ELSEVIER

Journal of Chromatography A, 725 (1996) 67–83

JOURNAL OF CHROMATOGRAPHY A

Analysis of microcontaminants in aqueous samples by fully automated on-line solid-phase extraction–gas chromatography–mass selective detection

A.J.H. Louter*, C.A. van Beekvelt, P. Cid Montanes[1], J. Slobodnik, J.J. Vreuls, U.A.Th. Brinkman

Free University, Department of Analytical Chemistry, De Boelelaan 1083, 1081 HV Amsterdam, Netherlands

Abstract

The trace-level analysis of unknown organic pollutants in water requires the use of fast and sensitive methods which also provide structural information. In the present study, an on-line technique was used which combines sample preparation by means of solid-phase extraction (SPE) on a small precolumn packed with a hydrophobic phase, and capillary gas chromatography (GC) with mass spectrometric (MS) detection. Sample preparation was carried out in a fully automated SPE module which was connected to the GC system via an on-column interface. The on-column interface was selected because of its wide application range. The mass spectrometer was preferably used in the full-scan acquisition mode because of the intended identification. The total system including the SPE module, was controlled by the MS software which allowed unattended analysis of a series of samples.

The feasibility of on-line SPE–GC–MS was demonstrated by analysing a variety of surface water samples in order to detect and identify non-target compounds. With a sample volume of only 10 ml various micropollutants could be identified, and also quantified, at levels below 0.1 μg/l. The system proved to be flexible, and the sample preparation could easily be adapted to analyse organochlorine pesticides by adding 30 vol.% of methanol to the raw sample. Samples were taken from several European (Axios, Greece; Ebro, Spain; Meuse, Netherlands; Nitra, Slovakia; Rhine, Germany; Thames, UK; Varta, Poland) and American (Sacramento, USA; Amazon, Brazil) rivers. An example of the identification of unknown microcontaminants in waste water is also presented, which is further evidence of the robustness and flexibility of the SPE–GC–MS analyzer.

Keywords: Water analysis; Automation; Environmental analysis; Solid-phase extraction; Sample preparation; Pesticides

1. Introduction

The monitoring of water samples for the presence of unknown pollutants at the trace-level requires fast, sensitive and selective methods. The determination of organic substances in water commonly involves isolation of the compounds of interest and subsequent separation by means of a chromatographic technique. On-line techniques, which combine sample preparation and separation-plus-detection in one analytical set-up, are relatively new. For such on-line systems, solid-phase extraction (SPE) is generally preferred to liquid–liquid extraction as the isolation technique, because it is less laborious, uses smaller

* Corresponding author. Tel.: +31 (20) 444 7525; Fax: +31 (20) 444 7543.

[1] Present address: University of California, Richmond, CA, USA.

0021-9673/96/$15.00
SSDI 0021-9673(95)00979-5

amounts of organic solvent, and yields better analyte enrichment [1,2].

In most instances, capillary gas chromatography (GC) should be the first choice as a separation technique because of its excellent separation efficiency, high speed of analysis and the wide range of sensitive detection devices available. For the GC analysis of unknown pollutants the best detector available is the mass spectrometer (MS) with its excellent detection and identification potential for amounts of analytes of, typically, 1 ng or less [3,4].

Analysis by means of GC has one weak point: sample introduction. The main problem is that, certainly until recently, and in many instances even today, the injection volumes often are 1–5 μl only. Since, after suitable sample treatment, the volume of a final extract typically is between 50 and 500 μl, this implies that in the last step prior to GC analysis, some 95–99% of the analytes collected is discarded. For the successful performance of (ultra-)trace analysis, i.e. to attain the required detection limits, it is advantageous to inject a much larger proportion of the sample [5]. To quote one example, in the European Union (EU) the detection limits for individual pesticides in tap water and surface water which is used for tap water production are 0.1 μg/l [6]. Since on-line SPE–GC allows the quantitative transfer of the enriched analytes to a GC–MS system, a sample volume of 10 ml will be sufficient to achieve these levels. When such a modest sample volume is enriched on a 10 mm×2–4 mm I.D. LC-type precolumn, which is packed with a polystyrene-divinylbenzene copolymer, SPE-related problems like early analyte breakthrough are unlikely to occur [7,8], except for highly polar analytes such as phenol [9]. Desorption of this type of precolumn can be carried out with 50–100 μl of ethyl acetate [10] which can be directly injected on a gas chromatograph via retention gap techniques [11] or a programmed temperature vaporizer [12]. The on-column interface, a retention gap technique using partially concurrent solvent evaporation [13] has frequently been used to interface SPE and GC, mainly because of its wide application range [14,15]. The state of the art in on-line sample preparation–GC has been reviewed recently [16,17].

The set-up, automation and operation of an SPE–GC–MS system, and its usefulness for the identification and quantification of target compounds, has been discussed in earlier papers, but the number of practical applications was rather limited [18,19]. The present paper reports two years of experience with the automated SPE–GC–MS water analyzer, and illustrates its potential for the detection and identification of unknown compounds at the (sub)-μg/l level when using sample volumes of only 10 ml. Samples were taken from many different rivers and transported to the laboratory in volumes of, in many instances, only 20–30 ml, which is a distinct advantage over the large-scale field sampling which has to be considered when off-line procedures are used. Prior to the analysis of these samples, the application range of the system, in terms of analyte volatility, was studied. Sample analysis included a study of the effect of the sample nature on system performance, and on robustness. The potential for target analysis when using time-scheduled selected-ion monitoring (SIM) or multiple-ion detection (MID) was also explored.

2. Experimental

2.1. Chemicals

Atrazine, benzothiazole, 2,5-dichloroaniline, 2,6-dimethylanaline, lindane, metolachlor, mevinphos, 2-nitroanisole, parathion-ethyl, propazine, simetryn were purchased from Riedel de Haen (Seelze, Germany) and were all of P.A. grade. Nitrobenzene, 1,1,2,2-tetrachloroethane, 1,4-dichlorobenzene, 1,2-dimethoxybenzene, *n*-propylbenzene, *n*-tributylphosphate, 1,2,4-trichlorobenzene, 1,3,5-trimethylbenzene and triphenyl-phosphine oxide were purchased from Aldrich (Milwaukee, WI, USA) and of 96–99% purity. Ethyl acetate, methanol and HPLC-grade water were from J.T. Baker (Deventer, Netherlands) and were all of P.A. grade. Ethyl acetate and methanol were glass-distilled prior to use. All river water samples were filtered through a 0.45-μm membrane filter (Schleicher and Scheull, Dassel, Germany) prior to preconcentration.

2.2. SPE system

Trace enrichment was performed on a PROgrammable Solid-Phase EKsTraktion (PROSPEKT) sample preparation system of Spark Holland (Emmen,

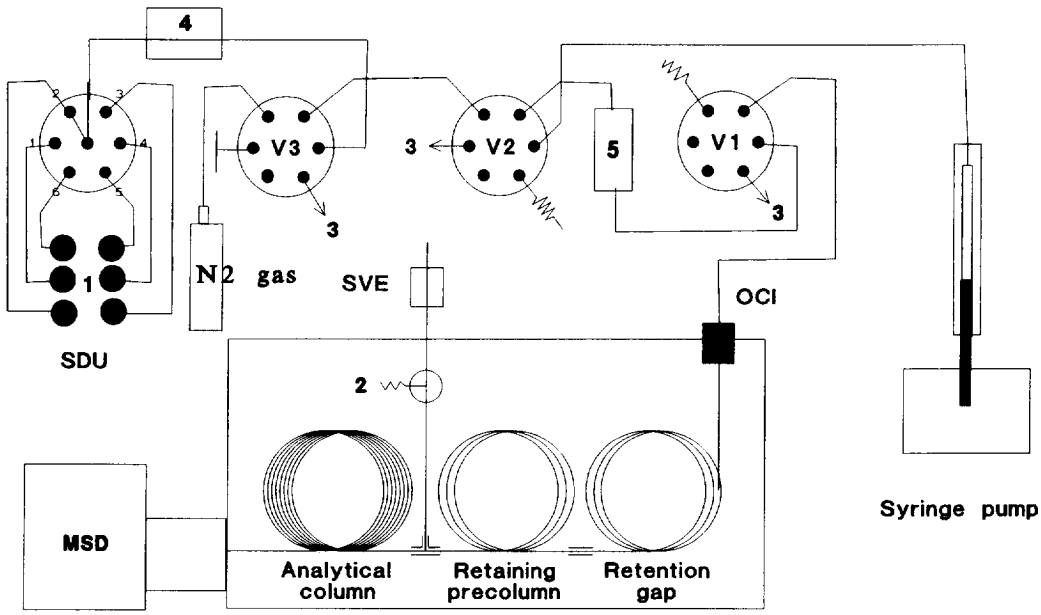

Fig. 1. Set-up of system for automated on-line SPE–GC–MS. 1, solvent channels; 2, purge leak restriction; 3, waste; 4, single-piston LC pump; 5, SPE precolumn; V1–V3, PROSPEKT valves; SDU, solvent delivery unit; SVE, solvent vapour exit; OCI, on-column injector.

