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Gas chromatographic determination of acid herbicides in surface water samples with electron-capture detection and mass spectrometric confirmation

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Abstract

The development of a multi-residue method for the determination of eight polar acidic herbicides (MCPA, MCPB, mecoprop, 2,4-D, dichlorprop, bentazone, dicamba and dikegulac) in surface water is described. The method involves an off-line solid-phase extraction (SPE) procedure prior to instrumental analysis. The herbicides are isolated on an SPE C_{18} column and derivatized with pentafluorobenzyl bromide. After clean-up of the obtained solution on a disposable silica gel cartridge, the herbicide derivatives are determined by capillary gas chromatography with electron-capture detection and confirmed by capillary gas chromatography with mass selective detection using negative chemical ionization. The detection limits for the herbicides are in the range of 0.02–0.05 μg per litre surface water. The average recovery is 93%. A few hundreds of water samples were successfully analysed with this method.

Keywords: Water analysis; Environmental analysis; Solid-phase extraction; Derivatization, GC; Pesticides

1. Introduction

The analysis of polar acid compounds has become more important in the past few years. Acidic herbicides such as chlorophenoxy acids (MCPA, MCPB, mecoprop, 2,4-D, dichlorprop), bentazone, dicamba and dikegulac are widely used in agricultural and forestry applications. Due to their large-scale application, about 800 tonnes annually in the Netherlands, it is suspected that these compounds may be present in surface waters due to their persistent and polar character [1]. Therefore, if such surface waters are to be used for supply as drinking water, it is necessary to screen them on contamination by these herbicides. Dikegulac is an outsider compared to the other herbicides mentioned. Dikegulac is a by-product of vitamin C production appearing by draining in the River Rhine [2,3]. Besides, dikegulac is used occasionally as a plant growth regulator to reduce apical dominance and to promote side-branching and flower-bud formation in some ornamental plants [4]. A number of methods for the determination of these herbicides have been developed. Some publications have described liquid–liquid extraction [3,6–9] but solid-phase extraction (SPE) has gained in popularity in recent years. Most publications describe the use of modified silica gels, especially with C_{18} [10–15]. Other materials such as XAD-2 [8] and a combination of Carbopack B and SAX [16] have also been

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used. The herbicides have been determined by gas chromatography after derivatization [8–11] or by high-performance liquid chromatography [5,7,13–15]. Our aim was to develop a method that would cover all the herbicides mentioned at a level <0.1 μg/l in surface water as required by an EEC Directive [17,18]. Because of our choice of gas chromatography, derivatization is necessary. The detection of non-electron-capturing compounds (bentazone and dikegulac) can only be achieved by ECD, after derivatization with a reagent having an electronegative function. This paper describes a method for the SPE of eight polar acidic herbicides in surface water and subsequent esterification of the acidic functional groups with pentafluorobenzyl bromide.

2. Experimental

2.1. Reagents and apparatus

The acidic herbicides (99%) were obtained from Promochem (Wesel, Germany). Pentafluorobenzyl bromide (PFBB) was obtained from Pierce (Rockford, USA), cesium carbonate (99.9%) and the internal standard 2,4-dichlorobenzoic acid (98%) from Aldrich-Chemie (Steinheim, Germany). Standard solutions of the individual herbicides were in acetone and the internal standard in methanol (1 μg/ml). These solutions appeared to be stable for at least two years if stored at 4°C. A herbicide standard mixture was prepared in acetone. The herbicides-PFB derivatives and the internal standard mixture was prepared as described below in Section 2.4.2. A standard solution of the derivatives and the internal standard in 25% toluene–hexane (v/v) can be stored at 4°C for at least two years without degradation. A 10% (v/v) solution of PFBB was prepared in acetone. Solid-phase extraction was carried out with Bakerbond PolarPlus RP-C_{18} (octadecyl) of 6-ml cartridges (Baker, Philipsburg, USA). SEP-PAK silica cartridges were from the Waters Division of Millipore (Milford, USA). All other chemicals were of analytical grade and were checked for interfering impurities by means of control determinations. Evaporation of extracts was carried out at 40°C (water-bath) using a vacuum rotary evaporator.

