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# Automated solid-phase extraction coupled to gas chromatography with electron-capture detection: a combination of extraction and clean-up of pyrethroids in the analysis of surface water

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**Abstract**

The combination of automated solid-phase extraction (SPE) and large-volume introduction gas chromatography electron-capture detection (GC–ECD) is used for the determination of synthetic pyrethroids in surface and drinking water. The selectivity that is needed for the use of GC–ECD of environmental samples is achieved by addition of a polarity modifier to the sample. In this study, sufficient methanol was added to 19 ml of sample to obtain a level of 30% of modifier prior to SPE. The cartridge is washed with one additional ml of 30% methanol in water. After drying, the cartridge is eluted with toluene. GC–ECD analysis is performed by on-column introduction of 100 $\mu$l of the toluene extract. The whole procedure was automated by using an automated solid-phase extraction apparatus. Limits of detection (LODs) for the pyrethroids in surface water are in the range of 1 to 8 ng/l (signal-to-noise ratio = 3); even lower limits of detection are possible for drinking water.

## 1. Introduction

Recently ecotoxicological evaluation of 243 pesticides showed that synthetic pyrethroids are amongst the most toxic pesticides for aquatic organisms such as fish and crustaceans [1]. Hence, sensitive analytical methods allowing the reliable analysis of those pesticides at levels even below the EU maximum residue limit of 0.1 $\mu$g/l for drinking water are needed. Moreover, the gas chromatographic (GC) analysis of pyrethroids in environmental water samples containing elevated amounts of organic carbon requires selective sample enrichment techniques, especially if electron-capture detection (ECD) is used.

Conventional pesticide residue analysis of organochlorine insecticides and pyrethroids in environmental samples is often laborious since it involves manual sample extraction, clean-up and several concentration steps. Moreover, these conventional methods are often rather inefficient because only about 0.1% of the original sample taken in preparation is finally injected onto the GC system [2,3]. Obviously, the combination of automated sample pretreatment coupled to GC

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and large-volume injections is a promising technique for the enhancement of both selectivity and sensitivity in the determination of pesticides in environmental samples.

In an earlier paper we proposed a semi-automated method for the determination of organochlorine pesticides and pyrethroids in which manual liquid–liquid extraction of aqueous samples was followed by automated clean-up over silica SPE cartridges and large-volume GC introduction [4], using a sophisticated LC autosampler. Such a method can be executed fully automated by also performing the liquid–liquid extraction step with the LC autosampler [3]. However, even if a single liquid–liquid extraction step is sufficient to obtain complete recovery of the compounds of interest, drying and evaporation will have to be implemented in the automated procedure prior to clean-up, thereby making the procedure complicated and difficult to automate. SPE has shown to be a good alternative for manual liquid–liquid extraction and is advantageous in its potential for automation, if sample volumes can be kept within reasonable limits.

In several applications typically 0.4–5 l of surface water are enriched on $C_{18}$ cartridges, followed by clean-up over a Florisil column prior to capillary GC–ECD analysis [5,6]. The combination of $C_{18}$ sample enrichment with clean-up on a silica cartridge in an automated procedure is complicated due to the poor compatibility of both the nature and the amount of the desorbing solvents for the $C_{18}$ cartridge with the requirements for the normal-phase clean-up step.

SPE has proven to be a powerful tool for the analysis of herbicides in water by GC–MS [7,8]. In these cases clean-up of the samples was less of a problem, because the MS is less sensitive to interferences from environmental samples than the ECD; the same holds true for flame photometric and thermionic detectors. One of the critical steps in SPE followed by GC is the drying step applied just before desorption. Small quantities of water can result in a rapid deterioration of the GC system. In the on-column introduction technique this problem can be alleviated to some extent by using properly deactivated retention gaps [9]. Another option is the use of membrane extraction disks, which are more easy to dry due to their much lower bed volumes [10,11]. The loss of the more volatile pesticides during the drying step, however, remains difficult to control.

In this study a method is described for the determination of pyrethroids at the low ng/l level using an automated SPE method combined with large-volume GC injection.

