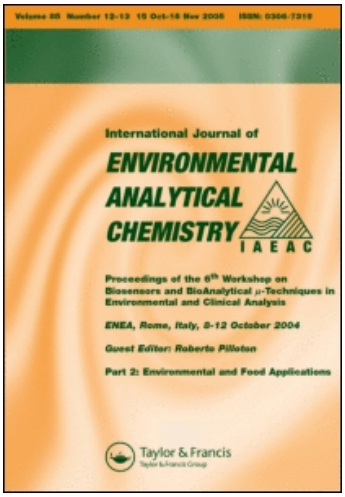

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Analysis of Polar Thermally Labile Pesticides using Different Solid-Phase Extraction (SPE) Materials with GC and HPLC Techniques

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To cite this Article Eisert, R. , Levsen, K. and Wüsch, G.(1995) 'Analysis of Polar Thermally Labile Pesticides using Different Solid-Phase Extraction (SPE) Materials with GC and HPLC Techniques', International Journal of Environmental Analytical Chemistry, 58: 1, 103 — 120
To link to this Article: DOI: 10.1080/03067319508033117
URL: http://dx.doi.org/10.1080/03067319508033117

Intern. J. Environ. Anal. Chem., Vol. 58, pp. 103-120
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ANALYSIS OF POLAR THERMALLY LABILE PESTICIDES USING DIFFERENT SOLID-PHASE EXTRACTION (SPE) MATERIALS WITH GC AND HPLC TECHNIQUES

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(Received, 10 October 1993; in final form, 12 December 1993)

In the present study, an efficient method for extraction, separation and determination of a limited number (30) of polar pesticides in aqueous matrices has been developed. Pesticides were extracted with high recoveries (usually >85%) from 1 L water samples, using the solid-phase extraction (SPE) technique. Affinities to different SPE materials (C-18 and XAD resins) have been studied for all pesticides. Special attention has been paid to the following 5 pesticides (which have classified by the EC as compounds which are particularly difficult to analyse): benazolin, bromofenoxim, ethofumesate, fenamiphos and phenmedipham. Thermally labile compounds have been determined with high pressure liquid chromatography (HPLC) and UV detection in comparison to TSP-LC-MS. Absolute limits of detection (LODs) for the HPLC technique are usually below 1 ng at 220 nm. Thermospray LC-MS determination shows usually limits of detection of 1–10 ng (SCAN) and 60–800 pg (SIM). All pesticides, which are amenable to GC have been detected in a comparative study with the following detectors: flame ionization detector (FID), nitrogen-phosphorus detector (NPD), electron capture detector (ECD) and atomic emission detector (AED). Element-specific detection of various functional groups of these pesticides has been achieved using GC-AED. Thus, while the FID has the lowest specificity, the AED is the most specific detector. LODs are usually <300 pg (FID < 20 pg, NPD < 1 pg, ECD < 1 pg, AED < 300 pg). Spiked river water samples (from the River Leine and River Weser in Lower Saxony, Germany) have been used to test the employed method. With the spiked surface water samples recoveries were usually >80%.

KEY WORDS: Pesticides, water analysis, solid-phase extraction (SPE), GC-AED, thermospray LC-MS, atomic emission detector.

INTRODUCTION

Pesticides are widely used in agriculture to protect plants from unwanted pests, e.g. rodents, locusts, weeds. In the past, many pesticides used had a low water solubility. Modern pesticides are more polar and thus often thermally labile. As a result of their solubility in water, they represent a greater risk for the pollution of ground and surface water.[1,2] The determination of pesticides in aqueous samples has found increasing interest, since the EC drinking water guideline demands analytic methods, which allow the determination of 0.1 μg/L for an individual compound and 0.5 μg/L for the total amount of pesticides, including the toxic metabolites.[3]

However, for many pesticides mentioned in the "Water Pollution Research Report" of the EC, there are are still no satisfactory methods for their determination in aqueous matrices at trace levels.[1] Thus, the emphasis of this study is on the development of methods for the compounds which are difficult to analyze, i.e. benazolin, bromofenoxim, ethofumesate, fenamiphos and phenmedipham.[1] Pesticides which are amenable to GC have been mainly analyzed by gas chromatography coupled with a variety of selective detectors: i.e., FID, NPD, ECD, and AED. For the extraction of pesticides, two SPE materials have been compared with respect to their recoveries. C-18 adsorbent material has been used previously for the extraction of pesticides from water samples by many authors.[4,5,6]

EXPERIMENTAL SECTION

SPE procedure

Solid-phase extraction (SPE) was normally used with 2 g of adsorbent filled in 6 ml cartridges, where the SPE apparatus used allows the extraction of up to 12 cartridges in parallel. These cartridges were first conditioned before extraction using 5 mL acetone, 5 mL methanol and 5 mL Milli-Q water. Then, 1 L water sample was extracted at a flow of 9–10 mL/min. After a drying step using a gentle stream of nitrogen for approximately half an hour, elution of the analytes from the SPE material was achieved with five times 1 mL methanol collected in a sample vial. This stepwise elution is more effective than using 5 mL methanol in a single step. For GC analysis, the combined eluent was concentrated in volume to 1 mL using a gentle stream of nitrogen, and for HPLC analysis to 0.5 mL. To this final sample volume, a chromatographic internal standard, 1-chloro-2,4-dinitrobenzene (for GC and HPLC) or 2,2′-dinitrobiphenyl (for GC), was added, where adequate; HPLC extracts were added up to 1 mL with water. Two different types of adsorbent material for SPE were used in this study: C-18 (Amchro®, Sulzbach-Taunus, Germany) and a styrene-divinylbenzene polymer (envi™-chrom P, Supelco Inc., Bellefonte, USA).

Instruments

SPE A solid-phase extraction system from Supelco in conjunction with a supplementary drying unit (Visiprep and Visidry) was used in this study.

