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Determination of residues of phenoxy acid herbicides in soil and cereals by gas chromatography–ion trap detection☆

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Abstract

The analysis of several phenoxy acids in soil and cereals was carried out by gas chromatography with ion trap detection, after derivatization with BF_3–methanol. Soil was extracted with methylene chloride, at acidic pH, on an orbit shaker, and plants were extracted with a 0.1 *M* NaOH solution in a Sorvall homogenizer. The extracts were cleaned up by liquid–liquid partition, the organic solvents evaporated and residues methylated. Herbicides residues were determined by gas chromatography–ion trap detection on a BP-1 capillary column with helium as carrier gas. Recovery through the method was studied in the range of 0.2 to 2 μg/g and was found higher than 80% for each herbicide in both matrixes. Residues of phenoxy acids were determined by selecting the base peak of their spectra, after acquisition of the total-ion chromatogram of the sample. The limit of detection in the selected-ion mode was 0.005 μg/g in soil and 0.04 μg/g in plant samples.

1. Introduction

Phenoxy acids are an important group of herbicides widely used to control broad leaf weeds. (2,4-Dichlorophenoxy)acetic acid (2,4-D), (4-chloro-2-methylphenoxy)acetic acid (MCPA) and (4-chloro-2-methylphenoxy)-propionic acid (MCPP or mecoprop) are the phenoxy acid herbicides most used in Spanish winter cereals, due to their low cost and good selectivity.

Several organic solvents, like acetonitrile, acetone, diethyl ether and methylene chloride, have been proposed for extraction of phenoxy acids from soils and cereals [1–5].

Determination of phenoxy acid residues has been usually carried out, after esterification, by gas chromatography (GC) with electron-capture detection [6,7], although other methods, like reversed-phase liquid chromatography [8,9], have been used too.

Capillary GC is a technique with high selectivity and sensitivity, suitable for the determination of multiple components, at residue level, in environmental samples [10]. Nevertheless, phenoxy acids are highly polar and with inadequate volatility to allow direct GC analysis. Conversion of acids into the corresponding methyl esters has been accomplished using diazomethane [11], or boron trifluoride–methanol [12]. Other reagents have also been used to

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obtain halogenated alkyl esters [13–15], in order to improve the response of electron-capture detector, especially important for compounds with a low halogen content, like MCPA and MCPP.

The purpose of this paper is to study the determination of several commonly used phenoxy acids, in soil and cereal samples, at trace level. The proposed methods are based on the determination by GC with the highly sensitive and specific ion trap detection (ITD), after esterification of the acids with BF_3–methanol.

2. Experimental

2.1. Chemicals

Herbicide standards were obtained from commercial sources. The compounds used were 2,4-D from Condor (Middlesex, UK), MCPA and MCPP from Akzo (Rotterdam, Netherlands).

The internal standard solution of MCPA propyl ester was prepared in the laboratory. A 2-ml volume of acetyl chloride–propanol (1:5), previously cooled, was added to 50 mg of MCPA and the mixture heated at 100°C in a sand bath for 1 h. After cooling, 2 ml of acetate buffer (pH 4.6) were added and the solution transferred to a 100-ml volumetric flask with methanol.

All solvents used were analytical-reagent grade from Panreac (Spain). Boron trifluoride–methanol was purchased from Merck (Germany).

2.2. Equipment

GC–ITD analysis was performed with a Perkin-Elmer 8500 chromatograph equipped with a Finnigan ion trap detector. A fused-silica capillary column, BP-1 (12 m × 0.22 mm I.D.) bonded phase, 0.25 μm film thickness, was used with helium as carrier gas at 10 p.s.i.g. (1 p.s.i. = 6894.76 Pa). The oven temperature was held at 85°C for 1 min, programmed to 250°C at 25°C/min and then held for 5 min. A 2-μl volume was injected splitless, with the split valve closed for 1 min.

