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Determination of dinitroaniline herbicides in environmental samples by gas chromatography

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Abstract

Simultaneous determination of several dinitroaniline herbicides in environmental samples (soil, plant and air) was performed by gas chromatography with ion trap and nitrogen–phosphorus detection.

Soil was extracted with ethyl acetate on an orbit shaker and plants were extracted with methanol in a Sorvall homogenizer. The plant extract was purified on a Florisil column before gas chromatographic analysis. The dinitroaniline herbicides volatilized from soil were trapped on a Florisil column, eluted with acetone and then analyzed by gas chromatography.

The concentrations of these compounds were determined by gas chromatography with nitrogen–phosphorus detection on a HP-1 capillary column and with ion trap detection on a BP-1 capillary column. Helium was used as carrier gas.

In all cases, the average recoveries were higher than 75%. The limit of detection for these herbicides was, at least, 0.01 μg/g in soil, 0.05 μg/g in plant and 1 ng/l in air with both gas chromatographic methods.

1. Introduction

Dinitroaniline herbicides are used to control some broad-leaved weeds and the major annual grasses in a wide variety of agronomic crops. Although the dinitroaniline herbicides are chemically related, they differ in volatility, persistence in soil and absorption by crops and, for this reason, may differ in their effects on soil [1,2], plants [3,4] and air [5].

Determination of dinitroaniline herbicide concentrations in soil and plants has usually been carried out by gas chromatography (GC) with electron capture detection [6–8], after sample extraction with an organic solvent and purification using Florisil cartridges [9] or glass chromatography columns packed with Florisil [7]. Liquid chromatography (HPLC) has also been used for the analysis of these herbicides [10] in soil and water.

Concentrations of these herbicides in air have generally been determined by means of different kinds of trapping apparatus [11,12] and a selective trapping phase, such as Florisil [12] or xylene [13].

The aim of the present work is to study the simultaneous determination of butralin, dinitramine, ethalfluralin, pendimethalin and trifluralin in soil, plants and air, at residue level, by GC with nitrogen–phosphorus detection (NPD) and ion trap detection (ITD).

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2. Experimental

2.1. Chemicals

Butralin [4-(1,1-dimethylethyl)-N-(1-methylpropyl)-2,6-dinitrobenzenamine], dinitramine [N^3,N^3-diethyl-2,4-dinitro-6-(trifluoromethyl)-1,3-benzenediamine] and pendimethalin [N-(1-ethyl-propyl)-3,4-dimethyl-2,6-dinitrobenzenamine] were obtained from CFPI (Gennevilliers, France), Condor (Middlesex, UK) and American Cyanamid (NJ, USA), respectively. Ethalfluralin [N-ethyl-N-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl)benzenamine] and trifluralin [2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine] were supplied by Eli Lilly (IN, USA).

The internal standard, the isopropyl ester of 2,4-dichlorophenoxyacetic acid (2,4-D), was prepared in our laboratory following a procedure previously described [14].

Ethyl acetate, methanol, *n*-hexane, acetone and methylene chloride, all analytical grade, were supplied by Panreac (Barcelona, Spain). Florisil (60–100 mesh) was obtained from Serva (Heidelberg, Germany). Anhydrous sodium chloride and anhydrous sodium sulfate were obtained from Merck (Darmstadt, Germany).

2.2. Equipment

GC–NPD

A Hewlett-Packard 5890 Series II gas chromatograph equipped with a nitrogen–phosphorus detector was used (Hewlett-Packard, Hoofddorp, Netherlands). A fused-silica capillary column, HP-1 (12.5 m × 0.20 mm I.D.), with 0.33 μm film thickness from Anorsa (Madrid, Spain), was employed with helium as the carrier gas (flow-rate 1 ml/min). Injection port and detector temperatures were maintained at 270°C and 300°C, respectively. The oven temperature was kept at 120°C for 1 min, then programmed to 180°C at 15°C/min, held at 180°C for 0.5 min, again programmed to 250°C at 10°C/min, and kept at the final temperature for 1 min. A 1-μl volume was injected splitless, with the split valve closed for 1 min.

