

Analytical Methods for the Determination in Soil of Herbicides Used in Forestry by GC–NPD and GC/MS

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Analysis of several herbicides used to control weeds in forestry (simazine, hexazinone, pendimethalin, and thiazopyr) has been performed by GC–NPD and GC/MS. A method based on the extraction of soil samples in small columns has been used for the determination of these compounds in soil. Acetone/water (90:10) was used for the extraction of all four compounds, and ethyl acetate can be used when the determination of hexazinone is not required. The recoveries through the method were always >80%, and the detection limit was <0.01 ppm for GC–NPD and GC/MS. Soil samples from experimental fields, taken at different times after treatment from the plow layer, were analyzed according to this method, and values similar to those obtained by a conventional method using mechanical shaking extraction were obtained.

Keywords: Hexazinone; pendimethalin; simazine; thiazopyr; soil; extraction

INTRODUCTION

Herbaceous weeds compete for water and nutrients available in soil with plants used in reforestation, and weed control is then necessary to increase the survival and growth of woody plants in young plantations (Creighton et al., 1987; Glover et al., 1989). Hexazinone, simazine, and pendimethalin (Figure 1) are herbicides often used for herbaceous weed control in forestry (Pehl and Shelnut, 1990; White and Newton, 1990; Reeder et al., 1994), and a new pre-emergence herbicide, thiazopyr, has been recently registered (Valera et al., 1992). These herbicides have a certain persistence in soil, which depends on, besides the properties of the compounds, the soil characteristics and the environmental conditions. This persistence in soil is important for obtaining good control of weeds during the growth season, although it may in turn produce contamination of ground and surface waters.

The determination of herbicide residual levels is needed to know the behavior in soil of these compounds, and methods are available for the determination of each of these herbicides in soil, alone or in combination with other pesticides (McIntosh et al., 1984; Sánchez-Brunete et al., 1994; Tadeo et al., 1996); however, we have not found in the literature an analytical procedure for the combined determination of all four compounds.

Analysis of these herbicides has been commonly carried out by gas chromatography (GC) with nitrogen–phosphorus detection (NPD) (Roy et al., 1989; Sánchez-Brunete et al., 1994; Pardue, 1995; Pérez et al., 1997) or in some cases by electron capture detection (Smith et al., 1995) and also by reversed-phase liquid chromatography with UV detection (McIntosh et al., 1984; Battista et al., 1988; Lydon et al., 1991; Ely et al., 1993). GC coupled with mass spectrometry (MS) has been used

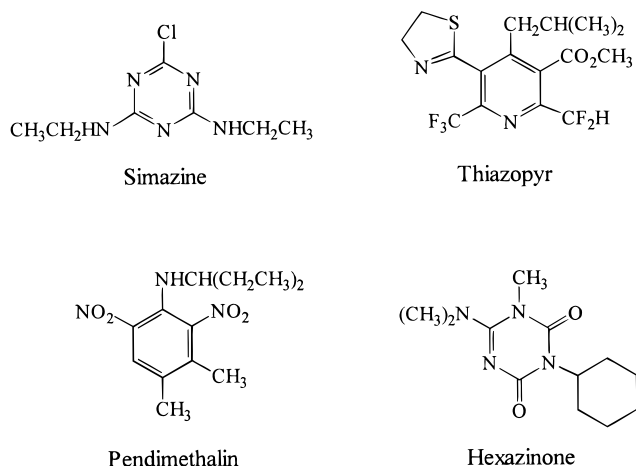


Figure 1. Chemical structures of the herbicides.

sometimes for the confirmation of residues (Felding, 1992; Sánchez-Brunete et al., 1994; Pérez et al., 1997).

Extraction of these compounds from soil is accomplished generally by mechanical shaking or Soxhlet extraction with a suitable solvent. Recently, supercritical fluid extraction (SFE) has been used for the extraction of some herbicides from soil (López-Avila et al., 1993; Dean, 1996; Goli et al., 1997), although this technique requires the use of expensive equipment and suffers from important matrix effects on the extraction efficiency. The commonly used conventional methods of extraction employ large volumes of organic solvents that are frequently toxic and must be concentrated before the chromatographic determination following a laborious procedure and using a great amount of glassware.

The aim of this work is to develop a small scale method, based on the extraction of soil samples placed in plastic columns with low volumes of an organic solvent, for the determination of simazine, thiazopyr, pendimethalin, and hexazinone in soil by GC–NPD and confirmation by GC/MS. The results of the proposed

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method are compared with those obtained with the conventional methods using mechanical shaking extraction.

