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Element-selective detection of pesticides by gas chromatography–atomic emission detection and solid-phase microextraction

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Abstract

The analysis of samples contaminated by organic compounds, especially pesticides, is an important tool of environmental monitoring. A new isolation method has been developed for the determination of pesticides in environmental water samples using solid-phase microextraction (SPME). Thus, the extraction and preconcentration steps of sample preparation are focused in a single process step. For the determination of organophosphorus pesticides using SPME extraction and preconcentration steps a GC–atomic emission detection coupling system was used. This coupling technique is a very selective analytical tool. Element-characteristic chromatograms acquired by using different element emission lines can be obtained, enhancing the selectivity of the method in environmental monitoring, and they can be used to identify even unknown compounds in environmental samples. A fused-silica fiber coated with a polymer (polydimethylsiloxane) phase is used to extract organic compounds and transfer them into a GC injector for thermal desorption and analysis. Volatile pesticides can be efficiently isolated from aqueous environmental samples, as demonstrated for organophosphorus pesticides. This method shows a precision of 8–12% (R.S.D.), depending on the compound. Furthermore, it is capable of limits of detection in the ppb and sub-ppb range. The adsorption and desorption times to carry out the optimum equilibrium and thermodesorption conditions, have been optimized. Determination of pesticides in spiked river water samples with this technique is reported and a comparison of SPME to established extraction techniques, i.e. solid-phase extraction is also carried out. The results demonstrate the suitability of the SPME approach for analysis of these polar compounds.

1. Introduction

The aim of the present work is to show the sensitivity, element-characteristic and -selective detection of compounds in environmental water samples using GC–atomic emission detection (AED) coupling. Pesticides, which are amenable to GC, can be detected using a wide spectrum of GC detection methods: i.e. flame ionization detection (FID), nitrogen–phosphorus detection (NPD), or mass spectrometry (MS). All these detection methods show extreme differences concerning their response selectivity. The element-specific AED shows a tunable detection specificity and is therefore a useful tool for elemental characterization of compounds [1].

The analysis of samples contaminated by organic compounds, especially pesticides, is an

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important tool of environmental monitoring [2–5]. A new isolation method has been developed for the determination of pesticides in environmental water samples using solid-phase microextraction (SPME). Thus, the extraction and preconcentration steps of sample preparation are focused in a single process step. A fused-silica fiber coated with a polymer [polydimethylsiloxane (PDMS)] phase is used to extract organic compounds from water and transfer them into a GC injector for thermal desorption and analysis. Analytes are extracted until the partition equilibrium has been reached. After this step the fiber is directly transferred to the heated GC injector, where the adsorbed organic substances are thermally desorbed, and subsequently separated and quantified. This technique has been previously applied to substituted benzenes [6] and polar compounds, i.e. phenols [7], in water. The sample preparation step does not require the use of solvent.

The elemental characterization of pesticides in environmental water samples by solid-phase extraction (SPE) was compared with SPME. For both techniques the determination of the pesticides by GC–AED is developed, which leads to a very high selectivity of the method. Element-characteristic chromatograms are obtained from this detection technique, which show only minor matrix interferences. The isolation using SPME was first applied to the analysis of benzene, toluene, ethyl benzene and xylenes in groundwater [6]. In the new isolation technique, SPME, a fused-silica fiber was used, coated with PDMS for adsorption of the analytes (pesticides and here especially organophosphorus pesticides) from the aqueous sample. Determination of pesticides using this screening method is possible in the low ppb (w/w) range.