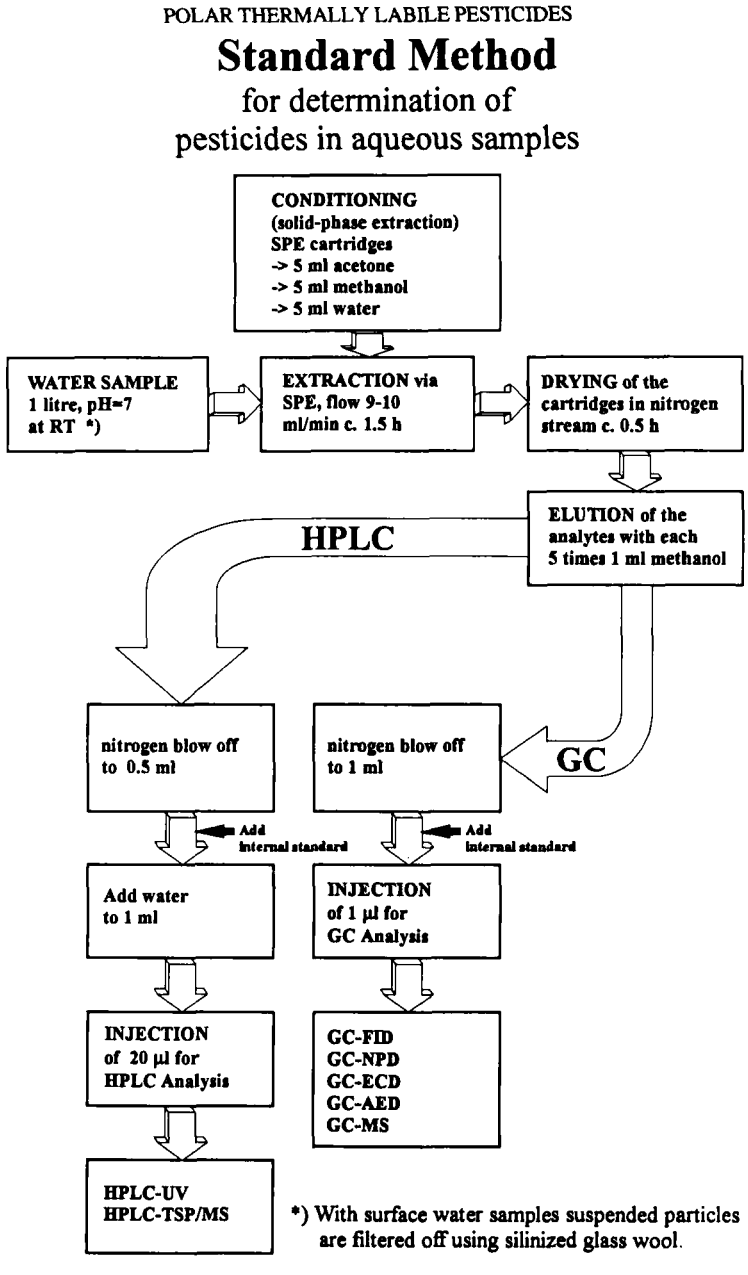

Figure 1 Standard method for extraction and determination of pesticides from aqueous matrices, used and developed in this study

GC Gas chromatographic investigations were carried out using two instruments from Hewlett Packard (Avondale, USA) type 5890, series II, equipped with FID, NPD and with ECD. For GC-AED measurement the Hewlett Packard atomic emission detector 5921 A, an

5890, series II, gas chromatograph and a GC/SFC injector 7673, were used. Helium supply was only of quality 5.0 (both for GC separation and AED plasma). For lower limits of detection (LOD) a helium gas purification up to a better quality of 6.0 should be achieved. The emission lines of the following eight elements were monitored: nitrogen (N 174.200 nm), phosphorus (P 178.079 nm), sulfur (S 181.379 nm), chlorine (Cl 480.192 nm), hydrogen (H 486,133 nm), carbon (C 495.724 nm), fluorine (F 690.466 nm) and oxygen (0 777.302 nm). A DB 5.625 column (J&W Scientific, Fisons Instruments, Folsom, CA, USA), 30 m, 0.32 mm i.d., 0.25 μm d_f, helium as carrier gas and a split/splitless injector were used for all investigations with the following temperature program: 60°C for 1 minute, 60–150°C at 15°C/min, 150°C for 1 minute, 150–201°C at 3°C/min, 201°C for 1 minute. In general, 1 μL was injected into the GC.

HPLC For HPLC investigations, an instrument from Varian (Palo Alto, CA, USA), model 5000 gradient liquid chromatograph, was employed, using a Waters photodiode-array (PDA) detector type 990. For pesticide analysis, an RP-select B LiChrospher® 60 (Merck, Darmstadt, Germany) 4 × 125 mm, 3 μm particle size, was used in this work. Two gradient programmes were developed: C_1 for typical pesticides and C_2 for very polar pesticides. Pesticides were eluted using a linear gradient elution or isocratic steps, with methanol/water as mobile phase. For C_1 the solvent composition was linearly programmed from 25% to 90% methanol in about 40 minutes. Polar pesticides (C_2) were separated using the following solvent gradient: 0–5 minutes 100% water, 5–40 minutes 0–90% methanol.

Samples were introduced via a 20 μL sample loop from Rheodyne (Cotati, CA, USA), model 7125.

TSP-LC-MS The thermospray interface (Vestec, Houston, TX, USA) was used coupled on a Finnigan MAT (San José, CA, USA) model 4500 mass spectrometer. A Shimadzu (Duisburg, Germany) LC-9A pump was installed for the postcolumn addition of a 175 mM ammonium acetate solution and connected with a low-dead-volume tee (Valco, Houston, TX, USA). A flow rate of 1.0 mL/min in the TSP vaporizer was used for all measurements, 0.6 mL/min was maintained through the column and 0.4 mL/min of ammonium acetate solution was added postcolumn. The typical thermospray interface operation conditions were as follows: vaporizer control temperature ≈140°C; vaporizer temperature 195–215°C; vaporizer tip temperature 270°C; source temperature ≈250°C; source jet temperature ≈240°C; and exit line pressure 3–4 Torr (1 Torr = 133,322 Pa). The exit line pressure depends on the composition of the mobile phase, which changes during the gradient. The mass spectrometer was operated in the positive ion mode (PI).