GC–ITD

A Perkin-Elmer 8500 gas chromatograph equipped with a Finnigan ion trap detector was used (Perkin-Elmer, Norwalk, CT, USA). A fused-silica capillary column, BP-1 (12 m × 0.22 mm I.D.), 0.25 μm film thickness from Sugerlabor (Madrid, Spain), was used with helium as the carrier gas at 10 psi (1 psi = 6894.76 Pa). The injection port and detector temperatures were 270°C and 300°C, respectively. The oven temperature was maintained at 85°C for 1 min and then programmed at 20°C/min to 180°C, kept at 180°C for 1 min and then again programmed at 10°C/min to 250°C. A 2-μl injection in splitless mode, followed by a waiting time of 1 min was utilized. The mass spectrometric acquisition parameters were as follows: mass range, 120–400 u; scan rate, 0.5 s/scan, 3-μscans; radiofrequency voltage, 1.1 MHz and 0–7.5 kV; automatic gain control from 78 μs to 25 ms; solvent delay, 5 min.

2.3. Procedure

Soil

A 20-g amount of air-dried soil fortified with dinitroaniline herbicides (1, 0.5 or 0.1 μg/g) was extracted with 100 ml ethyl acetate on an orbit shaker for 45 min. After shaking, the extract was decanted and the soil again extracted with 100 ml ethyl acetate for 45 min. Soil extracts were filtered through Whatman No. 1 filter paper and the filter cake was washed with an additional 20 ml of ethyl acetate. The combined ethyl acetate extracts were carefully evaporated to dryness, under vacuum, using a rotary evaporator (35°C), and the residue transferred to a tube with ethyl acetate and concentrated to an appropriate volume before GC analysis.

Plants

Plant samples (5 g), fortified with the herbicides, were extracted twice with 20 ml methanol in a Sorvall homogenizer and filtered through Whatman No. 1 filter paper, after which the filter cake was washed with 10 ml methanol. An aliquot of the plant extract (20 ml) was transferred to a separatory funnel, which contained 40

ml of 5% sodium chloride solution plus 0.5 ml of 0.1 *M* NaOH, and extracted with methylene chloride (2 × 20 ml). The organic phase was passed through anhydrous sodium sulfate and carefully evaporated to dryness on a rotary evaporator, under vacuum. The residue was dissolved in 5 ml hexane–ethyl acetate (98:2) for the clean-up on a Florisil column. A glass column was packed with 10 g Florisil (deactivated with 2% water) with 2 g anhydrous sodium sulfate on top. The extract residue was added at the top of the column and eluted with 100 ml *n*-hexane–ethyl acetate (98:2). The organic solvent was removed under vacuum and the residue dissolved in ethyl acetate to an appropriate volume before GC analysis.

Air

The apparatus used to trap herbicides volatilized from soil has been described previously [15]. The system consisted of a chamber (10.5 cm diameter glass round-bottom flask) mounted in a water bath, an air cylinder and a pressure regulator. Soil samples were placed in the chamber and air, at a flow-rate of 12 l/h, was passed through the volatilization chamber at a set temperature. The vapours were trapped in a column (7.7 cm × 2.2 cm I.D.) containing 12 g Florisil. The Florisil column was eluted with 50 ml acetone, the solvent evaporated to dryness on a rotary vacuum evaporator (35°C) and the residue dissolved in 1 ml ethyl acetate before GC analysis.

Recovery was studied by adding 1 ml of a standard solution (0.1, 0.5 or 1 μg/ml) to the trapping Florisil column. This column was included in the volatilization system and air was passed through the system at a flow-rate of 12 l/h for 5 h.

A volatilization assay was also carried out at 35°C with 20 g of soil (10% of moisture content) treated with 25 μg/g of each herbicide. The experiment was carried out over a period of 5 h and the trapped herbicides were determined as described above.