2. Experimental

2.1. SPME procedure

A fused-silica fiber coated with 100 μm PDMS phase was used. Vials of 5 ml were filled with 3 ml of sample for the adsorption process of the compounds from the aqueous sample using SPME. An optimized adsorption time (20 min) has been used in this study, unless stated otherwise. Thermal desorption of the pesticides has been carried out for 3 min. After this period, the liner purge of the GC injector has been closed, and the liner was purged by a helium flow. During the following 5–8 min the fiber was still kept in the liner. Possible memory effects of compounds, which may persist in the fiber for longer than 3 min under temperatures of 205°C, can be totally reduced from the fiber after such a period of time. However, no further regeneration mode for the fiber assembly was considered necessary. Several tests of a still blank value after this period have been completely negative. There is no necessity for further purification and concentration ("clean-up") before extraction and determination. GC detection of all SPME experiments was carried out using temperature program B, which is described below. See Fig. 1 and Table 1.

2.2. SPE procedure

A 1-l water sample was used for SPE. Cartridges (6 ml) were filled with 2 g of C_{18} adsorbent material (Amchro, Sulzbach-Taunus, Germany). These cartridges were first conditioned before extraction using 5 ml acetone, 5 ml methanol and 5 ml Milli-Q water. The sample was passed through the C_{18} material under vacuum at a flow of 9–10 ml/min. After drying the adsorbent, using a gentle stream of nitrogen for approximately 20 min, elution of the analytes from the SPE material was achieved using five 1-ml volumes of methanol. The combined eluent was concentrated in volume to 1 ml using a gentle stream of nitrogen. A 1-μl volume was injected for GC analysis using the temperature program A, which is described below.

2.3. Instruments

SPE

A SPE system from Supelco (Bellefonte, PA, USA) in conjunction with a supplementary dry-

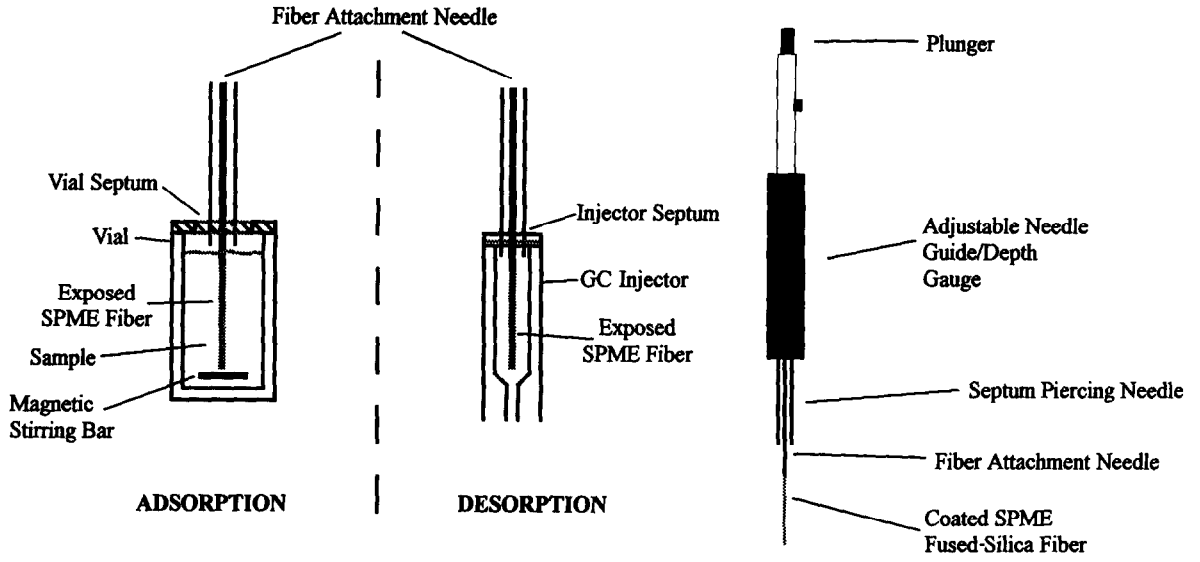

Fig. 1. Schematic description of the SPME unit and adsorption and desorption techniques.

ing unit (Visiprep and Visidry) was used in this study for the comparison experiments.

SPME

A SPME system from Supelco equipped with a fused-silica fiber coated with 100 μm PDMS phase was used for trapping the analytes from the aqueous matrix.

