

This article was downloaded by:

On: 18 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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 Phenoxy-carboxylic Acids and Other Acidic Compounds in Tap, Ground, Surface and Sewage Water at the Low ng/1 Level

Th. Heberer^a; S. Butz^a; H. -J. Stan^a

^a Institute of Food Chemistry, Technical University of Berlin, Berlin, Germany

To cite this Article Heberer, Th. , Butz, S. and Stan, H. -J.(1995) 'Analysis of Phenoxy-carboxylic Acids and Other Acidic Compounds in Tap, Ground, Surface and Sewage Water at the Low ng/1 Level', *International Journal of Environmental Analytical Chemistry*, 58: 1, 43 – 53

To link to this Article: DOI: 10.1080/03067319508033111

URL: <http://dx.doi.org/10.1080/03067319508033111>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

ANALYSIS OF PHENOXYCARBOXYLIC ACIDS AND OTHER ACIDIC COMPOUNDS IN TAP, GROUND, SURFACE AND SEWAGE WATER AT THE LOW ng/l LEVEL

Th. HEBERER, S. BUTZ and H.-J. STAN

*Institute of Food Chemistry, Technical University of Berlin, Gustav-Meyer-Allee 25,
D-13355 Berlin, Germany*

(Received, 10 September 1993; in final form, 29 December 1993)

Solid-phase extraction with RP-C18 phase has been successfully applied for the determination of more than 30 acidic herbicides and related compounds from environmental water samples. Detection of these contaminants was performed after pentafluorobenzoylation at the low ng per liter level using gas chromatography/mass spectrometry. With multiple-component SIM programming simultaneous detection of all compounds in one single gas chromatographic run was possible.

Increased reliability of acidic herbicide analysis from water samples with high matrix content was achieved by using a surrogate as well as an internal standard. 2-(4-chlorophenoxy) butyric acid, being a structural isomer of clofibric acid and mecoprop, was chosen as surrogate standard because clofibric acid was found to be a widespread contaminant in environmental water samples from the Berlin area. Mecoprop, dichlorprop and 1-naphthylacetic acid were also found in field studies of some of these samples. A few examples of positive findings in tap, ground, surface and sewage water samples are presented.

KEY WORDS: Acidic herbicides, pentafluorobenzoylation, solid-phase extraction, gas chromatography-mass Spectrometry (SIM), drinking water, surface and sewage water.

INTRODUCTION

The analysis of polar contaminants has gained much importance in recent years. Phenoxyalkanoic acids which are applied to defeat "broad leaf weeds" are potential water contaminants because of their widespread use^{1,2}.

Identification and quantitation of these compounds at a concentration level of 100 ng per liter is required to meet the maximum tolerances set by the EC commission tolerances for drinking water. Therefore, methods with high sensitivity and reliability have to be developed. A method complying these requirements to enable the detection of such low concentration levels and concentrations clearly below the 100 ng/l level has recently been elaborated by our group^{3,4}. In this method the water samples are extracted with solid-phase

extraction (SPE) using carefully checked RP-C18 material with recovery rates of more than 70% and convenient standard deviations for almost all compounds investigated⁴. Pentafluorobenzyl bromide is used for derivatization to form the pentafluorobenzyl esters of the acidic herbicides. Detection is performed with capillary gas chromatography/mass spectrometry (GC-MS) with electron impact ionization applying selected ion monitoring (SIM). This method makes the recognition possible of 1 to 10 ng of the target compounds in 1 liter of tap water with clear identification³.

The method, originally developed with tap water samples, has been modified for the application to environmental water samples. Many samples of different origin such as drinking, ground, river and sewage water have subsequently been investigated in field studies. In this paper, the extended method is described and its potential is demonstrated by presenting chromatograms of positive results.

