ELSEVIER

Journal of Chromatography A 822 (1998) 75–82

JOURNAL OF CHROMATOGRAPHY A

Automated solid-phase extraction on-line coupled to gas chromatography[1]

Petra Enoch, Aggi Putzler, Dieter Rinne*, Jörg Schlüter

Landesamt für Wasserwirtschaft Rheinland-Pfalz, Am Zollhafen 9, D-55118 Mainz, Germany

Received 14 April 1998; received in revised form 10 July 1998; accepted 10 July 1998

Abstract

A novel system with autosampling and automated solid-phase extraction on-line coupled to gas chromatography is reported. This system is unique in routine organic trace analysis of water constituents. The performance date of the analytical method developed for determination of lindane, musk ketone, and musk xylene are matching the requirements of the European Union directives for drinking water and have the same quality as the formerly used liquid–liquid extraction method. The recovery of spiked samples of surface water is excellent.

Keywords: Extraction methods; Water analysis; Automation; Lindane; Musk ketone; Musk xylene; Pesticides

1. Introduction

One of the main differences between organic and inorganic trace analysis of water samples is the fact that in organic trace analysis mostly an extraction step has to be applied. This is to concentrate the compounds and to transfer the components to be analyzed to a suitable phase for better subsequent handling e.g. further sample preparation or direct measurement.

This important step of sample preparation can be carried out as liquid–liquid, liquid–solid, and liquid–gas extraction depending on the physical properties of the compounds, and on other sample preparation steps to be carried out or the method of the final measurement.

With the exception of the liquid–gas extraction of highly volatile compounds followed by direct GC determination all these extraction steps have to be done batchwise and are very time-consuming in the laboratory.

Theoretically, solid-phase extraction (SPE) gives the opportunity to automate the whole analysis if no additional pre-chromatographic step is required.

Two different systems are possible, namely a system for automated sample preparation leading to a measuring solution and a system for automated sample preparation and direct transfer to the chromatographic system (GC or HPLC), a so called on-line method. The later system can also lead to further miniaturisation.

2. On-line SPE systems and scope

In the literature, so far only some commercial systems using automated SPE coupled to HPLC [1,2] and only one on-line SPE–GC system [2,3] are

*Corresponding author.

[1]This article is dedicated, with many thanks, to my teacher Professor Dr. A. Blaschette on the occasion of his 65th birthday

0021-9673/98/$19.00
PII: S0021-9673(98)00576-7

described. These publications and our work are all based on the fundamental work of Brinkman and co-workers [4,5].

In all these systems the filtered water sample or an aliquot thereof is passed over a cartridge with conditioned SPE material. After washing the SPE material with deionized water and after drying with an inert gas the cartridge is eluted with a suitable organic solvent. The eluate then is transferred onto the column of the chromatographic system. During the chromatographic run the cartridge is flushed back/cleaned and made ready for the next extraction step.

In our laboratory the devices Autoselect 2000 and Autoloop 2000 manufactured by Interchro [3] are coupled to a GC–electron-capture detection (ECD) system. To complete automatisation an autosampler is attached to create a real on-line system. So the possibility of overnight/over-weekend measurements is given as reported for an SPE–HPLC system [2].

The GC system was equipped with a device to transfer the eluate simultaneously to two chromatographic columns with stationary phases of different polarity.

The instrument configuration described above is the only real on-line system so far for the routine organic trace analysis of water.

The Autoselect 2000 controls the transport of solvents and samples through the piping system and the cartridge, the Autoloop 2000 controls the transfer of the eluate from the cartridge onto the GC columns.

To cope with the relatively high volume of solvent transferred from the cartridge to the GC column, a system of precolumns is required. The retention gap serves to evaporate the solvent and the substances. It works similar to an injector in a normal gas chromatograph. The retaining precolumn to retain the substances on the stationary phase after evaporation while the solvent is separated at a given temperature via a separate exit valve before the chromatographic column.

In detail the systems work as follows.

SPE controlled by the Autoselect 2000: (i) rinsing the piping system with solvent, (ii) rinsing the cartridge with solvent, (iii) rinsing the piping system with ultra-clean water, (iv) rinsing the cartridge with ultra-clean water, (v) rinsing the piping system with water sample (vi) passing the sample through the cartridge and enrichment of the compounds on the solid-phase material, (vii) washing the pipe system with solvent, (viii) washing the cartridge with solvent, and (ix) start of the Autoloop 2000.

