



ELSEVIER

Journal of Chromatography A, 677 (1994) 63–74

JOURNAL OF  
CHROMATOGRAPHY A

# Determination of phenoxyalkanoic acids and other acidic herbicides at the low ppt level in water applying solid-phase extraction with RP-C<sub>18</sub> material

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First received 22 September 1993; revised manuscript received 1 March 1994

## Abstract

A method for the determination of 34 phenoxyalkanoic acids and other acidic compounds in water samples was developed. Recoveries were made from 1 l of drinking water samples using solid-phase extraction (SPE). Different SPE materials and blends of octadecyl (RP-C<sub>18</sub>) and phenyl (RP-Phe) were tested. After method optimization, 26 out of the 34 compounds could be extracted with recoveries better than 70% on the most suitable RP-C<sub>18</sub> material. The acidic compounds in the extract were derivatized with pentafluorobenzyl bromide and the resulting esters determined by capillary gas chromatography with mass selective detection employing selected-ion monitoring with time window programming. Detection limits between 1 and 10 ng/l were obtained with spiked drinking water samples. This method has been used successfully for the analysis of drinking and groundwater samples in field studies.

## 1. Introduction

The determination of acidic compounds by GC-MS after derivatization with pentafluorobenzyl bromide (PFBBBr) was the subject of a previous paper [1]. The derivatization procedure has been demonstrated to permit the sensitive determination of the target compounds at levels down to 1–100 pg injected when measured with selected-ion monitoring (SIM) and electron impact ionization (EI-MS). The low detection limits that can be achieved with test substances make this method promising for application to drinking water samples. The identification and determination of these compounds at a concen-

tration level of 100 ng/l in water for a single compound is necessary to meet the maximum tolerances set by the European Community's drinking water regulation [2]. To determine phenoxyalkanoic acids and related acidic herbicides at such low tolerance levels, the target compounds have first to be extracted from the water sample with high recovery rates. A number of publications have described liquid-liquid extraction (LLE) using diethyl ether [3–5], dichloromethane [6–9], ethyl acetate [10–12] and benzene [13]. Solid-phase extraction (SPE) has gained in popularity in recent years. A variety of materials are available that have been used successfully for the extraction of phenoxyalkanoic acids. Most publications describe the use of modified silica gels, especially RP-C<sub>18</sub> [14–23]

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or RP-C<sub>8</sub> [24]. The use of the polymeric materials Amberlite XAD-4 [25], PLRP-S, PRP-1 [26,27] or Wofatit Y 77 [28–30] has also been reported. An ion exchanger [31] and a combination of Carbo-pack B and SAX [32] have also been used.

Methods for the determination of polar contaminants are mostly performed for a few well known compounds such as the acidic herbicides 2,4-D and 2,4,5-T. The determination of a larger number of acidic compounds has been described in only a few publications [9,14,22,27]. Our aim was to develop a method that would include a wide range of acidic contaminants that need to be determined at the low ng/l level in drinking water.

In this paper, a method for the SPE of 34 phenoxyalkanoic acids and other acidic herbicides from drinking water and groundwater is described.

## 2. Experimental

### 2.1. Materials

All solvents were Pestanal products from Riedel-de Haën (Seelze, Germany). Pentafluorobenzyl bromide was obtained from Aldrich (Steinheim, Germany) and triethylamine from Merck (Darmstadt, Germany). Sample vials, screw-caps and septa were purchased from Zinsser (Frankfurt, Germany) and 200- $\mu$ l inserts for the sample vials from CS-Chromatographie Service (Langerwehe, Germany). All pesticide standards were of analytical purity from Promochem (Wesel, Germany) or of Pestanal quality from Riedel-de Haën. Stock solutions of all compounds were prepared in toluene or methanol.

Solid-phase extraction was carried out with cartridges of polypropylene with a volume of 6 ml from Baker (Frankfurt, Germany). The RP-C<sub>18</sub> material labelled C was obtained from Eurochrom (Berlin, Germany) (Europrep 60–30 C<sub>18</sub>; 60 Å, 20–45  $\mu$ m, irregular) and the other two RP-C<sub>18</sub> materials, labelled A and B, were from Baker and ICT (Frankfurt, Germany),

respectively. RP-phenyl (RP-Phe) material was purchased from Baker. Adjustable transferpettors (1–10 and 10–100  $\mu$ l) were supplied by Brand (Wertheim, Germany). A Beta I freeze-drier from Christ (Osterode, Germany) was used in several experiments.

### 2.2. Sample preparation

A tap water sample of 1 l was spiked by adding a mixture of pesticides dissolved in methanol to obtain a concentration of 100 ng/l of each active compound. The internal standard 2,4-dichlorobenzoic acid, was added at a concentration of 200 ng/l. The sample was then acidified to pH < 2 with HCl. Each SPE cartridge was filled with 1 g of RP-C<sub>18</sub> adsorbent. Conditioning was performed successively with 10 ml of acetone, 10 ml of methanol and finally 10 ml of distilled, deionized water (pH < 2). The solvents were drawn through the cartridges by means of a gentle vacuum and the cartridge was not permitted to run dry during the whole conditioning procedure. The water sample spiked with the herbicides was then percolated through the cartridge at a flow-rate of ca. 8 ml/min applying a low vacuum. After drying the cartridge for 2–3 h under a gentle stream of nitrogen, the herbicides were eluted with 2.5 ml of methanol. The eluate was dried under a gentle stream of nitrogen.