GC–AED

GC–AED investigations were carried out using an Hewlett-Packard atomic emission detector 5921 A and a 5890, series II, gas chromatograph. All injections were performed manually. Helium was of quality better 6.0 (both for GC separation and AED plasma) using a helium gas purification unit (VICI Valco, TX, USA). In general, the emission lines of the following elements were monitored: nitrogen (N 174.200 nm), phosphorus (P 178.079 nm), sulfur (S 181.379 nm), carbon (C 193.032 nm and C 495.724 nm), chlorine (Cl 480.192 nm), hydrogen (H 486,133 nm), bromine (Br 478.578 nm) and oxygen (O 777.302 nm). A DB-5.625 column (J & W Scientific, Fisons Instruments, Folsom, CA, USA), 30 m × 0.32 mm I.D., film thickness 0.25 μm, helium as carrier gas and a split/splitless injector were used for all investigations with the following two temperature programs: (A) 60°C for 1 min, 60–150°C at 15°C/min, 150°C for 1 min, 150–201°C at 3°C/min, 201°C for 1 min and (B) 50°C for 4 min, 50–180°C at 30°C/min, 180°C for 1 min, 180–202°C at 3°C/min, 202°C for 5 min. In general, 1 μl was injected into the GC. See Tables 2 and 3.

Table 1
Optimized conditions for SPME and analysis of organophosphorus pesticides using GC–AED

SPME Fiber	100 μm PDMS
Sample volume	3-ml water sample in 5-ml vial
Extraction temperature	Room temperature (21°C)
Extraction times	20 min
Desorption temperature	205°C
Desorption time	3 min
Injection port	split/splitless (purge delay for 3 min)
Detector (AED)	Atomic emission detector HP 5921 A
Solvent vent time (AED)	0.8–4.8 min

2.4. Materials

All pesticide standards used in this study were purchased from Promochem (Wesel, Germany)

Table 2
GC–AED operating parameters (see also Table 3)

Injector parameters	
Injection volume	1 μl or thermal desorption of the SPME fiber
Injection temperature	205°C
Injection port	split/splitless
GC parameters	
Column	DB 5.625 (30 m × 0.31 mm I.D., film thickness 0.25 μm)
Column head pressure	100 kPa He
Oven program (for SPME)	50°C (4 min hold) 50–180°C with 30°C/min 180°C (1 min hold) 180–202°C with 3°C/min 202°C (5 min hold)
Interface parameters	
Transfer line	DB 5.625 column
Transfer line temperature	250°C
Scavenger gases	
Hydrogen: 99.999% (purity)	$5 \cdot 10^5$ Pa
Oxygen: 99.995%	$2 \cdot 10^5$ Pa
Nitrogen–methane: 99.99%–99.5%	$5 \cdot 10^5$ Pa
AED parameters:	
Spectrometer purge flow	2.5 l/min nitrogen
Cavity temperature	280°C
Helium make-up flow	60 ml/min
Helium supply pressure	30 p.s.i. (207 kPa)
Cavity pressure	1.5 p.s.i. (10.35 kPa)
Column-detector coupling	Column to cavity

and Riedel-de Haën (Seelze-Hannover, Germany). They were of purity >98% and used as received. Methanol (Pestanal quality) and acetone (Pestanal quality) were also from Riedel-de Haën. Water was obtained from a Milli-Q water-purification system (Millipore, Bedford, MA, USA).

3. Results and discussion

Environmental water samples often show two types of problems during the preconcentration and extraction; first a matrix interference from non-target compounds, and second a strong adsorption effect of the matrix. Therefore, a selective preconcentration and extraction step is necessary for a specific determination in environmental analysis. SPME offers an elegant sample preparation step, which is more efficient than flushing 1-l samples through a cartridge filled with adsorbent material, i.e. 2 g C_{18} material. The adsorption equilibrium of most analytes is almost reached after 15–20 min, which is demonstrated in Fig. 2.