EXPERIMENTAL PROCEDURES

Materials. Herbicide standards were obtained from commercial sources: simazine (6-chloro-*N,N*-diethyl-1,3,5-triazine-2,4-diamine) from Ciba-Geigy (Switzerland); thiazopyr [methyl-2-(difluoromethyl)-5-(4,5-dihydro-2-thiazolyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3-pyridinecarboxylate] from Monsanto (St. Louis, MO); pendimethalin [*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine] from American Cyanamid (Princeton, NJ); and hexazinone [3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione] from DuPont (Wilmington, DE). Anhydrous sodium sulfate was obtained from Merck (Darmstadt, Germany), and sodium chloride was purchased from Panreac (Barcelona, Spain). The solvents acetone, dichloromethane, ethyl acetate, hexane, methanol, and toluene AR (Panreac) were used without further purification. Propylene columns (20 mL) with polyethylene frits of 20 μm pore size (Varian, Harbor City, CA) at the end and Whatman No. 1 filter paper circles of 2 cm diameter (Whatman International Ltd., Maidstone, England) were used in the column extraction of soil samples. Screw-type valves were employed to close the columns.

Apparatus. A Hewlett-Packard model 5890 gas chromatograph equipped with a nitrogen-phosphorus detector and automatic injector was used for the analysis of herbicides. A fused silica capillary column, HP-1 (12.5 m \times 0.20 mm i.d.) and 0.33 μm film thickness, was employed, with helium as carrier gas at 1 mL/min. The column temperature was maintained at 100 $^{\circ}\text{C}$ for 1 min, then programmed at 15 $^{\circ}\text{C}/\text{min}$ to 250 $^{\circ}\text{C}$, and held 1 min. Injector port and detector temperatures were 270 and 300 $^{\circ}\text{C}$, respectively.

A Hewlett-Packard model 5890 gas chromatograph equipped with a model 5989A mass spectrometer was used for GC/MS analysis. Gas chromatography was performed under the same conditions used in GC-NPD analysis. Mass spectrometric acquisition parameters were the following: interface temperature, 250 $^{\circ}\text{C}$; electron energy, 70 eV; mass range, 60–400 Da; solvent delay, 3 min.

An ultrasonic water bath (Raypa, Barcelona, Spain) was used in the extraction of samples; the generator of this ultrasonic bath has an output of 150 W and a frequency of 35 kHz. A 12-port vacuum manifold (Scharlau, Barcelona, Spain) was employed for removing the organic phase from soil samples.

Column Extraction. Soil (5 g) was placed in a plastic column. In the recovery assays, samples were weighed in a weighing funnel (6 mL) and fortified with 0.5 mL of a mixture of the different compounds to give soil concentrations in the range of 0.2–1 $\mu\text{g}/\text{g}$, allowing 10 min for solvent evaporation before the samples were placed in the plastic columns. Soil samples were extracted with ethyl acetate, methanol/water (90:10) or acetone/water (90:10) (2 \times 4 mL) for 15 min in the ultrasonic water bath. The water level in the bath was adjusted to equal solvent level inside the column. Solvent was filtered on the multiport vacuum manifold, the extract was collected in a graduated tube, and the soil was washed with additional solvent (2 mL). The ethyl acetate extract was concentrated to an appropriate volume before GC analysis. The extract obtained with methanol/water or acetone/water was evaporated to dryness under vacuum, and the residue was transferred to a graduated tube with an appropriate volume of ethyl acetate; an aliquot was analyzed by GC under the conditions described above.

Mechanical Shaking Extraction. Soil (20 g) was weighed in a glass flask. In the recovery assays, samples were fortified before extraction with 1–2 mL of mixtures of herbicides of known concentration. Samples were extracted with ethyl acetate, methanol/water (80:20), or acetone/water (80:20) (2 \times 100 mL) by shaking for 45 min on an orbit shaker. The extract was filtered under suction through Whatman No. 1 filter paper and the filter cake washed with 20 mL of solvent.