### 2.3. Derivatization

Derivatization was performed at 90°C using 200  $\mu$ l of pentafluorobenzyl bromide (PFBr) (2% in toluene) and 2  $\mu$ l of triethylamine as catalyst as described previously [1]. The derivatized sample was then dried under nitrogen and finally dissolved in 100  $\mu$ l of toluene.

### 2.4. GC-MS parameters

All mass spectrometric measurements were performed with a Hewlett-Packard HP 5970 mass-selective detector combined with an HP 5890 gas chromatograph fitted with a 25 m  $\times$  0.2 mm I.D.  $\times$  0.33  $\mu$ m HP-5 capillary column and a

1.5 m × 0.32 mm I.D. × 0.17 μm HP-5 precolumn. The carrier gas was helium (purity 99.999%) set to a head column pressure of 100 kPa. The oven temperature was held at 100°C for 1 min following injection, then programmed at 30°C/min to 150°C, which was held for 1 min, then at 3°C/min to 205°C followed by 10°C/min to 260°C and finally held for 23 min. The injection port and transfer line temperatures were 210 and 250°C, respectively. Amounts of 2 μl of sample were injected by means of an HP 7673 autosampler using hot splitless injection with the split closed for 0.9 min. For SIM three characteristic ions were selected for each compound and scanned using corresponding time windows with dwell times between 100 and 200 ms per ion. Mass spectrometer tuning was performed weekly using the autotuning macro. The precolumn and insert liner were exchanged after not more than 50 injections.

### 3. Results and discussion

#### 3.1. Target compounds

To meet the objectives for the surveillance and monitoring of acidic herbicides in water samples, a routine method with low detection limits for all active compounds had to be developed and evaluated. After having demonstrated in a previous study [1] that phenoxyalkanoic acids and other acidic herbicides can be easily detected by GC-MS as their PFBBr esters at picogram levels, the aim of this study was to find the extraction procedure best suited for sample preparation and trace enrichment. In recent years in our laboratory, LLE with dichloromethane and SPE using RP-C<sub>18</sub> material were frequently applied in parallel to the same water samples to check the reliability of SPE results. We have come to the conclusion that before using SPE as a routine method, the RP-C<sub>18</sub> material and the extraction conditions must be carefully evaluated, otherwise the results vary dramatically.

The target compounds include phenoxyalkanoic acids and their esters, other acidic pesticides and related compounds of environmental

interest, and are representative of a variety of chemical structures containing acidic protons. The structural formulae of all the compounds studied are presented in Fig. 1.

All experiments were carried out under conditions that match the requirements of water monitoring analysis with respect to the maximum tolerances for pesticides in drinking water. Therefore, all drinking water samples were spiked with a mixture of all 34 target compounds to obtain a concentration level of 100 ng/l or lower. The whole procedure of sample extraction and derivatization is presented in Fig. 2.

#### 3.2. Influence of adsorbent drying on the recovery

Our first recovery experiments were carried out with RP-C<sub>18</sub> material from supplier A. According to earlier observations, the influence of the drying process of the adsorbent has been found to be a critical step in SPE. Independent of the type of pesticides or environmental contaminants determined in water, sometimes irreproducible results were obtained and these results correlated in many instances with incomplete drying of the RP-C<sub>18</sub> material before eluting the adsorbed compounds. Two drying procedures are executed in addition to the first drying of the column by vacuum. Some users of SPE prefer freeze-drying and, others flushing the extraction column with a gently stream of nitrogen. Both drying procedures were investigated in parallel in this study.

On comparing the recovery values for drying with nitrogen and for freeze-drying, no significant differences in the average recoveries could be observed. Therefore, nitrogen flushing was used as the standard procedure in all further experiments because of its simplicity.

#### 3.3. Selection of RP adsorbent material

As a few of the active compounds, such as clopyralid, 4-chlorophenoxyacetic acid, flurenol and 2,4-DB in particular, were found to give inadequate recoveries, adsorbents with other chemical structures were tested. RP-Phe and a

mixture of RP-Phe and RP-C<sub>18</sub> (1:1) were used for the extraction of the target compounds from water. Using a mixed material, improved recoveries were expected because of the operation of a mixed interaction process in adsorption, taking advantage of the favourable properties of the individual phases.

RP-C<sub>18</sub> material from supplier A on average showed better recoveries than those with the RP-Phe material and the blends. The same holds true if the number of compounds with an aimed recovery of better than 70% is compared. Surprisingly, only two herbicides were found to be extracted significantly better from water with RP-Phe than with RP-C<sub>18</sub> from supplier A, namely fluroxypyr and picloram.

The influence of the solvation effect was then studied with the addition of methanol to the water sample. The recoveries with RP-C<sub>18</sub> from

supplier A and a mixture of RP-C<sub>18</sub> and RP-Phe (1:1) after the addition of methanol to the sample were found to be only slightly changed. Whereas with the mixed phase no better recoveries could be achieved, the recoveries with RP-C<sub>18</sub> were found to be slightly better. Adding methanol to the water sample prior to extraction, however, generally led to better reproducibility.

