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Use of a presolvent to include volatile organic analytes in the application range of on-line solid-phase extraction–gas chromatography–mass spectrometry

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Abstract

The application range of the on-line solid-phase extraction–gas chromatographic (SPE–GC) analysis of aqueous samples has been extended to volatile analytes. In the new set-up, after conventional aqueous-sample loading and drying of the SPE cartridge with nitrogen gas, 30–50 μl of an organic solvent, the so-called presolvent, such as methyl acetate or ethyl acetate are introduced into the retention gap prior to the actual desorption to ensure that a solvent film is already present in the retention gap when the introduction of the analyte-containing desorption solvent starts. This procedure allows the recovery of analytes as volatile as monochlorobenzene and xylene. Aspects such as the type of retaining precolumn, and the type and amount of presolvent have been studied systematically to explain the performance of the novel set-up. Actually, when using 50 μl of presolvent, the use of a retaining precolumn did not have any significant influence on the recovery of the volatile analytes. The modified SPE–GC procedure was tested by analysing 10 ml of river Rhine water spiked at the 0.5 μg/l level with about 80 microcontaminants covering a wide range of volatility. The test compounds included chlorobenzenes, substituted and nonsubstituted aromatic compounds, anilines and phenolic compounds and organonitrogen and organophosphorus pesticides. The system performance in terms of recovery (typically 70–115% at the 0.5 μg/l level) and repeatability (R.S.D. values typically 1–9%; $n=7$) was satisfactory, even for monochlorobenzene, the most volatile analyte of the test mixture. Low recoveries due to early breakthrough (polar analytes) or adsorption to the tubing (apolar analytes) were observed for a few analytes only. The detection limits in SPE–GC–MS using full-scan acquisition generally were 20–50 ng/l.

Keywords: Automation; Presolvents; Water analysis; Environmental analysis; Volatile organic compounds

1. Introduction

The trace-level analysis of aqueous samples to determine organic microcontaminants requires fast, sensitive and selective methods. In this context, the on-line coupling of the sample preparation and the separation-cum-detection procedure in one integrated system is desirable to allow automation and increase sensitivity. In such a system, solid-phase extraction (SPE) is preferred for the transfer of the analytes from the aqueous phase into an organic solvent. The analytes are desorbed from the SPE cartridge into the GC system with 50–100 μl of organic solvent. Several applications have been reported for the SPE–

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GC analysis of pesticides using an on-column [1,2] or a loop-type [3] interface and a variety of selective detectors, including mass selective (MS) [1,4] and atomic emission [5] detectors.

Fully automated on-line SPE–GC is ideally suited as an early-warning system for the at-site screening of river water quality. In this case, it is desirable to have volatile analytes such as lower chlorinated benzenes included in the procedure. MS detection generally is preferred because of its identification potential. When the application range has to cover volatile analytes, an on-column interface should be one's first choice because of the solvent effects then operational for trapping of the analytes [6]. However, also with large volume on-column injection, the loss of a not fully-trapped analyte, e.g., toluene in pentane, was observed by Grob and Neukom when injecting 70 μl instead of 0.7 μl on-column [7]. They attributed the loss to incomplete reconcentration of partially solvent-trapped bands by phase soaking, because phase soaking only slows down the migration of early escaped volatiles, but does not stop it, and is therefore only active up to a certain injection volume. Deans [8] proposed the introduction of pure solvent in front of the sample plug to serve as a barrier against escaping solvent and showed an example for a 40-μl injection in packed-column GC. Several related studies [9–12] have been reported, but none of these used the approach for large-volume on-column injections into a retention gap in a GC.

On-line SPE–GC of volatile analytes has not been studied in much detail. Only Picó et al. reported the on-line SPE–GC determination of some chlorobenzenes and other rather volatile analytes [13]. In their set-up, a drying cartridge was inserted between the SPE module and the GC to remove traces of water from the organic SPE extract. However, the recoveries of 3-chlorotoluene and 1,2-dichlorobenzene were only 34 and 50%, respectively. In addition, in one of the real life examples shown several other dichlorobenzenes also showed up with rather low recoveries. These results indicate that there is an experimental problem.

The goal of this study was to extend the application range of on-line SPE–GC of aqueous samples to include volatile analytes next to higher-boiling compounds. To this end, the role of the drying step which is necessary to remove the water left in the SPE cartridge after the sampling step, the choice of the desorption solvent and the use of a so-called presolvent (i.e. the transfer of pure organic solvent into the GC prior to the analyte-containing fraction) were studied. The total system was used for the SPE–GC–MS determination of some eighty microcontaminants covering a wide volatility range, i.e. from monochlorobenzene to dioctyl phthalate, in river water at the sub microgram per litre level.

2. Experimental

2.1. Chemicals

HPLC-grade water, ethyl acetate, methyl acetate and isopropanol, all of analytical-reagent grade, were purchased from J.T. Baker (Deventer, The Netherlands). The organic solvents were glass-distilled prior to use. A stock solution of all test compounds at a concentration of about 20 ng/μl in dichloromethane, which was a gift from the Institute for Inland Water Management and Waste Water Treatment (RIZA, Lelystad, The Netherlands), was kept at −20°C. For the microcontaminants used as test analytes, which came from various sources and were all of analytical-reagent quality, one is referred to Table 6 below. For the optimization of the amount of presolvent and the comparison of several retaining precolumns, a stock solution of 29 test compounds in methyl acetate or hexane was prepared (Nos. 1, 4, 5, 6, 7, 9, 11, 13, 15, 16, 18, 20, 22, 23, 25, 26, 27, 35, 39, 40, 51, 54, 55, 60, 66, 70, 77, 81 and 82 of Table 6). Water samples were spiked prior to analysis by adding an aliquot of a (diluted) stock solution. River water samples were filtered through 0.45-μm membrane filters (Schleicher and Schüll, Dassel, Germany).

2.2. Equipment

The total system (Fig. 1) consisted of a Prospekt (Spark Holland, Emmen, The Netherlands) equipped with a solvent delivery unit (SDU), for sample preparation, and a GC–MSD system for analysis.

2.2.1. SPE system

The Prospekt system consisted of three pneumatic

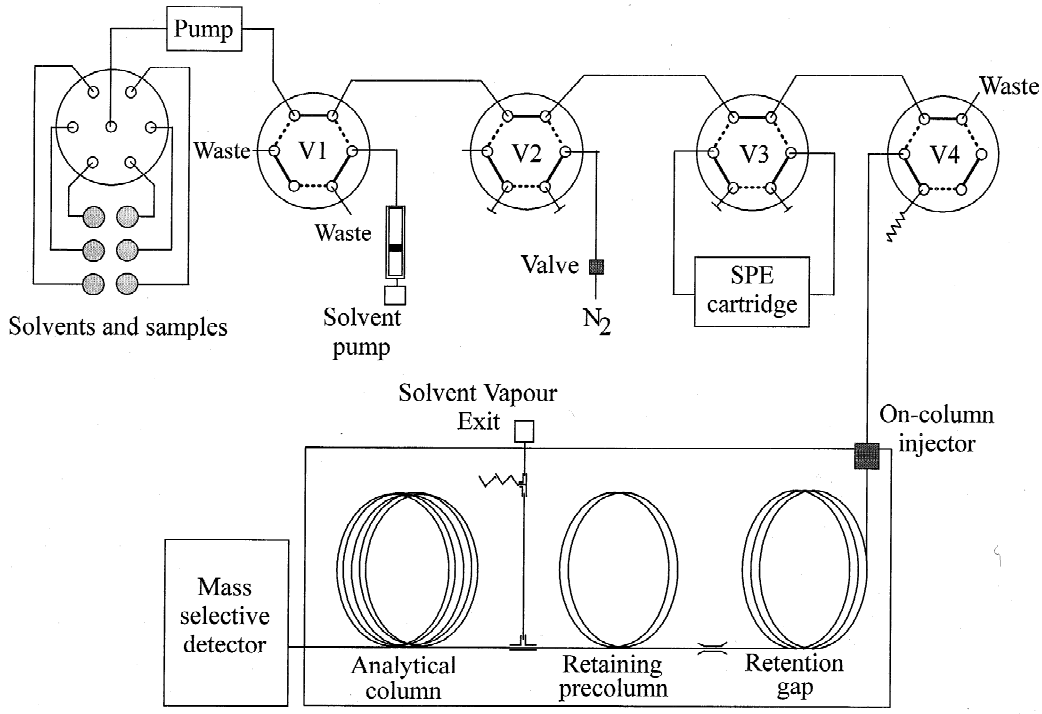

Fig. 1. Scheme of the on-line SPE–GC–MS system.