Transfer of the compounds to the GC system controlled by the Autoloop 2000: (i) filling the loops with solvent, (ii) emptying of the two loops simultaneously; the solvent of the first loop conditions the stationary phase of the retaining precolumn to retain the compounds quantitatively; the solvent of the second loop desorbes the compounds from the cartridge, (iii) transfer onto the retention gap and retaining precolumn; due to the relatively high volume of the solvent from both loops (ca. 200 μl) the pressure increases. The eluate is transferred into the retention gap where the solvent and the compounds are evaporated; both the compounds and the solvent are migrating into the retaining precolumn where the compounds are retained and hold back on the stationary phase; in the meantime the solvent is released through an exit valve, and (iv) start of the gas chromatograph. A signal is produced by the falling pressure of the releasing solvent and at a given pressure difference the gas chromatograph is started. A function scheme is given in Fig. 1.

Up to now trace analysis for the determination of lindane (γ-hexachlorocyclohexane), musk ketone {1-[4-(1,1-dimethylethyl)-2,6-dimethyl-3,5-dinitrophenyl]-ethanone}, and musk xylene {1-(1,1-dimethylethyl)-3,5-dimethyl-2,4,6-trinitrobenzene} in surface water and ground water is done by extraction of 1 L water sample with about 100 ml hexane. With this analytical method a limit of detection/determination [6,7] for each compound of 0.010 $\mu g\,l^{-1}$ and a standard deviation of the procedure of less than 10% is to be achieved. Hexane is supposed to be cancerogenic and therefore should be substituted by another extraction reagent.

The above described new system promises as a SPE on-line method to reach the targets of the mentioned criteria of the analytical method. Furthermore the required sample size could be smaller (10–100 ml) and the amount of manpower needed could be reduced.