Materials All pesticide standards used in this study were purchased from Promochem (Wesel, Germany) and Riedel-de-Haën (Seelze-Hannover, Germany). They were of purity >98% and used as received. Methanol (CHROMASOLV, HPLC grade) and acetone (PESTANAL quality) were also from Riedel-de-Haën. Water was obtained from a Milli-Q-Water purification system (Millipore, Bredford, MA, USA). The solvents were passed through a 0.45 μm filter (Sartorius, Göttingen, Germany) before use. Dichloromethane was from Rathburn (Walkerburn, Scotland) and sodium chloride (98% quality) from Aldrich

(Milwaukee, USA). Ammonium acetate (p.a) was obtained from Merck (Darmstadt, Germany).

RESULTS AND DISCUSSION

Solid-phase extraction (SPE)

First a general analysis scheme for the determination of pesticides from aqueous matrix was developed, as summarized in Figure 1. 1 L water spiked with 2 µg/L of each pesticide were used for extraction. This leads to an enrichment factor of about 1000, if the final sample volume is 1 mL.

Table 1 Recoveries (REC in %) and coefficient of variation $\pm CV_{rel.}$ (%) for the extraction of 30 pesticides fom water[a] (1 L) with two different solid extraction materials[b]

No.	*Compound*	*C-18 REC (%)*	*C-18* $\pm CV_{rel}$ *(%)*	*chrom-p REC (%)*	*chrom-p* $\pm CV_{rel}$ *(%)*
1	Alachlor	94	6	75	7
2	Aldicarb	93	6	44	5
3	Ametryn	86	6	75	6
4	Atrazine	90	3	82	3
5	Benazolin	10	6	37	8
6	Bromofenoxim	80	10	37	8
7	Carbaryl	83	2	73	6
8	Carbofuran	86	4	75	6
9	Chloridazon	97	4	81	7
10	Chlorotoluron	87	3	80	5
11	Cyanazine	86	2	73	5
12	Diuron	91	3	75	6
13	Ethofumesate	92	2	76	8
14	Fenamiphos	90	2	20	6
15	Linuron	87	2	75	6
16	Metamitron	120	10	130	15
17	Metolachlor	92	6	60	6
18	Metribuzin	92	6	77	5
19	Monuron	87	5	77	5
20	Pendimethalin	73	10	40	6
21	Phenmedipham	85	8	71	10
22	Propachlor	91	10	57	6
23	Propazine	90	4	83	4
24	Sebuthylazine	90	1	84	4
25	Simazine	97	4	81	4
26	Terbacil	89	2	84	5
27	Terbuthylazin	87	5	66	5
28	Triadimefon	110	6	86	8
29	Trifluralin	80	5	38	8
30	Vinclozolin	97	5	71	4

[a] water from Milli-Q purification unit
[b] n = 3

The recoveries for solid-phase extraction of 30 pesticides, using two different adsorbents and a concentration of 2 µg/L, are summarized in Table 1. The table demonstrates, that high recoveries (in general >85%) are achieved with most pesticides using a C-18 adsorbent. Only very polar compounds, such as benazolin, are not well extracted from water under these conditions. Lowering of the pH or reduction of the sample volume (to reduce the breakthrough) may improve the recovery. With four exceptions, the coefficient of variation, CVrel. is <5%. Addition of sodium chloride (100 g/L) before extraction has led to a small increase in recoveries of some pesticides by about 5–10%. When compared with the other adsorbent, in general, C-18 material shows higher recoveries than XAD resins, which give slightly lower recoveries (usually >75%, see Table 1). These recoveries were determined at pH ≈7. XAD resins increase their adsorbent capacity at lower pH levels. Hence, recoveries at pH values from 4 to 7 show higher values.

Figure 2 shows the recovery of simazine as a function of the amount of methanol used for elution. Optimum elution requires a volume between 3 and 5 mL. One can conclude from Figure 2, that elution of analytes is more efficient, if done in five steps of 1 mL instead of one step with 5 mL. The gradients of elution are steeper in the former case, which leads to an increase of total recoveries. A similar dependency has been found for other pesticides.

Gas chromatography: Comparison of different detectors

Gas chromatography (GC) is well suited for separation and identification of thermally stable compounds. Baseline separation of all 19 pesticides selected for GC determination was

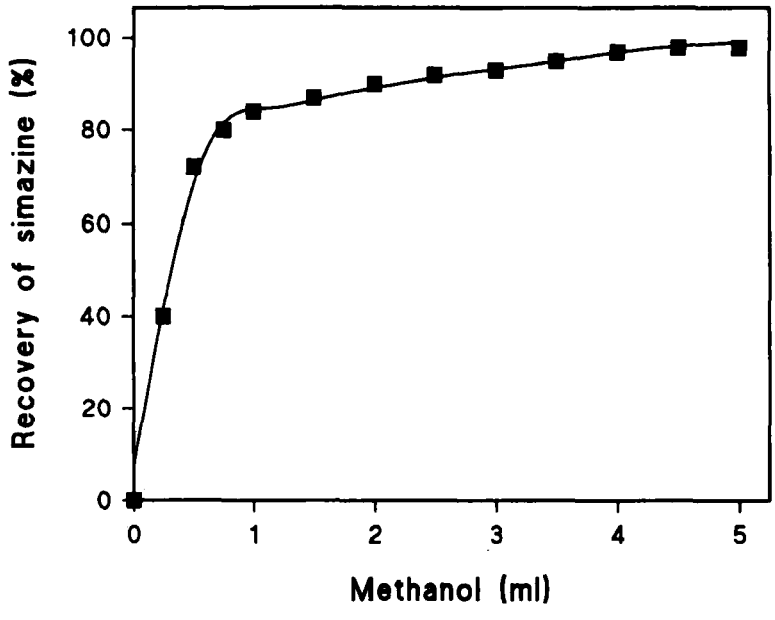

Figure 2 Recovery of simazine (in %) vs. total amount of methanolic solution, used for extraction of the analyte from adsorbent material

Table 2 Limit of detection (LOD) and peak assignment for the GC determination with FID/NPD/ECD of 19 pesticides and two chromatographic standards (S/N=3)