EXPERIMENTAL

Material

All solvents were Pestanal products from Riedel de Haen. Pentafluorobenzyl bromide was obtained from Aldrich (Steinheim, Germany) triethylamine from Merck (Darmstadt, Germany). Sample vials, screw caps and septa were purchased from Zinsser (Frankfurt, Germany) 200 μ l inserts for the sample vials from CS-Chromatographie Service (Langerwehe, Germany). All pesticide standards were of analytical purity purchased from Promochem (Wesel, Germany) or Pestanal quality from Riedel de Haen (Seelze, Germany). Stock solutions of all compounds were prepared in toluene or methanol. 2-(4-chlorophenoxy) butyric acid was synthesized according to a procedure described elsewhere⁵. Solid-phase extraction was carried out with cartridges of polypropylene with a volume of 6 ml from Baker, (Frankfurt, Germany). The RP-C18 material is obtained from Eurochrom (Europrep 60–30 C18; 60 \AA , 20–45 μ m, irregular) (Berlin, Germany.) Adjustable transferpettors (1–10 μ l and 10–100 μ l) were from Brand (Wertheim, Germany).

Sample preparation

Procedure A. A water sample of 1 l was mixed with 100 μ l of a solution of 2,4-dichlorobenzoic acid in methanol (2 ng/ μ l) as an internal standard to give 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-C18 adsorbent. Conditioning was performed successively with 10 ml acetone, 10 ml 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 was then percolated through the cartridge at a flow rate of about 8 ml/min applying a low vacuum. After drying the cartridge for 2–3 hours 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.

Procedure B. A water sample of 1 l was mixed with 100 μl of a solution of 2-(4-chlorophenoxy) butyric acid in methanol (1 $\text{ng}/\mu\text{l}$) to give a concentration of 100 ng/l . The sample was then acidified to $\text{pH} < 2$ with HCl. SPE was carried out as described in procedure A. The eluate from the SPE-cartridge containing the target compounds was mixed with 100 μl of a solution of 2,4 dichlorobenzoic acid in methanol (2 $\text{ng}/\mu\text{l}$) as internal standard to give the same concentration of 200 ng/l as in procedure A. The eluate was dried under a gentle stream of nitrogen.

Procedure C. Recovery experiments for checking the method with the various types of water were carried out by spiking a sample of 1 liter water by adding a mixture of pesticides dissolved in methanol to obtain a concentration of 100 ng/l or less of each active compound. The protocol then followed procedure A or B.

Derivatization

Derivatization was performed at 90°C for one hour using 200 μl of pentafluorobenzyl bromide (2% in toluene) and 2 μl of triethylamine as catalyst as previously described³. The derivatized sample was then dried under nitrogen and finally dissolved in 100 μl toluene.

GC-MS parameters

All mass spectrometric measurements were performed with a Hewlett-Packard HP 5970 MSD combined with an HP 5890 gas chromatograph fitted with a 25 m \times 0.2 mm i.d. \times 0.33 μm HP-5 capillary column and a 1.5 m \times 0.32 mm i.d. \times 0.33 μm HP-5 precolumn. 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. Injection port and transfer-line temperatures were 210°C and 250°C, respectively. 2 μl quantities of sample were injected by means of an HP 7673 autosampler using hot splitless injection with the split closed for 0.9 min. Using SIM three characteristic ions were selected for each compound and scanned with corresponding time windows between one and three minutes with dwell times of 100 to 200 ms per ion as described elsewhere³. Several target compounds were grouped in one window when eluting so close from the capillary column that switching of the indicative ions was not feasible. Mass spectrometer tuning was carried out weekly using the autotuning macro. Precolumn and insert liner were exchanged after at least 50 injections.

RESULTS AND DISCUSSION

Analytical method

The method for determining acidic herbicides and related compounds recently elaborated

in our group^{3,4}, has been evaluated and tested with water samples of different origin in field studies for more than one year. Sample preparation was carried out over the first months following procedure A. In the course of the field study it turned out that clofibric acid (4-CP) was the contaminant of greatest importance in water samples from the Berlin area⁶. Two other herbicides were also found in a few of the ground and river water samples, namely mecoprop and dichlorprop. Therefore, a surrogate standard was selected which greatly resembles the structure of 4-CP and also mecoprop. This is an isomer with only one methyl group shifted in the molecule compared to 4-CP, namely 2-(4-chlorophenoxy) butyric acid. This compound was synthesized in our laboratory⁵ and its occurrence in the environment is totally improbable.