When samples were extracted with ethyl acetate, solvent was carefully evaporated to dryness under vacuum and the

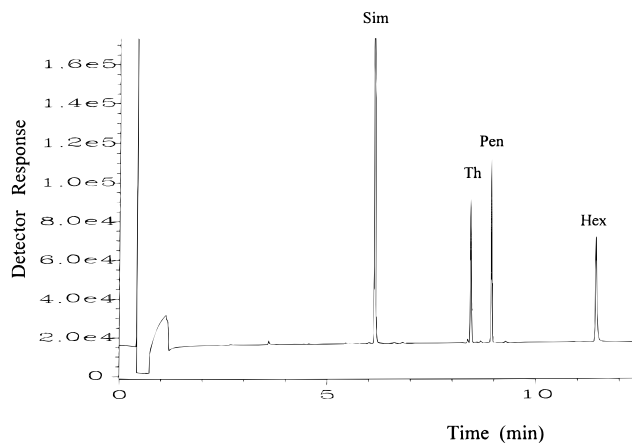


Figure 2. GC-NPD chromatogram of a mixture of simazine (Sim), thiazopyr (Th), pendimethalin (Pen), and hexazinone (Hex) (1 $\mu\text{g}/\text{mL}$).

Table 1. Recovery of Herbicides from Soil with Ethyl Acetate as Extracting Solvent

herbicide	added ($\mu\text{g}/\text{g}$)	recovery ^a (%)	
		column	mechanical shaking
simazine	1.0	100.7 \pm 8.3	93.8 \pm 9.2
	0.5	102.7 \pm 6.5	96.8 \pm 5.9
	0.2	97.0 \pm 3.6	97.2 \pm 4.1
thiazopyr	1.0	97.6 \pm 7.6	95.7 \pm 4.7
	0.5	102.8 \pm 6.3	96.9 \pm 6.2
	0.2	97.5 \pm 4.6	97.5 \pm 4.1
pendimethalin	1.0	97.8 \pm 8.1	96.3 \pm 4.9
	0.5	101.4 \pm 6.1	97.6 \pm 6.0
	0.2	95.7 \pm 2.8	96.1 \pm 3.5
hexazinone	1.0	5.6 \pm 1.6	22.0 \pm 3.5
	0.5	6.8 \pm 2.3	25.5 \pm 3.3
	0.2	8.2 \pm 0.7	27.0 \pm 2.0

^a Results are the mean of four replicates \pm standard deviation.

residue transferred to a tube with ethyl acetate prior GC analysis. When mixtures with water were used, the organic solvent was removed under vacuum on a rotary evaporator, the residual aqueous fraction was transferred to a separatory funnel, 20 mL of a saturated sodium chloride solution was added, and extraction was performed with 3 \times 70 mL of dichloromethane. The organic solvent was filtered through anhydrous sodium sulfate, toluene (1 mL) was added, and dichloromethane was evaporated under vacuum; small amounts of hexane were added to the residue and evaporated again to remove dichloromethane completely. The residue was transferred to a tube with ethyl acetate and an aliquot analyzed by GC under the conditions described above.

The concentration of each compound was calculated by comparing the peak area obtained in the sample with the area found for mixtures of herbicides of known concentration. Statistical comparisons were made between the two extraction techniques using a paired *t* test (Cardone, 1983).

RESULTS AND DISCUSSION

Determination of Herbicides in Soil by GC-NPD. Soil samples were fortified with 0.2, 0.5, and 1.0 $\mu\text{g}/\text{g}$ of simazine, thiazopyr, pendimethalin, and hexazinone and analyzed following the procedures described above. The determination was accomplished by GC-NPD, and a chromatogram of a mixture of these herbicides is depicted in Figure 2.

Table 1 shows the herbicide recoveries obtained when ethyl acetate was used as extracting solvent. Ethyl

Table 2. Recovery of Herbicides from Soil with Methanol/Water or Acetone/Water as Extracting Solvent