The concentrations of these compounds were determined by comparing the ratios of the peak areas in the sample with those found for mixtures of the herbicides and the internal standard of known concentration.

3. Results and discussion

The total ion chromatogram obtained for a mixture of the dinitroaniline herbicides and the internal standard is shown in Fig. 1. The results of the qualitative analysis, retention times and main ions found in the mass spectra are summarized in Table 1.

The herbicides trifluralin, butralin and pendimethalin gave base peaks at *m/z* 306, 266 and 252, respectively, corresponding to $[M - CH_2 - CH_3]^+$. The mass spectrum of ethalfluralin showed a base peak at *m/z* 276 and dinitramine presented the base peak at *m/z* 305. These ions were used for quantitation of the herbicides. Good linearity was obtained for all herbicides studied in the range 0.1–2 ng.

Soil samples were spiked with 0.1, 0.5 and 1 μg/g of the studied herbicides and analyzed by GC–ITD and GC–NPD following the procedure

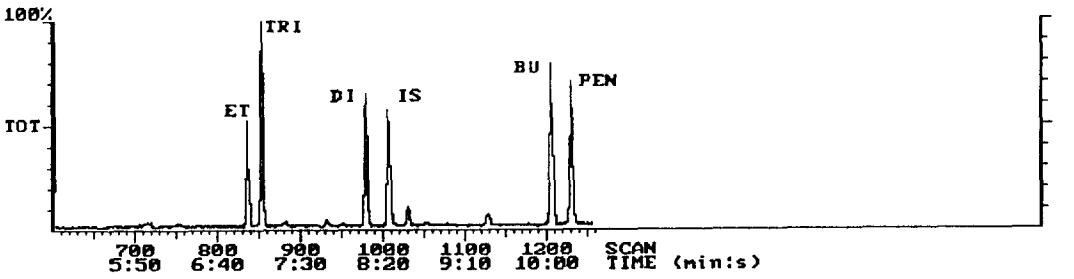

Fig. 1. Total ion chromatogram of a mixture of dinitroaniline herbicides (1 μg/ml) and the internal standard (IS) (0.5 μg/ml).

Table 1
GC retention times (t_R) and main ions in the mass spectra of dinitroaniline herbicides

Herbicide	t_R (min)		m/z
	HP-1[a]	BP-1[b]	
Ethalfluralin	5.61	6.58	**276**, 292, 316, 333
Trifluralin	5.78	7.08	264, 290, **306**, 336
Dinitramine	6.91	8.09	261, **305**, 322
Butralin	8.95	10.04	250, **266**, 295
Pendimethalin	9.14	10.17	**252**, 281
IS[c]		8.24	**276**

[a] Fused-silica capillary column: 0.33 μm film thickness and 12.5 m × 0.20 mm I.D.
[b] Fused-silica capillary column: 0.25 μm film thickness and 12 m × 0.22 mm I.D.
[c] Internal standard = isopropyl ester of 2,4-D.

described above. The average recoveries varied from 88 to 98% with a relative standard deviation between 1 and 5% for GC–ITD, and from 75 to 111% with the relative standard deviation ranging from 1 to 7% for GC–NPD (Table 2), with good agreement between the two GC methods.

Fig. 2 shows a GC–ITD chromatogram of a soil sample from a field treated with ethalfluralin and pendimethalin. The concentrations of these herbicides were determined by both chromatographic methods and confirmed by their mass spectra. The detection limit, in soil samples, of the dinitroaniline herbicides studied was near 0.01 μg/g for both GC–NPD and GC–ITD with selected-ion monitoring.

Extraction of these herbicides from plant samples was carried out with methanol [7], followed by clean-up of the extracts on a Florisil column. Table 3 shows the recoveries of these compounds added to tomato plants in the range 0.1 to 1 μg/g fresh weight and analyzed using the proposed method. The average recoveries ranged from 84 to 104% for GC–ITD and from 82 to 105% for GC–NPD, with the relative standard deviation ranging between 2 and 11%. Agreement between GC–NPD and GC–ITD was good.