six-port valves, an automatic cartridge exchanger and an SDU equipped with a six-port solvent selection valve and a single-piston HPLC pump. All timed events were programmed via a software package (Hewlett-Packard, Waldbronn, Germany) into the Prospekt controller unit. Additional equipment was programmed via auxiliary contact closure events of the Prospekt. A Phoenix 30 syringe pump (Carlo Erba Strumentazione, Milan, Italy) used for the delivery of the organic desorption solvent was modified to switch the flow on/off by an auxiliary event. An electrically actuated Must six-port valve (Spark Holland) was used as transfer valve, and a 24 V solenoid gas valve for actuating the nitrogen flow for drying of the cartridge. The nitrogen was purified with a carbon trap (20–40 mesh Carbotrap C; Supelco, Bellefonte, PA, USA). The water samples were preconcentrated on a commercial 10 mm×2 mm I.D. cartridge packed with 20 μm, 100 Å PLRP-S styrene–divinylbenzene copolymer (Spark Holland). One cartridge could be used for at least 50 water analyses. The tubing between valves V3 and V4 had a dead volume of 6 μl, and was occasionally used as sample loop for the simulation of an SPE–GC transfer. The SPE module was interfaced to the on-column injector of the GC system via a 0.25 m×75 μm I.D. deactivated fused-silica capillary.

2.2.2. GC–MS system

A Hewlett-Packard (Palo Alto, CA, USA) Model 5890 Series II gas chromatograph equipped with a pressure-programmable on-column injector and a Model 5972 mass selective detector (MSD) was used for GC–MS. MS ionization was achieved by electron impact, and ions with m/z 47–335 were monitored at 1.5 scans/s. The electron multiplier voltage was set at 1800 V. The injector was connected to a 5 m×0.32 mm I.D. retention gap (BGB Analytik, Zürich, Switzerland) and a 1.5 m×0.32 mm I.D. retaining precolumn containing PS-264 (5% diphenyl polysiloxane and 95% dimethylsiloxane) with a film thickness of 0.25 μm. An early solvent vapour exit (SVE) was inserted between the retaining precolumn and the GC column (HP5MS, 27 m×0.25 mm I.D., 0.25 μm film) to vent most of the solvent vapour [14]. The SVE was connected to the press-fit T-

splitter (BGB Analytik) between the retaining precolumn and GC column (see Fig. 1). The laboratory-made SVE was installed on the top of the split/splitless injector and kept at 150°C to prevent solvent condensation.

One other retention gap and several other retaining precolumns were used in a brief comparative study (see Table 5 below). The OV-1701-OH coated retention gap (0.32 mm I.D.) and the retaining precolumn (0.32 mm I.D.) coated with PS-264 (5% phenyl, 95% methylsilicone) with several film thicknesses were obtained from BGB. The retaining precolumns (0.32 mm I.D.) coated with DB-1701 (0.25 μm film thickness) and DB-1 (1 μm film thickness) were from J&W (Folsom, CA, USA).

2.3. Procedures

2.3.1. SPE procedure

The final time schedule of the SPE procedure is shown in Table 1. Each run started with conditioning of the SPE cartridge with 100 μl of desorption solvent and, next, 2.5 ml of HPLC-grade water. The HPLC pump and all connecting capillaries up to valve V3 were then flushed with 10 ml of sample in order to cover active sites and, thus, reduce the loss of apolar analytes due to adsorption on capillary walls and the HPLC pump during sampling. Next, 10 ml of sample were loaded on the SPE cartridge at 2.5 ml/min. Some clean-up to remove salts and very polar compounds was effected by flushing the cartridge with 1.9 ml of HPLC-grade water. The cartridge was then dried for 30 min with 70 ml/min of nitrogen at ambient temperature. During drying, the HPLC pump was cleaned with 2.5 ml of isopropanol, which will remove all air from the pump and, thus, prevent malfunctioning. The analytes were subsequently desorbed with 50 or 100 μl of methyl or ethyl acetate and transferred via the transfer line to the GC at the optimized flow-rate (see below). The

Table 1
Time schedule of sample preparation programme of on-line SPE–GC–MS

Time (min:s)	Solvent selection valve	Flow[a] (ml/min)	Valves[b]				Auxiliary events[c]			Comment
			V1	V2	V3	V4	1	2	3	
00:00	1	2.5	1	0	1	0	Off	Off	Off	Condition cartridge with MeOAc
02:00			0							Condition cartridge with water
03:00	3	5			0					Preflush pump/tubing with sample
04:55		2.5								Decrease flow of pump
05:05					1					Preconcentrate 10 ml of sample
09:05	1	5			0					Clean pump with water
09:25		2.5								Decrease flow of pump
09:35					1					Clean-up with 1.9 ml of water
10:20		0		1				On		Start drying for 30 min
10:30	2	5	1							Clean pump with i-PrOH
11:30	1									Clean pump with water
12:30		0								Stop flow of pump
37:00							On			Start of MeOAc pump
40:20								Off		Depressurize after drying
40:50				0						Fill cartridge with MeOAc
42:37					0					Preflush tubing with MeOAc
43:18									On	Start of GC
43:30						1			Off	Transfer of 50 μl pure MeOAc as presolvent
44:22					1					Transfer of analytes with 50 μl MeOAc
45:39						0				End of transfer, cleaning of cartridge with MeOAc
47:00							Off			Stop flow of MeOAc pump
47:00										End of sample preparation

[a] Flow of SDU pump.
[b] V1–V4: position 0 refers to position in Fig. 1.
[c] 1, Syringe pump on/off; 2, nitrogen valve on/off; 3, start of GC.
Abbreviations: i-PrOH, isopropanol; MeOAc, methyl acetate.

modification of the SPE procedure required when using a presolvent, which is discussed in Section 3.2, is included in Table 1. To increase sample throughput, pretreatment of the next sample was started after the transfer and subsequent cleaning of the SPE cartridge with 200 μl of methyl or ethyl acetate. This reduced the sample throughput time from 79 to 47 min.

2.3.2. SPE–GC transfer

During the transfer of solvent into the GC under partially concurrent solvent evaporation conditions, the SVE was open. The oven temperature was 54°C or 75°C when using methyl or ethyl acetate, respectively. The SVE was closed just before the last microlitres of solvent evaporated. The head pressure of the GC was increased from 60 kPa to 130 kPa at 500 kPa/min before the transfer, and decreased at 300 kPa/min to 60 kPa after the transfer. During the temperature programme of the GC run, the head pressure was programmed to provide constant flow. After 6 min the GC oven temperature was increased from the injection temperature to 280°C at 10°C/min, and then kept at 280°C for 5 min. The same temperature and pressure programme was used for 2-μl or 5-μl on-column injections carried out for reference purposes, except for the fact that the pressure was kept constant at 60 kPa during injection. Only during the study of several retaining precolumns (see Table 5 below), the head pressure was kept constant at 80 kPa during the transfer and the whole run. When injecting ethyl acetate, the head pressure was 90 kPa and programmed to provide constant flow during the GC run, and the GC oven temperature was increased 5 min after the start of the transfer at 10°C/min as described above.