Linear calibration curves can be obtained for all pesticides using SPME in a concentration range of 2–200 ng/ml. This linear relationship of these compounds is shown in Table 4. Correlation coefficients are better than $r = 0.996$ for all investigated compounds. The repeatability of the injections is in the range of 8–12% (R.S.D.). For

Table 3
GC–AED operation parameters: wavelengths and plasma conditions (see also Table 2)

Measurement set	Elements	λ (nm)	Scavenger gas conditions	Filter
1	C 496	495.724	O_2	No
1	H 486	486.133	O_2	No
1	Br 478	478.578	O_2	No
1	Cl 479	480.192	O_2	No
2	N 174	174.200	O_2,H_2	No
2	S 181	181.379	O_2,H_2	No
2	C 193	193.032	O_2,H_2	No
3	O 777	777.302	N_2–CH_4 (90:10)	Vis
4	P 178	178.079	H_2, high flow	No

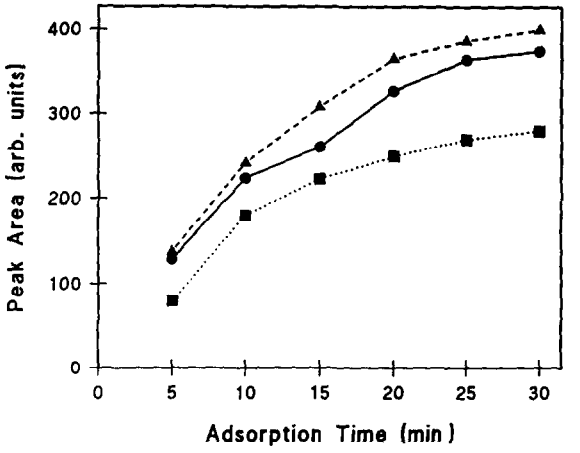

Fig. 2. The effect of varying adsorption times for SPME; optimized conditions are shown for three investigated organophosphorus compounds; equal amounts are injected; figure displays the peak area of sulfur at 181 nm versus the investigated adsorption time. ● = Diazinon; ▲ = parathion-methyl; ■ = parathion-ethyl.

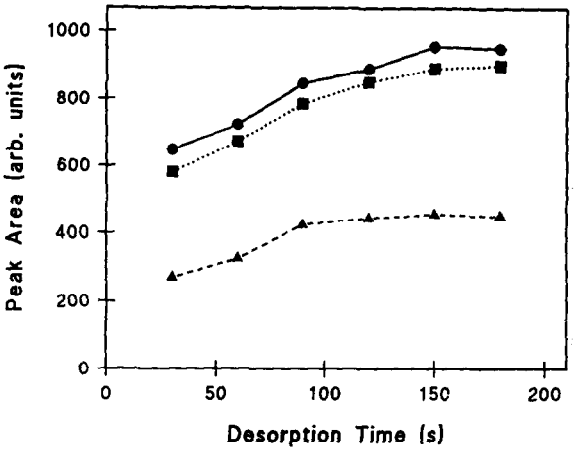

Fig. 3. The effect of varying desorption times for SPME; optimized conditions are shown for three investigated organophosphorus compounds; equal amounts are injected; figure displays the peak area of sulfur at 181 nm versus the investigated desorption time. Symbols as in Fig. 2.

the desorption of the analytes the time of the fiber exposed into the GC injector should be above 2 min, which is displayed in Fig. 3. Typical limits of detection (LODs) for all investigated compounds are between 0.5 and 5 μg/l using the emission lines of carbon (C 193 nm) and sulfur (S 181 nm), which are summarized in Table 5.