## 2. Experimental

### 2.1. Chemicals

Fenpropathrin, a mixture of *cis*- and *trans*-permethrin, a mixture of *trans*-D-/*cis*-A-/*cis*-B-/*trans*-C-cypermethrin and deltamethrin with a purity of >99% were obtained from Dr. S. Ehrenstorfer (Promochem, Wesel, Germany). Stock solutions were prepared in *n*-hexane, methanol, acetone, acetonitrile (ACN) and toluene from Rathburn (Walkerburn, UK). Anhydrous sodium sulphate was obtained from Baker (Deventer, Netherlands) and was heated at 300°C for 16 h before use.

### 2.2. SPE equipment

Solid-phase extraction was performed with an ASPEC-XL from Gilson (Villiers-le-Bel, France) equipped with a 10-ml syringe and a 401 Dilutor, programmed by a Compaq 386/20s using Sample manager 718 software V3.1 from Gilson.

The Bakerbond cartridges used in the ASPEC system contained 100 mg $C_8$, $C_{18}$ or Phenyl material which were packed in a polypropylene cartridge with nylon frits. Furthermore 100 mg $C_{18}$ cartridges from Baker made of glass with PTFE frits were used. All SPE sorbents had a particle size of 40 $\mu$m.

### 2.3. SPE procedure

An 8-ml volume of methanol was added to 19 ml water sample. This mixture containing 30% of methanol was transferred to a 100-mg $C_{18}$

cartridge which was conditioned with, subsequently, 5.0 ml acetone, 5.0 ml methanol and 5.0 ml methanol–water (3:7, v/v). After sample loading, the cartridge was rinsed with 1 ml methanol–water (3:7, v/v). The SPE cartridge was dried by the ASPEC with twice 9 ml of air at a volumetric flow of 9 ml/min and 36 ml/min, respectively.

Elution of the pyrethroids was performed with 1500 μl toluene yielding an organic extract of 1300 μl (as a result of the dead volume of 200 μl of the SPE cartridge). In order to remove traces of water a mixing step was performed with anhydrous sodium sulphate (1.5 g), already present in the collection tube before sample elution. Fig. 1 shows a scheme of the entire SPE procedure, carried out using the ASPEC system.

An aliquot of 100 μl of the SPE eluate was transferred to the storage loop, which was mounted on a 10-port valve, and the contents of the loop were introduced onto the GC system via a home-built on-column interface.

### 2.4. Apparatus

The equipment used for the automated analysis of pyrethroids in water samples is depicted in Fig. 2.

The injection valve of the ASPEC system (HV-1) was used to fill the 100-μl storage loop mounted on the 10-port valve from Valco Instruments (Houston, TX, USA) (HV-2). The actual LC–GC interface consisted of a 0.5 m × 75 μm I.D. capillary fused-silica transfer line (T) from the 10-port valve which was led through the on-column injector of the Series 5300 Mega gas chromatograph from Carlo Erba Strumentazione (Milan, Italy). The contents of the injection loop were introduced onto the GC by means of a HPLC pump from ABI (Ramsey, NJ, USA). The valve-switching as well as the start of the oven programme was controlled by the ASPEC.

### 2.5. Large-volume injection

Solvent introduction was performed in a 10 m × 0.53 mm I.D. retention gap obtained from Gimex (Macherey and Nagel, Düren, Germany)