Netherlands). The PROSPEKT system (see Fig. 1) consists of three pneumatic Rheodyne six-port valves, an automated cartridge exchanger and a solvent delivery unit (SDU) equipped with a six-port solvent delivery valve and a single-piston LC pump. Timed events such as valve switching, solvent selection and switching auxiliary channels on/off could be programmed on the PROSPEKT controller unit. Water samples were preconcentrated on a 10 mm×2.0 mm I.D. precolumn containing 15–25 μm PLRP-S copolymer (Spark Holland, Emmen) which was mounted between valves V1 and V2 of the PROSPEKT system.

A microMetric syringe pump from Milton Roy (Riviera Beach, FL, USA) was used to deliver the desorption solvent, ethyl acetate.

A 0.30 m×100 μm I.D. PEEK capillary coupled to a 0.15 m×110 μm I.D. stainless-steel capillary was used to interface valve V1 of the PROSPEKT module with the GC on-column injector.

2.3. GC system

A Hewlett-Packard Model 5890 Series II gas chromatograph (Palo Alto, CA, USA) equipped with a pressure-programmable on-column injector and a Model 5971A mass-selective detector was used for GC analysis. The injector was connected to a 5 m×0.32 mm I.D. retention gap, which essentially is an uncoated fused-silica capillary, deactivated with diphenyltetramethyldisilazane (DPTMDS) (BGB Analytik, Zurich, Switzerland), a 2 m×0.20 mm I.D. retaining precolumn and a 40 m×0.20 mm I.D. capillary GC column, both containing BGB-5 (5% diphenyl-polysiloxane and 95% dimethyl siloxane (BGB Analytik) with a film thickness of 0.12 μm, unless stated otherwise. Helium was the carrier gas at an inlet pressure of 200 kPa. Connections were made with conventional glass press-frits, a glass press-frit Y-piece (BGB Analytik) and a Swagelock T-piece which was connected to a solvent vapour exit (SVE).

SVE open time

The delay time for filling the cartridge and the interface capillary was 50 s. For a transfer volume of 85 μl of ethyl acetate 60 s were needed. That is, the total transfer time was 110 s. The SVE was opened after 45 s, just before introduction of the desorption solvent into the retention gap started. The SVE was

Table 1
SPE procedure

Conditioning	85 μl ethyl acetate (85 μl/min)
	2.5 ml HPLC-water (2.5 ml/min)
Sample loading	10 ml river water (1 ml/min)
Clean-up	1.0 ml HPLC-water (1 ml/min)
Drying	30 min N_2-gas at 3 bar
Desorption	85 μl ethyl acetate (85 μl/min)

closed after 159 s just before all the ethyl acetate had evaporated, thus leaving the volatile analytes in a small zone.

Procedures

The SPE procedure is outlined in Table 1 and was carried out as discussed in Ref. [18]. The SDU was used as an autosampler, that is, four of the solvent channels were used for water samples, one channel was used for HPLC-grade water and one for methanol. After each series of four samples the sample lines were flushed with 25 ml of methanol to prevent cross-contamination from previous samples.

Table 2 summarizes all relevant GC–MS parameters. The total set-up of the SPE–GC–MSD system is shown in Fig. 1.

Quantification of the detected compounds was performed by running calibration curves with the full SPE–GC–MS procedure with spiked HPLC-grade water (range, 0.1–2 μg/l; four data points in duplicate) on the same day as the sample was analysed. Quantification was performed on the basis of the peak areas of the two ions with the highest abundance above, if possible, *m/z* 100.

Table 2
Relevant GC–MSD analysis parameters

Temperature programming	
Initial temperature (°C)	85
Initial hold time (min)	7
Rate (°C/min)	10
Final temperature (°C)	280
Final hold time (min)	10
Carrier gas	He
SVE open time (min)	2.25
Column head pressure (kPa)	200
Interface temperature (°C)	290
Mass range (amu)	35–450
Scans/s	1.7
Threshold (abundance units)	500

3. Results and discussion

The present study was intended to demonstrate the potential of on-line SPE–GC–MS for the detection of non-target compounds in river water. On the basis of previous experience [14,15,18,19], it was expected that sample volumes of 5–10 ml would suffice to obtain detection limits of around 0.1 μg/l in the full-scan acquisition mode. Since loading such small samples will considerably help to enhance sample throughput, no attempt was made to use larger volumes. Firstly, the range of analytes that can be handled was investigated. Secondly, attention was devoted to the unattended analysis of samples from the rivers Amazon (Brazil), Axios (Greece), Ebro (Spain), Nitra (Slovakia), Sacramento (USA), Thames (UK) and Varta (Poland) as well as waste water from a greenhouse, a variety of surface water samples to demonstrate the practicality of the present SPE–GC–MS procedure.

3.1. Investigation of the application range

The application range of the system in terms of analyte volatility was studied by analysing a tap water sample which was spiked at a level of 1.0 μg/l with a mixture of compounds ranging from 1,4-dichlorobenzene (most volatile) to triphenylphosphine oxide (least volatile). Fig. 2 shows the SPE–GC–MS analyses of 10 ml of blank and spiked tap water. From *n*-propylbenzene (peak No. 1; b.p. 159°C) to triphenylphosphine oxide (peak No. 17) the analyte recoveries were in the range of 85–101%. The highly volatile 1,4-dichlorobenzene (b.p. 174°C) and 1,3,5-trimethylbenzene (b.p. 165°C) could still be detected in the total ion current (TIC) trace; however their recoveries were only 2–5%. Somewhat surprisingly, the later-eluting *n*-propylbenzene (peak No. 1), which has a lower boiling point than the two compounds mentioned above, showed a better recovery (but a poor MSD response). Since the most volatile compounds could be detected in off-line SPE–GC using the same sample preparation procedure, the losses obviously occurred during the SPE–GC transfer. In summary, *n*-propylbenzene is the most volatile analyte that can be handled by the present system.

With regard to analyte detectability, Fig. 2 enables

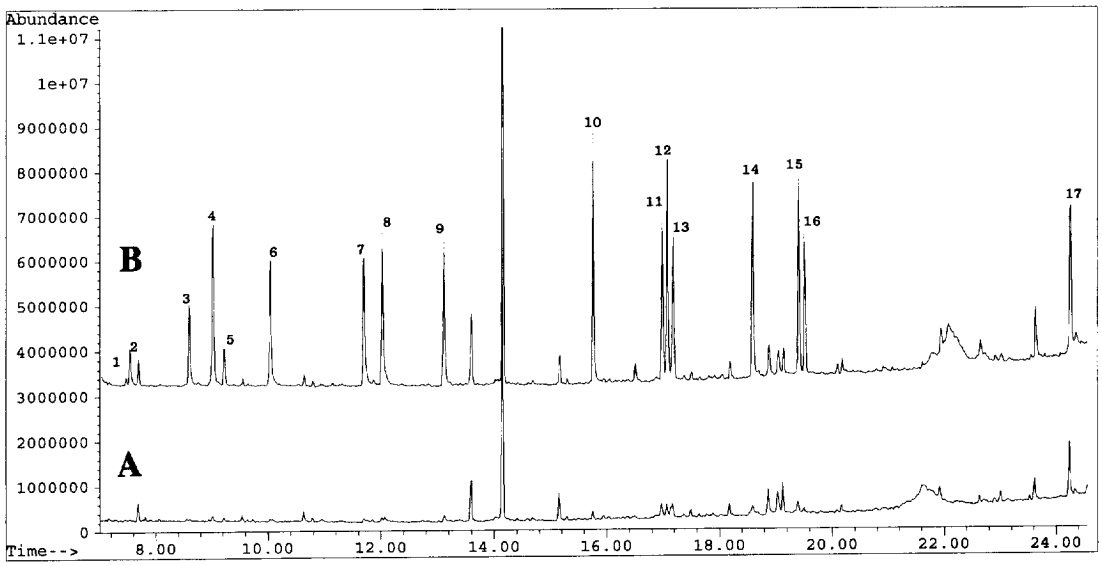

Fig. 2. SPE–GC–MS chromatograms obtained after trace enrichment of 10 ml of (A) blank and (B) spiked (1 μg/l) Amsterdam tap water. Peak assignments: 1, *n*-propylbenzene; 2, nitrobenzene; 3, 1,2-dimethoxybenzene; 4, 2,6-dimethylanaline; 5, 1,2,4- trichlorobenzene; 6, benzothiazole; 7, 2,5-dichloroaniline; 8, 2-nitroanisole; 9, mevinphos; 10, tri-*n*-butyl phosphate; 11, atrazine; 12, propazine; 13, lindane; 14, simetryn; 15, metolachlor; 16, parathion-ethyl; 17, triphenylphosphine oxide. GC analytical column 28 m×0.25 mm I.D. HP5-MS (d_f=0.25 μm), retaining precolumn, 2 m×0.25 mm I.D. HP5-MS (d_f=0.25 μm).