herbicide	added ($\mu\text{g/g}$)	recovery ^a (%)			
		column		mechanical shaking	
		MeOH/H ₂ O (90:10)	acetone/H ₂ O (90:10)	MeOH/H ₂ O (80:20)	acetone/H ₂ O (80:20)
simazine	1.0	93.9 \pm 3.6	95.5 \pm 5.4	88.4 \pm 5.2	89.5 \pm 3.7
	0.5	nd ^b	99.2 \pm 1.9	nd	99.2 \pm 3.8
	0.2	93.3 \pm 3.4	99.6 \pm 5.1	90.7 \pm 3.7	92.2 \pm 6.3
thiazopyr	1.0	84.9 \pm 4.3	84.4 \pm 3.6	87.3 \pm 5.2	87.5 \pm 2.7
	0.5	nd	90.7 \pm 5.7	nd	93.8 \pm 3.7
	0.2	85.1 \pm 3.1	91.3 \pm 4.0	93.9 \pm 3.6	93.8 \pm 8.8
pendimethalin	1.0	82.4 \pm 4.1	85.2 \pm 3.8	75.9 \pm 4.8	73.4 \pm 3.5
	0.5	nd	87.8 \pm 4.5	nd	82.1 \pm 4.3
	0.2	82.8 \pm 3.9	88.8 \pm 5.2	75.3 \pm 6.2	81.4 \pm 8.0
hexazinone	1.0	92.3 \pm 6.2	95.5 \pm 8.5	98.5 \pm 4.0	98.2 \pm 5.0
	0.5	nd	93.7 \pm 6.1	nd	98.1 \pm 9.5
	0.2	98.0 \pm 5.4	96.0 \pm 8.5	103.3 \pm 4.3	96.2 \pm 10.7

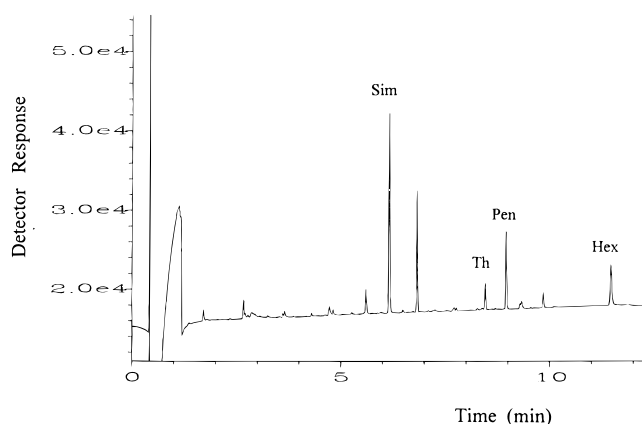
^a Results are the mean of four replicates \pm standard deviation. ^b nd, not determined.

acetate was first selected because it has been used for the extraction from soil of some of the studied herbicides (Sánchez-Brunete et al., 1994; Pérez et al., 1997). The average recoveries obtained with both extraction procedures, column and mechanical shaking, were >95% for all compounds but hexazinone, with standard deviations <10%. Recovery of hexazinone was very low with both methods, and therefore another solvent is needed for the extraction.

Good recoveries of hexazinone have been reported using acetone/water (80:20) (Feng, 1987) or methanol/water (80:20) (Lydon et al., 1991), and soil samples fortified with the herbicides studied were extracted with these solvents. The proportion of water assayed in the column extraction was somewhat lower (10%) to facilitate solvent evaporation. The average recoveries obtained for hexazinone were >92% with both extraction procedures and solvents (Table 2). High recoveries were also obtained for the other herbicides, although they were somewhat lower than those obtained with ethyl acetate, particularly for pendimethalin and thiazopyr. Pendimethalin recoveries attained with the mechanical shaking procedure, Table 2, were significantly lower than those obtained with column extraction ($p < 0.05$, t test), probably due to the higher vapor pressure of this compound and the greater amount of solvent used in the extraction by mechanical shaking. Therefore, solvent must be carefully evaporated in this sample preparation procedure, and a small amount of toluene was added prior solvent evaporation to avoid losses of pendimethalin.

In general, the column extraction method used in the analysis of all four compounds gave good recovery results, which were similar to, or even better than in the case of pendimethalin, those obtained with the conventional method using mechanical shaking. In addition, the proposed column method is more rapid and uses less volume of organic solvent: 10 mL instead of >400 mL required by the conventional method. Acetone/water (90:10) was selected for the extraction of these compounds since this solvent is easier to evaporate and less toxic than methanol/water, while the recoveries obtained are similar (Table 2).

The detector response was linear in the range of concentrations studied, 0.2–2 $\mu\text{g/mL}$, the correlation coefficient obtained in all cases being >0.99.

**Figure 3.** GC–NPD detection limit of these herbicides in soil samples (0.01 $\mu\text{g/g}$).**Table 3. Main Ions Found in the Mass Spectra of Herbicides**

herbicide	m/z (%)
simazine	201 (100), 186 (60), 173 (56)
thiazopyr	396 (82), 363 (34), 327 (100)
pendimethalin	281 (20), 252 (100), 162 (25)
hexazinone	252 (4), 171 (100), 128 (12)

The detection limit of these compounds in soil samples was, at least, 0.01 $\mu\text{g/g}$ (Figure 3), which is considered sufficient for the determination of residual levels of these herbicides.