It is well known by users that the material from a supplier can vary in its quality from batch to batch. Therefore, it is common practice to check batches with the compounds under investigation before buying a greater stock. Since we undertook our first experiments with an adsorbent selected for less polar pesticides such as polycyclic aromatic hydrocarbons and polychlorinated biphenyls, a check of RP-C<sub>18</sub> materials from other suppliers was carried out. The

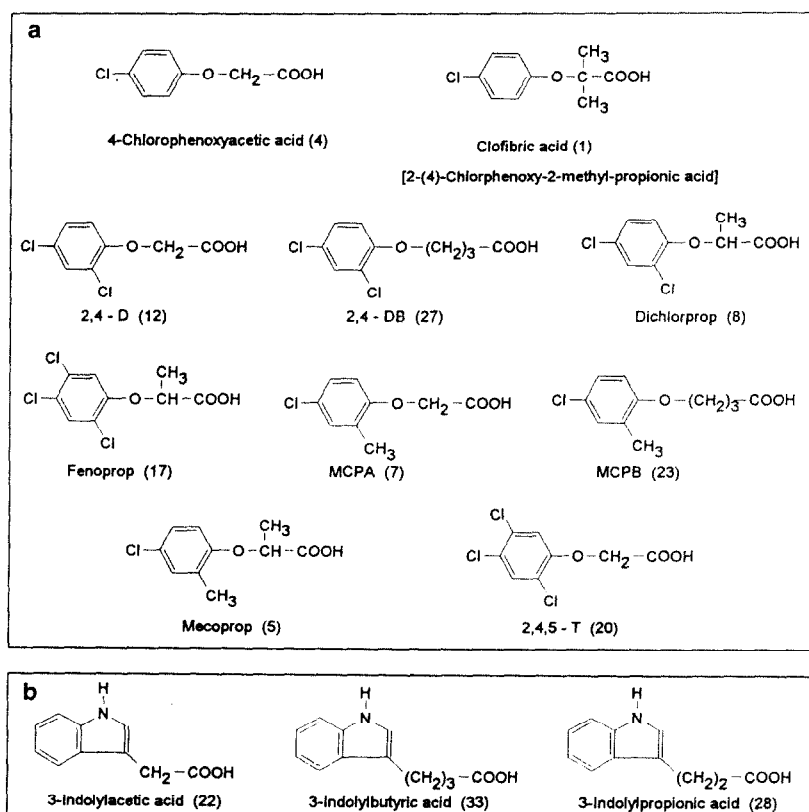


Fig. 1.