It was expected that its behaviour in the extraction and derivatization procedure would reflect that of 4-CP and mecoprop. The gaschromatographic properties of the three isomers is such that all compounds appear in the chromatogram with a distance of about 1 minute. The mass spectral fragmentation patterns of the three isomers contain the same molecular and similar fragment ions. Therefore, the application of this "ideal" surrogate standard renders the detection and quantitative analysis of both clofibric acid and mecoprop extremely reliable.

The merits using this surrogate standard has recently been proven very impressively. In a survey investigation of 70 tap water samples four of them could not be evaluated because the surrogate standard was not recovered and consequently no clofibric acid was found. In all four cases, samples from the same water tap taken a week before or later did not show any peculiarities. At present we have no idea what the reason for the interference could have been.

In Table 1 the retention times and the three indicative masses used for SIM are compiled together with their relative abundances in full mass spectra. The knowledge of these relative abundances is a prerequisite for enabling the identification of the individual compounds by calculating the peak area ratios of the ion traces. All gaschromatographic—mass spectrometric measurements were performed according to the SIM program described in detail elsewhere³.

The analytical method originally elaborated for the investigation of drinking water has been applied successfully to ground, surface and even sewage water. In these studies with many positive results the target compounds have been detected at the low ppt level. No additional clean-up steps were necessary even with sewage water samples. A few samples were selected to demonstrate the potential of the method.

Application to drinking water

A survey analysis of ground water in Berlin carried out in 1991 and 1992 including capillary gas chromatography with element specific detection (AED) resulted in finding the compound 2-(4-chlorophenoxy)-2-methyl propionic acid (4-CP) which was recognized as the drug clofibric acid⁵. This was the immediate reason to improve the detection sensitivity of the analytical method for acidic herbicides and other acidic compounds with special focus on clofibric acid in order to be able to detect these target compounds at lower concentration

Table 1 GC and GC-MS Data of the PFB derivatives of the Target Compounds.

In brackets the relative intensity of the charged mass fragment in the EI mass spectrum with the basepeak = 100.

Compound:	Rt (min)	Mass 1 (rel.abund.)*	Mass 2 (rel.abund.)*	Mass 3 (rel.abund.)*
Clofibric acid	25.42	128 (100)	130 (32)	394 (13)
2,4-Dichlorobenzoic acid	25.65	173 (48)	370 (42)	372 (28)
Clopyralid	26.18	147 (66)	175 (40)	308 (9)
p-Chlorophenoxyacetic acid	26.28	366 (100)	141 (51)	368 (33)
Mecoprop	26.43	169 (100)	394 (94)	142 (59)
2-(4-Chlorophenoxy) butyric acid	26.63	128 (93)	394 (77)	169 (70)
Dicamba	27.28	203 (79)	400 (31)	402 (20)
MCPA	27.48	380 (95)	141 (83)	382 (32)
Dichlorprop	27.79	162 (65)	414 (46)	416 (32)
Chlorflurenol-methyl**	28.31	215 (100)	152 (42)	217 (33)
Flurenol-butyl**	28.40	152 (27)	153 (13)	282 (5)
2,4-D	28.72	175 (48)	400 (42)	402 (27)
Chlorfenac	28.93	195 (60)	383 (17)	418 (11)
Bromoxynil	29.07	161 (6)	457 (3)	455 (2)
1-Naphthylacetic acid	29.17	141 (100)	366 (84)	115 (19)
Triclopyr	29.56	210 (30)	435 (20)	437 (19)
Fenoprop	30.03	196 (46)	448 (24)	450 (24)
Fluazifop-p-butyl**	30.28	282 (100)	383 (51)	254 (38)
Flamprop-isopropyl**	30.92	105 (100)	276 (15)	363 (2)
2,4,5-T	31.12	434 (27)	436 (26)	211 (26)
Bentazon	31.17	378 (33)	420 (15)	341 (11)
3-Indolylacetic acid	31.45	130 (100)	355 (57)	356 (11)
MCPB	31.54	267 (25)	142 (5)	408 (3)
Chloramben	31.75	385 (100)	387 (66)	161 (26)
Fluroxypyr	31.94	434 (36)	209 (28)	436 (23)
Flurenol	32.14	152 (31)	153 (17)	406 (12)
2,4-DB	32.87	267 (24)	162 (8)	428 (1)
3-Indolylpropionic acid	33.28	130 (100)	369 (67)	370 (15)
Fluazifop	34.34	282 (100)	254 (58)	507 (53)
Benazolin	35.22	170 (100)	423 (87)	198 (41)
Picloram	35.48	196 (100)	198 (96)	420 (6)
Haloxypop	36.85	316 (100)	288 (63)	541 (44)
3-Indolylbutyric acid	36.91	130 (100)	383 (57)	384 (11)
Flamprop	39.64	105 (100)	276 (11)	501 (4)
Acifluorfen	42.96	345 (77)	511 (16)	541 (10)