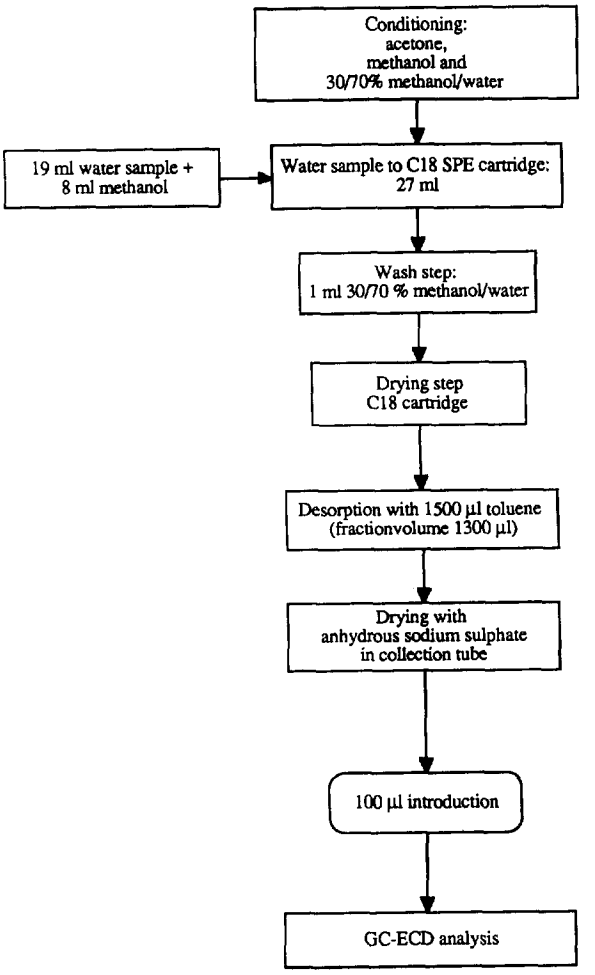


Fig. 1. Flow scheme of the automated procedure for the analysis of pyrethroids in water

which was coupled to a 3 m × 0.32 mm I.D. HP-1 retaining precolumn with a film thickness of 0.17 μm from Hewlett-Packard (Avondale, PA, USA). A three-way press-fit was used to connect the precolumn system to the early solvent vapour exit which consisted of 0.4 m × 0.32 mm I.D. uncoated fused-silica capillary from Gimex and the analytical 22 m × 0.32 mm I.D. HP-1 (film thickness 0.17 μm) GC column from Hewlett-Packard. The valve of the early solvent vapour exit was heated to a temperature of 200°C in order to avoid recondensation of the evaporated solvent. The oven temperature was programmed as follows: 108°C during 5 min, at

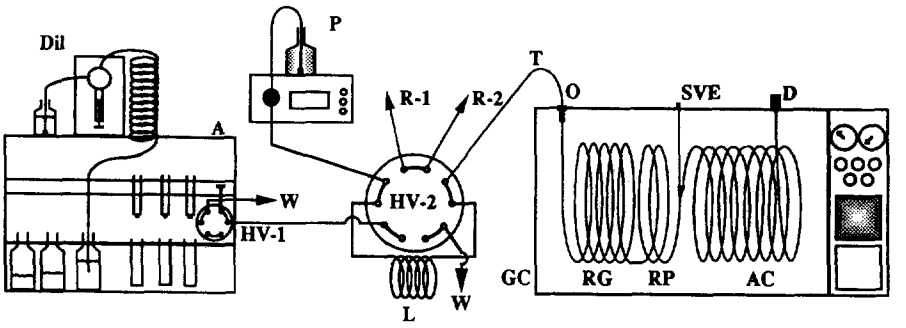


Fig. 2. Schematic representation of SPE–GC–ECD equipment used. (A) Autosampler with water samples and SPE cartridges; (Dil) dilutor; (P) pump; (HV-1 and HV-2) high-pressure 6- and 10-way valves; (L) storage loop; (R-1 and R-2) fused-silica restrictions; (GC) gas chromatograph; (T) fused-silica transfer line; (RG) retention gap; (RP) retaining precolumn; (AC) analytical column; (O) on-column interface; (SVE) solvent vapour exit; (D) ECD; (W) waste.

20°C/min to 220°C, at 2°C/min to 260°C, 10 min hold at 260°C. The helium inlet pressure was set to 100 kPa, The ECD temperature was set at 310°C, and argon–methane (95:5, v/v) was used as make-up gas at 150 kPa, which corresponds with a volumetric flow of 35 ml/min.

Non-automated analysis was performed with the same gas chromatograph equipped with an AS-550 on-column injector with large-volume option. A sample volume of 13 $\mu$l was injected in a 3 m × 0.53 mm I.D. retention gap which was connected to an SE-54 analytical column with a length of 25 m × 0.32 mm I.D. (film thickness 0.35 $\mu$m) from Gimex. The oven temperature was programmed as follows: 75°C during 5 min, at 20°C/min to 260°C, at 2°C/min to 290°C, 10 min hold at 290°C. The other conditions were essentially the same as in the automated procedure.