2.3.3. Optimization of introduction flow-rate

The flow-rate used to introduce the solvent, methyl or ethyl acetate, into the retention gap of the on-column injector was optimized by means of repetitive 100-μl injections of an *n*-alkane standard solution. For these (and other) 100-μl injections, a 120-μl loop was inserted between valves V3 and V4. This loop and the tubing between valves V2 and V3 was filled by means of a syringe, which was mounted on valve V2 and replaced the nitrogen line. Next, the sample was pushed into the retention gap by organic solvent from the syringe pump.

The introduction flow-rate was stepwise increased until peak distortion of the analytes was observed, which indicated flooding of the retaining precolumn with solvent [15]. The flow-rate was then set at a value 4 μl/min below that for which flooding has been observed. This procedure ensured that a solvent film was always created in the retention gap during the transfer step without undue risk of flooding of the retaining precolumn. Typical flow-rates were 40–50 μl/min.

3. Results and discussion

In the present paper, we first studied the loss of volatile analytes occurring with a conventional SPE–GC set-up. Next, the procedure was improved by including the addition of a presolvent and examining various related aspects. Finally, the optimized method was put to the test by analysing spiked surface water.

3.1. Loss of volatile analytes with conventional on-line SPE–GC

3.1.1. On-line SPE–GC: critical parameters

To investigate the potential of conventional on-line SPE–GC for the determination of volatile analytes, a 2-μl on-column injection of a standard solution of a test mixture (Fig. 2C) was used for comparison. Next, 10 ml of HPLC-grade water spiked with the same test mixture at the 0.2 μg/l level were analysed (Fig. 2A). (To ensure that the SVE would not be closed too late, i.e., that some solvent would still be left in the retention gap at the moment of closure, the time difference between the end of the solvent peak, monitored by the pressure gauge of the MSD, and the moment of closure of the SVE, was made 0.5–1 min longer than the dead time of the analytical column.) Comparison of the chromatograms shows that the more volatile analytes (compounds Nos. 1–21 in Fig. 2) did not show up in the on-line SPE–GC–MS chromatogram at all, and that most of the semi-volatiles (Nos. 22–44) were only partly recovered. From quinonine (No. 45) on, most analytes were recovered quantitatively. For practical reasons, the chromatogram is shown up to 3-nitroaniline (No. 60).

The observed loss of volatile analytes can occur

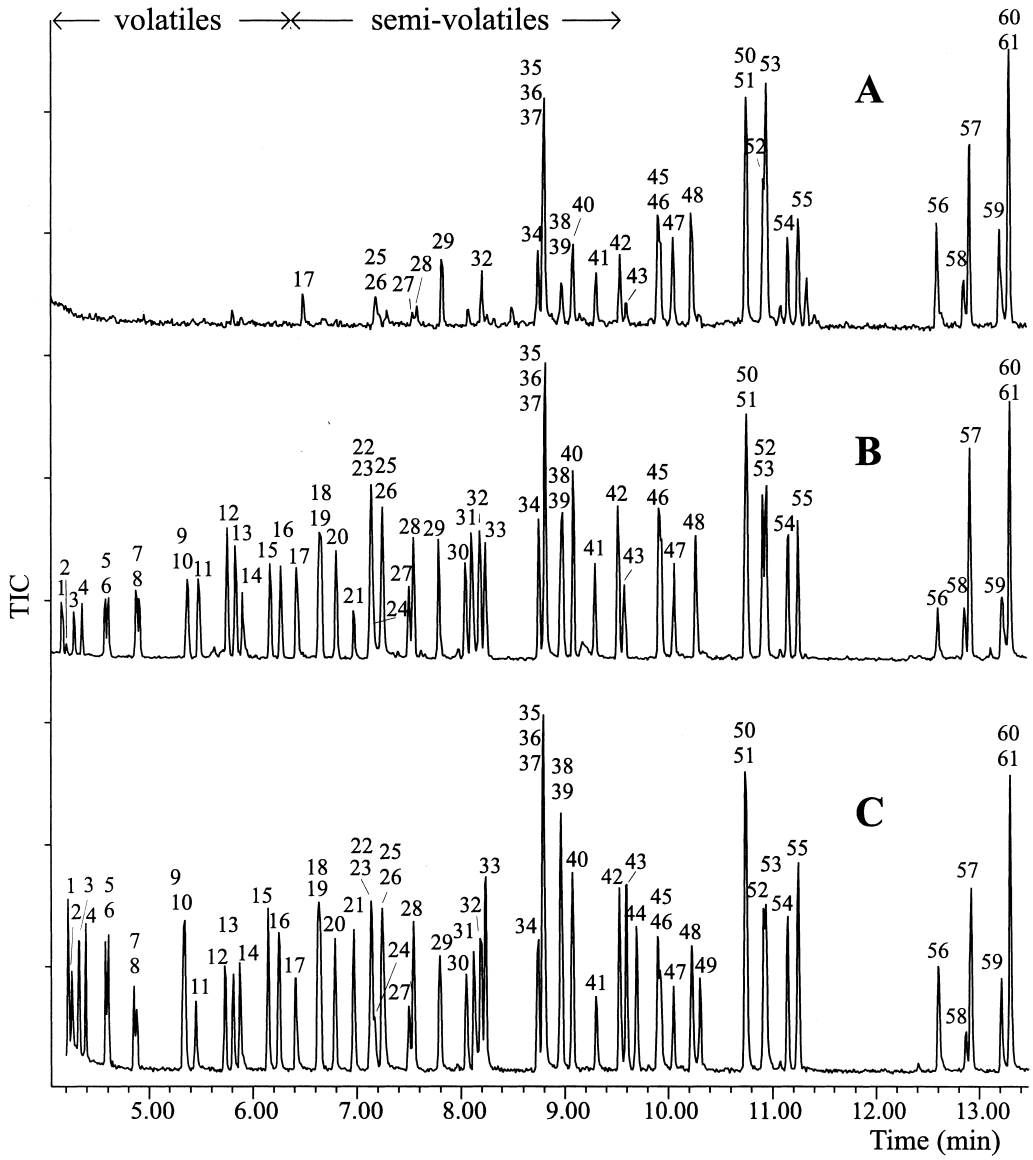

Fig. 2. On-line SPE–GC–MS of 10 ml HPLC-grade water spiked at the 0.2 μg/l level (A) and off-line SPE and GC–MS of 10 ml HPLC-grade water spiked at the 1 μg/l level (B). In the latter case, 100 μl out of the 250-μl extract were injected. For comparison, a 2-μl on-column standard injection of the test mixture is shown (C). In all cases, the total ion current (TIC) GC–MS chromatograms are shown. For peak assignment, see Table 6.

during several stages of the total SPE–GC procedure. One possibility is early breakthrough during sample loading on the SPE cartridge [16]. Another possibility, strong adsorption to the walls of the tubing [5,17] is much less likely with the present set of compounds. Self-evidently, losses may also be due to the drying with nitrogen [16,18] or to incomplete desorption of the SPE cartridge. Finally, losses of volatile analytes can occur during their transfer to the GC. The transfer temperature and the open time of SVE time are critical parameters in this respect.

As regards the role of the SPE procedure, the trace enrichment of a 10-ml HPLC-grade water sample was repeated at the spiking level of 1 μg/l. In this instance, desorption of the analytes was carried out with 260 μl of ethyl acetate into an autosampler vial and a 100-μl aliquot of the extract was injected into the GC. Fig. 2B shows that the volatile analytes now all show up in the full-scan GC–MS chromatogram. Actually, all analytes that were eluted later than trimethyl thiophosphate (No. 12) were quantitatively recovered. This result indicates that the losses of volatile analytes observed in the SPE–GC procedure occurs during the transfer into the GC. However, the losses cannot be attributed to the transfer temperature or the SVE open time, because they were the same as in the earlier experiment. Obviously, the essential remaining difference between the off-line large-volume injection and the on-line transfer is the distribution of the (volatile) analytes over the length of the solvent film which is uniform in the former case, but probably not in the latter.