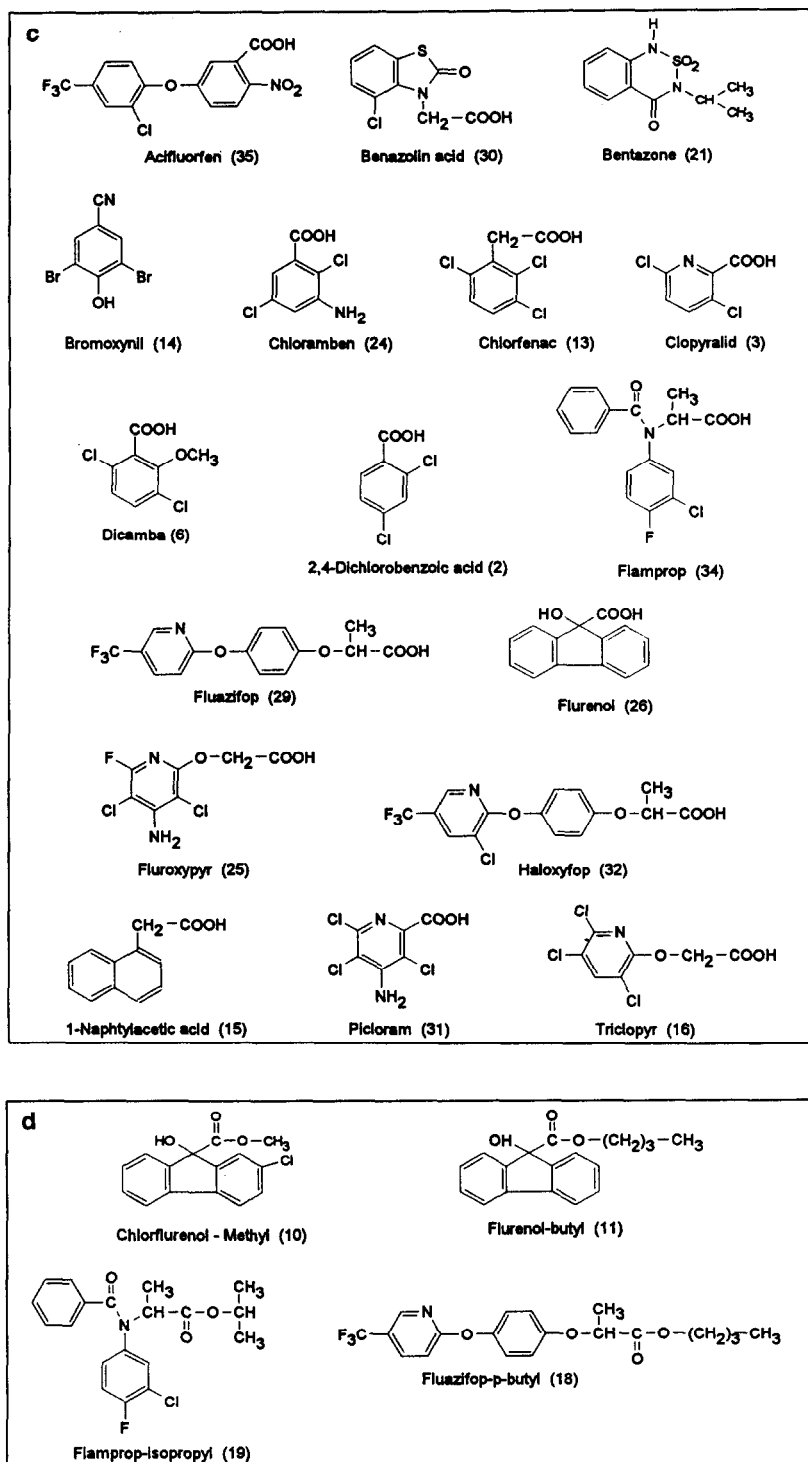


Fig. 1. (a) Phenoxyalkanoic acid herbicides and the drug clofibric acid; (b) indolycarboxylic acids; (c) other acidic herbicides and the internal standard (2); (d) herbicidal esters of considerable stability against hydrolysis.

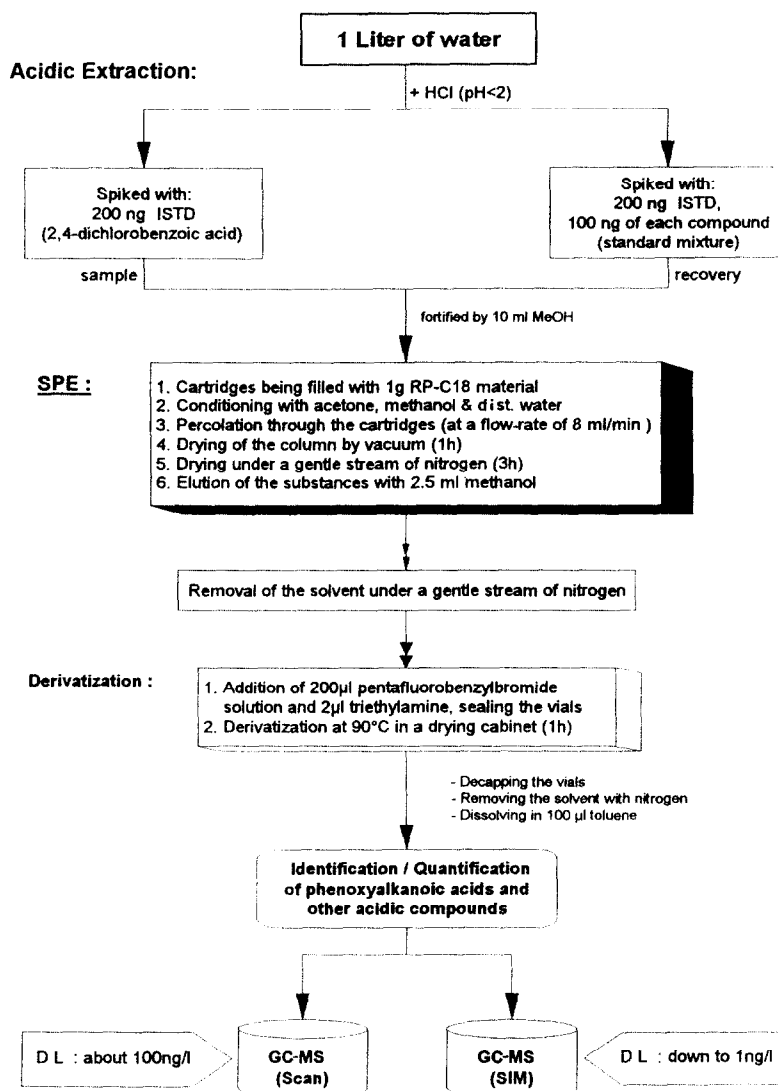


Fig. 2. Solid-phase extraction of acidic contaminants followed by pentafluorobenzylation and GC-MS determination. ISTD = Internal standard.

same recovery experiments were performed using RP-C<sub>18</sub> material A, B and C and a mixture of RP-C<sub>18</sub> A and RP-Phe. All experiments were carried out with the addition of methanol. The results of a series of sixfold experiments are compiled in Table 1.