an estimate of the sensitivity that can typically be obtained in the full-scan mode. The detection limits of the spiked compounds in tap water are in the 0.03–0.1 μg/l range for a signal-to-noise ratio (*S/N*) of 3, except for compounds Nos. 1, 2 and 5 (0.2–0.3 μg/l). This typically meets the requirements of the EU drinking water directives for pesticides (see above). Analyte detectability and selectivity can of course be substantially improved by using, e.g. selected-ion monitoring (SIM). However, whereas such an approach should be preferred in target analysis, it is not to be recommended in the present, more complicated situation where detection and identification of unknowns are among the goals included; much valuable mass spectral information will not be recorded and will thus be lost. In Fig. 2 the TIC was recorded over the *m/z* 35–435 range. The benefit of post-run ion extraction is illustrated in Fig. 3 which shows the extracted-ion traces of *m/z* 138 and 213 which represent the main ions in the mass spectra of 1,2- dimethoxybenzene (t_{ret}, 8.54 min) and simetryn (t_{ret}, 18.66 min), respectively. In both traces the largest peaks could be assigned to the compounds of interest. The recorded mass spectra and their corresponding library matches from the NBS and HPPEST libraries are shown as inserts. The match qualities were fully satisfactory, viz. 91 and 96 for 1,2-dimethoxybenzene and simetryn, respectively, with the better result being observed for the higher *m/z* value, as is to be expected.

The system performance in terms of recovery was tested for a series of River Nitra (Chalmova, Slovakia) and Amsterdam tap water samples which were spiked with 1 μg/l of propazine. The analyte recovery was 93±6% from tap water, and 89±6% from river water samples. On two separate days six Nitra water samples which were spiked separately with 1 μg/l of propazine, were analysed. On both days the within-day response showed a relative standard deviation of 6% (n=6). The observed day-to-day difference in the mean response of the separate days was less than 1%.

3.2. Apolar pollutants: organochlorine pesticides

To study the potential of the system to analyse apolar compounds, a mixture of fourteen organochlorine pesticides ranging from α-HCH to DDT

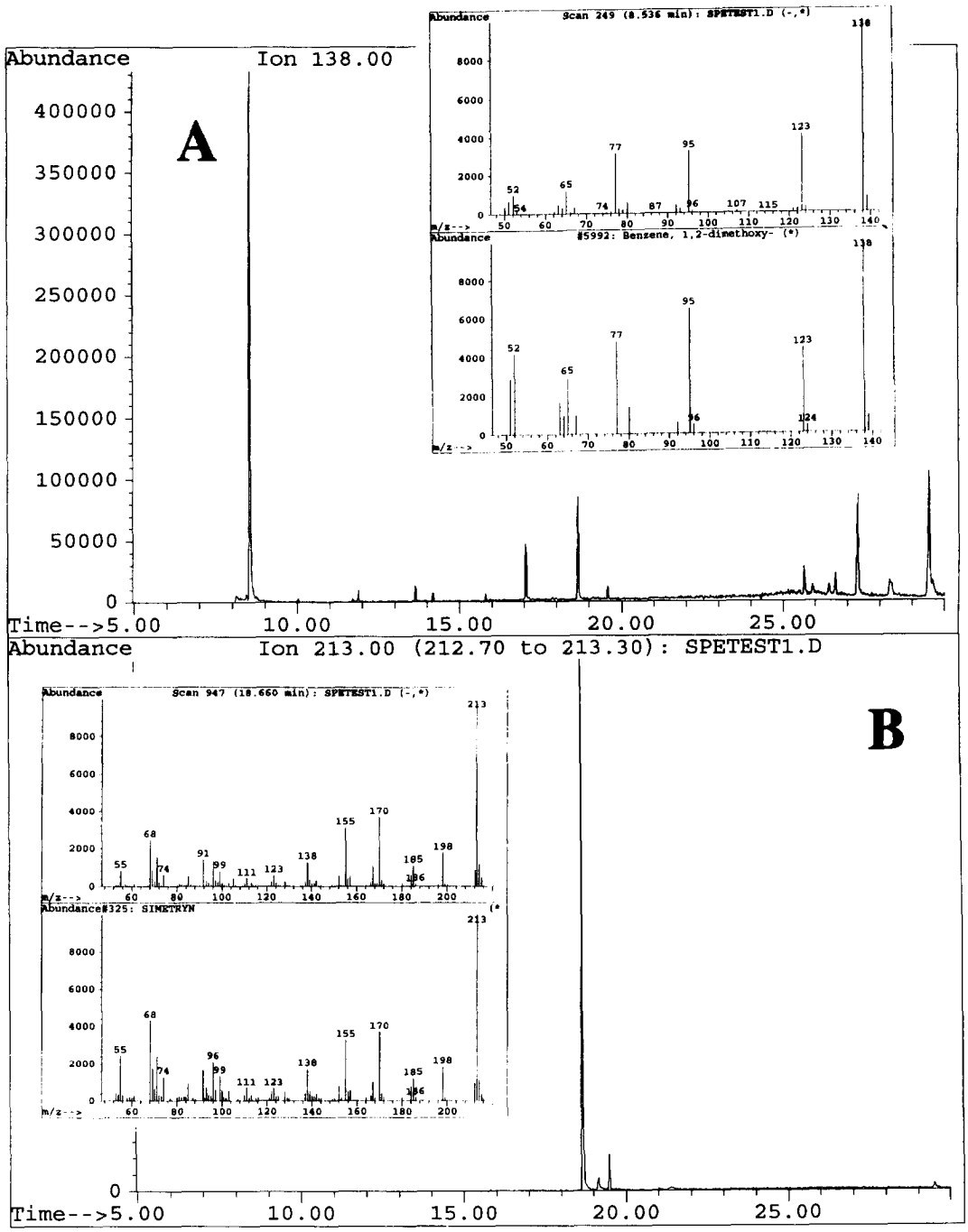

Fig. 3. Extracted-ion traces from TIC of Fig. 2: (A) m/z 138 and (B) m/z 213. Inserts: recorded mass spectra at 8.54 and 18.66 min, respectively, with corresponding NBS and HPPEST library matches.

Table 3
Analytical data on SPE–GC–MS of organochlorine pesticides

Compound	t_{ret} (min)	Recovery (%)		R^2*
		a	b	
α-HCH	20.61	94	93	0.999
γ-HCH	21.38	90	92	0.999
δ-HCH	22.03	102	99	0.999
Heptachlor	23.00	56	53	0.999
Aldrin	23.67	38	100	0.999
Heptachlorepoxide	24.73	86	90	0.998
o,p'-DDE	25.12	26	99	0.999
Endosulfan	25.37	96	95	0.998
Dieldrin	25.93	96	95	0.999
o,p'-DDD	25.93	96	97	0.999
Endrin	26.38	95	96	0.999
p,p'-DDD	26.56	95	95	0.999
o,p'-DDT	26.67	74	81	0.998
p,p'-DDT	27.40	16	80	0.998

a=10 ml of 1.0 μg/l spiked HPLC-grade water; $n=2$; b=10 ml of 1.0 μg/l spiked HPLC-grade water; $n=2$; 30% methanol added.
* Range 0.01–1 μg/l: five data points in duplicate.

was used. Relevant results are presented in Table 3. Acceptable recoveries (74–115%) were obtained for all analytes, except heptachlor (56%), aldrin (28%), *o,p'*-DDE (26%) and *o,p'*-DDT (16%). The low recoveries were probably caused by adsorption to valves and tubing, as was also observed by Noroozian et al. for an earlier SPE–GC set-up [20]. To overcome this problem, a modifier was added to the spiked samples: 30% of methanol was needed to achieve the maximum possible recovery for compounds like *p,p'*-DDT (see Table 3). The linearity of the total procedure was tested over the 0.01–1 μg/l range (five data points, $n=2$). The MS acquisition was run in a time-scheduled multiple-ion detection (MID) mode. The regression coefficients invariably were in the 0.998–0.999 range (Table 4), and were equal to those recorded for conventional on-column injections. Fig. 4 shows SPE–GC–MS (time-scheduled MID; two ions recorded per analyte) chromatograms of the analysis of 10 ml of raw (trace A) and spiked (0.1 μg/l; trace B) Amsterdam tap water (30% methanol added). All analytes were easily detected and detection limits of most of the later-eluting compounds are well below 0.01 μg/l. In the chromatogram of the raw sample two peaks were observed which showed overlap with γ-HCH (peak No. 2) and heptachlorepoxide (peak No. 6), respectively. Despite the analyte identity suggested by the MID detection mode, full-scan acquisition clearly revealed the absence of the pesticides from the sample.