So the evaluation of an analytical method for the

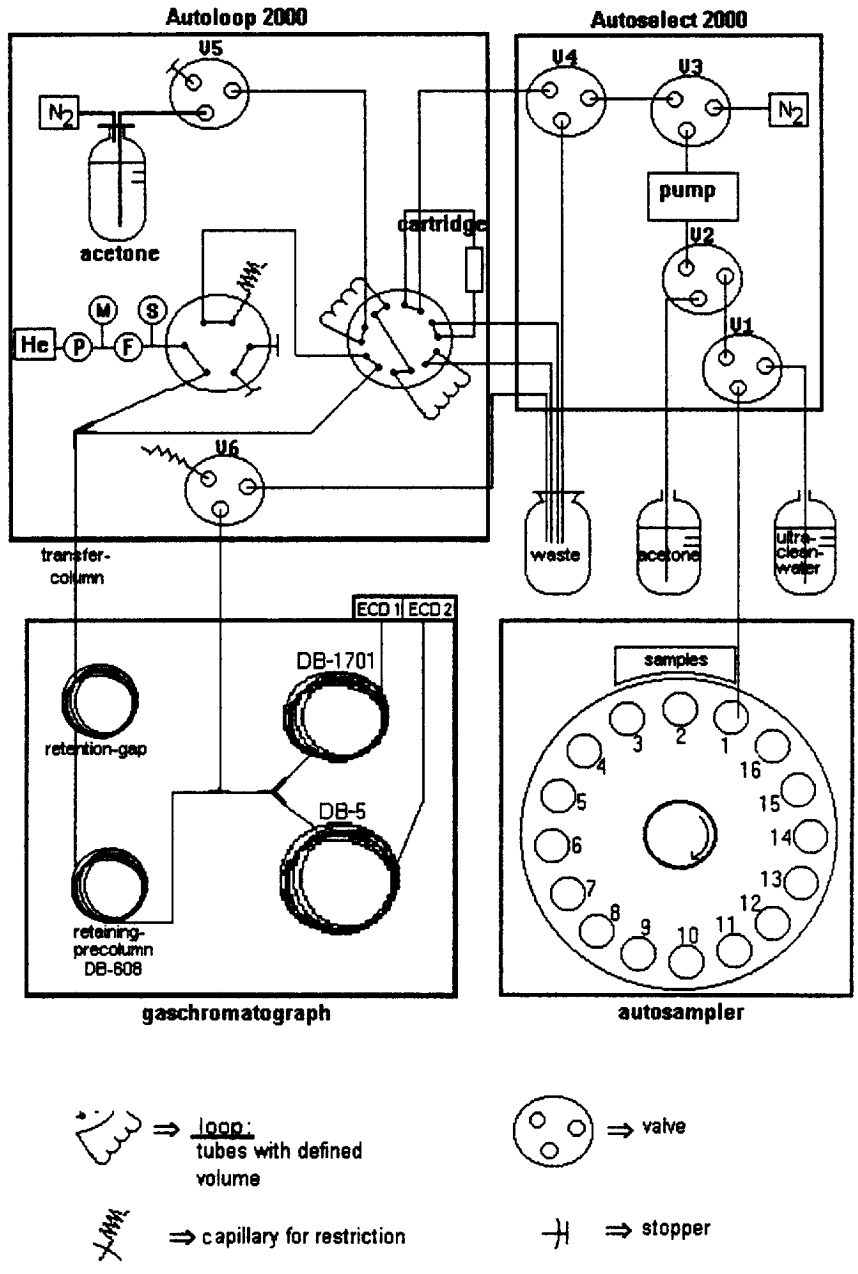

Fig. 1. Function scheme on-line SPE–GC system.

determination of the mentioned compounds had to be carried out including sample preparation, enrichment conditions, influences of the retention gap and retaining precolumn, evaluation of the instrument settings, GC conditions, and recovery rate for a given limit of determination (detection) and standard deviation of the procedure.

Also the questions of the lifetime of the cartridges

and service-free work of the on-line system besides other economical items had to be answered.

3. Experimental

It had to be pointed out first that all solvents used and the water sample itself has to be membrane filtered prior to the SPE step. This is essential to avoid clogging of the piping system and the cartridges.

So after addition of 0.2% of methanol to 100 ml of the water sample to avoid wall effects it was filtered through a 0.45 μm filter. The filter is washed with 1 ml of methanol to desorbe compounds from the filter material and the suspended matter.

The cartridge is filled with 35 mg of RP C_{18} material, closed at both end with a 5 μm frit. For washing ultra-clean water and for drying N_2 (5.0 grade) are used. The elution process is carried out with nano-grade acetone.

The working steps and times of the devices and the reagents with their volumes used are given in Tables 1 and 2 for the Autoselect 2000 and the Autoloop 2000, respectively.

The GC conditions for the determination of lindane, musk ketone, and musk xylene after SPE and on-line transfer onto the GC-columns are given in the Table 3.

Table 1
Working steps of auto select

No.	Working step	Material	Time
1	Start delay		1 s
2	Pump: on		
3	Rinsing the piping system	Acetone	1.0 min
4	Rinsing the cartridge	Acetone	1.0 min
5	Rinsing the piping system	Ultra-clean water	1.0 min
6	Rinsing the cartridge	Ultra-clean water	2.5 min
7	Rinsing the piping system	Water sample	1.0 min
8	Enrichment of compounds		5.0 min
9	Rinsing the piping system	Ultra-clean water	1.0 min
10	Rinsing the cartridge	Ultra-clean water	0.5 min
11	Drying the cartridge	Nitrogen	20.0 min
12	Start of Autoloop 2000		

Table 2
Working steps of autoloop

No.	Working step	Material	Time
1	Filling the loops	Acetone	0.2 min
2	Emptying loop 1	Acetone (50 μl)	
	Emptying loop 2	Acetone (150 μl)	2.0 min
3	Opening of release valve		135 s
4	Start GC		

4. Results and discussions

4.1. Influence of reagents, temperatures and parts of the device

In the experiments with different solid-phase materials C_{18} material turned out to yield the highest recovery for the tested compounds in combination with acetone as solvent for elution. Acetic acid methyl ester was rejected because it affected the phase of the retaining precolumn.

It is therefore essential to record carefully the signal intensities of standard compounds. In routine analysis about 120 measurements (including calibration and standards) could be carried out depending on the sample matrix without interferences. This is shown in Table 4 with standards which are inserted for quality control during the measurement of real samples.