*: relative abundances of the corresponding masses in the full mass spectrum

**: other esters

levels. A field study was carried out in 1993 with special attention given to the occurrence of clofibric acid in drinking water. The presence of this compound has subsequently been checked for more than two hundred water samples applying the method described above, initially by using procedure A and later procedure B. In most of the samples no herbicides could be detected, but 4-CP was frequently present at varying levels of concentration ranging from 10 to 165 ng/l. The Multiple Ion Detection (MID) chromatogram of a tap water sample analysed following procedure A and containing 20 ng/l of 4-CP is shown in Figure 1. This small amount of 4-CP gives a very clear peak. Besides the compounds 4-CP and the internal

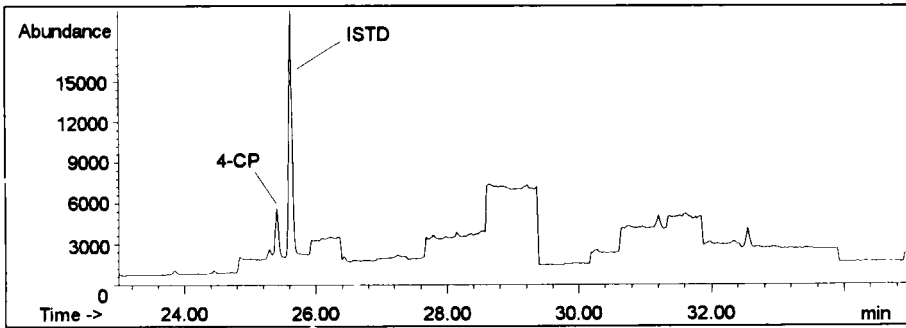


Figure 1 MID chromatogram of a tap water sample containing 20 ng/l clofibric acid (4-CP). 200 ng per liter 2,4 dichlorobenzoic acid added (ISTD).

standard 2,4 dichlorobenzoic acid (ISTD), hardly any peak appears in the chromatogram. Note that the steps observed in the baseline of the chromatogram reflect the switches in the ion traces recorded in the various time windows.

Application to ground water

The following example was chosen from the survey of ground water samples from sewage fields near Berlin.

In this study 4-CP was again found in approximately half of the analysed samples at concentrations ranging from 1 ng/l up to a few $\mu\text{g/l}$. In Figure 2 the MID chromatogram of a ground water sample containing 1500 ng 4-CP and, additionally, only 11 ng/l mecoprop is presented. When taking into account the high amount of 20 mg per liter dissolved organic carbon (DOC) measured for this sample, the determination of the trace level concentration of mecoprop without interferences was even more remarkable. On the other hand, the large amount of 4-CP found in a water sample taken from a depth of about 40 m is an indication