Table 4
Comparison of detection limits in full-scan and MID modes

Compound	LOD[a] (pg) of on-column injections			
	Full-scan		MID	Ions extr.
	TIC[b]	Extr. TIC		/MID
α-HCH	105	20	2	181/219
γ-HCH	115	30	2	181/219
δ-HCH	165	40	3	181/219
Heptachlor	145	65	6	100/272
Aldrin	265	40	4	263/265
Heptachlorepoxide	185	150	20	183/217
o,p'-DDE	105	15	2	246/248
Endosulfan	275	300	35	195/197
Dieldrin	190	40	4	79/263
o,p'-DDD	200	15	2	235/237
Endrin	205	300	25	263/345
p,p'-DDD	185	40	4	235/237
o,p'-DDT	110	60	6	235/237
p,p'-DDT	110	60	6	235/237
Compound	LOD[c] (ng/l) in 10 ml River Rhine water			
	Full-scan		MID	Ions extr.
	TIC[d]	Extr. TIC		/MID
Mevinphos	30	2	0.4	127/192
Diazinon	15	3	0.3	197/304
Fenitrothion	20	2	0.3	277/260
Fenthion	20	3	ND[e]	125/278
Triazophos	30	10	1.1	161/257
Coumaphos	30	2	0.3	226/362

[a] LOD=limit of detection, calculated from 1 ng injections.
[b] Recorded *m/z* range, 35–435.
[c] LOD=limit of detection, calculated from 0.1 μg/l spiking level.
[d] Recorded *m/z* range, 50–375.
[e] ND=not determined.

3.3. MID versus full-scan acquisition

The potential of MID and the full-scan acquisition mode were compared for the detection of organochlorine and organophosphorus pesticides. Relevant data on detection limits are presented in Table 4. For both classes of compounds, ion extraction is seen to cause a 3–10-fold improved analyte detectability compared with the full-scan acquisition in almost all

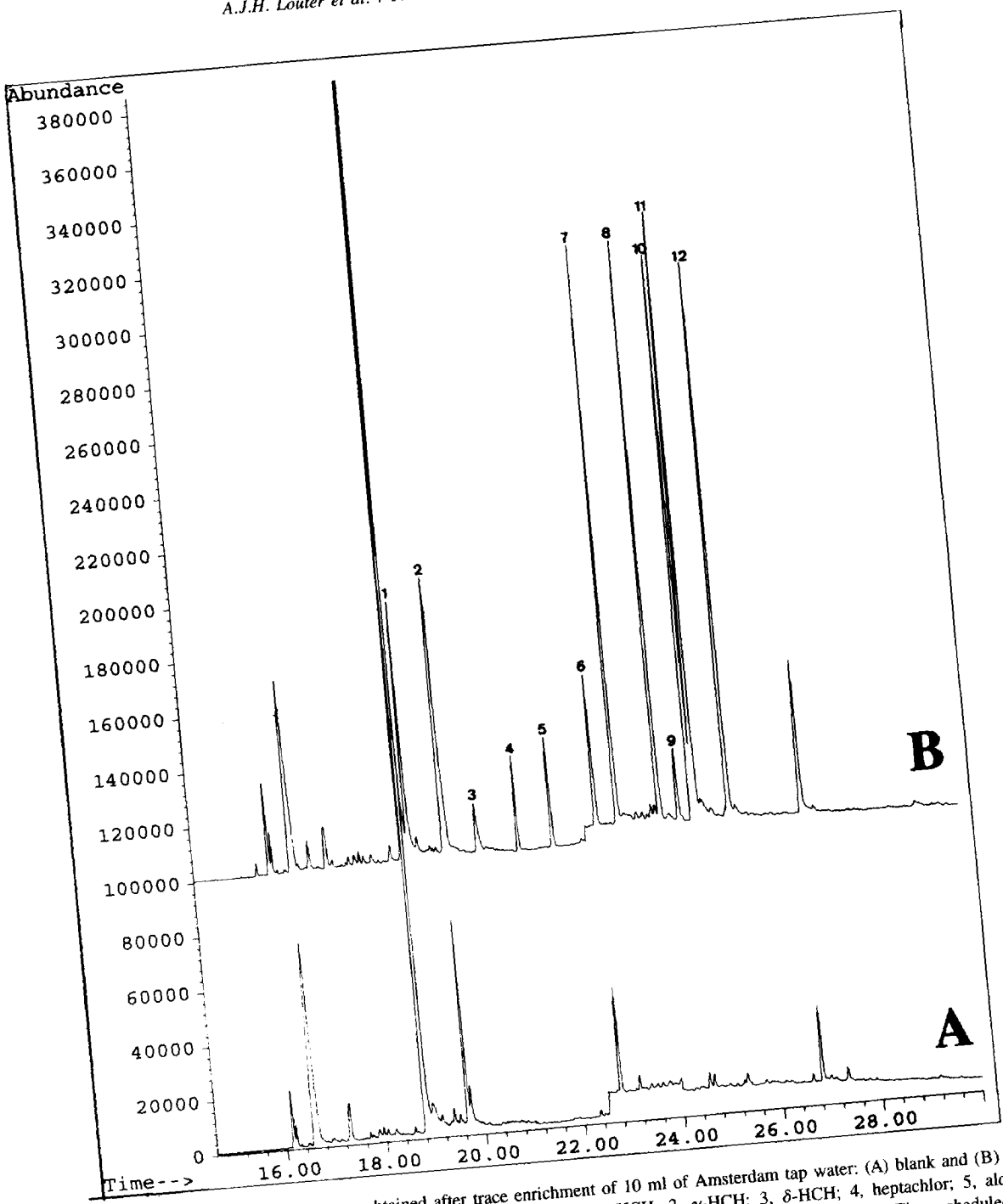

Fig. 4. SPE–GC–MS (MID) chromatograms obtained after trace enrichment of 10 ml of Amsterdam tap water: (A) blank and (B) spiked with 0.1 μg/l of twelve organochlorine pesticides. Peak assignments: 1, α-HCH; 2, γ-HCH; 3, δ-HCH; 4, heptachlor; 5, aldrin; 6, heptachlorepoxide; 7, *o,p'*-DDE; 8, dieldrin and *o,p'*-DDD; 9, endrin; 10, *p,p'*-DDE; 11, *o,p'*-DDT; 12, *p,p'*-DDT. Time-scheduled MID: 21–23.5 min (*m/z* 181, 219), 23.5–25 min (*m/z* 100, 272, 263, 265), 25–26.45 min (*m/z* 185, 253, 246, 248, 195, 197), 26.45–28 min (79, 263, 235, 237, 345).

cases. The obvious exceptions (heptachlorepoxide, endosulfan and endrin) are due to the severe fragmentation in the mass spectrum of these compounds. A further 10-fold improvement is achieved by using MID detection (two ions per analyte). This corresponds with detection limits of, typically, approx. 10 pg or, in other words, 1 ng/l for only 10-ml surface water samples. As an example, Fig. 5 shows SPE–GC–MS chromatograms recorded for the analysis of 10 ml of River Rhine (Lobith, Netherlands) water with and without spiking with 0.1 μg/l of the six organophosphorus pesticides in the full-scan (trace A) and the MID mode (trace B). The improved analyte detectability of MID, obtained at the cost of sacrificing much of the identification potential, is obvious.