2.2. Gas chromatography

A Hewlett Packard 5890A gas chromatograph equipped with two electron-capture detectors (ECD) was used. The instrument was equipped with an autosampler and two fused-silica capillary columns: Ultra-2 (cross-linked methyl siloxane), 25 m×0.32 mm I.D. film thickness 0.17 μm (Hewlett Packard, USA) and a DB-1701, 30 m×0.31 mm I.D., film thickness 0.25 μm (J&W Scientific, Rancho Cordova, USA). Helium was used as carrier gas (constant pressure 70 kPa). The temperatures of the injection port and the detector were 230°C and 300°C, respectively. A 1-μl sample volume was injected splitless onto the column at 60°C. After 60 s the carrier gas splitting was started and after another 60 s an oven temperature programme was started as follows: 25°C/min to 180°C, held for 1 min, then 2°C/min to 205°C, held for 3 min, then 10°C/min to 260°C, held for 12 min, then cooled to the initial temperature of 60°C.

2.3. Gas chromatography–mass spectrometry

The gas chromatograph–mass spectrometer (Carlo Erba MEGA 5000-QMD) was equipped with a fused-silica capillary column: DB-1701 30 m×0.31 mm I.D., film thickness 0.25 μm (J&W Scientific). Helium was used as carrier gas (constant pressure 70 kPa). The injection port temperature was 240°C. A 1-μl sample volume was injected splitless onto the column at 60°C. After 60 s the carrier gas splitting was started and after another 60 s an oven temperature programme was started as follows: 15°C/min to 200°C, then 5°C/min to 260°C, held for 5 min, then cooled to the initial temperature of 60°C. The mass spectrometer was operated in the negative-ion chemical ionization mode with methane as moderator gas (source pressure 10^{-4} mbar) and a electron energy of 70 eV. The ion source temperature of the mass spectrometer was 170°C. Spectra were recorded with a scan range of m/z 135–300 and a scan time of 0.5 s. Confirmation took place under selected-ion monitoring (SIM).

Table 1
Results of recovery experiments in surface waters

Herbicide added to water	Concentration (μg/l)	Recovery (%) (mean±S.D.)	R.S.D. (%) (n=12)
MCPA	0.1	93.2±4.2	4.5
	1.0	95.3±3.9	4.1
Mecoprop	0.1	90.5±3.1	3.4
	1.0	91.5±4.1	4.5
MCPB	0.1	89.7±5.8	6.5
	1.0	90.4±6.4	7.1
2,4-D	0.1	98.2±6.7	6.9
	1.0	106±1.9	1.8
Dichlorprop	0.1	98.2±6.7	6.9
	1.0	93.4±3.2	6.9
Bentazone	0.1	89.4±9.1	10
	1.0	90.3±3.1	3.4
Dicamba	0.1	83.4±4.5	5.4
	1.0	86.2±9.0	10
Dikegulac	0.1	97.6±7.2	7.3
	1.0	102±4.5	4.5

2.4. Determination

Extraction procedure

A 500-ml water sample was acidified to pH 2.4–2.6 with 2 *M* HCl. An amount of 5 ml of methanol and 1.0 ml of 1 μg/ml 2,4-dichlorobenzoic acid solution were added. The PolarPlus RP-C_{18} cartridge was conditioned with 10 ml of methanol and washed with 10 ml of Millipore-Q water acidified with HCl to pH 2.4–2.6. The cartridge was not allowed to run dry during this procedure. The water sample was then percolated through the C_{18} cartridge under vacuum at a rate of ca. 15 ml/min. The cartridge was air-dried under vacuum for about 5 min and centrifuged for 15 min at 500 *g* to remove the remaining water. The cartridge was washed with 0.75 ml of methanol and the washing discarded. Finally, the column was eluted with 2×2 ml portions of methanol into a graduated test tube under vacuum at a rate of about 2 ml /min. The eluate was adjusted to 10.0 ml with methanol and mixed.