2.3. Mass spectrometric acquisition parameters

The following conditions were used: transfer line temperature, 250°C; mass range, 40–350 u; scan rate, 0.5 s/scan, 2-μscans; radio frequency voltage, 1.1 MHz and 0–7.5 kV; automatic gain control, from 78 μs to 25 ms; solvent delay, 3 min.

2.4. Procedure

Soil (20 g) was extracted with 100 ml of methylene chloride, plus 15 ml of water acidified to pH 1.2 with 9 *M* H_2SO_4, on an orbit shaker for 1 h. Solvent was decanted and soil extracted again with another 100 ml of methylene chloride. The flask content was filtered under suction through Whatman No. 1 filter paper and Celite, and the filter cake washed twice with 50 ml of methylene chloride. The extract was transferred to a separatory funnel and extracted twice with 75 ml of 0.05 *M* NaOH (pH 8–9). The aqueous phase was acidified to pH 1.6 with 9 *M* H_2SO_4 and extracted with methylene chloride (2 × 100 ml). The organic phase was filtered through anhydrous sodium sulphate and solvent was evaporated to dryness using a rotary evaporator.

Plant samples (5 g) were extracted with 0.1 *M* NaOH (2 × 25 ml) in a Sorvall homogenizer, based on a previously published method [16]. The extract was filtered under suction and the filter cake washed twice with 5 ml of the basic aqueous solution. To the extract, 25 ml of saturated sodium chloride solution were added, the pH was lowered to near 5 by the addition of 2 *M* H_2SO_4, the solution let stand for 15 min and the liquid decanted. Then the pH of the solution was lowered to approximately 1, the solution was transferred to a separatory funnel and extracted with diethyl ether (2 × 50 ml). The organic phase was extracted with 0.5 *M* $NaHCO_3$ (2 × 25 ml), the combined aqueous solution acidified to pH 1 by adding carefully 3 *M* H_2SO_4 (10 ml), and extracted with chloroform (2 × 25 ml). The organic phase was filtered through anhydrous sodium sulphate and solvent concentrated to dryness under vacuum.

2.5. Esterification

The residue from the extraction procedure was transferred to a tube with methanol (1–2 ml) and 4 ml of BF_3–methanol were added. The mixture was heated at 70°C for 30 min in a water bath. After cooling the reaction mixture in an ice bath, 10 ml of hexane and 10 ml of water were added, the tube shaked for 1 min and then the hexane phase was transferred to a 10-ml tube, dried over sodium sulphate and analyzed by GC.

3. Results and discussion

Phenoxy acid herbicides, applied in the form of salts or esters, are mainly found in the acid form in soils, since ester hydrolysis to the parent compounds occurs in a few days, under field conditions [17]. Extraction of phenoxy acids from soil samples has been carried out with different solvents at acidic or basic pH [1,10,18]. In our case, the acidic extraction with methylene chloride produced cleaner extracts than those obtained at basic pH.

Acidic herbicides have been extracted from plant samples with organic [19] or aqueous [16] solvents. These compounds are best released from plant tissues at basic pH and several authors included a hydrolytic step through extraction with alkaline aqueous solutions [20]. Cereals were extracted following a previously reported method [16] and good results were obtained with this procedure.

Esterification of phenoxy acids, prior to GC determination, has been accomplished by BF_3–methanol [21], a reagent less dangerous than diazomethane, and good conversion of the three studied herbicides was obtained.