3.4. Detection of unknown compounds

River Ebro

On five different days samples were taken at two locations along the River Ebro (Spain) (see Table 5). A typical chromatogram obtained by SPE–GC–MS of 10 ml of river water (80 km upstream from estuary) is shown in Fig. 6. For the five most prominent peaks in the chromatogram no satisfactory matches could be found with any entry in the mass spectral libraries available to us. Results for two of the three peaks that could be identified are shown in the inserts of Fig. 6. Quantification revealed concentration levels of 0.1–0.5 μg/l for both compounds (see Table 5). The concentrations in the samples taken farther upstream (80 km) were distinctly higher than those in the samples taken closer to the estuary; this can be attributed to dilution. The detection limits estimated for the two compounds when using ion extraction from the TIC were 0.01 μg/l.

River Nitra

Analysis of samples from the River Nitra (Slovakia) which is a tributary of the Danube, yielded SPE–GC–MS chromatograms as shown in Fig. 7. Mass spectra for two peaks that could be assigned, viz. to D-limonene and bis(2-chloro-1-methylethyl) ether (NBS library name: 2,2′-oxybis[1-chloropropane]), and the corresponding library spectra are shown as inserts to Fig. 7. The molecular mass of the latter compound is 170.2 ($C_6H_8Cl_2O$), but its molecular ion was not observed in either the SPE–GC–MS or the NBS library spectrum as is to be expected for this type of compound. The peaks at m/z 121/123 can be assigned to the $C_5H_7ClO^+$ fragment, with its chlorine isotopes. The m/z 77 peak can be assigned to the $C_3H_3Cl^+$ fragment, where the m/z 79 peak is a mixture of the ^{37}Cl isotope and the $C_2H_4ClO^+$ fragment (^{35}Cl isotope). The most prominent peak in the mass spectrum, at m/z 45, can be assigned to the $C_2H_5O^+$ ion. The prominent peak assigned to bis(2-chloro-1-methylethyl) ether was present in such a high concentration that both the GC column and the MSD multiplier were overloaded. This implies that the concentration level typically was between 10 and 100 μg/l. 'Modern' pesticides such as are frequently found in surface water of rivers in western Europe were conspicuously absent from all samples studied, except for atrazine. Chlorinated compounds were also detected in this sample when using off-line GC–AED with large-volume injections (100 μl) [21].

In the present study, water samples were taken at six different locations along the river. Selected results are presented in Fig. 8. For bis(2-chloro-1-methylethyl) ether, the largest concentration was observed at the Chalmova sampling site, just downstream from the location of heavy chemical industry at Novàky, which is known to produce several chlorinated products. The observed decrease in concentration at the more downstream sampling sites can be attributed to dilution.

Other river water samples

In the course of the present project, surface water samples that were offered for analysis included samples from the rivers Axios (Greece), Ebro (Spain), Meuse (Netherlands), Nitra (Slovakia) Rhine (Germany), Thames (UK), Varta (Poland), Sacramento (USA) and Amazon (Brazil). No special problems were ever encountered when analysing such samples, and 10-ml volumes invariably were sufficient to reach detection and identification limits of 1 μg/l or below. A selected list of compounds detected is included in Table 6. As an illustration, Fig. 9 shows the extracted-ion chromatogram at m/z 217 recorded for a sample taken from the river Axios

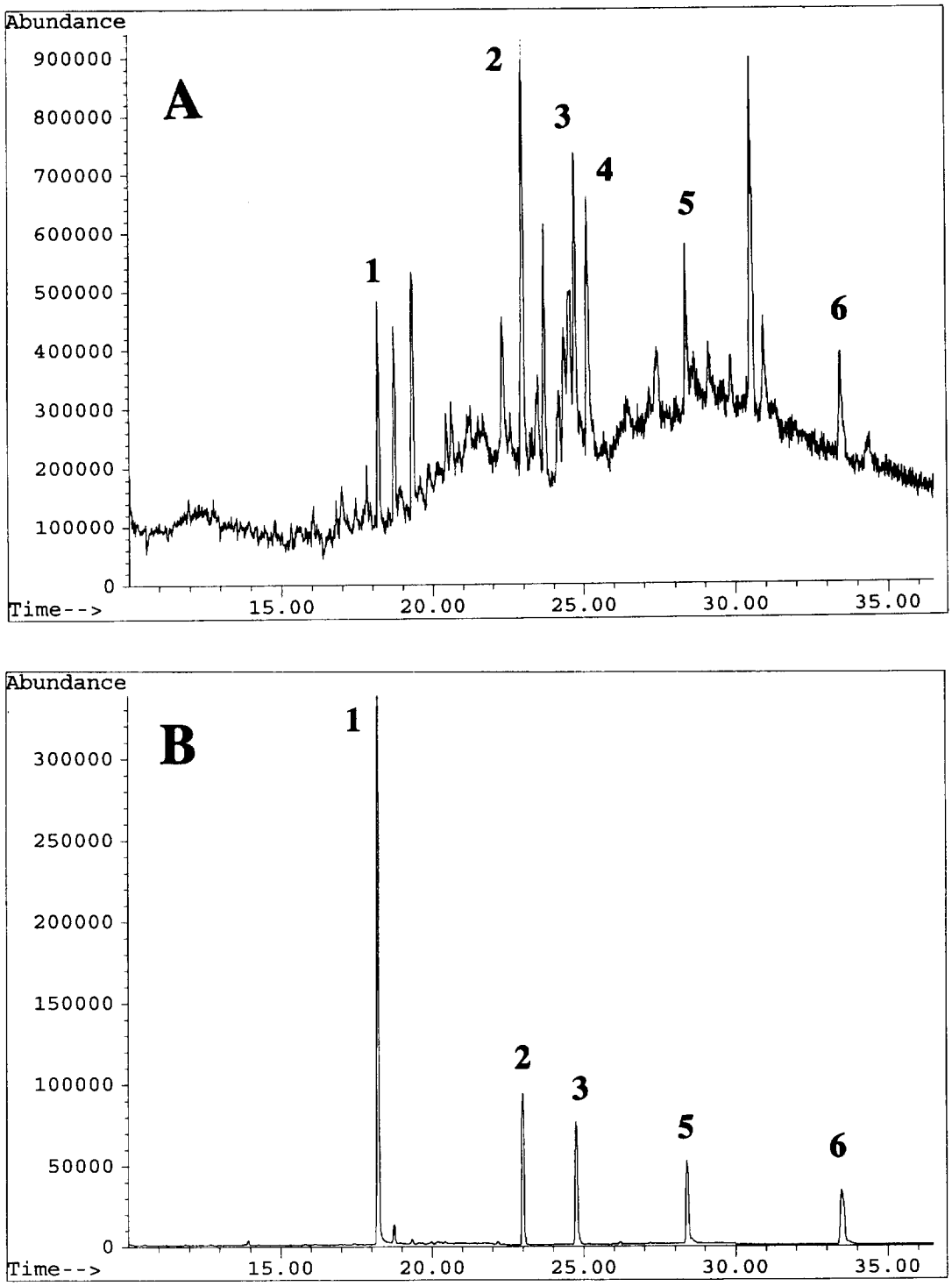

Fig. 5. SPE–GC–MS chromatograms obtained after trace enrichment of 10 ml of River Rhine water spiked at the 0.1 μg/l level. (A) Full-scan mode (m/z 50–375). (B) Time-scheduled MID mode (for ions used see Table 4). Peak assignments: 1, mevinphos; 2, diazinon; 3, fenitrothion; 4, fenthion; 5, triazophos; 6, coumaphos.

Table 5
Concentrations of atrazine and metolachlor in River Ebro samples ($n=2$)

Sample No.	Date	Location upstream from the estuary (km)	Atrazine (μg/l)	Metolachlor (μg/l)
1	15-08-93	2	0.1	0.2
2	16-08-93	2	0.15	0.2
3	22-08-93	80	0.5	0.4
4	25-08-93	80	0.5	0.5
5	17-08-93	2	0.1	0.15

which was suspected to contain α-HCH. The mass spectrum recorded for the prominent peak at 18.15 min (compare the minute peak in the TIC trace!) showed a good match with the α-HCH spectrum from the HPPEST library (quality, 91); the concentration was found to be 0.5 μg/l. The retention time is different from that reported in an earlier section because a different GC column was used in the present instance.