The temperature of the GC oven has a substantial influence on the sample transfer from the cartridge to the GC columns.

Our experiments showed that at 70°C several smaller signals appeared in front of the compound signals in question indicating poor evaporation and delay of the substances. This starting temperature was to low.

At a higher temperature of 100°C there were additional signals behind compound signals in question.

Finally, at 85°C a gas chromatogram with highly symmetric signals and no additional peaks was obtained (see, Fig. 2).

The retention gap is an empty tube made of fused-silica. During every evaporation of the sample eluate the non-volatile compounds retained in the

Table 3
GC conditions

Detection	ECD
Detection temperature	300°C
Carrier gas	Helium 5.0
Flow-rate	1.3 ml min^{-1} for each column
Columns	DB-1701; 30 m×0.25 mm I.D.; 0.25 μm film thickness
	DB-5; 30 m×0.25 mm I.D.; 0.25 μm film thickness
Retention gap	Mid-polar desactivated fused-silica column; 4 m×0.53 mm I.D.
Retaining precolumn	DB-608; 4 m×0.32 mm I.D.; 0.5 μm film thickness
Temperature program	85°C (0.5 mm); 11°C min^{-1} to 200°C (16.45 mm); 10°C min^{-1} to 240°C (6.1 mm); 10°C min^{-1} to 260°C (3.95 mm)

gap. The gap getting dirty causes a reduction of signal intensity of the compounds in question as shown in Fig. 3.

The retaining precolumn had to trap the substances after evaporation in a narrow chromatographic starting zone during the split of the solvent.

The capability of the trapping had to be tested because some stationary phases are not able to swell sufficiently when washed with the solvent. This leads to losses in trapping of the substances and they were removed partly with the solvent. Examples are given in Fig. 4.

4.2. Performance characteristics of the analytical procedure

To compare analytical methods some data like limits of determination/detection, relative standard deviation of the procedure, slope of the calibration curve, recovery rate and precision had to be evaluated.

The performance data detection/determination limits, relative standard deviation of the procedure and slope of the calibration curve were evaluated according to the German Standards [7] from cali-

Table 4
Time dependence of measurements

Date	No. of injections	Peak area of standards (40 ng l^{-1} each compound) column: DB-5 (mV s)								
		Lindane Peak area	Mean±S.D.	R.S.D. (%)	Musk xylene Peak area	Mean±S.D.	R.S.D. (%)	Musk ketone Peak area	Mean±S.D.	R.S.D. (%)
21 August 1997	5	159 230	165 425±5312	3.21	23 607	22 990±1081	4.70	83 555	80 465±2547	3.16
21 August 1997	14	172 203			23 893			77 318		
21 August 1997	23	164 842			21 470			80 525		
27 August 1997	27	219 038	224 887±5849	2.60	44 483	43 506±978	2.25	182 808	197 702±3107	1.73
27 August 1997	37	230 736			42 528			176 595		
17 September 1997	60	102 129	105 916±3787	3.58	18 033	17 985±48	0.27	57 359	61 656±4297	6.97
17 September 1997	68	109 703			17 937			65 953		
6 October 1997	73	97 683	97 274±3522	3.62	16 159	16 323±379	2.32	69 937	68 019±2913	4.28
6 October 1997	83	92 771			16 847			63 902		
6 October 1997	93	101 369			15 962			70 218		
7 October 1997	98	110 735	116 974±4785	4.09	22 863	20 757±1557	7.50	79 589	81 905±1638	2.00
7 October 1997	106	122 362			20 262			83 019		
7 October 1997	114	117 826			19 146			83 107		
22 October 1997	117	74 475	77 314±2839	3.67	13 957	13 681±276	2.02	37 289	40 680±3391	8.34
22 October 1997	123	80 153			13 405			44 071		