A comparison of the recoveries of the adsorbents from the three suppliers reveals considerable differences between their trapping properties. Whereas with material A only 9 out of the

34 target compounds give recoveries greater than 70%, with material B 17 and with material C 26 compounds show recoveries greater than 70%. A comparison of the average recoveries of all the target compounds in Table 1 demonstrates the excellent properties of adsorbent C, with an average recovery of 87% compared with 71% for adsorbent B and only 59% for adsorbent A. Four of the investigated compounds were excluded from the evaluation of average recoveries

Table 1

Recoveries (%) with standard deviations ( $n = 6$ ) of acidic herbicides with SPE using various adsorbent materials with water samples containing 1% of methanol

No.	Compound	C <sub>18</sub> <sup>a</sup> - Phe	S.D. (%)	C <sub>18</sub> A	S.D. (%)	C <sub>18</sub> B	S.D. (%)	C <sub>18</sub> C	S.D. (%)
1	Acifluorfen	43	8	68	5	58	19	77	13
2	Benazolin	38	6	37	5	75	7	89	11
3	Bentazone	67	8	76	7	56	11	71	24
4	Bromoxynil	52	24	72	24	59	15	75	27
5	Chloramben	20	4	17	3	40	5	58	6
6	Chlorfenac	54	8	72	3	109	12	92	9
7	Chlorfurenol-methyl	76	7	88	4	92	8	109	2
8	4-Chlorophenoxyacetic acid	18	3	28	3	19	2	72	11
9	Clofibrac acid	78	10	96	5	81	6	106	7
10	Clopyralid	22	10	33	4	55	11	79	5
11	2,4-D	36	7	51	5	106	8	79	16
12	2,4-DB	24	13	36	6	53	6	53	5
13	Dicamba	51	9	63	3	95	9	101	10
14	2,4-Dichlorobenzoic acid	56	8	76	5	60	3	90	9
15	Dichlorprop	43	7	67	6	77	9	94	10
16	Fenoprop	54	6	65	5	70	14	100	7
17	Flamprop	53	7	60	4	75	10	88	8
18	Flamprop-isopropyl	89	7	98	7	100	8	109	14
19	Fluazifop	48	8	64	5	60	9	91	11
20	Fluazifop- <i>p</i> -butyl	55	8	65	3	79	4	101	6
21	Flurenol	26	4	25	13	20	10	33	1
22	Flurenol-butyl	75	7	81	2	95	8	109	2
23	Fluroxypyr	21	4	23	3	63	6	87	10
24	Haloxypyr	48	6	58	2	59	9	88	10
25	3-Indolylacetic acid <sup>b</sup>	13		12		40		42	
26	3-Indolylbutyric acid <sup>b</sup>	8		6		12		10	
27	3-Indolylpropionic acid <sup>b</sup>	40		9		40		56	
28	1-Naphthylacetic acid	49	8	56	8	75	15	104	6
29	MCPA	41	8	55	5	76	10	85	10
30	MCPB	42	4	41	8	74	6	69	6
31	Mecoprop	51	7	64	4	68	10	89	8
32	Picloram <sup>b</sup>	27		6		—		9	
33	2,4,5-T	75	17	82	8	88	5	102	14
34	Triclopyr	57	6	67	4	79	8	107	5
Average		49		59		71		87	
No. of compounds with recovery $\geq 70\%$		5		9		17		26	
No. of compounds with recovery $\geq 50\%$		15		22		26		29	

<sup>a</sup> With RP-C<sub>18</sub> material A.

<sup>b</sup> Not taken into account for averaging owing to unsatisfactory recovery.

because their recoveries were low with all the materials tested. These compounds are the three indolealkanoic acids and picloram. Whereas the indole-3-alkanoic acids are certainly of only

limited interest in general environmental monitoring, picloram may be the target of environmental monitoring. In the course of this study RP-Phe was found to be best suited for picloram

whereas RP-C<sub>18</sub> seems not to be suitable for the extraction of this compound.

The recoveries using material C demonstrate that compounds containing more than one functional group show lower recoveries. Note that with increasing aliphatic chain length the recoveries of the phenoxyalkanoic acids unexpectedly decrease from 2,4-D to 2,4-DB and from MCPA to MCPB, whereas aliphatic chain branchings increase the recoveries such that dichlorprop is better extracted than 2,4-D and mecoprop better than MCPA.

The results of our investigations showed clearly that material C is in this case superior to all the other materials tested. Therefore, it was chosen for the screening of acidic compounds in water samples. It should be emphasized that the RP-C<sub>18</sub> adsorbents A and B work satisfactorily in other applications such as with chlorinated pesticides, triazine herbicides and polycyclic aromatic hydrocarbons.

#### 3.4. Recovery experiments at low concentration levels

To check the potential of the described extraction method, recovery experiments were carried out by spiking of a series of drinking water samples with all the target compounds at concentrations below the 100 ng/l level. In recovery experiments, the practical detection limits for each compound were determined by analysing 1 l of drinking water spiked with 50, 25, 10, 5 and 1 ng of the standard mixture. At each concentration, a threefold determination was carried out. In Fig. 3 the multiple ion detection (MID) chromatogram obtained during the analysis of the spiked drinking water is presented, which in this instance was spiked at a concentration level of 10 ng/l. The chromatogram shows that the detection limit achievable with this method for most of the target compounds is clearly below 10 ng/l.