Derivatization and column chromatographic clean-up

A 5-ml aliquot of the methanol extract was evaporated to dryness with the vacuum rotary evaporator at 40°C. The residue was dissolved in 10 ml of acetone. An amount of 200 μl of a 10% (v/v) PFBB solution, 25 mg of cesium carbonate and some pumic stones were added. The mixture was boiled under reflux (water bath 90°C) for 15 min, then 10 ml of 2,2,4-trimethyl pentane was added and the mixture concentrated to ca. 2 ml. Then another 10 ml of 2,2,4-trimethyl pentane was added and the mixture was again concentrated to ca. 2 ml. The concentrate was quantitatively transferred to a 10 ml volumetric flask, adjusted to the mark with 2,2,4-trimethyl pentane and mixed.

A silica SEP-PAK cartridge was fixed under an empty chromatographic column (30 cm×0.6 cm) and pre-washed with 5 ml of 25% (v/v) toluene–hexane and next with 5 ml *n*-hexane. A 4.0-ml portion of the 2,2,4-trimethyl pentane extract was transferred to the column. The column was washed with 20 ml 5% (v/v) toluene–hexane and the washing was discarded. Then the column was eluted with 100 ml 25% (v/v) toluene–hexane into a 250-ml round-bottom flask. This eluate contains MCPA, MCPB, mecoprop, 2,4-D, dichlorprop, dicamba and bentazone. Then the column was washed with 15 ml 5% (v/v) ethyl acetate–hexane and the washing was discarded. Finally, the column was eluted with 15 ml 10% (v/v) ethyl acetate–hexane into the same 250-ml round-bottom flask. This eluate contains dikegulac. The eluate was concentrated to 2 ml and mixed. This cleaned extract was examined by gas chromatography. Quantification was achieved by comparing the peak heights of the herbicides-PFB derivatives and the internal standard to those of standard solutions of comparable concentration.

3. Results and discussion

Recovery experiments were carried out by adding known amounts of the herbicides to 500 ml surface water. Recovery results were high and reproducible using 200 μl of the 10% PFBB solution. By using less PFBB (200 μl of a 1% or 5% solution) recoveries in surface water may be low or variable due to the consumption of PFBB by dissolved compounds [9]. For drinking water it was obtained that 200 μl of a 1% (v/v) PFBB solution was sufficient to obtain high and reproducible recoveries.