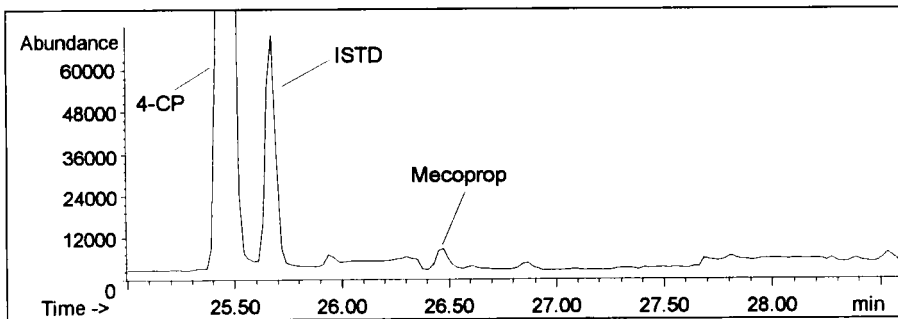


Figure 2 MID chromatogram of a ground water sample containing 1.5 μg clofibric acid and 11 ng mecoprop per liter.

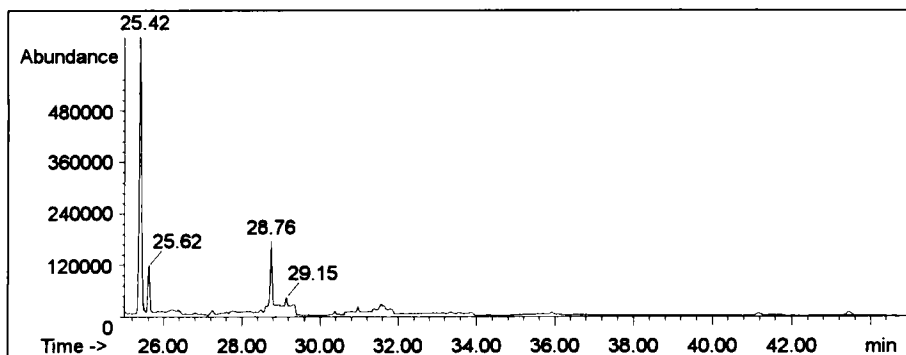


Figure 3 MID-chromatogram of an extracted sewage water sample, spiked-with 200 ng ISTD (at 25.62 min) per liter

of its high mobility in the environment. This ability of leaching seems to promote 4-CP as a tracer for the recognition of possible groundwater contamination in the Berlin area and elsewhere. The indicative ion peaks of mecoprop PFB ester occur in the chromatogram at the expected retention time without any interference which must be considered as a remarkable fact. Of course, the large amount of 4-CP could have easily been detected using full-scan acquisition, whereas the concentration of 11 ng/l mecoprop is far below the detection limit achievable in full scan mode.

Application to sewage water

Another example is given from investigations of sewage water samples of which one is presented with the MID chromatogram in Figure 3. One liter of the water sample has been extracted according to procedure A with 200 ng 2,4-dichlorobenzoic acid as internal standard. To our surprise a rather clear MID chromatogram resulted. The bulk of matrix compounds expected from the rather high DOC value of 80 mg per liter appeared obviously transparent with the time-programmed SIM. Four peaks are clearly recognizable with the dominating peak at 25.42 min which is caused by 4-CP followed by the internal standard at a retention time of 25.62 min. The identification of the four peaks was again performed by inspecting the individual ion chromatograms.

In Figure 4 the characteristic ion traces of 4-CP and the internal standard are presented. Both compounds were detected and clearly identified by their three indicative ion traces arising at the expected retention time to form a symmetrical peak with the relative abundances of the ions as calibrated. The amount of 4-CP in the sample was calculated with the three ion traces and determined to be 1200 ng per liter. The peak at 28.76 min matches the retention time of 2,4-D as can be seen from Table 1. However, the peak is dominated by the ion m/z 147 which is not an indicative ion, but only a minor fragment in the mass spectrum of 2,4-D. None of the most intense and characteristic ions forms a peak and therefore, 2,4-D is absent from the sample. Another minor peak in the MID-chromatogram of Figure 3 at