Compared to classical GC detection methods, the sensitivity is considerable poorer with AED, but AED is nevertheless much more selective. There may be interference in the emission lines of an element by an emission line of another element. Such interference can be revealed using the wavelength snapshot technique of AED. Using this three-dimensional technique an element is not characterized by only one but by all emission lines, which further enhances the selectivity. A typical example of this identification method is given in Fig. 5. The three-dimensional snapshot of bromophos-ethyl at retention time 18.46 min in a spiked surface water sample of the River Leine shows the typical three emission lines of chlorine (so-called "chlorine emission triplet"). If one of them is missing in the plot,

Table 4

Coefficients of correlation r for the calibration of six organophosphorus pesticides using SPME in Milli-Q water samples at a range of 2–200 ng/ml

Peak No.	Compound	a[a]	b[a]	r
1	Ethoprophos	−79.94	22.06	0.9998
2	Diazinon	−100.23	21.76	0.9997
3	Parathion-methyl	−14.57	10.77	0.99997
4	Parathion-ethyl	−150.74	25.78	0.9998
5	Bromophos-methyl	−170.19	24.59	0.9998
6	Bromophos-ethyl	0.29	12.43	0.9998

[a] Linear regression of type: $y = bx + a$.

Table 5
Peak assignment and limits of detection[a] of six organophosphorus pesticides using SPME and an adsorption time of 20 min; limits of detection are shown for all pesticides using the emission lines of carbon at 193 nm and sulfur at 181 nm

Peak No.	Compound	Molecular formula	Retention time (min)	Limit of detection[a], C 193 nm (μg/l water)	Limit of detection[a], S 181 nm (μg/l water)
1	Ethoprophos	$C_8H_{19}O_2PS_2$	10.98	0.5	1
2	Diazinon	$C_{12}H_{21}N_2O_3PS$	12.73	1	3
3	Parathion-methyl	$C_8H_{10}NO_5PS$	14.32	0.5	5
4	Parathion-ethyl	$C_{10}H_{14}NO_5PS$	16.06	1	3
5	Bromophos-methyl	$C_8H_8BrCl_2O_3PS$	16.58	0.5	2
6	Bromophos-ethyl	$C_{10}H_{12}BrCl_2O_3PS$	18.46	0.5	5

[a] Signal-to-noise ratio = 3.

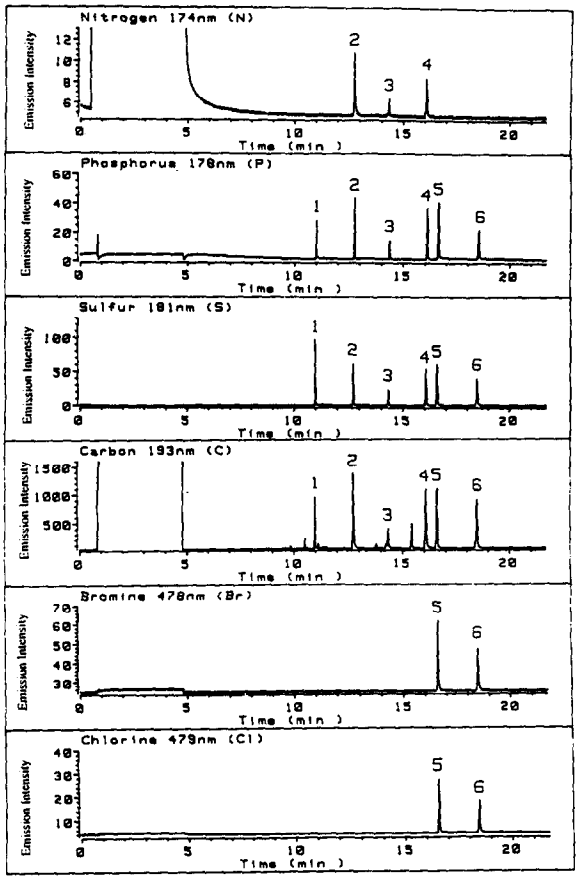

Fig. 4. Elemental characterization of a 60 ppb standard solution containing six organophosphorus pesticides [ethoprophos (1), diazinon (2), parathion-methyl (3), parathion-ethyl (4), bromophos-methyl (5) and bromophos-ethyl (6)] using SPME with a 100 μm PDMS coating; GC–AED response is shown for six different element emission lines (equal amounts of the pesticides are injected).

one can conclude that chlorine will be also missing in this compound. In the present case (see Fig. 5), chlorine could be identified, which enhances the presence of the pesticide bromophos-ethyl.