Since the loss of volatiles obviously is a critical aspect, methyl acetate was used as desorption solvent in the rest of this study. With this solvent, the polar and apolar analytes were desorbed from the SPE cartridge with a efficiency similar to that of ethyl acetate (see Table 2 below). However, because the boiling point of methyl acetate is 20°C [19] below that of ethyl acetate, the more volatile analytes will be recovered more efficiently [20].

3.1.2. Desorption and transfer profiles

The elution profile of a selected series of analytes from the SPE cartridge was determined by a number of on-line SPE–GC analyses of a spiked HPLC-grade water sample. The procedure was as follows. After drying of the SPE cartridge, a predetermined volume of desorption solvent (methyl acetate; 100, 50, 30, 20, 10 or 0 μl) was flushed to waste before a 100-μl fraction was transferred to the GC system. The amount of each analyte in the 0–10 μl, 10–20 μl, etc., fractions was calculated by subtraction (Table 2). No more analytes were found in desorption solvent collected after over 50 μl had been led to waste; no data for the 50–150 μl fraction are therefore given in Table 2. Actually, most of each analyte was desorbed in the 0–10 μl fraction and desorption generally was complete within 30 μl.

Table 2
Elution profile of several analytes in on-line SPE–GC[a]

Compound	Recovery (%) in fraction (in μl)				
	0–10	10–20	20–30	30–50	Σ 0–50
N,N-Dimethylphenol	78	10	4	0	92
Isoforon	79	9	7	0	95
Triethyl phosphate	95	0	0	0	95
1,2,4-Trichlorobenzene	83	2	0	0	85
Naphthalene	91	6	2	0	98
m-Nitrotoluene	90	7	0	0	97
Hexachlorobutadiene	64	9	0	0	73
1-Chloro-2-nitrobenzene	87	12	0	0	99
1,4-Diethoxybenzene	86	9	0	0	95
2-Methylisoquinoline	90	1	0	0	91
Ferrocene	86	6	4	1	97
1-Nitronaphthalene	99	6	0	0	105
Tributyl phosphate	90	10	5	2	107
Trifluralin	45	2	2	2	51
Hexachlorobenzene	40	5	1	0	46
Dimethoate	121	0	0	0	121
Atrazine	87	16	0	0	103
Phenanthrene	76	6	3	0	85
Diazinon	84	11	4	3	102

[a] After drying of the PLRP-S cartridge, a predetermined volume of desorption solvent (50, 30, 20, 10 or 0 μl) was flushed to waste before a 100-μl fraction was transferred to the GC; methyl acetate was used as desorption solvent.

However, to prevent carry-over due to memory effects in the transfer line, a desorption volume of 50 μl was chosen for the SPE–GC procedure used in further experiments.

Next, in order to further study the distribution of analytes in the solvent film in the retention gap during an on-line SPE–GC transfer, we deliberately transferred a series of *n*-alkanes (C_6–C_{20}) in the first or last microlitres (cf. below) of a 100-μl injection, and investigated whether they were deposited at the front end, or in any other part, of the solvent film. The presence of the alkanes at the front end will be indicated by peak distortion if conditions are selected which cause flooding of the retaining precolumn. In a first experiment, the analytes were 'located' in the first 6 μl of a 100-μl injection. By first transferring the content of the 6-μl loop between valves V3 and V4 (cf. Fig. 1) and, subsequently, 94 μl of pure solvent into the retention gap. As peak distortion was observed at a flow-rate at which flooding for a standard 100-μl injection just occurred (38 μl/min; cf. Section 2.3), it was evident that a considerable part of the alkanes was deposited in the front part of the solvent film. When, on the other hand, the analytes were transferred in the final 6 μl of a 100-μl injection, i.e. after the introduction of 94 μl of pure solvent, no peak distortion was observed even at a flow-rate of 80 μl/min, i.e. when about 60 μl of solvent flooded the retaining precolumn.

In conclusion, during an on-line SPE–GC transfer, the major part of all analytes tested will be situated in the front part of the solvent film in the retention gap, because they are desorbed and transferred with the first 10–20 μl of the desorption solvent (cf. Table 2).

3.1.3. Influence of the desorption volume

We next studied whether the amount of desorption solvent had an important influence on the loss of volatiles. When using 100 μl rather than 50 μl of methyl acetate for the on-line desorption step, and using the same injection temperature, pressure and injection rate, the loss of volatiles was higher. This was demonstrated for on-line SPE–GC of a 10-ml HPLC-water sample spiked at the 0.5 μg/l level. To quote two examples, the recoveries of *o*-chlorotoluene and indene decreased from 42 to 11% and 78 to 29%, respectively, when increasing the desorption volume from 50 μl to 100 μl. However, even with 50 μl, the losses were still significant for all analytes with an elution temperature of ca. 100°C or below (Table 3). The results of the on-line SPE–GC transfer were essentially the same as those obtained by means of a large-volume injection used to simu-

Table 3
Recoveries of 14 test compounds using on-line SPE–GC of 10 ml water or a transfer simulated by a large-volume injection (LVI)[a]

No.	Compound	Elution temperature (°C)	Recoveries (%) for desorption volume (μl) of			
			50 μl		100 μl	
			LVI transfer	10 ml water	LVI transfer	10 ml water
1	Chlorobenzene	54	8	8	0	1
4	*p*/*m*-Xylene	54	8	11	0	1
5	Styrene	57	23	27	0	4
6	*o*-Xylene	64	14	16	0	1
7	Methoxybenzene	72	45	47	7	17
9	*o*-Chlorotoluene	80	37	42	3	11
11	Benzaldehyde	84	74	73	42	51
18	1,2-Dichlorobenzene	99	70	74	31	50
20	Indene	101	71	78	32	29
27	Nitrobenzene	112	91	99	84	90
40	Naphthalene	127	92	94	79	87
51	Methylnaphthalene	144	97	99	91	95
60	Acenaphthene	170	99	98	98	98
81	Metolachlor	225	100	102	102	102

[a] In LVI, the first 5 μl of desorption solvent contained all analytes. For further details on desorption with 50 μl or 100 μl of methyl acetate, see text. All experiments were carried out in duplicate.

late an on-line SPE–GC transfer; here, the analytes were transferred in a plug of 6 μl, followed by 44 or 94 μl of pure solvent. This result further supports the hypothesis that the desorption-cum-transfer profile is the main cause of the loss of volatile compounds, and suggests that one should use only 50 μl of desorption solvent, as was found to be necessary above.

3.1.4. Summary

The combined results of the present section allow us to improve our earlier (cf. Section 3.1) classification of the analytes in three groups, i.e. volatile (compounds Nos. 1–10), semi-volatile (compounds Nos. 11 to 49) and high-boiling (compounds Nos. 50 to 81) analytes.

The volatile analytes are lost more or less completely (recovery below 20%) when using 100 μl of desorption solvent. With 50 μl, recoveries are still below 50%. Because they have an elution temperature 0–26°C above the injection temperature, these analytes are only partly trapped by the solvent film [21].