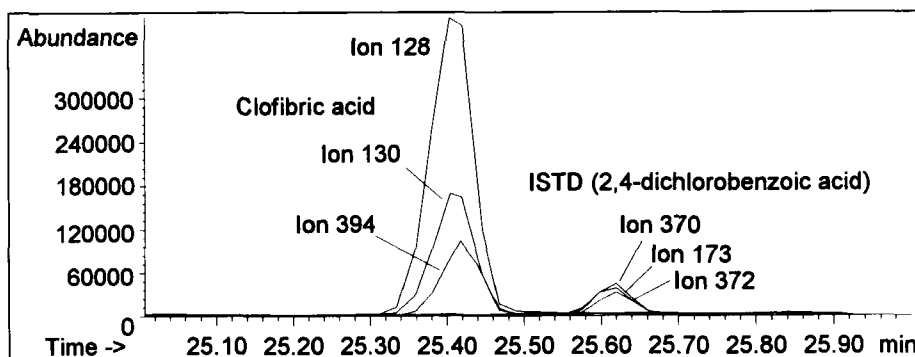


Figure 4 Characteristic ion traces of clofibric acid (at 25.42 min) and the internal standard (at 25.62 min), extracted from figure 3

29.15 min has been checked. With the indicative ion traces, the presence of 16 ng/l 1-naphthylacetic acid has been spotted and confirmed by calculating the ion intensity ratios. This trace amount of 1-naphthylacetic acid has been found in a sewage water with a DOC value as high as 80 mg per liter.

The investigations of sewage water samples made some modifications of the sample preparation necessary. The sample volume for sewage and surface water samples had to be frequently reduced to 500 or even 200 ml in order to avoid overloading the adsorbent and cartridge blocking by matrix compounds. Thus, with the smaller sample volume a constant flow of the percolating sample could be ensured.

With the large amount of matrix present in these samples varying recoveries were observed demanding a better control of sample preparation. This was the reason for introducing a surrogate standard which very much resembles the most important target compounds and for replacing the 2,4-dichlorobenzoic acid. This compound, however, was further used as the internal standard to control the reproducibility of the derivatization and the operation of the gas chromatographic system which is crucial in SIM analyses when working with narrow time windows. In the improved procedure B the surrogate standard 2-(4-chlorophenoxy)-butyric acid is used for recovery control and the internal standard for all steps following SPE.

Summarizing the properties of the surrogate standard: (a) it is not expected in environmental samples; (b) it gives 100% recovery from tap water; and (c) it is structurally similar to 4-CP and mecoprop, the most important target compounds monitored in our investigations. As mentioned above the surrogate is an isomer of these two compounds.

Application to river water

In the example shown in Figure 5, a Total Ion Current (TIC) chromatogram of a typical river water sample recorded in full scan is presented to demonstrate the high load of the GC-MS system arising from river water samples. In this case 500 ml of river water were extracted

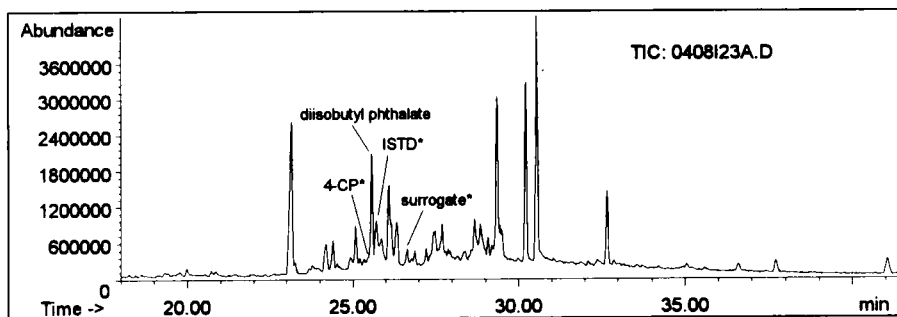


Figure 5 TIC chromatogram of a sample taken from the river Havel recorded in full scan mode (m/z 50–550). Sample spiked with 200 ng surrogate standard and 400 ng ISTD per liter. *Peaks resulting from matrix compounds overlapping the indicated target and standard compounds.

giving a very complex chromatogram. 4-CP as well as the surrogate and the internal standard are swamped by matrix compounds although peaks at the corresponding retention times suggest their presence. Nevertheless, the peaks are much too large to have originated from the target compounds, as can be seen from the evaluation of the Reconstructed Ion Chromatogram (RIC).