Surface water samples were taken from two rivers in Lower Saxony (Germany), the River Leine in Hannover and the River Weser in Holzminden. Suspended particles were filtered off using silanized glass wool. The samples were extracted using SPE and SPME. The chromatograms of the spiked River Leine sample (see Fig. 6), where extraction was done by the SPME technique, show less interferences of the matrix, especially of the emission line of carbon at 193 nm, as compared to the analogue determination of a spiked water sample from the River Weser (see Fig. 7 and Table 6) using the SPE technique. Thus, a chromatogram monitoring the carbon emission lines is even less selective than a chromatogram obtained by FID, as almost every matrix compound contains carbon and will thus give a response for the carbon-selective detection mode. Even more selectivity is gained if the sulfur emission line at 181 nm is monitored. From these observations, one can conclude that the SPME fiber leads to a more selective extraction of pesticides than the SPE adsorption material. The total number of non-target compound peaks, observed in a chromatogram taken in a non-specific detection mode is higher in SPE preconcentration than in SPME.

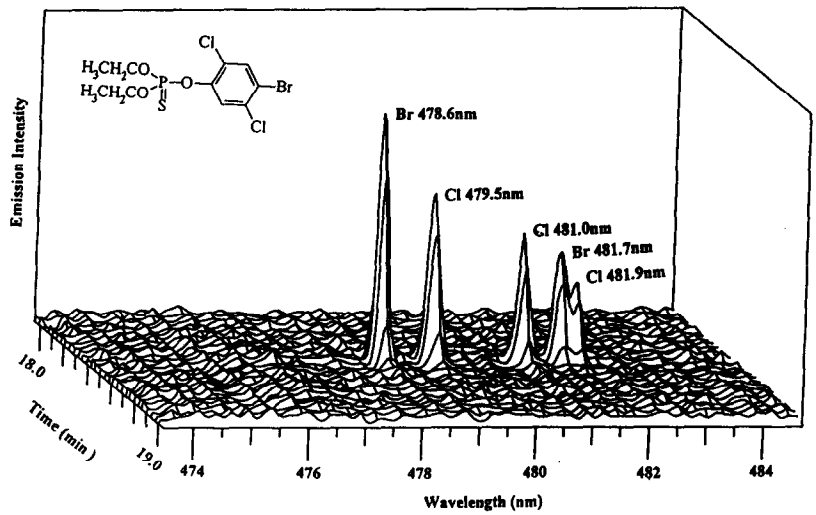

Fig. 5. Three-dimensional snapshot from the GC analysis of a spiked (60 ppb) environmental water solution (River Leine in Hannover) containing six organophosphorus pesticides using SPME (same mixture of pesticides as shown in Fig. 4); typical chlorine and bromine emission lines can be identified for the compound bromophos-ethyl at retention time 18.46 min.

4. Conclusions

The element-specific GC–AED allows a tunable specificity and is therefore a useful tool for element characterization of compounds. For instance, the presence of chlorine in a compound can be readily detected with AED in its normal operation mode (i.e. chlorine emission line Cl 479 nm) and confirmed by the wavelength snapshot technique (a small part of the emission spectra of about 50 nm; see three-dimensional snapshot of bromophos-ethyl in Fig. 5). Thus, an unknown compound in an environmental sample can be characterized as a substance which either contains the element chlorine or not. Identification of pesticides in environmental samples can be verified not only by one but by all characteristic element emission lines. The exclusion of