The semi-volatile analytes (elution temperatures 30–85°C above the injection temperature) showed recoveries between 29 and 99% depending on the analyte and the amount of desorption solvent. To quote examples, from analytes such as nitrobenzene, recoveries were above 90% for desorption with 50 μl, and above 75% for desorption with 100 μl of methyl acetate, while for analytes such as 1,2-dichlorobenzene the corresponding recoveries were ~70% and ~40%, respectively. In nearly all cases, peak deformation could be observed in the mass chromatogram; some fronting, taking the shape of a very low seat, was observed in front of the actual peak. These analytes are partially up to nearly fully trapped by the solvent film [21]. If no solvent film is present, as will occur when the SVE is closed only after all solvent has evaporated, these analytes are easily lost. It should be added that the analytes cover a wide polarity range with many of them having a polarity considerably different from that of the solvent. This obviously somewhat hampered solvent trapping.

The high-boiling analytes (elution temperature 90–171°C above the injection temperature) invariably showed recoveries of, at least, 91%. They were not lost if the SVE was closed too late, i.e., after evaporation of the last drops of solvent, and, no prepeaks were observed. These analytes are fully reconcentrated by the retention gap effect, i.e. during their transfer from the retention gap to the retaining precolumn which displays much higher retention ([22], p. 184), and do not require any solvent trapping. This is in agreement with data reported by Grob: analytes move through the retention gap at temperatures 100–140°C below their elution temperature and the reconcentration of analytes by internal cold-trapping on the analytical column requires a temperature difference of about 90°C between the injection and elution temperature ([22], p. 215).

Obviously, analytes showing low recoveries due to the SPE procedure itself have not been considered in the above discussion.

3.2. Use of a presolvent

Two aspects may be considered to be the cause of the (partial) loss of the volatile and semi-volatile analytes: (i) a delay in the formation of the solvent film at the start of the injection and (ii) an early escape of non-fully-trapped analytes deposited at the front end of the solvent film. Grob has reported that some of the solvent introduced into the retention gap will evaporate concurrently, because eluent evaporation starts immediately upon starting the transfer to the GC. However, Grob also found that this concurrent evaporation is a rather minor effect ([22], p. 246). Actually, the experiments of Table 3 on the much larger losses found with 100 μl rather than 50 μl of desorption solvent suggest that the amount of solvent introduced after the analytes themselves have been transferred is also important. During the transfer, a solvent film of about 3 m length (see footnote c of Table 5) containing about 20 μl of solvent was deposited in the retention gap (assuming a flooded zone of about 10 μl/min [23]). Although there was a strong pressure drop along this solvent film due to the presence of the SVE, there was no risk that the eluent reached a zone in which the boiling point equalled the column temperature ([22], p. 218), as the injection temperature of 54°C was below the boiling point of methyl acetate at atmospheric pressure, 57°C [19]. Therefore, a delay in the formation

of the solvent film at the start of the injection or concurrent evaporation of the solvent film further in the retention gap cannot fully explain our observations. The increase of the pressure during the transfer had no great influence, as transfers at a constant head pressure of 80 kPa resulted in a similar loss of the volatile and semi-volatile analytes (see Table 5, 0-μl presolvent data).

If an analyte is not fully trapped by the solvent film in the retention gap, i.e., if it is also present in the gaseous phase, it will move through the retention gap with a higher velocity than the front end of the solvent film. If such a compound catches up with this front, it will not be further retarded and will be lost through the SVE. This is schematically shown in Fig. 3A and B which depict this situation for a volatile compound which is deposited at the front end of the solvent film. During injection, that amount of the analyte already injected moves towards the front end of the film and then is lost through the SVE (Fig. 3A). At the end of the solvent evaporation process, the analyte has been lost completely (Fig. 3B). It should be kept in mind here that the loss of non-fully-trapped volatiles is more critical in on-line SPE–GC than with conventional large-volume injections because of the nonuniform distribution of the analytes in the solvent film, i.e. because the major part of the analytes is deposited in the front part of the solvent film.

The creation of a solvent barrier in front of the sample plug by introducing a small amount of organic solvent, so-called presolvent, to ensure that a solvent film is already present in the retention gap when the introduction of the analyte-containing desorption solvent starts (Fig. 3C), should prevent the loss of volatiles in on-line SPE–GC. To our best knowledge, the concept of a solvent barrier in front of the sample plug (although suggested by Deans for 40-μl injections in packed-column GC [8]) has not been applied to large-volume on-column injections yet. For the loop-type interface, injection of a co-solvent has been reported [24]. However, this approach was not studied by us, because the solvent peak of the additional higher boiling solvent may well obscure the early eluting compounds.

If the velocity of the analyte through the retention gap is lower than the movement of the rear end of the solvent film due to evaporation after the injection

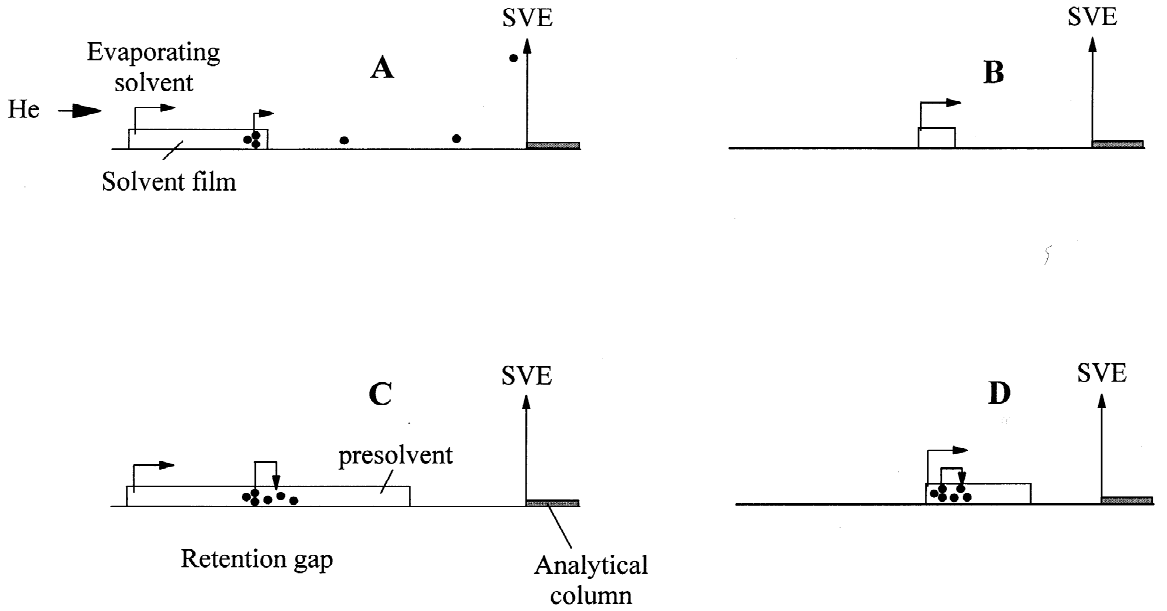

Fig. 3. Scenario for analytes (indicated by ·) which are not fully trapped by the solvent film during an on-line SPE–GC transfer. During injection these analytes are deposited (A) at the front of the solvent film if there is no presolvent, or (C) behind a solvent barrier if a presolvent is used. At the end of solvent evaporation, analytes (B) have been lost without presolvent, but (D) are recovered with presolvent.

has been completed, and enough solvent is present in front of the analyte, the analyte will be enriched in the rear part of the solvent film (Fig. 3D). It will only start to move through the retention gap towards the retaining precolumn after the last drop of solvent has evaporated. Analyte loss due to a delayed formation of the solvent film will also be prevented by the introduction of the presolvent prior to the desorption.

3.2.1. Amount of presolvent

The potential of using a presolvent for SPE–GC of volatile analytes was studied by simulating the analyte desorption by large-volume injections, i.e. a 6-μl sample plug containing the analytes and, next, 44 μl of pure methyl acetate were introduced into the GC (see above). Unlike earlier experiments, volumes of 10 to 50 μl of pure methyl acetate, the so-called presolvent, were introduced into the retention gap prior to the analyte transfer. The SVE was switched to the 'open' position prior to the introduction of the presolvent and closed before the last drop of solvent had evaporated. A 5 m×0.32 mm I.D. DPTMDS-deactivated retention gap and a 1.5 m×0.32 retaining precolumn (PS-264, 0.25 μm film thickness) were used. The test mixture contained 20 compounds.