When using RIC, as shown in Figure 6 however, the overlapped PFB esters can be recognized and identified. In the RIC most of the interfering matrix ions have been faded out by selection of seven indicative ions. Only two additional ion peaks (for m/z 128 and 169) caused by matrix can be seen in this time window occurring at the retention time of the internal standard. Both ion peaks originate from minor mass fragments of a matrix compound that was only partially resolved. On the other hand the ion peaks of the target compounds were not interfered by matrix as can be shown by comparing the peak area ratios for the individual compound with the relative abundances of the masses in its mass spectrum shown in Table 1. Assuming that this is the case, ion peaks can easily be evaluated. Thus, 4-CP was calculated with 150 ng/l for this sample, but the limitation of full-scan analysis with this type of sample becomes evident. This can be drawn from Figure 6 demonstrating individual ion traces with signal to noise ratios at the detection limit. Nevertheless, full-scan acquisition is not dispensable when investigating environmental samples because it gives an overview of the total matrix content of the sample and enables the search for a great number of target compounds by RIC analysis in a single full-scan run as demonstrated for only a few in Figure 6. Furthermore, when storing the full scan data of an analysis it is possible to check with RIC the presence of compounds at a later time in the case where new information about possible contamination is found.

In Figure 7 a MID chromatogram of the same river water sample is presented. The complex chromatogram resulting from full scan has turned into a clear chromatogram with the analyte peaks dominating.

As expected when examining the ion traces, as demonstrated in Figure 8, the signal-to-noise ratio is found to be much better than that of full-scan acquisition. The seven ion traces selected correspond to those chosen in Figure 6 for the RIC's. Besides the improved

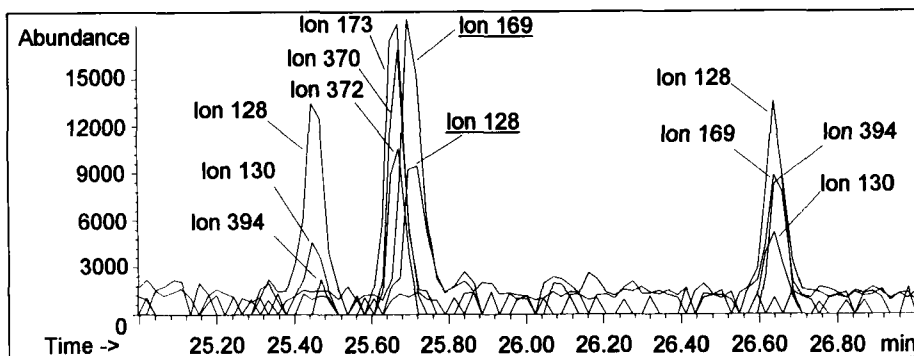


Figure 6 Restricted Ion Chromatograms (RIC's) taken from figure 5. Overlapping matrix ions underlined.

signal-to-noise ratio caused by increased dwell times for these indicative ions, it becomes evident that in the MID chromatogram the peaks of the target compounds are hardly interfered. Only a small ion peak for m/z 128 contributed to the MID peak of the internal standard, whereas the matrix ion peak for m/z 169 still visible in RIC (Figure 6) has been eliminated with the rest of interfering matrix ions by SIM programming. Due to the narrow time window setting the ion indicative for mecoprop and the surrogate standard did not have to be recorded before 26.00 min. It is obvious that the indicative ions selected for MID were hardly interfered even in the presence of high matrix content that can be drawn from the TIC in Figure 5. We suppose that with multiple SIM programming derivatization with PFBBr provides some advantages in comparison to other derivatization techniques such as methylation, although we did not prove this experimentally. PFBBr derivatization shifts the molecular weight of the acidic compounds by a remarkable 180 daltons resulting in much later retention times. Thus, low fragment ions such as the chlorophenol moiety (m/z 128) of clofibric acid PFB ester can not be interfered by smaller compounds eluting earlier. The higher masses of the molecular ions of the PFB esters, such as for instance m/z 394 for the