Fig. 3 shows a GC–ITD chromatogram of a sample of tomato grown in a field treated with pendimethalin. The concentration of this herbicide in the plant sample was determined by

Table 2
Recovery of dinitroaniline herbicides added to soil samples

Herbicide	Added (μg/g)	GC–ITD (mean ± S.D., %) ($n = 4$)	GC–NPD (mean ± S.D., %) ($n = 4$)
Ethalfluralin	1.0	96.3 ± 1.0	95.1 ± 2.6
	0.5	94.5 ± 3.7	94.9 ± 2.4
	0.1	98.5 ± 1.3	90.4 ± 5.0
Trifluralin	1.0	96.1 ± 2.0	92.8 ± 5.7
	0.5	96.2 ± 2.6	97.5 ± 3.2
	0.1	98.0 ± 3.5	92.1 ± 3.0
Dinitramine	1.0	93.0 ± 5.4	101.2 ± 6.9
	0.5	89.2 ± 1.7	78.1 ± 5.1
	0.1	88.0 ± 3.9	75.5 ± 5.7
Butralin	1.0	97.7 ± 3.3	90.2 ± 6.9
	0.5	97.5 ± 2.6	96.8 ± 5.1
	0.1	96.3 ± 1.5	91.0 ± 1.3
Pendimethalin	1.0	98.2 ± 1.7	89.5 ± 6.9
	0.5	96.0 ± 2.9	101.2 ± 6.3
	0.1	96.0 ± 4.9	94.8 ± 2.2

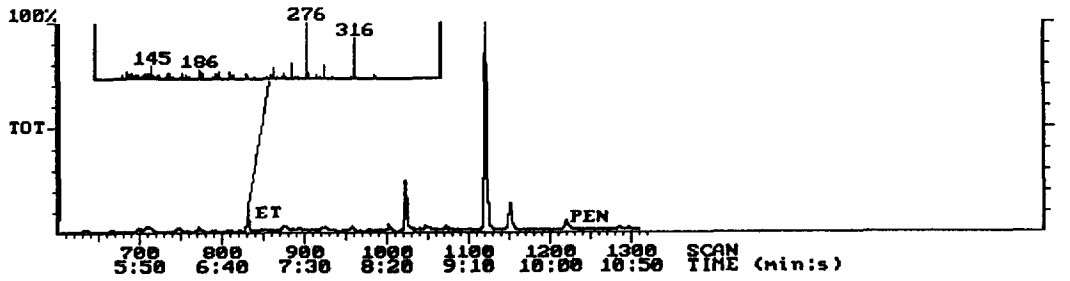

Fig. 2. Total ion chromatogram of a treated soil sample (0.17 μg/g of ethalfluralin and 0.013 μg/g of pendimethalin).

Table 3
Recovery of dinitroaniline herbicides added to plant samples

Herbicide	Added (μg/g)	GC–ITD (mean ± S.D., %) ($n = 4$)	GC–NPD (mean ± S.D., %) ($n = 4$)
Ethalfluralin	1.0	86.5 ± 6.2	85.3 ± 6.8
	0.5	97.4 ± 2.7	84.9 ± 7.5
	0.1	89.4 ± 7.7	87.3 ± 6.5
Trifluralin	1.0	96.7 ± 10.0	88.3 ± 5.6
	0.5	97.6 ± 7.5	90.9 ± 11.3
	0.1	97.4 ± 8.4	93.5 ± 8.7
Dinitramine	1.0	89.8 ± 9.6	83.9 ± 6.6
	0.5	86.8 ± 3.9	82.9 ± 4.0
	0.1	84.8 ± 11.0	94.6 ± 8.9
Butralin	1.0	89.9 ± 8.2	93.7 ± 1.8
	0.5	84.4 ± 10.3	96.1 ± 3.1
	0.1	94.7 ± 10.4	100.3 ± 6.7
Pendimethalin	1.0	90.6 ± 11.1	95.2 ± 2.0
	0.5	104.3 ± 3.8	105.5 ± 6.2
	0.1	96.1 ± 3.6	100.4 ± 5.3