As the data of Table 4 show, in the absence of presolvent, only methylnaphthalene, acenaphthene and metolachlor were recovered quantitatively. Even if only 10 μl of presolvent were used, the situation changed considerably. Now benzaldehyde, indene and all later eluted analytes were recovered quantitatively. With 20 μl of presolvent, the recoveries of the volatile compounds (Nos. 1 to 10) improved markedly, and with 30 μl all analytes were recovered quantitatively. A further increase to 50 μl of presolvent did not have any further beneficial influence. Chromatograms which vividly illustrate the marked effect of the presolvent are given in Fig. 4.

The above results indicate that mixing of the sample plug and the presolvent which may occur to some extent [10], does not ruin the effect of the introduction of the presolvent. Obviously, in the on-line SPE–GC–MS procedure, the SPE cartridge has to be filled nearly completely with desorption solvent prior to the transfer of presolvent and desorption of the analytes (cf. Table 1).

3.2.2. Influence of retention gap and retaining precolumn

Next, the influence of the retention gap and the type of coating and film thickness of the retaining precolumn (for details, see Table 5) were studied by varying the amount of presolvent used. In this case, a total volume of 100 μl of methyl acetate, i.e. of

Table 4
Dependence of analyte recoveries of a large-volume injection simulating an on-line SPE–GC transfer on amount of methyl acetate introduced as presolvent into the GC prior to desorption with 50 μl methyl acetate[a]

No.	Compound	Recoveries (%) for a presolvent volume of			
		0 μl	10 μl	20 μl	30 μl
1	Chlorobenzene	5	7	70	97
4	*p*/*m*-Xylene	7	8	72	95
5	Styrene	22	34	86	100
6	*o*-Xylene	9	14	85	99
7	Methoxybenzene	40	66	95	100
9	*o*-Chlorotoluene	33	54	94	96
11	Benzaldehyde	70	102	100	103
18	1,2-Dichlorobenzene	62	89	95	97
20	Indene	64	94	96	101
27	Nitrobenzene	88	100	95	100
40	Naphthalene	89	96	95	99
51	Methylnaphthalene	95	94	95	96
60	Acenaphthene	99	100	99	101
81	Metolachlor	99	100	102	99

[a] For the sake of convenience, not all analytes present in the test mixture are given in this table, for more details, see text.

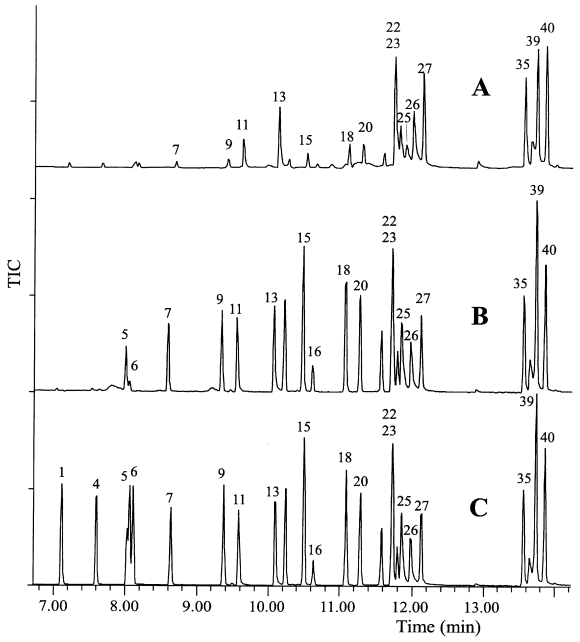

Fig. 4. TIC trace of a simulated on-line SPE–GC–MS transfer using (A) no, (B) 20 μl and (C) 50 μl of presolvent prior to desorption with 50 μl of methyl acetate. For further details, see text. For peak assignment, see Table 6.

presolvent plus desorption solvent, was always injected, because the same amount of solvent would then be left in the GC provided the SVE was closed at the same time.

When no presolvent was introduced before the 6-μl sample plug, most of the volatile and semi-volatile analytes were at least partly lost in all set-ups and essentially quantitative recovery started with methylnaphthalene (No. 51). As Table 5 shows, the type of retaining precolumn used was not particularly important. Even without a retaining precolumn, methylnaphthalene and later eluted analytes were quantitatively recovered, either with or without using a presolvent. The mutual differences found if no presolvent was used (No. 27 vs. No. 51), may well be caused by different delays in the formation of the solvent film at the start of the injection.

When 20 μl of presolvent were introduced, methoxybenzene (No. 7) was the first quantitatively recovered analyte in nearly all cases. With 50 μl of presolvent, all volatile analytes were quantitatively recovered irrespective of the set-up selected.

In conclusion, the introduction of presolvent prior to the transfer of the analytes is much more efficient in the trapping of volatile analytes than the use of a retaining precolumn. The increased recoveries in the presence of a presolvent are due to increased trapping by the solvent film in front of the analytes and not to increased phase soaking of the retaining precolumn, because similar results were obtained without a retaining precolumn. Here, it should be kept in mind that we used a rather polar solvent, because the desorption of polar as well as apolar analytes was our goal. With a different type of solvent, phase soaking may well have a larger

Table 5
Dependence of loss of volatile analytes for several set-ups using various amounts of presolvent

Retention gap[a]	Retaining precolumn		First recovered compound[b]		
	Type	Film (μm)	using presolvent volume of: 0 μl	20 μl	50 μl
DPTMDS[c]	No	No	51	7	1
DPTMDS[c]	HP-5-MS	0.25	27	7	1
DPTMDS	PS-264	0.25	51	7	1
DPTMDS	PS-264	0.5	51	7	1
DPTMDS	PS-264	1.0	27	7	1
DPTMDS	DB-1701	0.25	51	7	1
OV-1701	DB-1	1.0	51	11	1

[a] DPTMDS, diphenyltetramethyldisilazane-deactivated; OV-1701, coated with OV-1701-OH.
[b] First test compound of Table 4 with at least 90% recovery compared with 5-μl on-column injection; for compound number, see Table 4. On-line SPE–GC transfer simulated with LVI; in total 100 μl of methyl acetate were injected in all experiments.
[c] If no retaining precolumn was used, a laboratory-made 'flooding' detector was used for optimization and control of the injection [30]. The injection rate was chosen so that the flooded zone, which is further pushed into the GC after the end of the injection, reached the point where the 'flooding' detector was installed, i.e. after 3 m of retention gap, shortly after the end of the injection. To verify correct functioning, the 'flooding' detector was also used for one configuration containing a retaining precolumn.

influence on the trapping of the more volatile analytes.

3.2.3. Methyl acetate vs. ethyl acetate

When ethyl rather than methyl acetate was used for the (simulated) on-line SPE–GC analysis of volatiles (50 μl of presolvent prior to desorption with 50 μl of solvent; no retaining precolumn), the first compound that was quantitatively recovered was *o*-chlorotoluene. The recoveries of monochlorobenzene and *p*/*m*-xylene were a mere 45% and 34%, respectively, rather than the 95–97% obtained with methyl acetate (experiments of Table 5). Therefore, methyl acetate was preferred as desorption solvent.