Confirmation by GC/MS. Figure 4 shows the total ion chromatogram of a soil sample fortified with a mixture of these herbicides (1 $\mu\text{g/g}$) and the mass spectra of these compounds obtained by GC/MS. The main ions of their mass spectra were used as characteristic ions for confirmation purposes (Table 3), and the base peak of each spectrum was employed for the quantitation of herbicides. The detection limit of these compounds in soil samples was <0.01 $\mu\text{g/g}$ using selected ion monitoring (Figure 5).

Application to Real Samples. Soil from experimental fields treated with the studied herbicides was sampled at various times after treatment and analyzed following the extraction methods described above (Table 4). Both methods gave similar values of residues in soil samples taken along the sampling period studied. This indicates that the efficiencies of extraction for recently

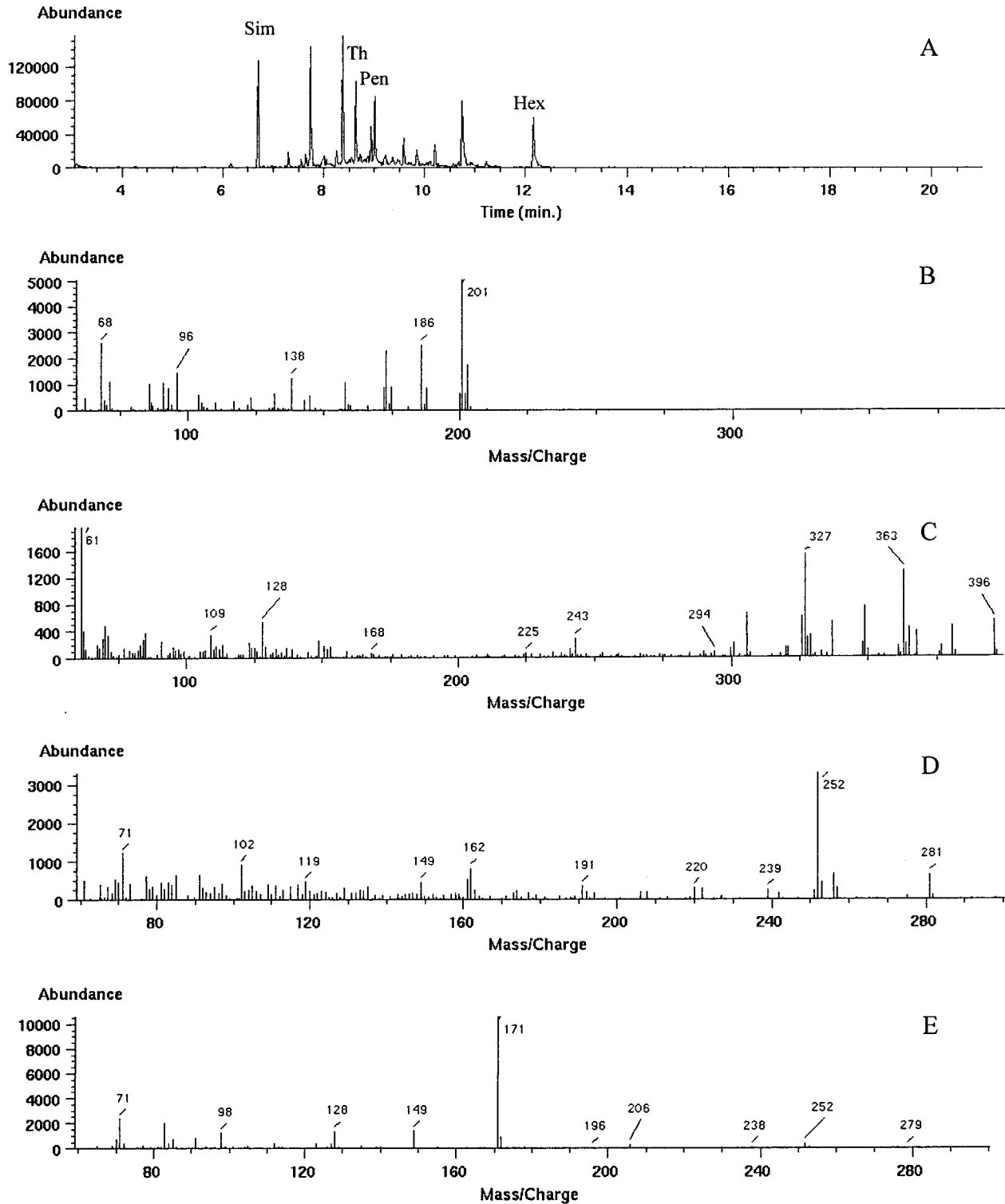


Figure 4. Analysis by GC/MS: (A) total ion chromatogram of a fortified soil sample (1 $\mu\text{g/g}$) and mass spectra of the herbicides (B) simazine, (C) thiazopyr, (D) pendimethalin, and (E) hexazinone.

applied herbicide as well as for aged residues in soil obtained with both analytical procedures are comparable. The times for 50% disappearance of simazine and hexazinone (t_{50}) calculated by fitting these values to a first-order equation were also similar for both methods. These results confirm the adequacy of the proposed column method for the determination of these herbicides in soil. Figure 6 shows representative chromatograms of soil samples treated with the different herbicides and analyzed following the column extraction method.