## 3. Results and discussion

### 3.1. SPE procedure

On the basis of earlier experience concerning the analysis of pyrethroids with GC–ECD, low to sub ng/l sensitivity can be obtained if the equivalent of approx. 2 ml of the original sample is injected in the gas chromatograph [4]. In order to facilitate automation one should not try to start with a larger sample volume than necessary. Besides, the enrichment of unnecessarily large sample volumes will also affect selectivity, since interferences will also be enriched. We therefore assumed that a sample volume of 20 ml would be sufficient even if some 90% of sample is discarded during the total analytical procedure.

Environmental analysis using ECD usually requires a clean-up step between enrichment and GC determination. In SPE techniques some clean-up can be established by the use of either washing steps, or the addition of a polarity modifier, e.g. methanol or acetonitrile, to the sample. Initial experiments showed that SPE cartridges filled with 100 mg $C_{18}$, $C_8$ or phenyl material, could retain only some 10% of the pyrethroids (fenpropathrin, a mixture of *cis*- and *trans*-permethrin, a mixture of *trans*-D-/*cis*-A-/*cis*-B-/*trans*-C-cypermethrin and deltamethrin) from 20 ml bidistilled water spiked at levels of about 2 $\mu$g/l. Analysis of the water that passed through the cartridge indicated breakthrough to be at least partly responsible for the loss of the analytes. With more complex (surface) water samples, recoveries were generally higher but never exceeded 60%.

Van Noort and Wondergem [12] and Brouwer et al. [13] reported a similar effect in the SPE of PAHs from water; they found improved extraction efficiency when an organic modifier was added to the water sample before solid-phase extraction. As pyrethroids are retained strongly on reversed-phase materials addition of a polarity modifier seems to be a viable way to go.

In order to evaluate the effect of modifier on

the extraction efficiency, different percentages of methanol were added to a spiked bidistilled water sample. The recovery percentages of the pyrethroids showed strong dependence on the modifier concentration. As can be seen from the data of Table 1, maximum recoveries were obtained at a methanol content of about 30%. Hence the addition of 8 ml of methanol to 19 ml of sample is an appropriate procedure, which will improve both the recovery and the selectivity of the sample enrichment procedure.

Washing of the cartridge was studied by flushing it with 1 ml methanol–water mixtures containing 10–50% of methanol. After LC analysis of the eluates, no pyrethroids were found in the eluates of the wash step using up to 30% methanol in bidistilled water; some breakthrough started to occur at a level of 35% methanol. A wash step with 1 ml of 30% methanol in water was therefore selected for all further work.

The cartridge was dried by dispensing air into it. An air volume of 18 ml was sufficient to remove the excess of methanol–water from the SPE column. With a subsequent third step of 9 ml air some loss of the analytes was observed.

### 3.2. SPE desorption

After the loading, washing and drying steps discussed above, the desorption volume to be used was determined by eluting the enriched SPE cartridge with *n*-hexane. GC–ECD analysis of subsequent 100-μl fractions showed a recovery of approx. 80% of the total amount of pyrethroids in the first three fractions after the dead volume of the cartridge, which was estimated to be approx. 200 μl. The remaining 20% of the pyrethroids were not recovered using *n*-hexane as an eluent. The experiment was repeated with toluene as eluent, because this solvent has stronger desorption capabilities. Using toluene the pyrethroids were eluted from the SPE cartridge within the first two 100 μl fractions after the dead volume. Hence, a desorption volume of 450 μl was chosen. Unfortunately the use of toluene in the final elution step also caused interfering peaks originating from the SPE cartridge to show up in GC–ECD. Therefore preconditioning of the cartridges with toluene was studied by rinsing the cartridges with 5 ml of toluene prior to the analytical procedure. Unfortunately, this step results in a drastic change in permeability of the cartridge for the subsequent conditioning steps with methanol and methanol–water. Therefore, acetone, which is more compatible with methanol–water mixtures, was tested as a solvent in the conditioning procedure of the SPE cartridge. This resulted in a cleaner final extract with less interfering peaks in the GC–ECD chromatogram.