Peak-No.	*Compound*	*Retention time (min.)*	*LOD-FID (pg)*	*LOD-NPD (pg)*	*LOD-ECD (pg)*
1	1-Chlor-2,4-dinitrobenzene (internal Stan.)	11.40	6	0.71	0.16
2	Propachlor	12.32	2	0.30	1.18
3	Trifluralin	13.70	3	0.24	0.09
4	Simazine	15.51	6	0.08	12.4
5	Atrazine	15.74	6	0.09	10.5
6	Propazine	15.94	4	0.09	9.6
7	Terbuthylazine	16.42	4	0.10	9.2
8	Terbacil	17.38	13	0.09	3.36
9	Sebuthylazine	18.06	5	1.20	8.8
10	Metribuzin	19.13	6	0.10	0.15
11	Vinclozolin	19.38	5	0.16	0.13
12	Alachlor	19.55	3	0.91	8.1
13	Ametryn	20.07	5	0.43	5.3
14	Ethofumesate	21.13	5	n.d.	12.2
15	Metolachlor	21.63	4	0.90	1.5
16	Cyanazine	22.21	10	0.09	1.8
17	Triadimefon	22.47	6	0.22	0.44
18	Pendimethalin	23.73	4	0.23	0.36
19	2,2'-Dinitrobiphenyl (internal Stan.)	24.06	6	0.70	0.26
20	Fenamiphos	27.20	13	0.29	2.8
21	Metamitron	28.80	150	3.30	15.0

n.d. = not determined

achieved using a deactivated column of low polarity (see Experimental Section) and an insert deactivated by silylation. Figure 3 shows a chromatogram of 19 pesticides and 2 chromatographic standards with FID (a), NPD (b) and ECD (c). The limits of detection (LOD) are compared in Table 2. The ECD combines high selectivity and relatively high sensitivity for compounds with halogen or nitro functionality.[7] Lowest limits of detection have been reached for trifluralin, vinclozolin and metribuzin. Note that even for halogenated compounds the LODs may vary by as much as two orders of magnitude (compare, for instance, the LODs for trifluralin and atrazine). Moreover, the LODs are comparable to those obtained with FID for many halogenated compounds. More specific and even sensitive detection for almost all investigated pesticides was achieved by means of the NPD. Moreover, as compared to the ECD this detector shows a more even response for most compounds. The detector is more sensitive than the FID by 1–2 orders of magnitude, except for ethofumesate, which lacks a nitrogen atom and is thus not detectable at all using an NPD.

The same standard solution of 19 pesticides and two chromatographic standards was analyzed using GC-AED, which allows an element-specific detection. The emission lines of the following elements were monitored: nitrogen, phosphorus, sulfur, chlorine, hydrogen, carbon, fluorine and oxygen. At 24 ng total amount of each pesticide, every compound shows peaks, which reflect the elemental composition (see Figure 4). The chromatogram of the

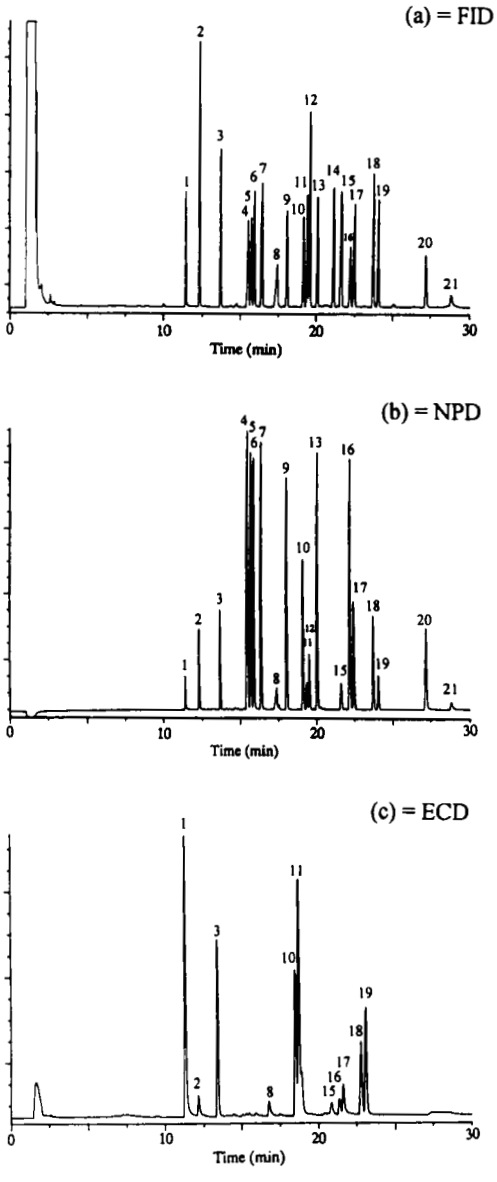

Figure 3 Gas chromatogram of a standard solution containing 19 pesticides and 2 chromatographic standards (24 ng total amount for each pesticide, for peak assignment see Table 2): a = FID, b = NPD, c = ECD

carbon line is comparable to an FID chromatogram. Limits of detection are shown in Table 3. It is apparent from this figure that the LODs vary substantially for the various elements, where the lower LODs are observed for the carbon and sulfur line, the highest for the fluorine line. It is expected that the LOD can be further reduced by using purer helium. Nevertheless,

Table 3 Limit of detection (LOD) and peak assignment for the GC determination with AED of 19 pesticides and two chromatographic standards (S/N=3) using all eight present element lines