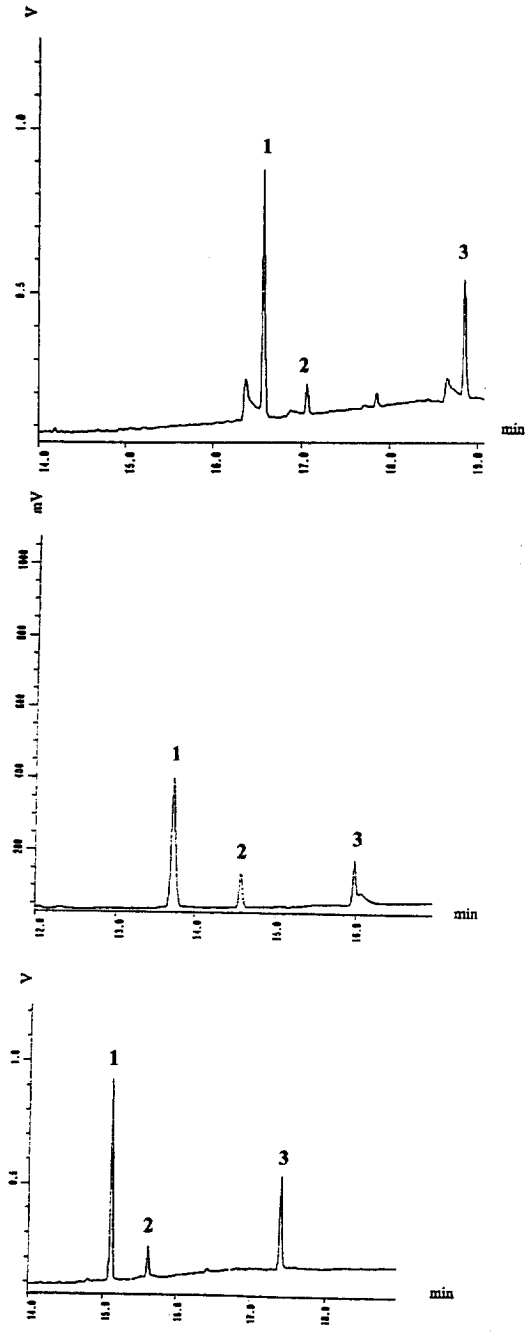

Fig. 2. Influence of oven temperature; 0.04 $\mu g\,l^{-1}$ of each compound, analytical column: DB-5 (Top) temperature during sample transfer: 70°C, (middle) temperature during sample transfer: 100°C, (bottom) temperature during sample transfer: 85°C. Peaks: 1=lindane; 2=musk xylene; 3=musk ketone.

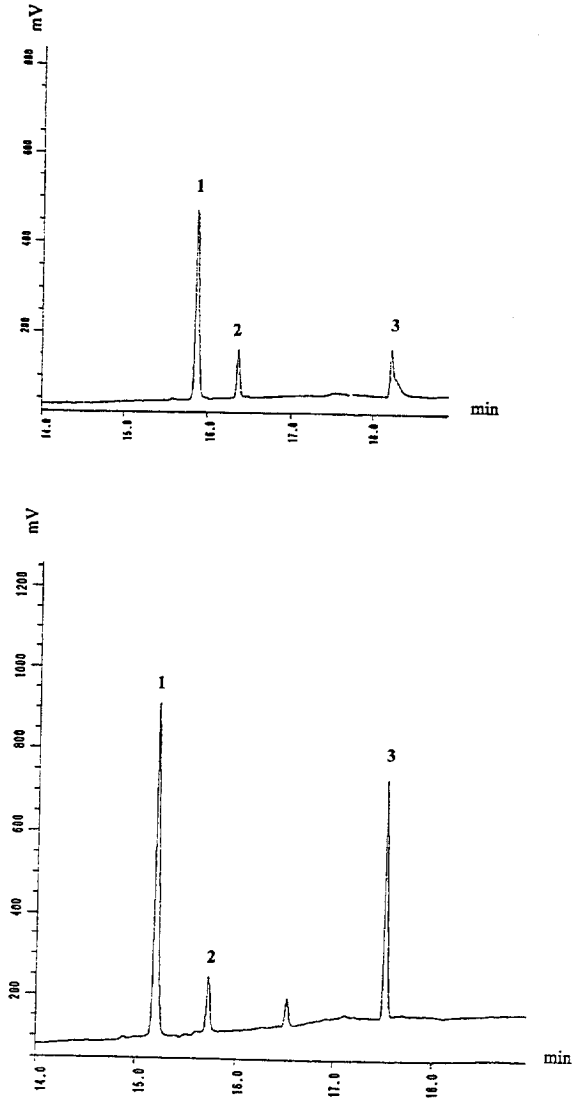

Fig. 3. Influence of retention gap; 0.04 $\mu g\,l^{-1}$ of each compound, analytical column: DB-1701. (Top) used retention gap, (bottom) new retention gap. Peak numbering as in Fig. 2.

