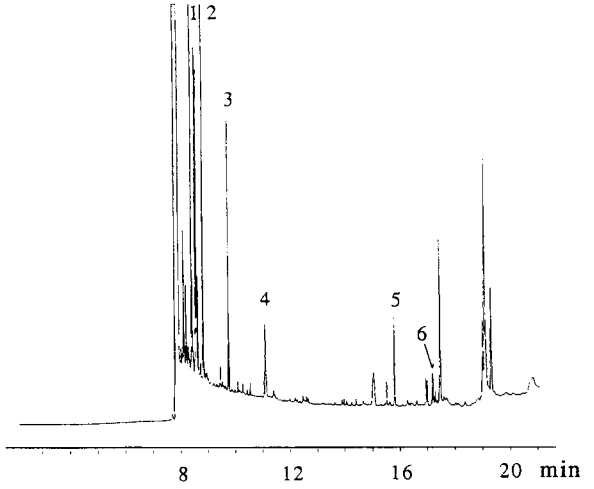

Figure 6
On-line extraction–GC of 0.5 ml of human serum spiked at a 30 ppb level. 1) toluene, 2) ethylbenzene, 3) *p*-dichlorobenzene, 4) 1,2,4-trichlorobenzene, 5) lindane, 6) heptachlor. Sorption flow rate, 100 µl/min; swelling agent, dichloromethane; desorption volume, 75 µl.

compounds from the test mixture at a 5 ppb level. A volume of 2.25 ml was sampled through the trap which was then flushed with 0.15 ml of distilled water. Chromatograms of a blank and a spiked river water sample are shown in **Figure 4**. No significant differences in recovery were observed when comparing the spiked river water sample with a 5 ppb test mixture in distilled water. The repeatability (RSD, $n = 4$) of this analysis was found to be 1.5–10%. Another example is the analyses of urine shown in **Figure 5**. 0.5 ml of urine spiked with a number of substituted benzenes and two organochloro pesticides at a 30 ppb level was sampled and then flushed with 0.5 ml water. Again, quantitative recoveries were obtained indicating that there were no adverse matrix effects. In principle, the use of open tubular traps for on-line extraction–GC also holds promise for direct injection of protein containing samples like blood serum, as is illustrated in **Figure 6**. When packed solid-phase extraction cartridges or extraction disks are applied for this type of samples, partial plugging of the pores by protein molecules often results in low recoveries and a poor repeatability.

4 Conclusion

Wall coated open-tubular traps can be used for on-line extraction–GC of organic compounds from aqueous samples. While some non-polar compounds can be trapped on a plain thick film polysiloxane phase, swelling the stationary phase with a suitable organic solvent is a prerequisite for trapping other components. Pentane-swollen traps are most suited for trapping non-polar analytes, breakthrough volumes larger than 10 ml are easily obtainable using two meter traps. Chloroform is best suited for trapping more polar compounds. For the analysis of specific groups of compounds, the use of other swelling agents can be beneficial from the point of view of selectivity. With the system described here quantitative recoveries for most compounds from a test mixture of priority pollutants is obtained for aqueous samples up to 5 ml. In this way detection limits in the ppt–ppb range are readily achievable with FID detection. Important advantages of open-tubular trapping columns are the non-susceptibility towards plugging and the ease of water removal.

Acknowledgment

The foundation for Chemical Research in the Netherlands (SON) is gratefully acknowledged for their financial support.

References

[1] *R.G. Melcher* and *P.L. Morabito*, Anal. Chem. **62** (1990) 2183–2188.

[2] *E.C. Goosens, R.G. Bunschoten, V. Engelen, D. de Jong*, and *J.H.M. van den Berg*, J. High Resolut. Chromatogr. **13** (1990) 438–442.

[3] *E. Noroozian, F.A. Maris, M.W.F. Nielen, R.W. Frei, G.J. de Jong*, and *U.A.Th. Brinkman*, J. High Res. Chromatogr. **10** (1987) 17–24.

[4] *J.J. Vreuls, W.J.G.M. Cuppen, G.J. de Jong*, and *U.A.Th. Brinkman*, J. High Res. Chromatogr. **13** (1990) 157–161.

[5] *E.C. Goosens, M.H. Broekman, M.H. Wolters, R.E. Stnijker, D. de Jong, G.J. de Jong*, and *U.A.Th. Brinkman*, J. High Res. Chromatogr. **15** (1992) 242–248.

[6] *E. Ballesteros, M. Gallego*, and *M. Valcázcel*, J. Chromatogr. **633** (1993) 169–176.

[7] *C.F. Poole* and *S.K. Poole*, Chromatography Today, Elsevier, Amsterdam, 1991.

[8] *J.J. Vreuls, R.T. Ghijsen, G.J. de Jong*, and *U.A.Th. Brinkman*, J. Chromatogr. **625** (1992) 237–245.

[9] *P.J.M. Kwakman, J.J. Vreuls, U.A.Th. Brinkman*, and *R.T. Ghijsen*, Chromatographia **34** (1992) 41–47.

[10] *W.P.N. Fernando, M.L. Larnve*, and *C.F. Poole*, Anal. Chem. **65** (1993) 588–595.

[11] *T. McDonnell* and *J. Rosenfeld*, J. Chromatogr. **629** (1993) 41–53.

[12] *H.G.J. Mol, J. Staniewski, H.-G. Janssen, C.A. Cramers, R.T. Ghijsen*, and *U.A.Th. Brinkman*, J. Chromatogr. **630** (1993) 201–212.

[13] *S. Folestad* and *M. Larsson*, J. Chromatogr. **394** (1987) 455–464.

[14] *J. Staniewski, H.-G. Janssen*,and *C.A. Cramers*, manuscript in preparation.

[15] *C.E. Werkhoven-Goewie, U.A.Th. Brinkman*, and *R.W. Frei*, Anal. Chem. **53** (1981) 2072–2080.

[16] *Y. Marcus*, Introduction to Liquid State Chemistry, Wiley Interscience, New York, 1977.

[17] *H. Stephan* and *T. Stephan*, Solubility of Inorganic and Organic Compounds, Vol. 1, Part 1, Pergamon, New York, 1963.

[18] *J. Staniewski* and *J.A. Rijks*, J. Chromatogr. **623** (1992) 105–113.

Ms received: May 27, 1993
Accepted: July 6, 1993