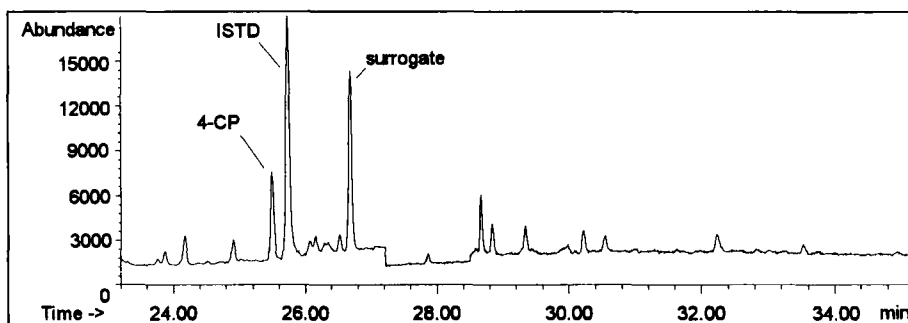


Figure 7 MID chromatogram recorded in SIM of the river water sample from figure 5. Sample with 74% recovery for the surrogate standard, containing 150 ng clofibric acid per liter.

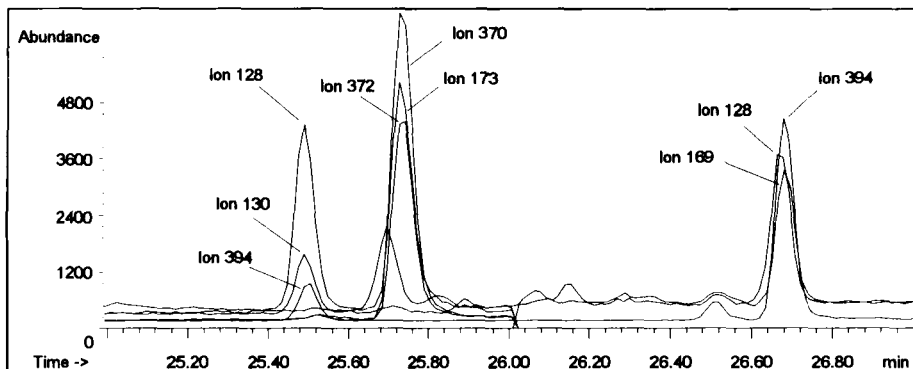


Figure 8 Ion traces taken from the MID chromatogram of the river water sample shown in figure 7.

esters of mecoprop, the internal standard and clofibric acid are obviously linked with a better signal to noise ratio. On the other hand fluorine derivatives elute from the used capillary column earlier than other molecules of the same molecular weight.

CONCLUSION

With the improved analytical method described in this paper trace level analysis of acidic herbicides is even possible from water samples with a high matrix content. The addition of the surrogate (2-(4-chlorophenoxy) butyric acid) and the internal standard 2,4-dichlorobenzoic acid as well has proven to increase the reliability of the results. The surrogate was designed as a structural isomer of the two most important target compounds clofibric acid and mecoprop with only one methyl group shifted in the molecule. The determination of the target compounds at low ng/l levels in water samples with high matrix content prove that the method worked excellent in our field studies.

References

1. H.-B. Lee, T. E. Peart, J. M. Carron and H. Tse, *J. Assoc. Off. Anal. Chem.*, **74**, 835–842 (1991).
2. C. Schlett, *Z. Wasser-Abwasser-Forsch.*, **23**, 32–35 (1990).
3. Th. Heberer, S. Butz and H.-J. Stan, *J. Assoc. Off. Anal. Chem.*, in press.
4. S. Butz, Th. Heberer and H.-J. Stan, *J. Chromatogr.*, in press.
5. H.-J. Stan and M. Linkerhügner, *Vom Wasser*, **79**, 75–88 (1992).
6. H.-J. Stan and Th. Heberer, in preparation.