bration experiments of artificial samples (matrix: deionized water) using five concentration levels with equidistant difference in the working ranges of 4–50 $ng\,l^{-1}$, 8–50 $ng\,l^{-1}$, and 4–50 $ng\,l^{-1}$ for lindane, musk ketone, and musk xylene, respectively. The results are summarized in Table 5.

The data indicate that the analysis with the device described above could be carried out at the desired

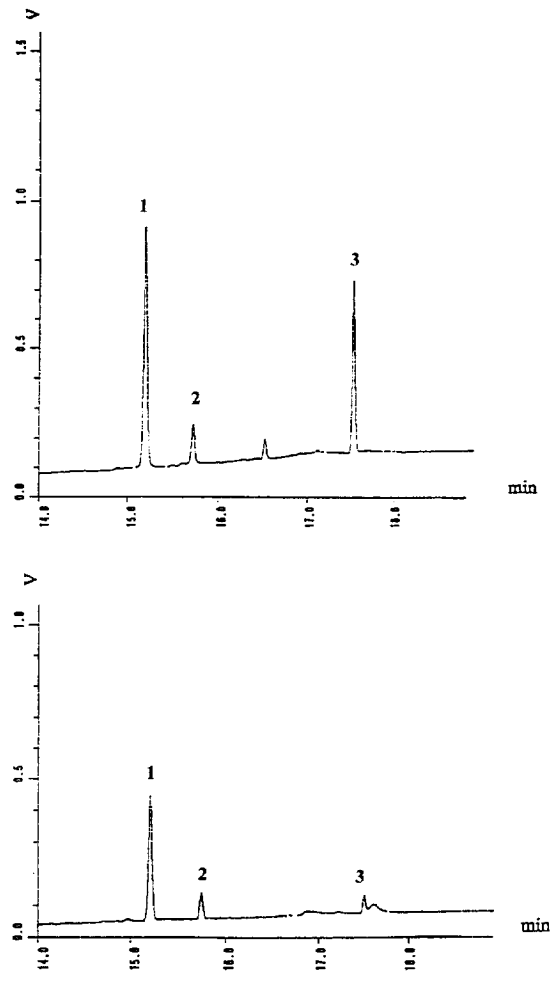

Fig. 4. Influence of retaining precolumn; 0.04 $\mu g\,l^{-1}$ of each compound, analytical column: DB-1701. (Top) retaining precolumn: DB-608, (bottom) retaining precolumn: DB-XLB. Peak numbering as in Fig. 2.

limits of detection/determination with a small standard deviation. These limits of detection/determination meet the requirements of the European Union (EU) directives for drinking water and are the same as reached with the formerly applied method based on liquid–liquid extraction using hexane.

To measure the precision 1 l of tap water was spiked with 0.020 $\mu g\,l^{-1}$ of each substance and analyzed ten times (see Table 6).

From these values standard deviations of 2.5% for Lindane, 6.1% for musk xylene, and 3.5% for musk ketone were obtained.

Furthermore to establish precision in real samples a surface water sample was spiked with 0.020 $\mu g\,l^{-1}$ of each substance (Table 7). Precision did not differ on columns with different stationary phases in use (DB-5, DB-1701). These results are also indicating a good reproducibility.