Table 1
Recovery of pyrethroids on $C_{18}$ cartridges with various percentages methanol added to the water sample

| MeOH in water (%) | Recovery (%) | | |
|---|---|---|---|
| | Fenpropathrin | Deltamethrin | Permethrin |
| 0 | 15 | 12 | 18 |
| 2 | 40 | 33 | 36 |
| 4 | 25 | 20 | 16 |
| 8 | 20 | 18 | 19 |
| 16 | 39 | 40 | 48 |
| 32 | 93 | 95 | 93 |
| 50 | 20 | 9 | 10 |

### 3.3. Automated SPE–GC–ECD

In the automated procedure the injection valve of the ASPEC system was used as 3-way valve: to fill the storage loop of the 10-port valve in one position and to rinse the transfer port of the ASPEC in the other position. Air-drying of the cartridge does not guarantee a completely dry extract, droplets of the sample may remain in the cartridge in some instances. Therefore drying of the extract with anhydrous sodium sulphate, added to the collection tube was introduced. This step requires a minimum amount of solvent to be present in the collection tube in order to prevent the salt to be injected in the GC. Therefore, in our first approach 1000 μl of toluene was added to the collection tube after desorption of the cartridge.

An injection volume of 100–200 μl is generally convenient in large-volume introduction technol-

ogy. Higher volumes will easily cause interferences in the chromatogram due to impurities in the solvent, while lower volumes will adversely affect the sensitivity. Hence an injection volume of 120 μl, being 100 μl of sample and 20 μl of dead volume in the transfer tubing, seemed to be appropriate.

Toluene has a rather high boiling point, 110°C at atmospheric pressure, the corrected boiling point of toluene under the actual injection conditions was estimated to be 150°C at 150 kPa [14]. Hence large-volume injection by means of a loop-type interface is unfavourable due to losses of volatile analytes. The use of the loop-type interface will therefore lead to losses of components eluting below approx. 240°C.

No literature values are known for the evaporation rate of toluene. Usually the process of solvent evaporation is monitored by ignition of the solvent vapours leaving the solvent vapour exit [14]. However, with toluene, the ignition of the vapour results in the formation of black smoke. Solvent evaporation was therefore monitored by recondensation of the toluene on the surface of a polished stainless-steel wrench which was cooled to approx. 10°C. Solvent evaporation took 164 s for a sample fraction of 120 μl introduced in 90 s. That is, the evaporation rate of toluene was 44 μl/min.

GC injection was achieved by an HPLC pump at a volumetric flow of 80 μl toluene/min during 90 s, thus introducing a volume of 120 μl toluene. After transfer to the GC, the injection loop was flushed with 1.0 ml of acetone in order to remove polar contaminants, 1.0 ml toluene to remove the acetone and 0.5 ml of air to remove the excess of toluene and avoid memory effects during the injection of the next extract.

### 3.4. Performance data

In order to obtain reliable results, care should be taken in the preparation of calibration solutions and samples for recovery experiments because of the low solubility of pyrethroids in polar (organic) solvents. Both tap and surface water samples were spiked with a mixture of pyrethroids which consisted of fenpropathrin (17 ng/l), a mixture of *cis*- and *trans*-permethrin (54 and 81 ng/l, respectively), a mixture of *trans*-D-/*cis*-A-/*cis*-B-/*trans*-C-cypermethrin (13, 11, 9 and 16 ng/l, respectively) and deltamethrin (18 ng/l). Initial experiments showed rather low recoveries for deltamethrin though not for the other analytes. Therefore the desorption volume was increased from 450 μl to 1500 μl, which caused an enhanced recovery of deltamethrin. It also caused a slightly higher baseline, but no extra peaks were observed in the chromatogram. A further increase of the desorption volume was not considered because it will merely lead to unacceptable losses in sensitivity, due to dilution of the sample. Table 2 shows recovery and reproducibility data for both tap water and surface water. Recovery percentages for most of the pyrethroids analysed are acceptable considering the level at which they had to be determined; the same holds true for the R.S.D. data. The lower recovery for deltamethrin can possibly be explained by a strong sorption to particulate matter in the matrix, since experiments with standards and samples that were spiked after the addition of methanol showed significantly better recoveries. For this particular analyte liquid–liquid extraction may be a more appropriate sample pretreatment procedure than SPE. Obviously the technique of choice will depend on the underlying (eco)toxicological question.