Note that although the extraction of 3-indolybutyric acid is not satisfactory with this method, a drinking water sample containing 10 ng/l of this compound gives a positive result, as can be observed from peak 32 in Fig. 3. The only

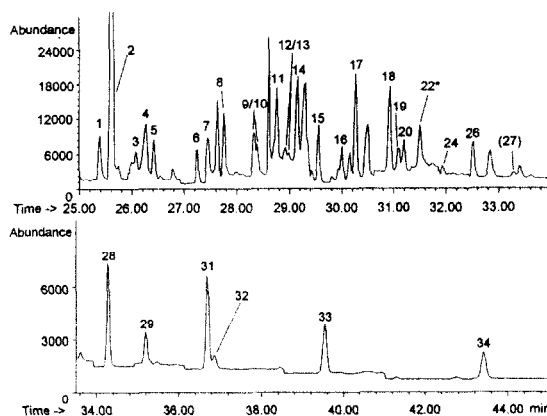


Fig. 3. MID chromatogram of an extract of a water sample spiked at 10 ng/l. Internal standard (2) added at a concentration of 200 ng/l. The asterisk indicates 3-indolyacetic acid PFB ester (21) coeluting.

compounds under investigation that could not be spotted using this procedure at the 10 ng/l concentration level were flurenol, chloramben and, of course, picloram. As can be seen from Fig. 4, a positive confirmation of the identity of any target compound is possible by means of the three indicative ion traces that are the source of the peak seen in the MID chromatogram.

In this particular instance the demonstration was done for the small peak of 3-indolybutyric acid seen in Fig. 3 as peak 32. All peaks that can be seen in the MID chromatograms represent the equivalent of 200 pg injected, presupposing a total recovery of the spiked target compounds.

The evaluation of all spike experiments down to a concentration of 1 ng/l was carried out to obtain an estimate of the detection limit of every target compound with real drinking water sam-

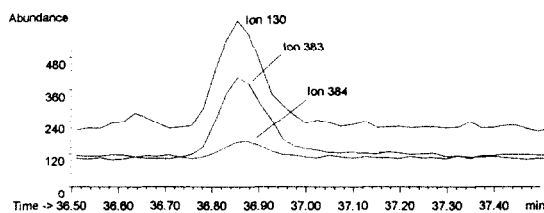


Fig. 4. Ion traces of *m/z* 384, 383 and 130 for 3-indolybutyric acid reconstructed from the MID chromatogram shown in Fig. 3.



ples. For every individual compound three indicative masses were recorded, as described in a previous paper [1] and demonstrated in Fig. 4 with one of them. Detection levels were determined by extracting the ion traces for each individual compound. This means a time-consuming procedure especially for quantification, because proper integration parameter setting is important and has to be checked individually. Therefore, we do not report detection limits

calculated from the calibration graphs obtained in the series of spike experiments rather than the lowest concentration level at which in three parallel analyses the target compound could definitively be seen with a signal-to-noise ratio of 3:1 or better. In Table 2 the detection limits for each compound are reported for the pure standard and in addition after extraction from drinking water samples. The detection limits for the individual compounds were found to be between

Table 2

Detection limits (DL) of the target compounds as their PFB derivatives in standard mixtures and in spiked tap water samples

No.	Compound	$t_R$ (min)	DL (standard) (pg)	DL (SPE) (ng/l) <sup>a</sup>
1	Clofibric acid	25.42	2	≤ 1
2	2,4-Dichlorbenzoic acid	25.65	4	≤ 1
3	Clopyralid	26.18	20	≤ 10
4	4-Chlorophenoxyacetic acid	26.28	10	≤ 10
5	Mecoprop	26.43	10	≤ 1
6	Dicamba	27.28	2	≤ 1
7	MCPA	27.48	2	≤ 1
8	Dichlorprop	27.79	1	≤ 1
9	Chlorflurenol-methyl <sup>b</sup>	28.31	10	≤ 10
10	Flurenol-butyl <sup>b</sup>	28.40	10	≤ 10
11	2,4-D	28.72	20	≤ 5
12	Chlorfenac	28.93	20	≤ 10
13	Bromoxynil	29.07	20	≤ 10
14	1-Naphthylacetic acid	29.17	2	≤ 5
15	Triclopyr	29.56	2	≤ 1
16	Fenoprop	30.03	2	≤ 5
17	Fluazifop- <i>p</i> -butyl <sup>b</sup>	30.28	1	≤ 1
18	Flamprop-isopropyl <sup>b</sup>	30.92	3	≤ 1
19	2,4,5-T	31.12	20	≤ 10
20	Bentazone	31.17	20	≤ 10
21	3-Indolyacetic acid	31.45	10	–
22	MCPB	31.54	20	≤ 10
23	Chloramben	31.75	20	≤ 25
24	Fluroxypyr	31.94	30	≤ 10
25	Flurenol	32.15	30	≤ 25
26	2,4-DB	32.87	30	≤ 10
27	3-Indolypropionic acid	33.28	10	–
28	Fluazifop	34.34	5	≤ 1
29	Benazolin	35.22	10	≤ 10
30	Picloram	35.48	30	–
31	Haloxypop	36.85	10	≤ 1
32	3-Indolybutyric acid	36.91	10	–
33	Flamprop	39.64	2	≤ 1
34	Acifluorfen	42.96	100	≤ 10

<sup>a</sup> Detection limits are not listed for compounds with unsatisfactory recoveries.

<sup>b</sup> Other esters.