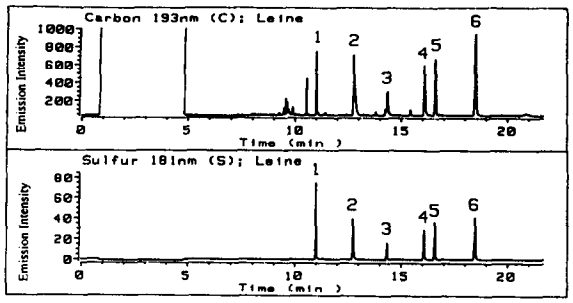

Fig. 6. Chromatogram of an environmental water sample from the River Leine in Hannover (Lower Saxony, Germany) using SPME; AED response of carbon at 193 nm and of sulfur at 181 nm is shown from obtained matrix compounds and six pesticides; sample was spiked (60 ppb) with six organophosphorus pesticides [ethoprophos (1), diazinon (2), parathion-methyl (3), parathion-ethyl (4), bromophos-methyl (5) and bromophos-ethyl (6)].

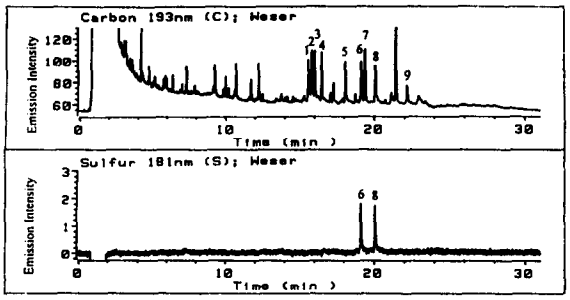

Fig. 7. Analysis of a spiked (1 ppb) environmental water sample from the River Weser in Holzminden (Lower Saxony, Germany) using SPE; AED response of carbon at 193 nm and of sulfur at 181 nm is that obtained from matrix compounds and nine pesticides [simazine (1), atrazine (2), propazine (3), terbuthylazine (4), sebuthylazine (5), metribuzin (6), vinclozolin (7), ametryn (8) and cyanazine (9)]; SPE sample preparation (C_{18} adsorbent).

Table 6
Analysis of a spiked (1 ppb) environmental water sample[a] from the River Weser in Holzminden[b] using SPE with C_{18} adsorbent material; limits of detection[c] are shown for all pesticides using the emission lines of carbon at 193 nm and sulfur at 181 nm

Peak No.	Compound	Molecular formula	Retention time (min)	Limit of detection[c], C 193 nm (pg)	Limit of detection[c], S 181 nm (pg)
1	Simazine	$C_7H_{12}ClN_5$	15.51	37	-
2	Atrazine	$C_8H_{14}ClN_5$	15.74	37	-
3	Propazine	$C_9H_{16}ClN_5$	15.94	32	-
4	Terbuthylazine	$C_9H_{16}ClN_5$	16.42	30	-
5	Sebuthylazine	$C_9H_{16}ClN_5$	18.06	34	-
6	Metribuzin	$C_8H_{14}N_4OS$	19.13	33	223
7	Vinclozolin	$C_{12}H_9Cl_2NO_3$	19.38	35	-
8	Ametryn	$C_9H_{17}N_5S$	20.07	48	300
9	Cyanazine	$C_9H_{13}ClN_6$	22.21	50	-

[a] Suspended particles of the sample are filtered off using silanised glass wool.
[b] River Weser in Holzminden (district of Lower Saxony, Germany), sampling date 9 May 1993.
[c] Limit of detection of the instrument; signal-to-noise ratio = 3.

spectral interferences is possible by observing all the characteristic element emission lines, i.e. sulfur (S 181.7 nm, S 182.0 nm and S 182.6 nm) or chlorine (Cl 479.5 nm, Cl 481.0 nm and Cl 481.9 nm). The tuning of selectivity using AED is limited due to the minimum detectable amount of a compound at different element emission lines (see Fig. 4). Environmental water samples show a wide range of disturbing matrix interferences from non-target pollutants despite some selective sample preparation steps. In these cases, additional selectivity is gained from the element-selective detection mode of GC–AED. The monitoring of sulfur at 181 nm allows a specific AED analysis of all investigated organophosphorus pesticides (see Fig. 8). The sulfur emission line was monitored, because it is much more sensitive than the phosphorus emission line, which shows always a very high specificity for these compounds. Furthermore, all matrix compounds, which interfere in the detection of carbon at 191 nm in some cases, could be