In Fig. 3 a typical chromatogram is shown for the analysis of pyrethroids in tap water at the low ng/l level. Fig. 4 shows an example of the automated analysis of a surface water sample spiked with pyrethroids in the range 9–81 ng/l by means of automated SPE–GC–ECD. LODs for the pyrethroids in surface water are in the range of 1–8 ng/l (signal-to-noise ratio = 3). Comparison of Figs. 3 and 4 and the data of Table 2 indicate that even lower detection limits can be expected for drinking water.

Screening of pyrethroids at the level of the EU drinking water limit (0.1 μg/l) does not require the LODs given above. If such detection limits are required, one can either reduce the sample volume, or alternatively, perform the analysis manually using a more conventional GC injection technique. The extract obtained after SPE

Table 2
Recoveries and reproducibility of pyrethroids in spiked tap- and surface water using the procedure depicted in Fig.1 (range 9–81 ng/l)

| No. | Component | Mean recovery (%) ± R.S.D. (% of %) | |
|---|---|---|---|
| | | Tap water[a] | Surface water[b] |
| 1 | Fenpropthrin | 104 ± 4 | 104 ± 16 |
| 2 | *cis*-Permethrin | 76 ± 7 | 69 ± 14 |
| 3 | *trans*-Permethrin | 82 ± 5 | 86 ± 20 |
| 4 | *trans*-D-Cypermethrin | 88 ± 2 | 70 ± 33 |
| | *cis*-A-Cypermethrin | 75 ± 6 | 58 ± 39 |
| | *cis*-B-Cypermethrin | 88 ± 2 | 85 ± 32 |
| | *trans*-C-Cypermethrin | 96 ± 4 | 81 ± 31 |
| 5 | Deltamethrin | 53 ± 18 | 33 ± 29 |

[a] $n = 3$.
[b] $n = 5$.

can than be transferred to an autosampler vial and subsequently placed in the autosampler tray. Using GC–ECD analysis in combination with 13-$\mu$l on-column injection, the results shown in Table 3 were obtained.

The low recovery of deltamethrin is in line

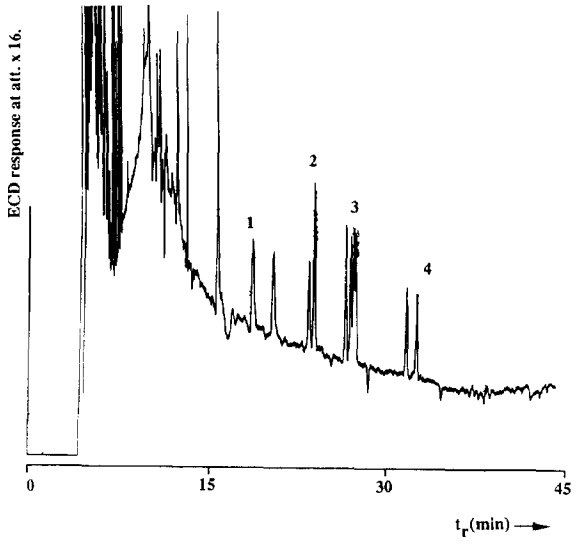


Fig. 3. Chromatogram obtained by automated SPE–GC–ECD of a tap water sample spiked with pyrethroids; range, 9–81 ng/l; sample size, 19 ml. Peaks: 1 = fenpropathrin (16.8 ng/l), 2 = mixture of *cis*- and *trans*-permethrin (53.5 and 80.9 ng/l), 3 = mixture of *trans*-D-/*cis*-A-/*cis*-B-/*trans*-C-cypermethrin (13.4, 10.9, 9.0 and 16.2 ng/l, respectively), and 4 = deltamethrin (18.2 ng/l).