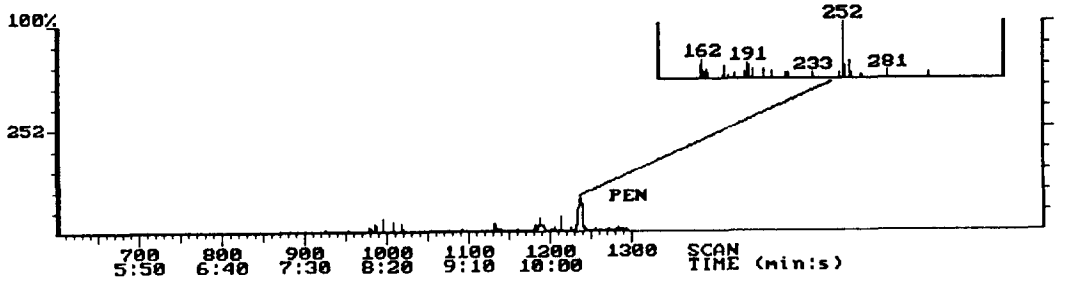

Fig. 3. Mass chromatogram (m/z 252) of a treated plant sample (0.11 μg/g of pendimethalin).

both methods and confirmed by its mass spectra. The detection limit, in plant samples, was near 0.05 μg/g for both methods.

Recovery of dinitroaniline herbicides from the Florisil trapping phase in the volatilization system was studied in the range 0.1 to 1 μg. The results obtained are shown in Table 4. Average recoveries ranged from 87 to 104% with a relative standard deviation between 2 and 9%, and from 88 to 105% with a relative standard deviation between 2 and 9% for all herbicides by GC–ITD and GC–NPD, respectively.

In the volatilization assay, ethalfluralin and trifluralin were the most volatile herbicides, with concentrations of 391 and 358 ng per litre of air, respectively; dinitramine, butralin and pendimethalin were moderately volatile, at 16, 23 and 21 ng/l air, respectively (Fig. 4). This relative order of the volatilities of these herbicides is similar to that found in other work [12]. The limit of detection of the proposed method was, under the conditions described, near 1 ng/l.