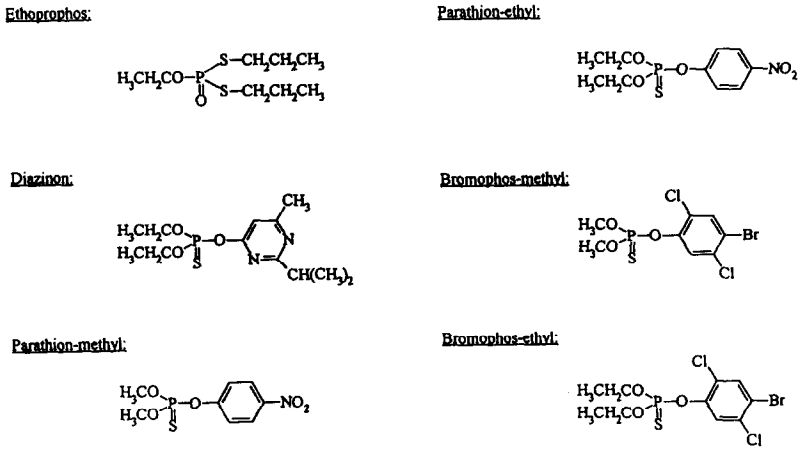

Fig. 8. Molecular structures of all investigated organophosphorus pesticides.

eliminated. In the analysis of real samples, it is suggested that the influence of non-target compounds might have been the major effect on the adsorbent material. So selectivity is most frequently gained from a detection system with a high specificity.

The selectivity of an analysis method which employs GC can be substantially enhanced when using element-specific detection such as AED, although AED is substantially less sensitive than conventional GC detectors. A MS detector would be even more specific than an AED, if pesticides have to be identified which are in the MS library. However, for unknown compounds (such as metabolites) and samples, the information gained from AED may even be superior to that from MS. Furthermore, typical element emission lines can be monitored using AED for verification of unknown compounds and for excluding interferences in the chromatogram [8,9]. Non-target substances can be separated into different compound classes, i.e. organochlorine compounds, using element-specific detection.

SPE is, in general, a useful determination technique of pesticides from aqueous matrix, where 1-l water sample spiked with 1 μg/l of each pesticide was used for extraction, as shown in Fig. 7. This leads to an enrichment factor of about 1000, if the final sample volume is 1 ml. If we compare the total amount of sample, which is necessary for the extraction and determination, SPE needs liter amounts and SPME only a few ml volume of the sample. Much more important for sample preparation steps is the time spent in using the different techniques. SPME is, however, very fast (20 min are needed for the total sample preparation up to the GC analysis step) compared to SPE, which needs about 2.5–3 h before the GC analysis can be done.

SPME is a simple, inexpensive, rapid and solvent-free sample preparation technique. Volatile pesticides can be efficiently isolated from aqueous environmental samples. This method shows a precision of 8–12% (R.S.D.), depending on the compound. Furthermore, this technique is capable of LODs in the ppb and sub-ppb range. Typical LODs for all investigated compounds are between 0.5 and 3 μg/l using AED. The adsorption and desorption times have been optimized. Typical saturation effects concerning the adsorption maximum can be observed at 15–20 min adsorption times for most pesticides. Determination of these pesticides in environmental water matrices, and in spiked river water has been shown. These samples can be detected with a high selectivity, which is gained from AED. Elements, which are only part of the target compounds and an even smaller part of non-target substances can be easily detected by their typical emission lines in these matrices and can be identified by them. The results demonstrate the suitability of the SPME approach to analysis of these polar compounds. Further investigations concerning the adsorption of different compound classes to the SPME fiber will be described by us in the future.

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