Conclusions. The results presented in this study indicate that the proposed method of extraction using small columns is suitable for the determination of simazine, thiazopyr, pendimethalin, and hexazinone in soil by GC-NPD and for the confirmation of residues by GC/MS. The method is reproducible and has good sensitivity for the analysis of these compounds at residue level. The extraction of herbicides from soil is carried out using a rapid procedure that uses a small volume of an organic solvent and does not require

Table 4. Herbicide Residues Found in Treated Soil Samples

time ^a	method	concentration ^e ($\mu\text{g/g}$)			
		simazine ^b	pendimethalin ^c	hexazinone ^b	thiazopyr ^c
0	column	2.57 \pm 0.07	3.18 \pm 0.23	0.97 \pm 0.08	3.78 \pm 0.15
	mechanical shaking	2.33 \pm 0.06	3.22 \pm 0.10	1.10 \pm 0.07	3.50 \pm 0.36
1st	column	0.98 \pm 0.07	1.21 \pm 0.13	0.89 \pm 0.04	1.73 \pm 0.06
	mechanical shaking	1.07 \pm 0.09	1.25 \pm 0.05	0.94 \pm 0.09	1.50 \pm 0.13
2nd	column	0.53 \pm 0.06		0.28 \pm 0.02	
	mechanical shaking	0.47 \pm 0.03		0.30 \pm 0.06	
3rd	column	0.29 \pm 0.02		0.13 \pm 0.02	
	mechanical shaking	0.23 \pm 0.02		0.14 \pm 0.07	
t_{50} ^d	column	35 (0.979)		43 (0.964)	
	mechanical shaking	32 (0.988)		41 (0.972)	

^a Sampling times: simazine, 0, 24, 64, 105 days; pendimethalin, 0, 31 days; hexazinone, 0, 41, 84, 133 days; thiazopyr, 0, 31 days.

^b Soil characteristics: sandy clay loam, OM (organic matter) = 0.71%, pH 7.35. Doses: Gesatop, 2 kg/ha simazine; Velpar, 0.9 kg/ha hexazinone. ^c Soil characteristics: sandy loam, OM = 1.75%, pH 6.68. Doses: Stomp LE, 2 kg/ha pendimethalin; Visor, 1.5 kg/ha thiazopyr.

^d t_{50} = time in days for 50% disappearance of each herbicide (correlation coefficient); average air temperature and rainfall: January, 6.9 °C, 128.8 L/m²; February, 4.4 °C, 23.9 L/m²; March, 8.6 °C, 19.6 L/m²; April, 11.7 °C, 16.5 L/m²; May, 14.7 °C, 109.7 L/m²; June, 20.3 °C, 1.8 L/m²; July, 23.4 °C, 0.3 L/m². Simazine was treated in January and hexazinone in March. ^e Values are the mean of three replicates \pm standard deviation.