Fig. 1 shows the total ion chromatogram, acquired in the electron impact (EI) mode, of the methyl esters of 2,4-D, MCPA and MCPP, 2 ng each, and the internal standard, the propyl ester of MCPA, 5 ng. Their retention times together with the main ions of their mass spectra are shown in Table 1. The molecular ion is abundant in the mass spectra of these compounds, being the base peak of the spectrum for MCPA and MCPP methyl esters. The spectrum of 2,4-D methyl ester shows the base peak at m/z 199. Other remarkable peaks of 2,4-D, MCPA and MCPP spectra are observed at m/z 175, 155 and 169, respectively, caused by the loss of the $-COOCH_3$ fragment. Also, loss of the $-CH_2-COOCH_3$ fragment is important in the MCPA ester. The internal standard shows the molecular ion m/z 242, as the base peak, and the ions m/z 141 and 125 caused by loss of the fragments $-CH_2-COO-(CH_2)_2-CH_3$ and $-O-CH_2-COO-(CH_2)_2-CH_3$, respectively (Table 1).

Residues of phenoxy acids were determined by selecting the base peaks of their spectra, after acquisition of the total ion chromatogram of the sample. The ions m/z 228, 214, 199 and 242 were selected for MCPP, MCPA, 2,4-D and the internal standard, respectively. The concentration was determined by comparing the ratio of the areas in the mass chromatogram of selected ions in the sample with the ratio found for mixtures of known concentration of the herbicides and the internal standard.

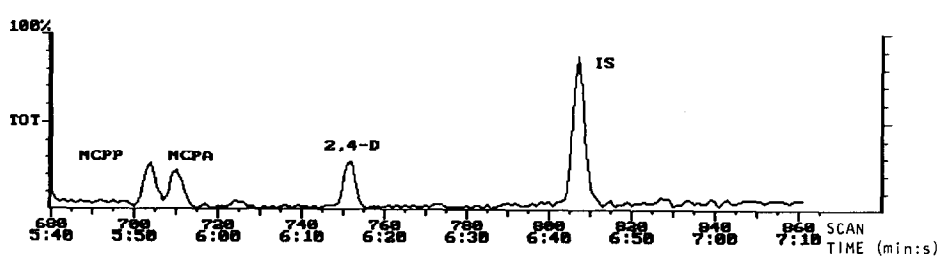

Fig. 1. Total ion chromatogram of the internal standard (IS) and the methyl esters of 2,4-D, MCPA and MCPP. A 5-ng amount of IS and 2 ng of each phenoxy acid were injected.

Table 1
GC retention times (t_R) and main ions in the EI mass spectra of methyl esters of phenoxy acids

Herbicide (methyl ester)	t_R (min)	m/z[a]	Fragment ion assignments
2,4-D	6.16	*199*	$[M-Cl]^+$
		235	$[M]^{+\cdot}$
		175	$[M\text{-}COOCH_3]^+$
MCPA	5.56	*214*	$[M]^{+\cdot}$
		155	$[M-COOCH_3]^+$
		141	$[M-CH_2COOCH_3]^+$
		125	$[M-OCH_2COOCH_3]^+$
MCPP	5.52	*228*	$[M]^{+\cdot}$
		169	$[M-COOCH_3]^+$
		141	$[M-CH(CH_3)COOCH_3]^+$
IS[b]	6.43	*242*	$[M]^{+\cdot}$
		125	$[M-OCH_2COO(CH_2)_2CH_3]^+$
		141	$[M-CH_2COO(CH_2)_2CH_3]^+$

[a] Base peak in italics.
[b] Internal standard: propyl ester of MCPA.

Recovery through the analytical method was studied with soil and cereals samples spiked before extraction by addition of 0.2, 1 and 2 μg/g of herbicides. The average recoveries varied from 80 to 106%, with a relative standard deviation between 1 and 12% (Table 2).

The detection limit of the GC–ITD method, with the total ion current, was near 0.01 μg/g for soil and 0.1 μg/g for plant samples. These limits can be improved with selected-ion monitoring (SIM) down to 0.005 μg/g for soil and 0.04 μg/g for plant samples (Fig. 2).