1 and 10 ng/l, with the exception of two compounds.

The detection limits of the four active compounds that give inadequate recoveries with the SPE procedure were omitted, but the detection limits of the GC–MS method with test compounds (standards) are reported in Table 2.

It should be emphasized that the detection limits given had been estimated conservatively. This becomes evident on looking at Fig. 3, with peaks 29 and 34 of benazolin or acifluorfen having signal-to-noise ratios better than 10:1 but an estimated detection limit of 10 ng/l as given in Table 2.

### 3.5. Application to ground water samples

Finally, the potential of the procedure for residue analysis of drinking water is demonstrated with an example from a survey of ground and tap waters in Berlin carried out in 1992 and 1993. The recovery experiments with spiked tap water showed that nearly all of the 34 target compounds could be detected in tap water with detection limits between 1 and 25 ng/l, as compiled in Table 2. None of the real tap water samples gave positive results for any of the herbicides. The investigation of ground water samples, especially those from sites that were used for the production of drinking water, resulted in only a few positives at concentration levels clearly below the maximum tolerance of 100 ng/l. In one ground water sample mecoprop was found at 11 ng/l, as demonstrated in Fig. 5.

All three indicative ions arise simultaneously to form a peak at the retention time expected,

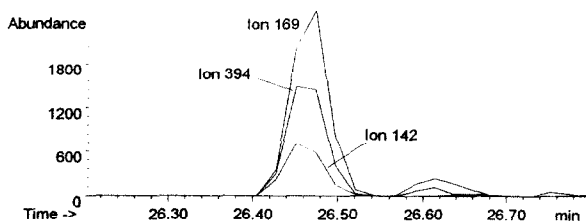


Fig. 5. Analysis of a ground water sample containing 11 ng/l of mecoprop. Ion traces of  $m/z$  394, 169 and 142 for mecoprop PFB ester.

exhibiting the intensity ratios as calibrated within an acceptable limit of variation, an essential result for positive identification. Other positive findings in raw water samples included mecoprop and dichlorprop.

In further investigations, this method was extended to the analysis of surface and sewage water samples. The performance of this method and the results of these investigations will be presented elsewhere [33].

### 3.6. Derivatization and mass spectrometric detection

The derivatization procedure and the mass spectrometric detection method are described and discussed in detail elsewhere [1]. Of course, the recoveries reported are not dependent on the final determination step. The eluates can equally be applied to the analysis with TLC using automated multiple development (AMD-TLC) [18] or HPLC.

Recently, the application of phase-transfer alkylation with PFBBr was reported as an alternative derivatization procedure [34]. In the same paper, a 100-fold increase in sensitivity by using electron-capture negative-ion chemical ionization MS (ECNCI-MS) was reported but could not be reproduced in our laboratory. Only a twofold increase compared with EI-MS with SIM was observed with derivatized standards applying ECNCI-MS with two different quadrupole MS systems (Finnigan 4000 and Hewlett-Packard 5989 A MS Engine). In preliminary studies, ECNCI-MS proved to be more prone to interferences from the matrix in real water samples with out quadrupole instruments. Thus, detection limits from environmental water samples were found to be surprisingly better with EI-MS-SIM. This results from target ions with much higher  $m/z$  values in EI-MS than those in ECNCI-MS caused by easy fragmentation of the PFB esters under ECNCI conditions. These matrix problems with ECNCI-MS detection might be overcome when using a high-resolution mass spectrometer as reported by Meiring *et al.* [34], but this type of instrument is not in widespread use in environmental analysis. In a normal environ-

mental laboratory, routinely achieving a resolution of 4000 with acceptable transmission would, in our opinion, involve too large a proportion of “down-time” when analysing “dirty” samples.

Using GC–EIMS with SIM, detection limits in the low-picogram range region can be achieved [1] for many phenoxy-carboxylic acid PFB esters and related compounds (see Table 2). When performing the extraction procedure described with RP-C<sub>18</sub> material A, detection limits down to 1 ng/l can be achieved for environmental water samples with a high load of matrix [33].

#### 4. Conclusions

Our investigations indicate that a careful selection and check of the adsorbent is a prerequisite in SPE. Adsorbents of the same type may vary so much in their ability to retain the analytes that an adsorbent from one supplier may be well suited whereas that from another supplier may give unsatisfactory results. Taking this into account, the method described has proved to be suitable for the sensitive screening of about 30 phenoxyalkanoic acids and other acidic compounds clearly below the concentration of 100 ng/l fixed by the EC as the maximum tolerance for drinking water. At a concentration level of 100 ng/l, 29 of the 34 compounds studied can be extracted with recoveries better than 50% and 26 compounds with recoveries better than 70%.