Analysis of greenhouse waste water

In addition to the above, waste water samples originating from greenhouses were screened for the presence of pesticides. These samples were dark yellow which suggested the presence of a fairly large concentration of humic substances. None of the pesticides which are commonly used on crops raised in these greenhouses could be identified on the basis of the TIC trace recorded after SPE–GC–MS analysis of 10-ml samples. However, selective-ion extraction indicated the presence of procymidone (t_{ret}, 23.57 min). Relevant data are shown in Fig. 10. To verify whether the large amount of humic substances did not cause early analyte breakthrough on the SPE cartridge, either by association with the analytes or by saturation of the sorbent [22–24], one sample was spiked with 0.5–2 μg/l of eight organophosphorus pesticides which were earlier shown to give good recoveries in SPE–GC with both HPLC-grade water and surface water [25]. Recoveries were 80–110%, except for bromophos (48%). These results were the same as those obtained in the earlier study, also even for bromophos, which is known to require the addition of a modifier (10% methanol) to obtain satisfactory recovery [26]. Obviously, the presence of the humic substances did not interfere with the procedure. This was convincingly demonstrated by analysing thirty such samples over a 48-h period. After that time no decrease in analyte recovery or in chromatographic performance was observed when running a 10-ml solution of the same pesticides in HPLC-grade water.

4. Conclusions

The potential of the present, fully automated and software-controlled on-line SPE–GC–MS system is demonstrated by the successful analysis of a wide variety of surface and waste water samples. Quite a number of microcontaminants were identified and quantified at levels down to 0.01–0.1 μg/l using a modest sample volume of 10 ml. The presence of, occasionally large, amounts of humic substances did not cause problems. The present system has been used for over two years without any special maintenance problems. The response (peak area) of the internal standard propazine was found to change less than 2-fold during a series of campaigns carried out over a period of one year. If the solvent delivery unit of the PROSPEKT system is used as a small autosampler (for four samples), samples can be run unattended. Today, solvent delivery systems with sixteen solvent channels are also available which increases the number of samples that can be run unattended to fourteen. The 100-μl transfers of ethyl acetate which are an inherent part of every analysis, or standard run, did not adversely affect the performance of the GC–MSD instrument. The PLRP-S precolumn could be used for at least 100 surface and/or tap water samples. Retention gaps were generally replaced after 50–100 real-life samples and/or standard runs; for a skilled operator this is a matter of a few minutes only. In other words, the present SPE–GC–MS system indeed is a powerful analyser for the detection of target compounds as well as unknown pollutants in water samples. In

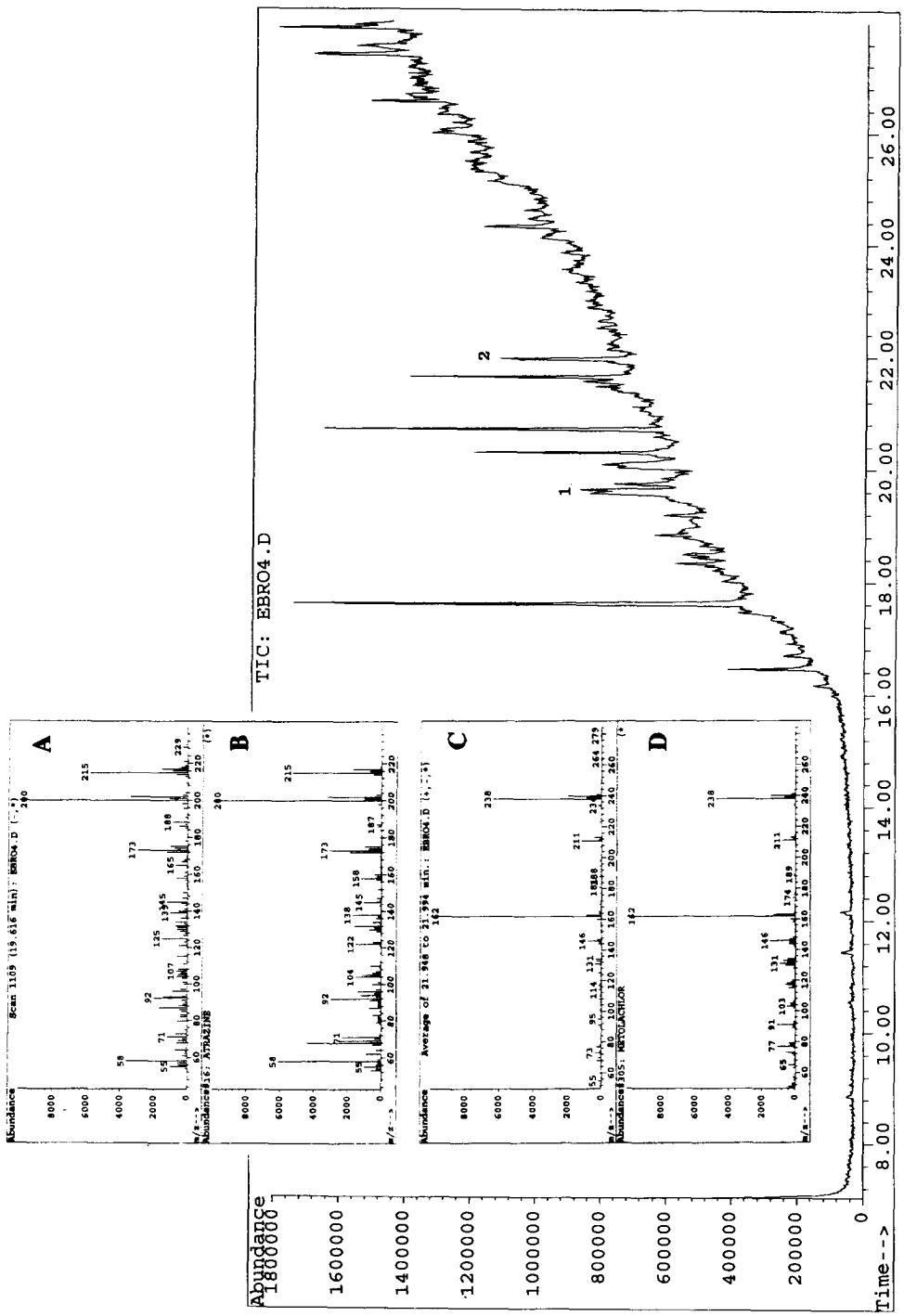

Fig. 6. SPE–GC–MS chromatogram obtained after trace enrichment of 10 ml of River Ebro water. Peak assignments: 1, atrazine; 2, metolachlor. Inserts: mass spectra from (A) peak at 19.61 min, and (B) atrazine from HPPEST library, (C) peak at 21.97 min, and (D) metolachlor from HPPEST library.