The results obtained showed that the proposed

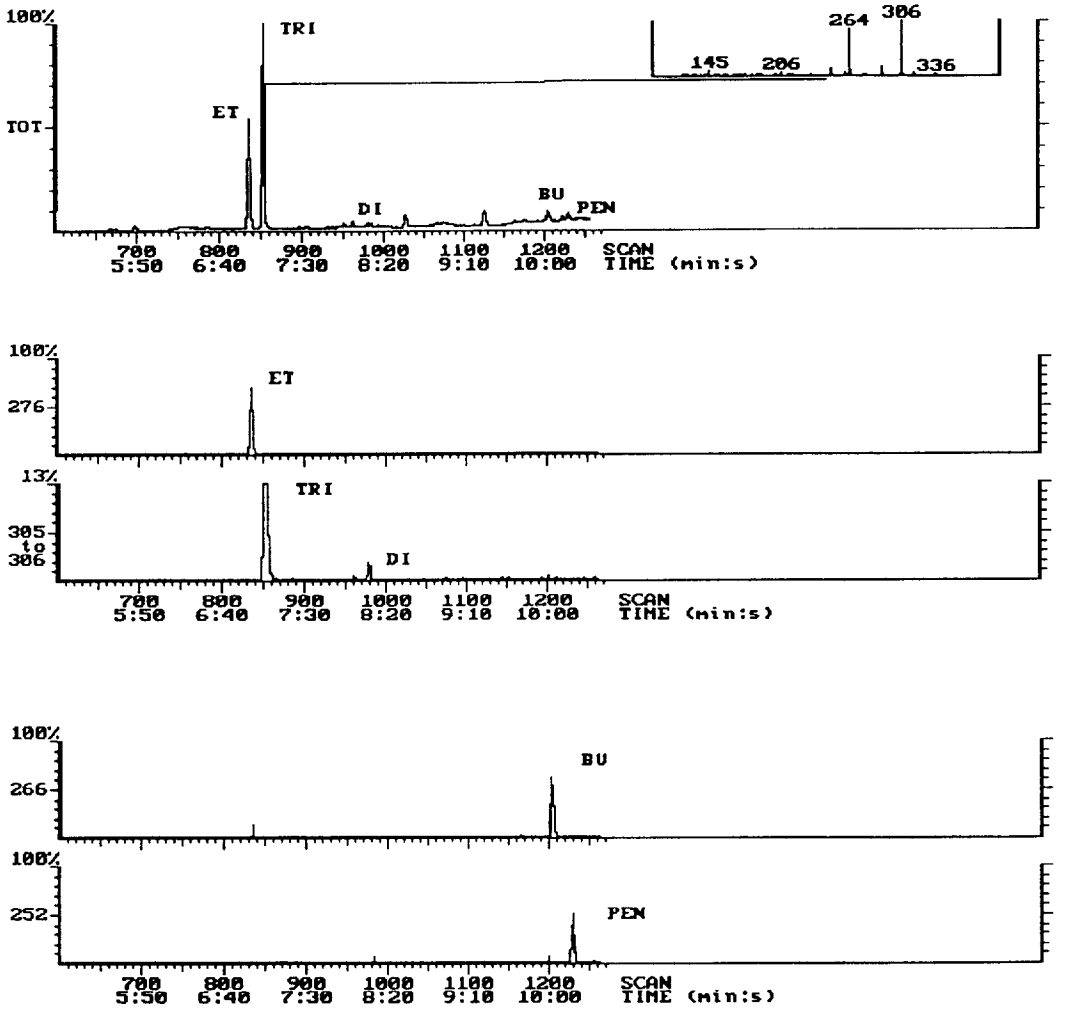

Fig. 4. Total ion chromatogram of a volatilization sample and the corresponding mass chromatograms: ethalfluralin (m/z 276, 391 ng/l), trifluralin (m/z 306, 358 ng/l), dinitramine (m/z 305, 16 ng/l), butralin (m/z 266, 23 ng/l) and pendimethalin (m/z 252, 21 ng/l).

Table 4
Recovery of dinitroaniline herbicides in the volatilization assays

Herbicide	Added (μg)	GC–ITD (mean ± S.D., %) ($n = 3$)	GC–NPD (mean ± S.D., %) ($n = 3$)
Ethalfluralin	1.0	101 ± 5.1	92.5 ± 4.9
	0.5	88.5 ± 9.4	88.4 ± 9.2
	0.1	103.4 ± 6.1	98.2 ± 8.9
Trifluralin	1.0	100.1 ± 4.5	89.9 ± 7.3
	0.5	85.1 ± 7.6	91.0 ± 8.5
	0.1	98.8 ± 8.5	87.8 ± 9.2
Dinitramine	1.0	104.4 ± 6.1	104.7 ± 2.0
	0.5	87.4 ± 2.3	94.5 ± 8.2
	0.1	99.6 ± 8.5	103.2 ± 3.1
Butralin	1.0	102.7 ± 5.6	96.7 ± 9.2
	0.5	102.9 ± 4.2	104.2 ± 8.1
	0.1	99.0 ± 4.9	104.0 ± 8.5
Pendimethalin	1.0	97.9 ± 3.7	99.4 ± 9.5
	0.5	101.6 ± 5.7	103.3 ± 1.7
	0.1	103.4 ± 2.1	104.1 ± 2.7

methods are appropriate and sensitive enough for the simultaneous determination of these dinitroaniline herbicides at residue level.

The two chromatographic methods (GC–NPD and GC–ITD) produced similar average recoveries, with good precision among replicate determinations, of dinitroaniline herbicides in soil, plant and air. An advantage of GC–ITD is that the herbicide residues can be identified by their mass spectra.

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