The recovery of the extraction of dikegulac at

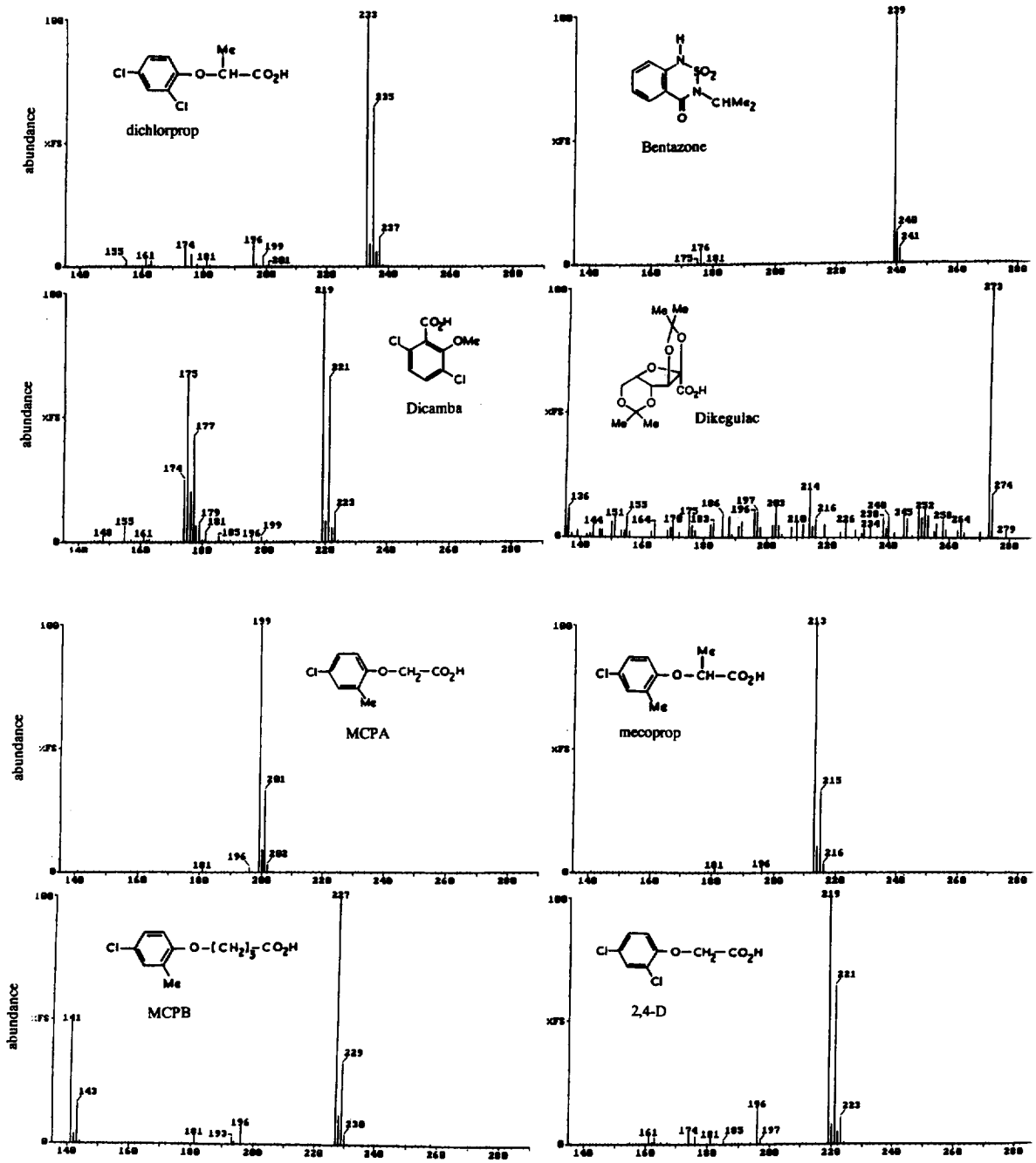

Fig. 1. NCI mass spectra of the pentafluorobenzyl (PFB) derivatives.

pH≤2 was about 30%. Dikegulac decomposes at pH≤2 [2,3]. Extraction at pH 3 resulted in a much better recovery, about 80%. However, at this pH the recovery of dicamba is only 45%. For all herbicides good recoveries were obtained at pH 2.4–2.6 with very acceptable standard deviations. The results of the recoveries are given in Table 1.

For derivatization with PFBB cesium carbonate was used to complete the reaction. The reaction time was not longer than 15 min which was substantially shorter than earlier described reaction times [9,10].

Surface water contains compounds [9] which may react with PFBB to form products that may strongly interfere during GC–ECD analysis. Therefore, extracts need a clean-up to remove most of these products. Also, excess of the reagent and by-products of the PFBB-reagent formed during the derivatization have to be removed. In Ref. [9] a combination of a silica gel column and gel permeation chromatographic (GPC) clean-up method has been described using a rather excessive amount of total solvents. This method is, however, rather time consuming (1.5 h per sample extract).

Because the here described procedure also saves on organic solvents for the extractions by using Bakerbond PolarPlus RP-C_{18} cartridges (relatively cheap) instead of liquid–liquid partition, it is less labourious and hence cheaper. Centrifuging the cartridges saves much time as compared to air drying [11] and hence the time to remove water from the cartridge was decreased substantially.

The response of the electron-capture detector and mass selective detector to the herbicide derivatives is linear up to at least 0.1 or 0.5 ng, respectively, with a minimum detectable amount of at least 0.0025 and 0.01 ng, respectively. Generally, in residue analysis positive samples should, if possible, be confirmed by mass spectrometry. The identity of herbicide derivatives was first investigated by negative chemical ionization (NCI) with methane as moderator gas, in the range of 80–500 m/z and a scan time of 0.5 s. The NCI mass spectra gave intensive fragment ions

Table 2
Mass fragments (m/z) used in SIM mode

Herbicide	Mass 1[a]	Mass 2[a]	R.T.-window (min)
MCPA	199(100)	201(33)	17–19
Mecoprop	213(100)	215(33)	15–17
MCPB	227(100)	229(33)	19–23
2,4-D	219(100)	221(63)	19–23
Dichlorprop	233(100)	235(63)	17–19
Bentazone	239(100)	240(11)	19–23
Dicamba	219(100)	221(67)	15–17
Dikegulac	273(100)	274(15)	17–19

[a] Relative abundance in parentheses.