Soil from a cereal field, treated with MCPP, was sampled several months after treatment. The

Table 2
Recovery of phenoxy acids added to soil and plant samples

Herbicide	Added (μg/g)	Soil (mean ± S.D., %) (n = 4–6)	Plant (mean ± S.D., %) (n = 4)
MCPP	0.2	106.0 ± 2.1	95.5 ± 6.3
	1.0	89.7 ± 8.0	101.0 ± 7.0
	2.0	97.0 ± 12.0	96.5 ± 6.3
MCPA	0.2	80.5 ± 6.3	104.0 ± 6.3
	1.0	91.7 ± 8.3	99.3 ± 10.3
	2.0	102.0 ± 10.2	100.0 ± 1.4
2,4-D	0.2	89.0 ± 1.4	96.0 ± 8.4
	1.0	87.5 ± 12.7	103.0 ± 7.0
	2.0	89.3 ± 6.2	97.0 ± 2.4

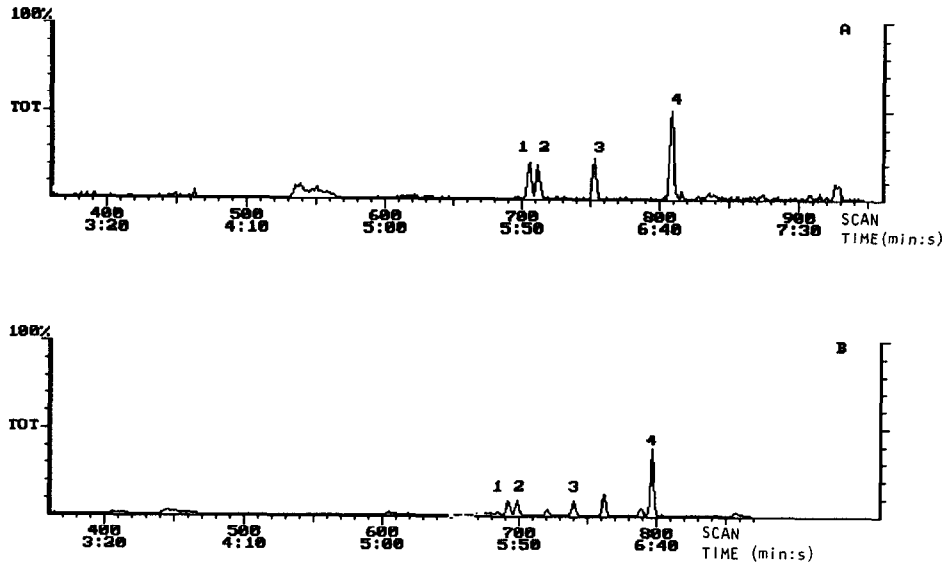

Fig. 2. SIM chromatograms of soil and plant extracts. (A) Soil sample (0.005 μg/g), (B) plant sample (0.04 μg/g). 1 = MCPP, 2 = MCPA, 3 = 2,4-D and 4 = internal standard.

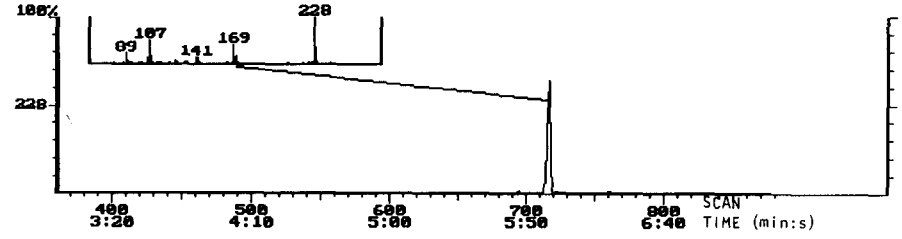

Fig. 3. Mass chromatogram (ion 228) of a treated soil sample (0.19 μg/g of MCPP).

sample was analyzed with the described method and MCPP was determined (0.19 μg/g) and identified by its mass spectrum (Fig. 3).

The proposed methods are reproducible and sensitive enough for determination of 2,4-D, MCPA and MCPP in soil and cereals, at residue level, by GC–ITD.

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