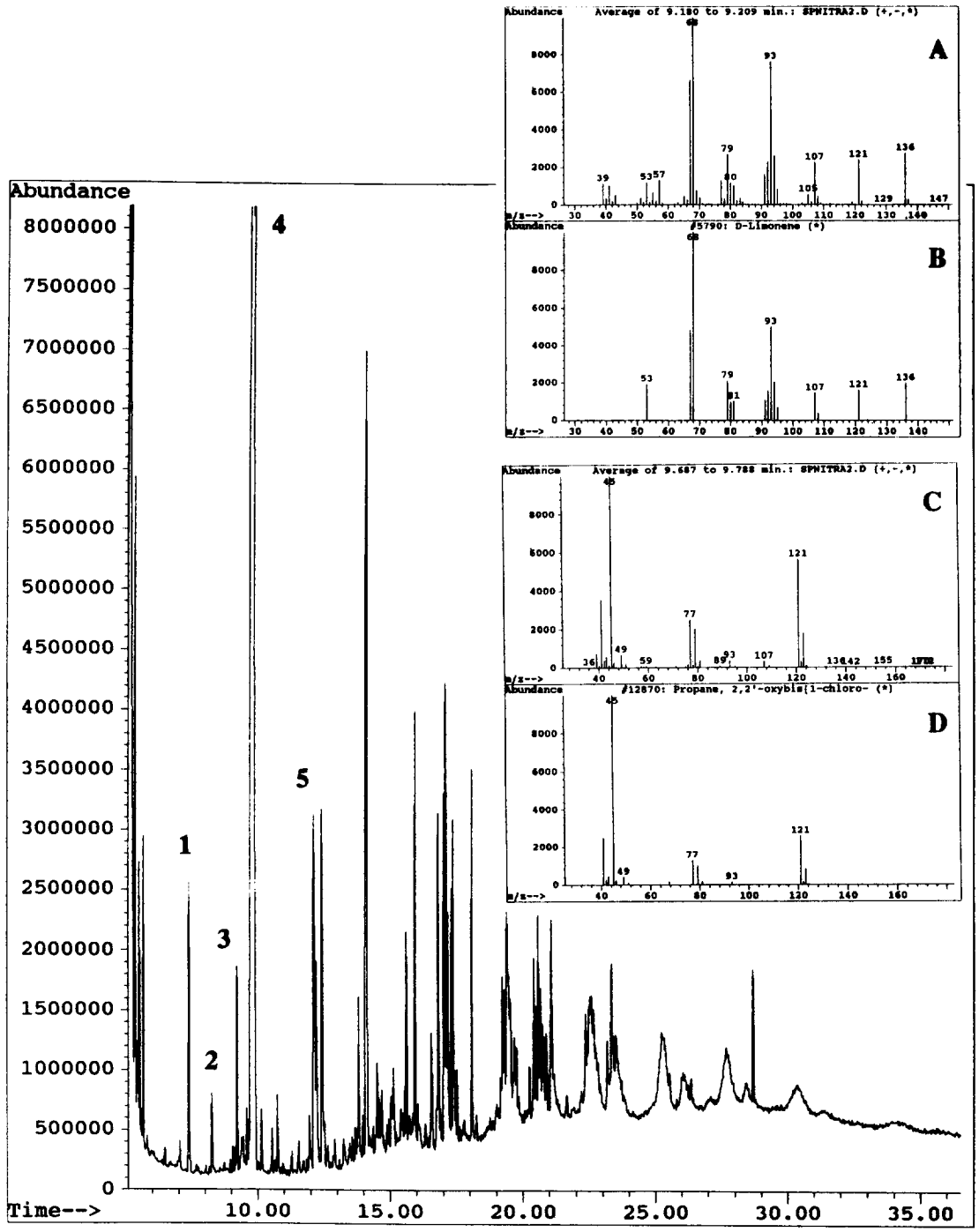

Fig. 7. SPE–GC–MS chromatogram obtained after trace enrichment of 10 ml of River Nitra water. Peak assignment (and NBS library match): 1, 5-methyl-3-heptanone (97); 2, bis(2-chloroethoxy)methane (74); 3, D-limonene (90); 4, 2,2′-oxybis[1-chloropropane] (90); 5, 1-[1-methyl-2[2-propenyloxy]]-2-propanol (83). Inserts: mass spectra from (A) peak at 9.19 min, and (B) D-limonene from NBS library, (C) peak at 9.73 min, and (D) 2,2′-oxybis[1-chloropropane] from NBS library.

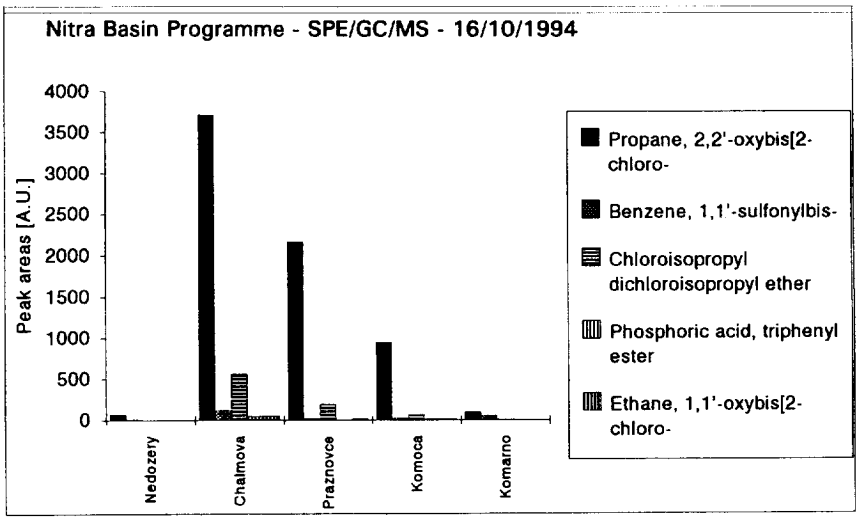

Fig. 8. Concentrations (in arbitrary units) of microcontaminants detected at six sample locations along the River Nitra. The locations of the sample sites are from Komarno to Nedozery in the upstream direction from the Nitra–Danube confluence.

principle, all analytes which can be trapped on the polymer precolumn, and desorbed by ethyl acetate and are GC-amenable, can be handled by the system.

Future research will be devoted to increasing the application range on the volatile ending by using a drying cartridge instead of a nitrogen purge for the drying step and to study the potential of SPE–GC–MS with detection in the chemical ionization mode.

Table 6
Survey of additional microcontaminants detected in various water samples using on-line SPE–GC–MS (10 ml samples)

Compound	Concentration (μg/l)	Water source	Spectral match[a]
Benzothiazole	1.1	River Meuse	91
n-Butylphosphate	0.70	River Thames	93
α-Hexachlorohexane	0.50	River Axios	91
Atrazine	0.05	River Rhine	87
	0.01[b]	Amsterdam tap	90
	–[c]	River Nitra	95
2,4-Dichloro-6-methylphenol	–	Westland greenhouse	86
s-Dichloroethyl ether	–	River Nitra	87
Diethylpentyl phosphate	–	River Varta	81
Diethyl phthalate	–	River Amazon	93
2,4,5-Trichlorophenol	–	River Sacramento	80
Triphenylphosphine oxide	1.05	River Rhine	92
	0.05	Amsterdam tap	80

[a] Match quality of NBS and HPPEST libraries.
[b] 50 ml sample used.
[c] –, no quantification performed.