Peak-No.	*Compound*	*N 174 (ng)*	*P 178 (ng)*	*S 181 (ng)*	*Cl 479 (ng)*	*H 486 (ng)*	*C 496 (ng)*	*F 690 (ng)*	*O 777 (ng)*
1	1-Chlor-2,4-dinitrobenzene (internal Stan.)	1,47	—	—	1,14	2,47	0,188	—	0,874
2	Propachlor	3,95	—	—	1,04	0,36	0,093	—	3,49
3	Trifluralin	2,25	—	—	—	0,576	0,153	18,2	1,166
4	Simazine	2,25	—	—	2,16	0,987	0,376	—	—
5	Atrazine	1,694	—	—	1,68	0,640	0,251	—	—
6	Propazine	1,636	—	—	1,65	0,531	0,218	—	—
7	Terbuthylazine	1,63	—	—	1,56	0,504	0,204	—	—
8	Terbacil	4,65	—	—	3,03	1,152	0,338	—	6,122
9	Sebuthylazine	2,0	—	—	1,83	0,586	0,240	—	—
10	Metribuzin	1,5	—	0,223	—	0,705	0,233	—	6,12
11	Vinclozolin	9,3	—	—	1,41	1,728	0,251	—	3,061
12	Alachlor	10,28	—	—	2,31	0,611	0,196	—	4,08
13	Ametryn	3,84	—	0,3	—	0,864	0,377	—	—
14	Ethofumesate	—	—	0,348	—	0,713	0,223	—	1,93
15	Metolachlor	13,09	—	—	3,32	0,777	0,245	—	5,25
16	Cyanazine	2,62	—	—	2,79	1,28	0,391	—	—
17	Triadimefon	2,82	—	—	3,12	1,02	0,228	—	5,65
18	Pendimethalin	3,69	—	—	—	0,785	0,239	—	2,38
19	2,2'-Dinitrobiphenyl (internal Stan.)	3,388	—	—	—	1,65	0,213	—	1,985
20	Fenamiphos	24,0	4,42	0,6	—	1,44	0,544	—	14,69
21	Metamitron	4,0	—	—	—	2,77	0,545	—	14,8

the LODs are several orders of magnitude higher than those achieved, e.g. with an FID. While the sensitivity is considerable poorer with an AED as compared to classical GC detectors, the AED is much more selective. Still, there may be interference in the emission lines of a given element by an emission line of another element. Such interference can be revealed using the wavelength snapshot technique of the AED. With this technique an element is not characterized by one but by all emission lines, which further enhances the selectivity. In this wavelength snapshot of propachlor (see insert in C1 479 of Figure 4), the pattern of the emitted wavelengths correspond to those of chlorine; the so-called "**chlorine triplet**".

HPLC determination

For thermally labile pesticides, which decompose during GC analysis, HPLC with UV photodiode-array (PDA) detection is a valuable alternative. Two gradients for separation of pesticides have been developed (see Experimental Section). The first gradient (C_1) is suitable for an analysis of pesticides of medium polarity. Using this gradient, a baseline separation of 12 pesticides is achieved. A baseline separation of 12 pesticides using gradient (C_1) and a chromatographic standard (1-chloro-2,4-dinitrobenzene) is shown in Figure 7. For very

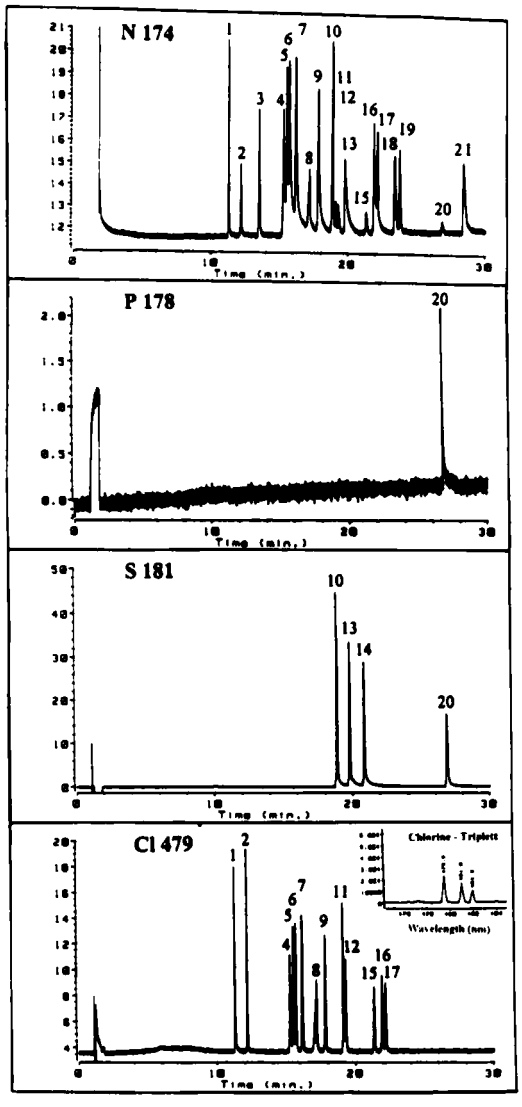

Figure 4 AED—gas chromatogram of a standard solution containing 19 pesticides and 2 chromatographic standards (24 ng total amount for each pesticide, for peak assignment see Table 3) for all eight present element lines (please note different scaling factors!), insert of Cl 479 in Figure 4 shows the *Chlorine—triplet* at retention time of 12.32 minutes (propachlor), used for identification of the element chlorine (Cl emission lines: 479.5, 481.0 and 481.9 nm)

polar compounds such as benazolin, a second gradient (C_2) is used. This gradient includes an isocratic step with 100% water at the beginning. Limits of detection for UV and TSP-LC-MS detection are summarized in Table 4. A standard TSP-LC-MS chromatogram