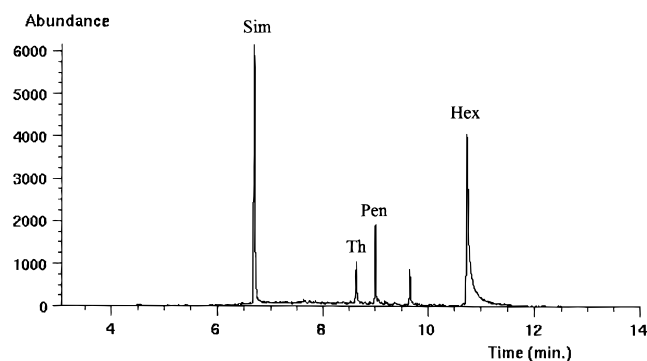


Figure 5. GC/MS detection limit of these herbicides in soil samples in selected ion monitoring (0.01 $\mu\text{g/g}$).

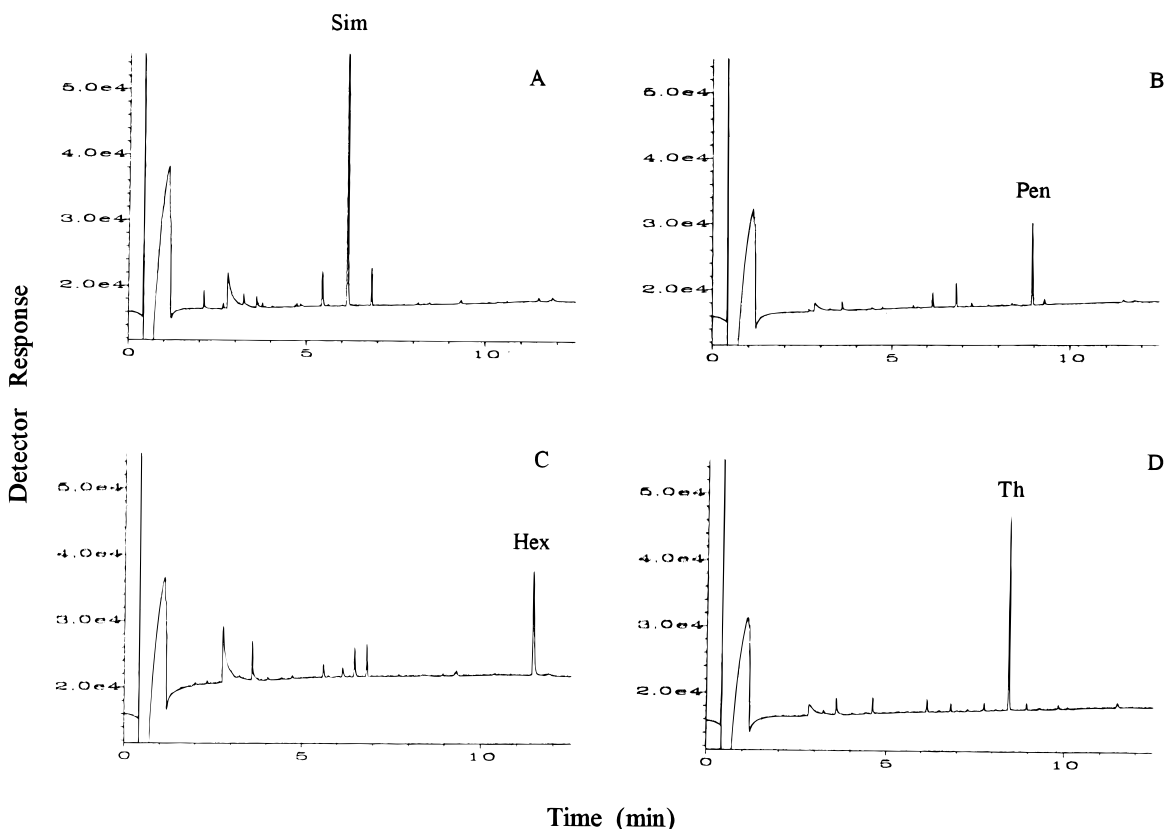


Figure 6. GC-NPD chromatograms of treated soil samples: (A) simazine (0.3 $\mu\text{g/g}$); (B) pendimethalin (0.3 $\mu\text{g/g}$); (C) hexazinone (0.9 $\mu\text{g/g}$); (D) thiazopyr (1.7 $\mu\text{g/g}$).

special equipment. Acetone/water (90:10) is used for the extraction of all four compounds, and ethyl acetate can be used when hexazinone is not present. Samples taken at different times after treatment from experimental fields were analyzed according to this method, and the results obtained were similar to those determined by the conventional method using mechanical shaking extraction. The proposed method of extraction in columns can then be used as a routine procedure for the analysis of these herbicides in soil samples.

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