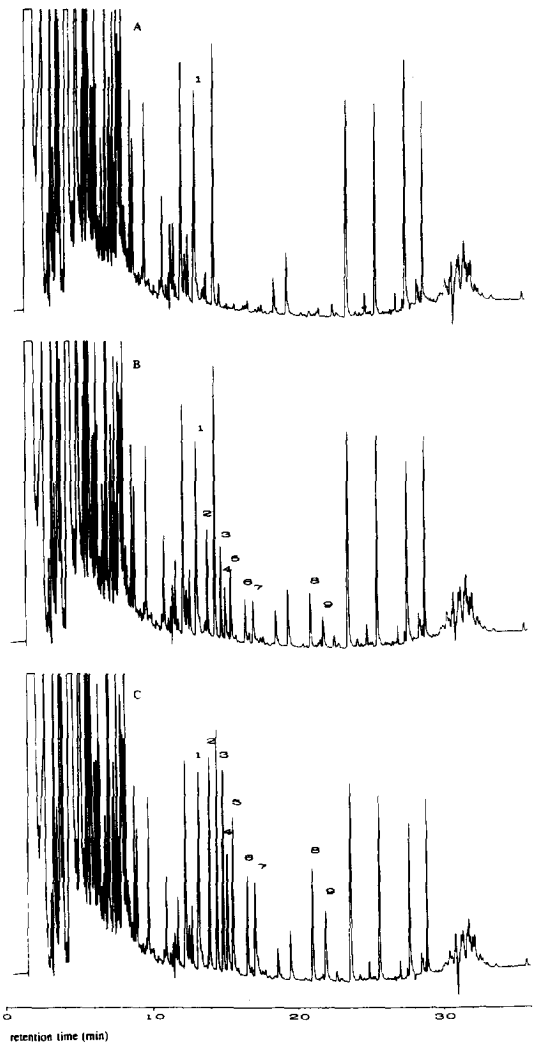

Fig. 2. ECD chromatograms of surface water obtained on an Ultra-2 fused-silica capillary column: (A) surface water; (B) fortified with 0.2 μg/l of herbicides; (C) fortified with 0.5 μg/l of herbicides. Pentafluorobenzyl (PFB) derivatives of: (1) 2,4-dichlorobenzoic acid (I.S.); (2) mecoprop; (3) dicamba; (4) MCPA; (5) dichlorprop; (6) dikegulac; (7) 2,4-D; (8) bentazone; (9) MCPB.

at $[M-181]^-$ for the derivatives investigated. However, these fragment ions are intensive but not selective. They belong to the coupled PFB group and, therefore, we measured again with a limited scan range of 135–300 *m/z*. This scan range gave selective-ion fragments such as the molecular ion (M^-) with a good relative abundance. These mass spectra are presented in Fig. 1. Using selected-ion monitoring (SIM), two characteristic ions were selected for each compound and scanned by using corresponding time windows with dwell times of 0.08 s per ion (Table 2). For positive identification the peak-area ratios of the indicative ion should match within ca. 20%. The relative abundances are given in Table 2.

An advantage of the method described is that bentazone, present in many formulations with chlorophenoxy acids, can be determined at the same time. An other advantage is that dikegulac can be determined separately via the SEP-PAK cartridge clean-up and hence only if required. With GC–ECD, detection limits of 0.02–0.05 μg/l surface water were obtained. Acid herbicides, special MCPA, mecoprop, 2,4-D and bentazone were found positive between ca. 0.02 and 2 μg per litre surface water in many samples.

Typical gas–liquid chromatograms of water samples spiked with the herbicides are shown in Fig. 2.

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