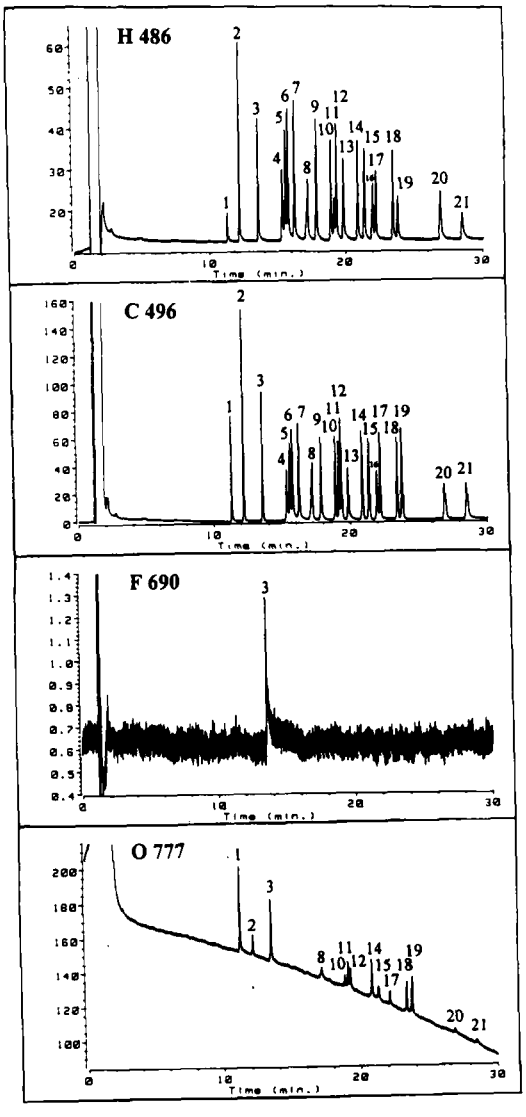

Figure 4 *continued*

of 12 pesticides using gradient C_1 is shown in Figure 5 (SCAN mode). Limits of detection are of the same level as observed with an UV-detector. However, monitoring of the characteristic positive ions such as $[M+H]^+$ or $[M+NH_4]^+$ using the SIM mode allows a specific and even more sensitive detection (by a factor of 10–100). The results are summarized in Table 4. A comparison of a SCAN detection (m/z 150–400, 30 ng total amount) for ethofumesate versus a SIM detection (m/z 304, 3 ng total amount) is shown in Figure 5,

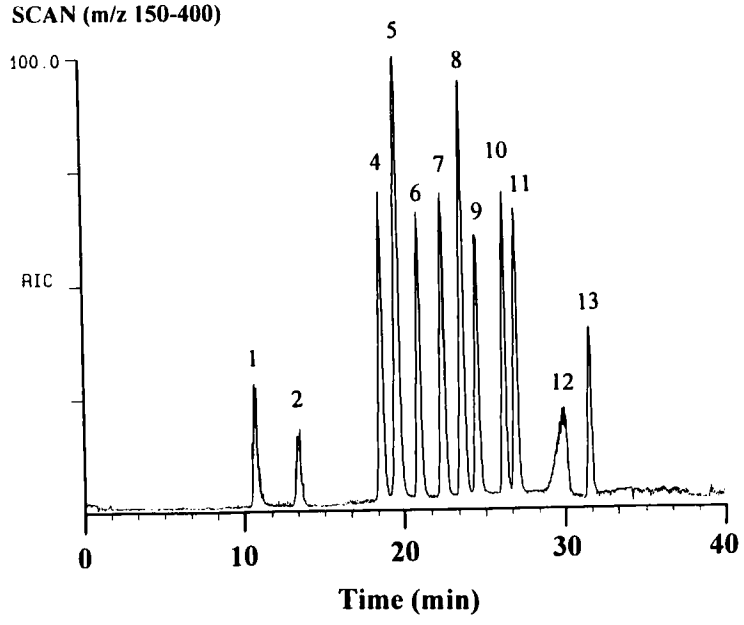

Figure 5 TSP-LC-MS chromatogram of 12 pesticides (SCAN modus, m/z 150–400, positive ions, 600 ng total amount for each pesticide, for peak assignment see Table 4), gradient C_1

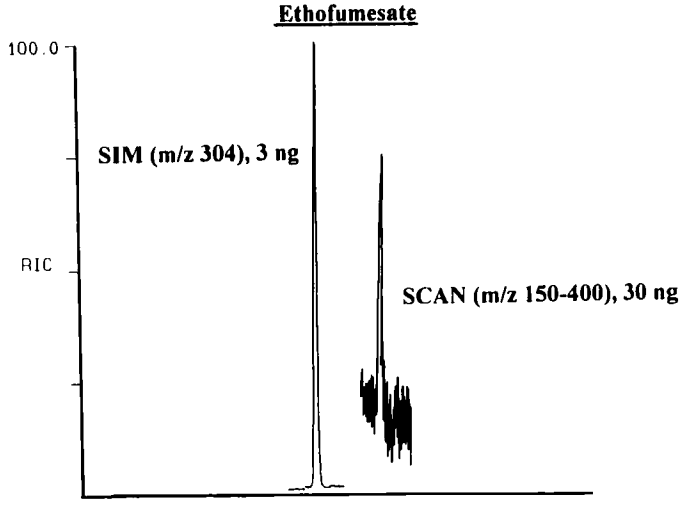

Figure 6 Two snapshots of ethofumesate using SCAN (30 ng total amount, m/z 150–400) and SIM (3 ng total amount, m/z 304), positive ions, gradient C_2

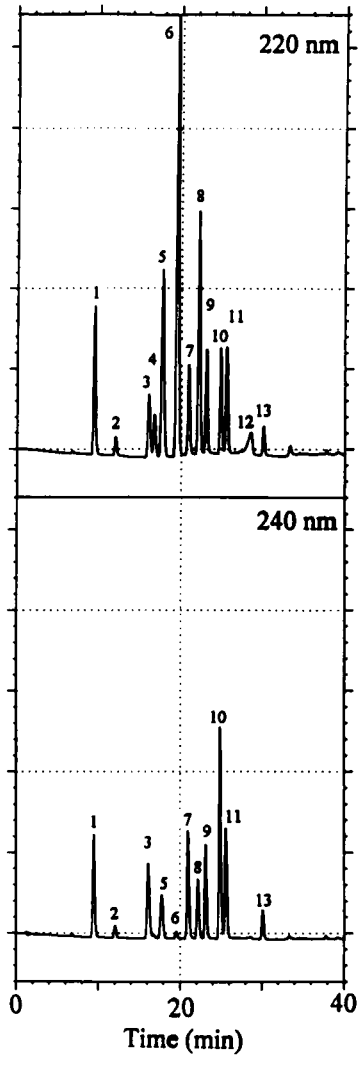

Figure 7 HPLC chromatogram of 12 pesticides and 1 chromatographic standard using UV detection at 220 nm and 240 nm (180 ng total amount for each pesticide, for peak assignment see Table 4), gradient C_1

which confirms the increase of sensitivity gained from this specific detection. The UV-chromatogram in Figure 7 has been recorded at two wavelengths (220 and 240 nm). When real environmental samples are determined by HPLC, determination at longer wavelengths is more specific, as interference from unknown environmental substances is reduced. This increase in specificity is, however, achieved at the expense of sensitivity. Thus, the UV spectra of chlorotoluron from 200 and 400 nm (extracted from run C_1 at a retention time of 21.05 min) contains two maxima at 210 and 245 nm, which differ in intensity by a factor of