#### 5. References

- [1] Th. Heberer, S. Butz and H.-J. Stan, *J. Assoc. Off. Anal. Chem.*, in press.
- [2] *EEC Drinking Water Guideline, 80/779/EEC, EEC No. L229/11-29*, Commission of the European Communities, Brussels, August 30th, 1980.
- [3] N.C. Jimenez, Y.H. Atallah and T.R. Bade, *J. Assoc. Off. Anal. Chem.*, 72 (1989) 840–844.
- [4] T. Tsukioka, R. Takeshita and T. Murakami, *Analyst*, 111 (1986) 145–149.
- [5] M.A.H. Franson, *Standard Methods for the Examination of Water and Wastewater*, 17th ed., Part 6000, Automated Laboratory Analyses, American Public Health Association, Washington, DC, p. 6-182–6-187.
- [6] H. Agemian and A.S.Y. Chau, *Analyst*, 101 (1976) 732–737.
- [7] W. Fresenius, K.E. Quentin and W. Schneider, *Water Analysis*, Springer, Berlin, 1988, pp. 587–588.
- [8] W. Schüssler, *Chromatographia*, 29 (1990) 24–30.
- [9] H.-B. Lee, T.E. Peart, J.M. Carron and H. Tse, *J. Assoc. Off. Anal. Chem.*, 74 (1991) 835–842.
- [10] A. Brown, R.D. Stephens and I.S. Kim, *Trends Anal. Chem.*, 10 (1991) 330–335.
- [11] I.S. Kim, F.I. Sasinios, R.D. Stephens, J. Wang and M.A. Brown, *Anal. Chem.*, 63 (1991) 819–823.
- [12] W. Weber, *Ergebnisse und Tendenzen der Analytik von Pflanzenbehandlungsmitteln und ähnlichen Stoffen sowie deren Metaboliten in Grund- und Trinkwässern, Schr.-Reihe Verein WaBoLu 68*, Gustav Fischer, Stuttgart, 1987, pp. 109ff.
- [13] J. De Beer, C.H. Van Peteghem and A.M. Heyndrickx, *J. Assoc. Off. Anal. Chem.*, 61 (1978) 1140–1154.
- [14] C. Schlett, *Z. Wasser-Abwasser-Forsch.*, 23 (1990) 32–35.
- [15] M.J.I. Mattina, *J. Chromatogr.*, 542 (1991) 385–395.
- [16] S.H. Hoke, E.E. Brueggemann, L.J. Baxter and T. Trybus, *J. Chromatogr.*, 357 (1986) 429–432.
- [17] A. Gratzfeld-Hüsgen, R. Schuster and R. Weber, *LaborPraxis*, 8 (1992) 800–803.
- [18] *DIN 38 407, Teil 11, Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, Gemeinsam erfaßbare Stoffgruppen (Gruppe F), Bestimmung ausgewählter organischer Pflanzenbehandlungsmittel mittels Automated Multiple Development (AMD)-Technik (F11)*, Beuth Verlag Berlin, December 1990.
- [19] *DIN 38 407, Teil 14, Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, Gemeinsam erfaßbare Stoffgruppen (Gruppe F), Bestimmung von Phenoxyalkancarbonsäuren mittels Gaschromatographie und massenspektrometrischer Detektion nach Fest-Flüssig-Extraktion und Derivatisierung (F14)*, Beuth Verlag Berlin, December 1990.
- [20] W.H. Weber, *Probenvorbereitung für die Bestimmung von Pflanzenbehandlungsmitteln und ähnlichen Stoffen aus Grund- und Trinkwässern mittels Festphasen-Extraktion*, Baker Lit. 223, Baker, Groß-Gerau, Germany.
- [21] H.J. Brauch and S. Schullerer, *Buch der Umweltanalytik*, Band 4, GIT, Darmstadt, 1992, pp. 83–88.
- [22] H.-J. Stan and Th. Heberer, *J. Chromatogr.*, 653 (1993) 55–63.
- [23] S. Butz and H.-J. Stan, *J. Chromatogr.*, 643 (1993) 227–239.
- [24] C. Sternbergh, *Chlorophenoxy Acid Herbicides Qualitative Screening (Liquid Chromatography, Ultraviolet Detection)*, ICT Lit. m 639, ICT, Frankfurt am Main, 1986.
- [25] S. Mierzwa and S. Witek, *J. Chromatogr.*, 136 (1977) 105–111.
- [26] R.B. Geerdink, A.A. Van Balkom and H.J. Brouwer, *J. Chromatogr.*, 481 (1989) 275–285.

- [27] I. Liska, E.R. Brouwer, A.G.L. Ostheimer, H. Lingeman and U.A.Th. Brinkman, *Int. J. Environ. Anal. Chem.*, 47 (1992) 267–291.
- [28] W. Dedek, K.D. Wenzel, F. Luft, H. Oberländer and B. Mothes, *Fresenius' Z. Anal. Chem.*, 328 (1987) 484–486.
- [29] W. Dedek, K.D. Wenzel, H. Oberländer, B. Mothes and J. Männig, *Fresenius' Z. Anal. Chem.*, 339 (1991) 201–206.
- [30] W. Dedek, L. Weil and L. Feistel, *Wasser*, 78 (1992) 155–164.
- [31] L. Renberg, *Anal. Chem.*, 46 (1974) 459–461.
- [32] A. Di Corcia, M. Marchetti and R. Samperi, *Anal. Chem.*, 61 (1989) 1363–1367.
- [33] Th. Heberer, S. Butz and H.-J. Stan, *J. Environ. Anal. Chem.*, in press.
- [34] H.D. Meiring, G. den Engelsman and A.P.J.M. de Jong, *J. Chromatogr.*, 644 (1993) 357–365.