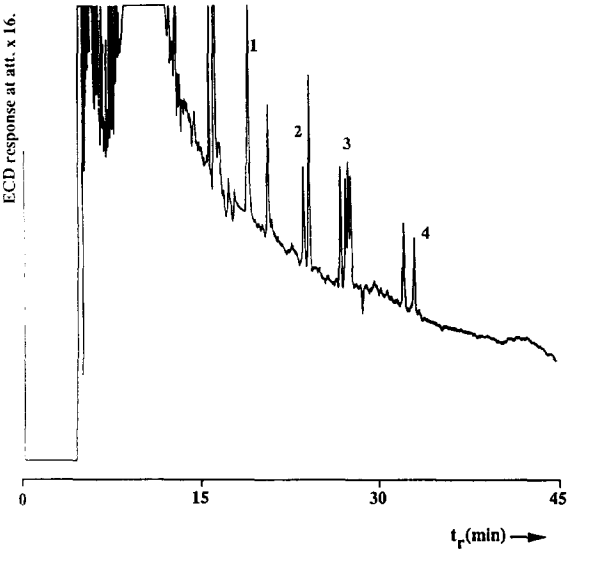


Fig. 4. Chromatogram obtained by automated SPE–GC–ECD of a surface water sample spiked with pyrethroids; range, 9–81 ng/l; sample size, 19 ml. Peaks: 1 = fenpropathrin (16.8 ng/l), 2 = mixture of *cis*- and *trans*-permethrin (53.5 and 80.9 ng/l), 3 = mixture of *trans*-D-/*cis*-A-/*cis*-B-/*trans*-C-cypermethrin (13.4, 10.9, 9.0 and 16.2 ng/l, respectively), and 4 = deltamethrin (18.2 ng/l).

Table 3
Recoveries and reproducibility of pyrethroids in spiked tap and surface water using the non-automated SPE–GC–ECD procedure (spike level 2 μg/l)

| No. | Component | Mean recovery (%) ±R.S.D. (% of %) | |
|---|---|---|---|
| | | Tap water[a] | Surface water[a] |
| 1 | Fenpropathrin | 96 ± 10 | 116 ± 10 |
| 2 | *cis*-Permethrin | 87 ± 8 | 97 ± 7 |
| 3 | *trans*-Permethrin | 90 ± 9 | 97 ± 6 |
| 4 | *trans*-D-Cypermethrin | 86 ± 6 | 73 ± 12 |
| | *cis*-A-Cypermethrin | 71 ± 9 | 55 ± 16 |
| | *cis*-B-Cypermethrin | 87 ± 8 | 79 ± 13 |
| | *trans*-C-Cypermethrin | 79 ± 13 | 65 ± 15 |
| 5 | Deltamethrin | 69 ± 18 | 58 ± 12 |

[a] $n = 8$.

with the findings in the automated procedure. Utilising this procedure detection limits of 50–100 ng/l are attainable.

## 4. Conclusion

Automated SPE can be combined with large-volume GC introduction techniques for the automated determination of pesticides in aqueous samples. For pyrethroids employing GC–ECD detection limits in the low ng/l range are attainable. Some clean-up can be achieved by adding a polarity modifier to the sample prior to trace-enrichment on a SPE cartridge. Considering the fact that fair chromatographic separations are usually achieved in isocratic reversed-phase LC with acetonitrile–water (70:30, v/v) as eluent, the pyrethroids investigated in this study can be classified as non-polar. From this retention behaviour one would expect efficient sorption of these compounds from aqueous samples on 100 mg $C_{18}$ cartridges. Surprisingly the addition of a polarity modifier to the sample leads to more efficient sample enrichment. Similar observations have recently been made by Wintersteiger et al. [15] and Brouwer et al. [16]. The seemingly anomalous behaviour of pyrethroids and other non polar compounds on $C_{18}$ cartridges will be a matter of future research.

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