Table 4 Limit of detection (LOD) and peak assignment for pesticides using HPLC-UV and TSP-LC-MS

Compound	*Retention time (min)*	*UV LOD* [a] *(ng)*	*TSP-MS LOD* [b] *(ng)*	*TSP-MS LOD* [c] *(pg) [SIM]*	*Peak-No.*	*Gradient*
Alachlor	28,79	1.30	10,4	825 [270]	12	C1
Aldicarb	12,32	2.68	3	610 [208]	2	C1
Atrazin	22,25	0.22	0,6	60 [216]	8	C1
Benazolin	6,65	0.45	n.d.	n.d.	—	C2
Bromofenoxim	29,51	4.80	n.d.	n.d.	—	C2
Carbaryl	19,99	0.11	1	300 [219]	6	C1
Carbofuran	16,90	0.90	1	230 [222]	4	C1
Chloridazon	9,50	0.42	1,3	1000 [222]	1	C1
1-Chlor-2,4-dinitrobenzene	16,20	0.52	n.d.	n.d.	3	C1
Chlorotoluron	21,32	0.53	1,8	230 [213]	7	C1
Diuron	23,45	0.52	6	930 [233]	9	C1
Ethofumesate	33,51	1.14	17,5	70 [304]	—	C2
Fenamiphos	30,52	1.06	2,1	90 [304]	13	C1
Linuron	25,99	0.51	3,6	830 [249]	11	C1
Monuron	16,25	0.52	—	—	—	C1
Phenmedipham	24,90	0.48	1,3	600 [185]	10	C1
Simazin	17,48	0.23	0,8	50 [202]	5	C1

[a] UV-detection at λ =220 nm
[b] SCAN modus (m/z 150–400)
[c] SIM modus [selected ion monitored]

~2. Hence, a determination at 245 nm decreases the sensitivity by this factor, which leads to a LOD of ~0.7 ng.

Analysis of spiked surface water samples

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 silynized glass wool. Extraction of 1 L water samples was carried out as described in Figure 1 using C-18 material followed by HPLC analysis. Both spiked and unspiked samples were studied. The HPLC chromatograms are shown in Figure 8 (a = Leine, b = Weser), the recoveries in Table 5. Recoveries of many investigated pesticides are comparable to those obtained with standard water solutions (compare Tables 1 and 5), while lower recoveries were observed with alachlor, aldicarb, carbofuran, phenmedipham and fenamiphos. Interactions with compounds from environmental samples may explain this result.

CONCLUSIONS

A careful optimization of solid-phase extraction of 30 pesticides leads to the following conclusions: Among the two adsorbents tested (C-18 and XAD), highest recoveries are achieved with C-18 material. Recoveries are usually >85% with coefficients of variation

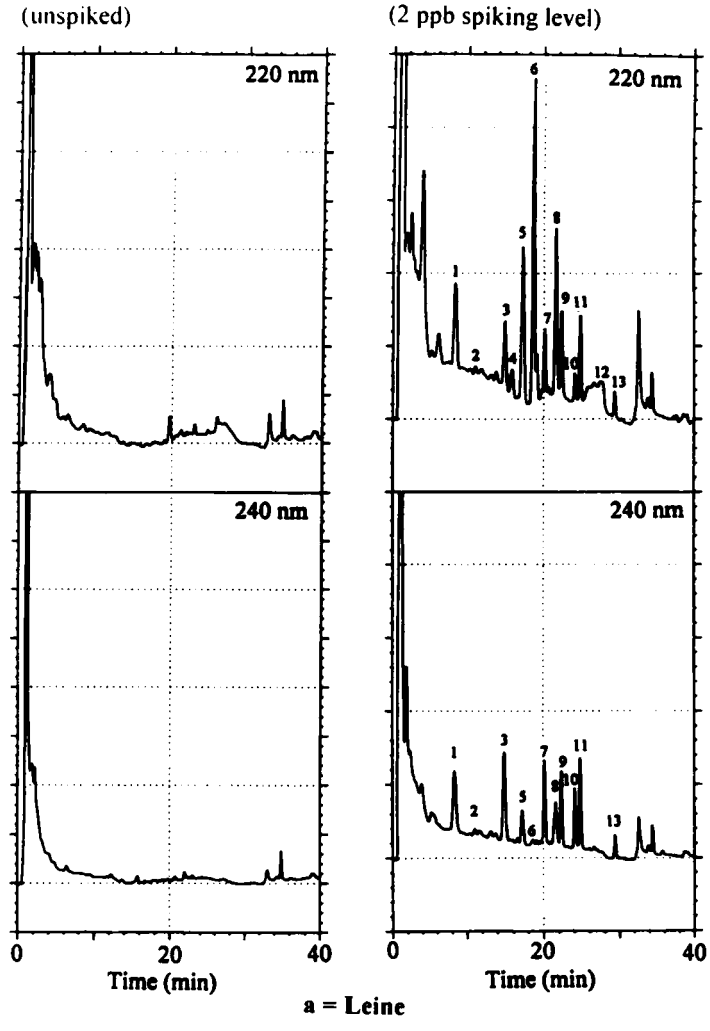

Figure 8 HPLC chromatogram of 12 pesticides and 1 chromatographic standard in two surface water samples (a = River Leine in Hannover, b = River Weser in Holzminden, both in Lower Saxony, Germany) using UV detection at 220 nm and 240 nm (2 μg/L spiking level for each pesticide), gradient C_1

(CVrel.) <5%. Only extremely polar compounds, i.e. benazolin, have lower recoveries up to 37% ($CV_{rel.}$ = 8%). An optimized elution of the pesticides from the adsorbent is achieved by using 5 times 1 mL methanol.