With a real on-line system it is impossible to measure the recovery rate of the extraction step

Table 6
Precision of measurements in spiked tape water (0.020 $\mu g\,l^{-1}$ of each compound)

No.	Lindane ($\mu g\,l^{-1}$)	Musk xylene ($\mu g\,l^{-1}$)	Musk ketone ($\mu g\,l^{-1}$)
1	0.02	0.019	0.02
2	0.02	0.021	0.022
3	0.021	0.021	0.021
4	0.02	0.021	0.021
5	0.02	0.02	0.02
6	0.02	0.02	0.021
7	0.02	0.018	0.02
8	0.021	0.02	0.021
9	0.021	0.019	0.022
10	0.02	0.018	0.021

Table 5
Performance data

Compound	Column	Limit of detection[a] ($ng\,l^{-1}$)	Limit of determination[a] ($ng\,l^{-1}$)	S.D. ($ng\,l^{-1}$)	R.S.D. (%)	Slope of calibration curve (count $ng^{-1}\,l^{-1}$)
Lindane	DB-5	4.3	14	1.1	5.1	40 000
	DB-1701	5.3	17	1.4	6.4	29 000
Musk ketone	DB-5	6.3	19	1.5	5.9	6000
	DB-1701	4.1	13	1.1	4.9	4900
Musk xylene	DB-5	8.4	27	2.3	10	5900
	DB-1701	5.1	16	1.4	6.1	4200

[a] According to the German Standard [7].

Table 7
Precision of measurements in spiked surface water (0.020 μg l^{-1} of each compound)

Compound	Concentration (μg l^{-1})	
	Original sample	Spiked sample
Musk xylene	0.01	0.025
	0.01	0.024
	0.01	0.026
Musk ketone	0.01	0.024
	0.01	0.024
	0.01	0.025
Lindane	0.029	0.051
	0.028	0.048
	0.029	0.05

itself. The recovery therefore only can be estimated by a standard addition experiment over the whole analytical procedure of real samples.

The recovery data of a spiking amount of 0.020 μg l^{-1} of each substance under investigation to surface water samples show a good recovery for all three substances (see Table 7).

5. Conclusions

The automated system for on-line SPE developed by Interchro coupled to an autosampler and a dual column gas chromatograph is an excellent tool for the determination of traces of lindane, musk ketone, and musk xylene in water.

The performance date of the analytical method based on this device such as limits of detection/determination, relative standard deviation of the procedure, and precision are in good agreement with the values of the former used liquid–liquid extraction method. Also the recoveries of spiked surface water samples are excellent.

Absolutely necessary is the filtration of all solvents used and the sample itself over a 0.45 μm filter prior to the SPE to avoid clogging of the piping system and the cartridge. Only this step had to be carried out batchwise in the whole analytical procedure. In addition due to our experiences other advantages are worthwhile to mention.

(1) Amount of reagents: in the on-line system the volume of 5 ml of solvents (acetone, methanol) is used compared with 100 ml (hexane) in the liquid–liquid extraction. Furthermore this on-line system needs only 35 mg of solid-phase material instead of 500 mg to 2 g in the off-line. These cartridges last approximately for 120 extractions. This long lifetime allows the whole system work for this amount chromatographic runs because it is more or less the lifetime of the retention gap. The sample volume is also reduced from 1 l to 10 ml.

(2) Working time: the working time for the sample preparation is reduced up to 8 h because the only handling to be done is the filtration. The system than works overnight/over-weekends. On the other hand the whole system is service-intensive. Beside analytical qualification the personal should be technically good trained to operate the system.

Overall the on-line SPE coupled to a GC fits in all laboratories applying SPE to the organic trace analysis of water samples.

References

[1] G. Schwedt, Nachr. Chem. Tech. Lab. 44(Suppl) (1996) 63.
[2] T. Renner, K.K. Unger, GIT Labor-Fachzeitschrift 40 (1996) 756.
[3] D. Jahr, J.J. Vreuls, A.J.H. Louter, W. Löbel, GIT Labor-Fachzeitschrift 40 (1996) 178.
[4] J.J. Vreuls, A.J.H. Louter, U.A.Th. Brinkman, Capillary GC with selective detection using on-line solid-phase extraction and liquid chromatography techniques, Chem. Plant Protect. 2 (1995) 1–30.
[5] H.G.J. Mol, H.G.M. Janssen, C.A. Cramers, J.J. Vreuls, U.A.Th. Brinkman, J. Chromatogr. A. 703 (1995) 277.
[6] W. Funk, V. Dammann, C. Vonderheid, G. Oehlmann (Eds.), Statistische Methoden in der Wasseranalytik, VCH, Weinheim, 1985.
[7] Deutsches Institut für Normung e.V.: Deutsche Norm DIN 32645