3.3. On-line SPE–GC–MS analysis using a presolvent

3.3.1. Analysis of river water

The optimized on-line SPE–GC–MS procedure was applied to the analysis of 10 ml of river Rhine water samples (sampled at Lobith, The Netherlands; 26 April 1995) spiked at the 0.5 μg/l level (Fig. 5A), with Fig. 5B showing the trace of the nonspiked sample. After drying of the SPE cartridge, the cartridge was nearly completely filled with methyl acetate, 50 μl of presolvent were injected into the GC and, then, the analytes were desorbed with 50 μl of methyl acetate (for details, see Table 1). According to our expectations, all analytes showed up in the chromatogram due to the use of 50 μl of presolvent.

For most analytes, recoveries were satisfactory (70–115%; 76 out of the 86 test compounds) or even very good (90–105%; 48 out of 86 test analytes) (Table 6). Lower recoveries can generally be attributed to adsorption to capillary walls and/or valves during sampling (compound Nos. 49, 63, 69 to 72 and 85) [17], early breakthrough during trace enrichment (No. 79) [25] or inefficient trapping by the solvent film (No. 3) [26]. The recoveries of the analytes which were partly lost due to adsorption could be increased by adding 30% of methanol to the

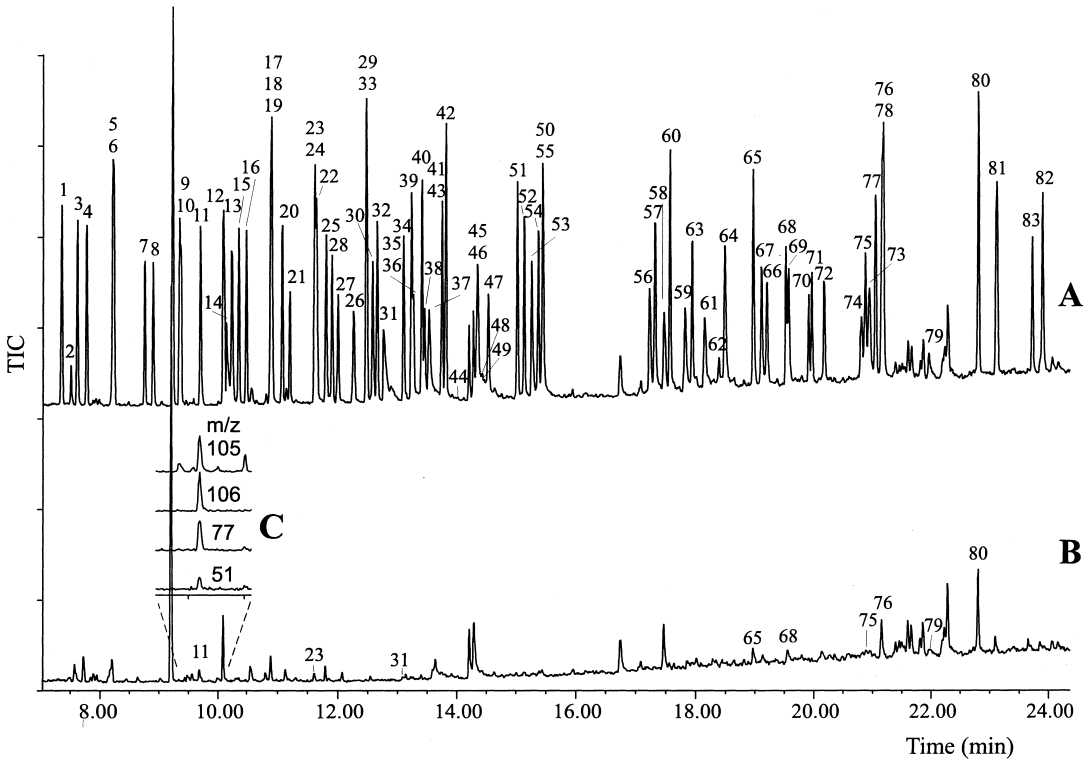

Fig. 5. TIC chromatogram for SPE–GC–MS of 10 ml of river Rhine water (B) nonspiked and (A) spiked at the 0.5 μg/l level with 86 microcontaminants. A 50-μl volume of methyl acetate was used as presolvent. For peak assignment, see Table 6; all peaks up to No. 83 are shown. The insert (C) shows the mass chromatograms of four characteristic masses of benzaldehyde (*m*/*z* 51, 77, 105 and 106). The time scale for the mass chromatogram is twice as large as for the TIC chromatogram.

Table 6
Analyte recoveries and R.S.D. data for on-line SPE–GC–MS of 10 ml of river Rhine samples spiked at the 0.5 μg/l level

No.	Compound	Recovery	(R.S.D.)[a]	No.	Compound	Recovery	(R.S.D.)[a]
		%	(%)			%	(%)
1	Monochlorobenzene	100	(4)	45	Quinoline	100	(14)
2	Chlorohexane	80	(4)	46	1-Chloro-4-nitrobenzene	107	(4)
3	Ethylbenzene	62	(8)	47	1-Chloro-2-nitrobenzene	103	(8)
4	*p*/*m*-Xylene	102	(7)	48	Isoquinoline	90	(16)
5	Styrene	103	(1)	49	Chlorodecane	25	(25)
6	*o*-Xylene	100	(2)	50	1H-Indole	101	(3)
7	Methoxybenzene	99	(9)	51	Methylnaphthalene	94	(2)
8	1,2,3-Trichloropropane	98	(2)	52	1,4-Diethoxybenzene	98	(2)
9	*o*-Chlorotoluene	94	(2)	53	2-Methylisoquinoline	93	(19)
10	Propylbenzene	97	(8)	54	Ferrocene	96	(14)
11	Benzaldehyde	107	(3)	55	1,2,4,5-Tetrachlorobenzene	76	(3)
12	Trimethylthiophosphate	98	(2)	56	3,4-Dichlorobenzeneamine	87	(4)
13	Benzonitrile	100	(2)	57	Dimethyl phthalate	101	(3)
14	2,4,6-Trimethylpyridine	90	(7)	58	1,3-Dinitrobenzene	110	(4)
15	1,3-Dichlorobenzene	94	(2)	59	4-Butoxyphenol	104	(1)
16	1,4-Dichlorobenzene	94	(1)	60	Acenaphthene	98	(1)
17	5-Ethyl-2-methylpyridine	110	(8)	61	3-Nitroaniline	83	(5)
18	1,2-Dichlorobenzene	97	(1)	62	1-Naphthalenol	99	(4)
19	Indane	97	(1)	63	Pentachlorobenzene	65	(1)
20	Indene	99	(1)	64	2,5-Diethoxyaniline	77	(2)
21	Butylbenzene	79	(3)	65	Diethyl phthalate	106	(1)
22	N-Methylaniline	95	(1)	66	1-Nitronaphthalene	108	(1)
23	Acetophenone	105	(2)	67	Sorbofuranose derivative[b]	102	(2)
24	1-Octanol	92	(12)	68	Tributyl phosphate	105	(1)
25	2-Methylbenzeneamine	83	(9)	69	1-Chlorotetradecane	61	(6)
26	*m*/*p*-Methylphenol	82	(15)	70	Trifluralin	57	(4)
27	Nitrobenzene	101	(3)	71	1,4-Dibutoxybenzene	57	(2)
28	N,N-Dimethylaniline	98	(2)	72	Hexachlorobenzene	51	(1)
29	N,N-Dimethylphenol	95	(5)	73	Dimethoate	108	(8)
30	Isoforon	98	(13)	74	Simazine	109	(8)
31	Triethyl phosphate	97	(19)	75	Atrazine	108	(2)
32	N-Ethylaniline	95	(2)	76	Tris(2-chloroethyl) phosphate	112	(3)
33	1,3,5-Trichlorobenzene	86	(3)	77	Phenanthrene	88	(1)
34	1,4-Dimethoxybenzene	99	(3)	78	Diazinon	103	(1)
35/36	2,4+2,6-Dimethylaniline	82	(13)	79	Caffeine	29	(8)
37	2,4-Dichlorophenol	94	(12)	80	Dibutyl phthalate	102	(1)
38	Methoxyaniline	84	(10)	81	Metolachlor	100	(1)
39	1,2,4-Trichlorobenzene	88	(3)	82	Fluoranthene	73	(1)
40	Naphthalene	100	(2)	83	Chlorooctadecane	74	(6)
41	*m*-Nitrotoluene	97	(3)	84	Pyrazone	113	(8)
42	1,2,3-Trichlorobenzene	92	(4)	85	Di-2-ethylhexyl phthalate	66	(2)
43	Hexachlorobutadiene	75	(7)	86	Dioctyl phthalate	74	(5)
44	α,α,α-Trichlorotoluene	9	(40)				