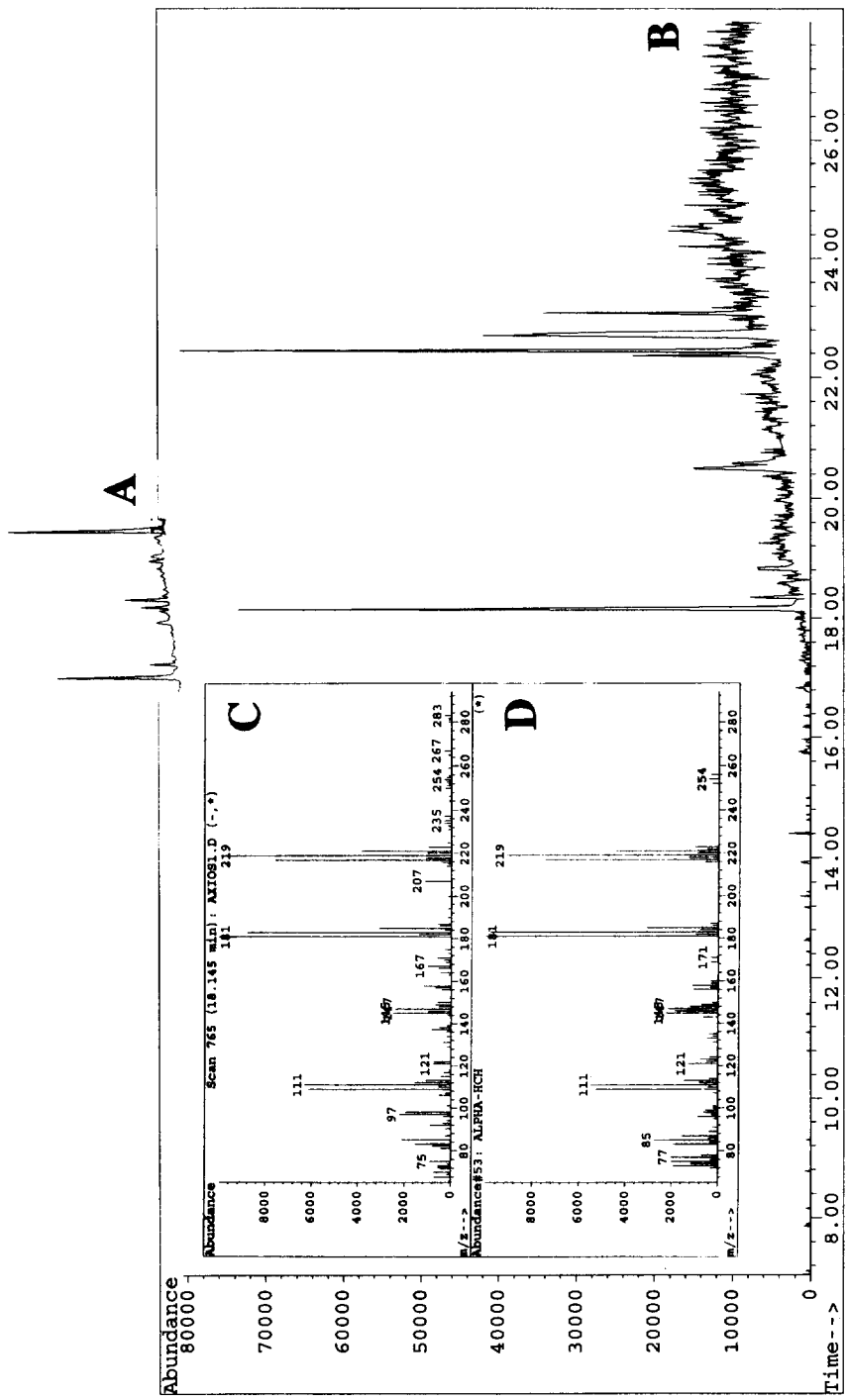

Fig. 9. SPE–GC–MS chromatograms of 10 ml of River Axios (Greece) water: (A) TIC; (B) extracted-ion chromatogram of m/z 217. Insert: (C) mass spectrum recorded at 18.15 min; (D) corresponding HPPEST library spectrum. GC analytical column, 28 m×0.20 mm I.D. SPB-1 (d_f=0.20 μm), retaining precolumn, 2 m×0.20 mm I.D. SPB-1 (d_f=0.20 μm).

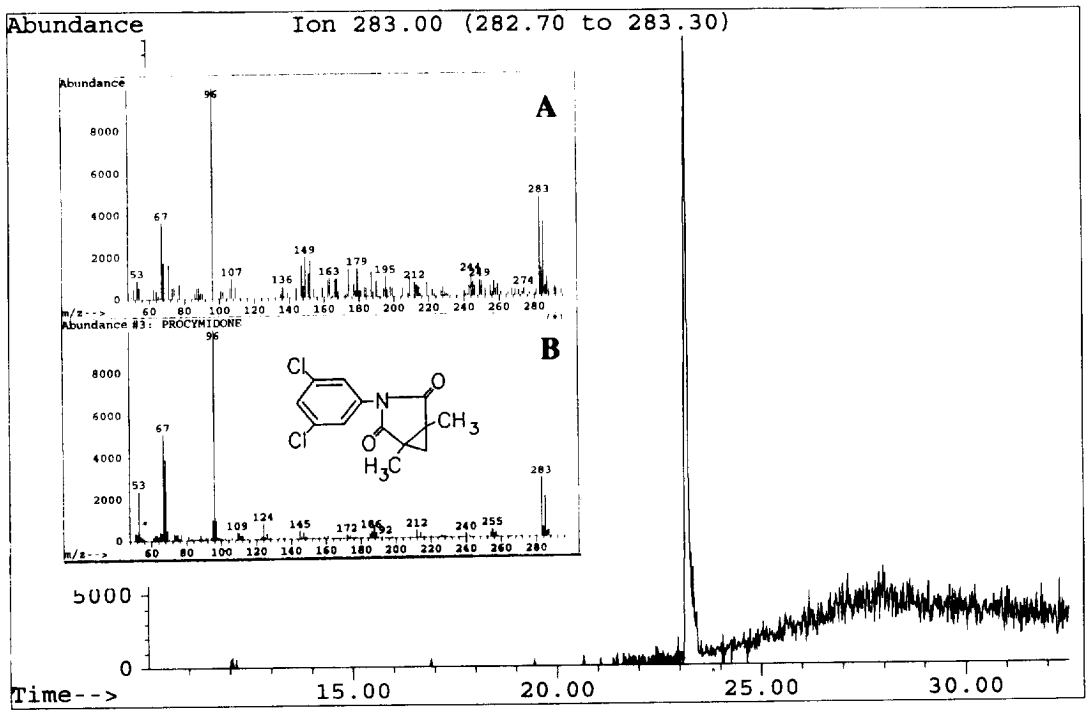

Fig. 10. Extracted-ion trace of m/z 283 obtained from SPE–GC–MS of 10 ml of greenhouse effluent water. Insert: mass spectra of (A) peak at 23.57 min and (B) procymidone from HPPEST library.

Acknowledgements

We thank the Rhine Basin Program (Amsterdam/Waldbronn) and the European Union (EV5V-CT92-0105) for their financial support. Dr. Ben van Baar is acknowledged for valuable discussions. Mr. Jan Brands (Supelco, Leusden, Netherlands) is acknowledged for the gift of the SPB-1 column.

References

[1] I. Liška, J. Krupčik and P.A. Leclerq, J. High Resolut. Chromatogr., 12 (1989) 577.
[2] M.C. Hennion, Trends Anal. Chem., 10 (1991) 317.
[3] D. Barceló, Analyst, 116 (1991) 682.
[4] K. Levsen, Org. Mass Spectrom., 23 (1988) 406.
[5] J.V. Hinshaw, LC–GC INT., 10 (1994) 560.
[6] EC Council directive relating to the quality of water intended for human consumption (80/778/EEC).
[7] I. Liska, E.R. Brouwer, A.G.L. Ostheimer, H. Lingeman and U.A.Th. Brinkman, Int. J. Environ. Anal. Chem., 47 (1992) 267.
[8] J. Slobodnik, E.R. Brouwer, R.B. Geerdink, W.H. Mulder, H. Lingeman and U.A.Th. Brinkman, Anal. Chim. Acta, 268 (1992) 55.
[9] M.W.F. Nielen, G.J. de Jong, R.W. Frei and U.A.Th. Brinkman, Int. J. Environ. Anal. Chem., 25 (1987) 37.
[10] J.J. Vreuls, W.J.G.M. Cuppen, G.J. de Jong and U.A.Th. Brinkman, J. High Resolut. Chromatogr., 13 (1990) 157.
[11] K. Grob, in On-line Coupled LC–GC, Hüthig Buch Verlag, Heidelberg, 1991.
[12] G. Schomburg, E. Bastian, H. Behlau, H. Husmann and F. Weeke, J. High Resolut. Chromatogr. Chromatogr. Comm., 7 (1984) 4.
[13] K. Grob, D. Frölich, B. Schilling, H.-P. Neukom and P. Nägeli, J. Chromatogr., 295 (1984) 55.
[14] J.J. Vreuls, A.-J. Bulterman, R.T. Ghijsen and U.A.Th. Brinkman, Analyst, 117 (1992) 1701.
[15] A.-J. Bulterman, J.J. Vreuls, R.T. Ghijsen and U.A.Th. Brinkman, J. High Resolut. Chromatogr., 16 (1993) 397.
[16] J.J. Vreuls, G.J. de Jong, R.T. Ghijsen and U.A.Th. Brinkman, J. Assoc. Off. Anal. Chem., 77 (1994) 306.
[17] J.J. Vreuls, A.J.H. Louter and U.A.Th. Brinkman, in H.-J. Stan (Editor), Chemistry of Plant Protection, Springer, Berlin, 1995, in press.
[18] A.J.H. Louter, U.A.Th. Brinkman and R.T. Ghijsen, J. Microcol. Sep., 5 (1993) 303.
[19] A.J.H. Louter, F.D. Rinkema, R.T. Ghijsen and U.A.Th. Brinkman, Int. J. Environ. Anal. Chem., 56 (1994) 49.

[20] E. Noroozian, F.A. Maris, M.W.F. Nielen, R.W. Frei, G.J. de Jong and U.A.Th. Brinkman, J. High Resolut. Chromatogr. Chromatogr. Comm., 10 (1987) 17.
[21] A.J.H. Louter, F.D. Rinkema and U.A.Th. Brinkman, Proceedinfs of the 16th Symposium on Capillary Chromatography, Hüthig, Heidelberg, 1994, p. 1423.
[22] A. Di Corcia and R. Samperi, Anal. Chem., 65 (1993) 907.
[23] I. Liska, E.R. Brouwer, H. Lingeman and U.A.Th. Brinkman, Chromatographia, 37 (1993) 13.
[24] W.E. Johnson, N.J. Fendinger and J.R. Plimmer, Anal. Chem., 63 (1991) 1510.
[25] F.D. Rinkema, A.J.H. Louter and U.A.Th. Brinkman, J. Chromatogr. A, 678 (1994) 289.
[26] Th. Hankemeier, A.J.H. Louter, F.D. Rinkema and U.A.Th. Brinkman, Chromatographia, 40 (1995), 119.