Despite the fact that interaction of analytes with sample matrix can generally influence recoveries, spiked surface water samples (from the Leine and Weser) have shown only little decrease in recoveries at about 5–10%, except alachlor, aldicarb, carbofuran, fenamiphos and in particular phenmedipham. The recovery of later compound was only 15% in the Leine sample and it was not recovered from the Weser sample indicating a strong interaction with the matrix.

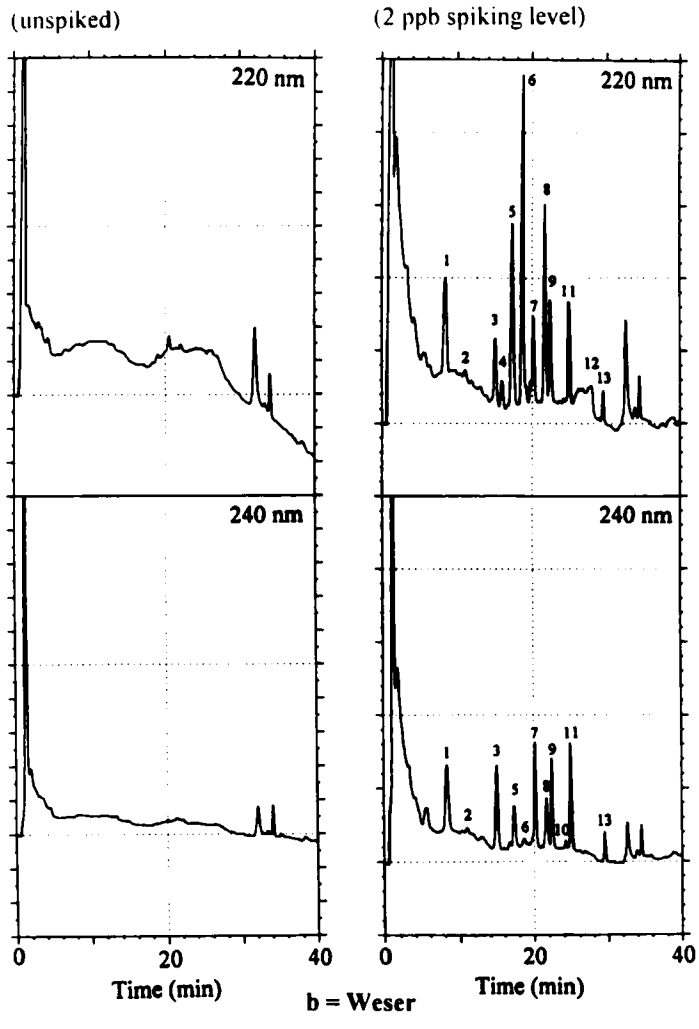

Figure 8 *continued*

For pesticides amenable to GC, the sensitivity and selectivity of four detectors, FID, NPD, ECD and AED, is compared. The ECD is more selective, but surprisingly not necessarily more sensitive than the FID for many chlorine-containing pesticides. For nitrogen-containing agents the NPD is often more sensitive than the ECD (even for chlorine-containing compounds) and more selective. The selectivity can be substantially enhanced using an element-specific detector (ESD) by employing an AED, although this detector is substantially less sensitive. A mass spectrometric (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, which are not in the library (such as metabolites), the information gained from the AED may even be superior to that from an MS. Furthermore, typical element

Table 5 Recoveries (REC in %) of 12 pesticides using C-18 adsorbent material in two spiked surface water samples, from the River Leine in Hannover and River Weser in Holzminden, both in Lower Saxony, Germany

Peak-No.	*Compound*	*Retention time (min)*	*LEINE-SAMPLE*[a] *recovery (%) (n=3)*	*WESER-SAMPLE*[b] *recovery (%) (n=3)*
1	Chloridazon	9.50	107	111
2	Aldicarb	12.10	60	78
4	Carbofuran	16.90	111	108
5	Simazine	17.85	82	93
6	Carbaryl	19.60	90	88
7	Chorotoluron	21.05	83	102
8	Atrazine	22.25	79	93
9	Diuron	23.20	86	106
10	Phenmedipham[c]	24.90	15	—
11	Linuron	25.65	70	80
12	Alachlor	28.50	66	59
13	Fenamiphos	30.20	56	72

[a] Leine in Hannover, 28.04.93, River in Lower Saxony, Germany
[b] Weser in Holzminden, 09.05.93, River in Lower Saxony, Germany
[c] Peak quantification difficult due to interactions

emission lines can be monitored using an AED for verification of unknown compounds and for excluding interferences in the chromatogram.[8,9]

Thermally labile pesticides have to be analyzed by HPLC and the separation of 16 pesticides using two different gradients for very polar compounds and compounds of medium polarity has been proposed. While instrument limits of detection for GC-NPD may be as low as 0.1 pg for some pesticides, the limits of detection of the HPLC (UV) method are considerably poorer (typically 0.5—1 ng). Moreover, any HPLC determination will be less specific than a GC determination due to the lower resolution of LC compared to GC. Using a photodiode array (PDA) detector, the selectivity can be enhanced. Compounds, i.e. chlorotoluron, with a second adsorption maximum at a longer wavelength (245 nm), can be detected more selectively and with less interference in environmental samples. Unfortunately, pesticides of the same compound class show almost identical UV spectra. Thus, a confirmation of pesticide analysis by LC-MS is carried out. Limits of detection (LOD) for 12 pesticides, studied with TSP-LC-MS, are in general between 1–10 ng (SCAN mode) and 50–1000 pg (SIM mode). This detection is much more sensitive (SIM mode) than UV detection but also more specific (typically $[M+H]^+$ and $[M+NH_4]^+$ can be observed). Effects on the ion abundances in thermospray mass spectra and an LC-MS multiresidue method for the determination of 95 pesticides have been described by us elsewhere.[10,11]

Acknowledgements

This study is supported by the Commission of the European Communities [EV5V-CT92-0061] and EC AVICENNE Programme [AVI*-CT92-0004], which are gratefully acknowledged.

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