[a] R.S.D.: $n=7$.
[b] 1,2:4,6-bis-O-(1-methylethylidene)-α-L-sorbofuranose.

sample prior to analysis. To quote two examples, the recovery of chlorodecane increased from 25 to 76%, and that of hexachlorobenzene from 51 to 99%. However, the recoveries of the more polar analytes such as compound Nos. 11 to 14 then, of course, decreased. Actually, if analytes spanning such a wide polarity range have to be monitored, two different SPE–GC–MS runs are the best solution to obtain

high recoveries for all, apolar and polar, analytes. As the aim of this study was to devise a method for monitoring river water in one run, no modifier was added to the sample. The low recovery for α,α,α-trichlorotoluene can be attributed to a slow reaction with water [27]. Analyte recoveries were fully comparable with those obtained using ethyl acetate as desorption solvent [28].

For the majority of all analytes (73 out of the 86 compounds) the repeatability was good with R.S.D. values of 1–9% ($n=7$). Interestingly, good repeatability was even obtained for the apolar analytes yielding low recoveries, such as trifluralin (R.S.D., 4%) and hexachlorobenzene (R.S.D., 1%). Higher R.S.D. values were observed when the recovery was below 30% (compound Nos. 44 and 49) and for some rather polar and slightly tailing compounds (Nos. 24, 26, 38, 45, 48 and 53). In the latter case integration problems were the main cause.

The linearity was determined by spiking river water in the 0.15–1 μg/l range (four data points). It was satisfactory for 76 out of the 86 compounds (regression coefficient better than 0.98), but less good for some apolar compounds (Nos. 49, 69, 80 and 83; probably due to adsorption on the capillary walls and valves), dibutyl phthalate (blank problem), caffeine (probably due to low recovery) and some volatile compounds (Nos. 2 to 4 and 10).

Data analysis was automated by means of the standard procedure of the GC–MS software package (for details, see [29]). For each compound the mass chromatograms of the target ion and three characteristic qualifier ions were reconstructed and integrated in the appropriate retention time window (expected retention time±0.5 min). When detecting a peak in the target ion trace at the expected retention time, the presence of the target compound was considered confirmed if the ratio of responses of the target ion and each of the three qualifier ions at the corresponding retention time did not deviate more than 30% from that of the target compound.

Using the automated procedure for the river water sample, nine compounds were identified at the 0.02–0.2 μg/l level (Table 7). As an example, the mass chromatograms of the target ion (m/z 105) and qualifier ions (m/z 106, 77 and 51) of benzaldehyde at the expected retention time (9.7±0.5 min) are shown in Fig. 5C. The target and qualifier ions had a retention time of 9.69 min, and the three qualifier ion ratios met the reference values. The limit of detection ($S/N=3$) for the mass chromatograms of the target and qualifier ions of benzaldehyde was 4–8 ng/l.

For the total set of analytes tested, the limits of detection were between 2 ng/l and 0.1 μg/l, the individual results being determined by the nature of the mass spectrum and the presence of interferences. In general, compounds present at the 0.02–0.05 μg/l level were detected in the target ion trace, and at 0.05–0.2 μg/l in the total ion current (TIC) trace. Above 0.1 μg/l, usually all qualifier criteria were met, as is true for tris(2-chloroethyl) phosphate and

Table 7
Result of automated data analysis of 86 micropollutants in 10-ml river water sample

No.	Compound	Identification		Concentration (μg/l)
		Correct qualifier ion ratios[a]	Qualifier value[b]	
11	Benzaldehyde	3	94	0.04
23	Acetophenone	3	81	0.02
31	Triethyl phosphate	1	41	0.02
65	Diethyl phthalate	2	81	0.04
68	Tributyl phosphate	3	89	0.03
75	Atrazine	2	74	0.05
76	Tris(2-chloroethyl) phosphate	3	96	0.10
79	Caffeine	2	70	0.11
80	Dibutyl phthalate	3	99	0.21

[a] Calculated ratio of the responses of each qualifier ion and the target ion was considered correct if it did not deviate more than 30% from that of the target compound.

[b] Qualifier value compares qualifier ion ratios with those of target compound in reference database on scale of 100 (for details, see [29]).

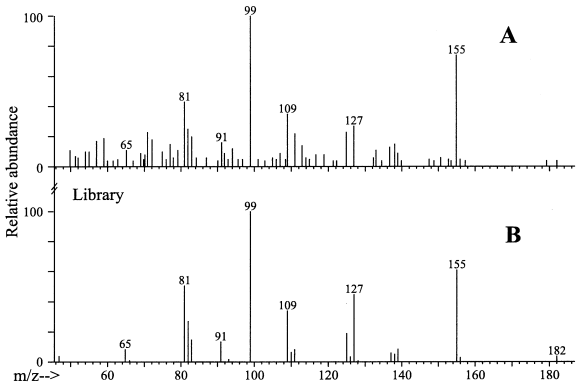

Fig. 6. (A) Mass spectrum of peak observed at 13.11 min in the SPE–GC–MS chromatogram of Fig. 5B and (B) library mass spectrum of triethyl phosphate.

dibutylphthalate in Table 7. The less good result for caffeine can be attributed to its low recovery of about 25%. At the 0.02–0.1 μg/l level, all qualifier ion ratios still gave the proper results for three out of the six compounds detected. If not all criteria are met, the qualifier value tends to become rather low (Table 7), and identification should be done by comparing the full mass spectra. Actually, the presence of all nine compounds detected in the river water was then confirmed satisfactorily. To illustrate, the mass spectrum acquired at 13.11 min for the nonspiked sample (Fig. 6A) is closely analogous to the reference spectrum of triethyl phosphate (Fig. 6B), i.e. all nine major mass peaks of the reference spectrum show up in the acquired spectrum, confirming the presence of triethyl phosphate.

The system proved to be robust and was used for the analysis of more than 200 tap and river water samples.

4. Conclusions

The application range of on-line SPE–GC–MS of aqueous samples has been extended to include volatile analytes down to monochlorobenzene. The introduction of about 30–50 μl of methyl acetate as a presolvent prior to the desorption of the analytes from the SPE cartridge with 50 μl of organic solvent is sufficient to recover the volatile analytes when using an on-column interface. Methyl acetate is superior to ethyl acetate as presolvent and desorption solvent, because more volatile analytes can be determined, while the desorption efficiency is the same. Actually, when using 50 μl of presolvent, the use of a retaining precolumn did not have any significant influence on the recovery of the volatile analytes. Over 80 microcontaminants which covered a wide range of volatility and polarity were determined in 10 ml of spiked and nonspiked surface water samples down to the 0.02–0.05 μg/l level using full-scan mass selective detection. For a large majority of the analytes studied, the recovery and repeatability data at the trace-level were highly satisfactory. Actually, with conventional off-line SPE the loss of volatiles like 1,4-xylene during sampling, drying and elution is rather critical [18], whereas with the present on-line SPE–GC system, losses do not occur because of the closed nature of the set-up.

In summary, the present system appears to be well suited for the screening of rather volatile as well as high(er)-boiling compounds, e.g., for the automated monitoring of the quality of river water.

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