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Note

A multi-residue extraction procedure for the gas chromatographic determination of the herbicides dichlobenil, dinitramine, triallate and trifluralin in soils

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Analytical procedures for the simultaneous extraction and gas chromatographic determination of residue combinations of several insecticides in soils are well established[1-3]. Although procedures for the multi-residue extraction of herbicides from soils for gas chromatographic analysis have been reported, these methods are mainly for the assay of herbicides belonging to specific groups, such as the triazines[4,5] or ureas[6].

In Saskatchewan, the carry-over of some soil-based herbicide residues from one growing season to the next has been reported[7]. The procedure to be described here was developed for the routine extraction and gas chromatographic estimation of four such persistent chemicals in soils, either alone or in combination.

MATERIALS AND METHODS

Soils

The composition and physical characteristics of the soils used in these studies are shown in Table I.

TABLE I

CHARACTERISTICS OF SOILS

Soil	*Clay (%)*	*Silt (%)*	*Sand (%)*	*Organic carbon (%)*	*pH in water (1:1)*
Jameson sandy loam	6	9	85	3.2	7.5
Regina heavy clay	69	26	5	4.2	7.7
Melfort silty clay	30	38	32	11.7	5.2

Herbicides

The following technical-grade herbicides were used in these studies: dichlobenil (2,6-dichlorobenzonitrile), dinitramine (N,N-diethyl-*α,α,α*-trifluoro-3,5-dinitrotoluene-2,4-diamine), triallate (S-2,3,3-trichloroallyl diisopropylthiocarbamate) and trifluralin (*α,α,α*-trifluoro-2,6-dinitro-N,N-dipropyl-*p*-toluidine). A combined stock solution was prepared containing 50 μg of each herbicide per milliliter of methanol.

Soil fortification

A portion (20 or 200 μl) of the mixed herbicide solution was added to each of several 20-g samples of the sieved air-dried soils in screw-capped glass bottles (capacity 70 ml). Thus, the soils were fortified with 1 or 10 μg of each individual herbicide to give a soil concentration of 0.05 or 0.5 ppm. After mixing to ensure distribution of the chemicals throughout the soil samples, the bottles containing the fortified soils were capped and frozen at −5° for 8 weeks, after which four replicate samples for each soil type and herbicide concentration were extracted and analysed.

Extraction procedure

Each fortified soil sample (20 g) was placed in a 100-ml beaker together with 60 ml of acetonitrile–water (9:1) and extracted for 2 min using a Sonic Dismembrator (Artek Systems Corp., Farmingdale, N.Y., U.S.A.) at maximum power. After settling, 30 ml of the acetonitrile solution, corresponding to 10 g of soil, were added to 150 ml of distilled water plus 20 ml of saturated aqueous sodium sulphate solution, and the mixture was shaken twice with 25-ml portions of *n*-hexane. Following extraction, the aqueous phase was discarded, the combined *n*-hexane layers were dried over anhydrous sodium sulphate, and 3 or 4-μl aliquots were examined by gas chromatography.

Gas chromatographic analysis

A Hewlett-Packard 5713 A gas chromatograph equipped with means for on-column injection and a nickel electron-capture detector (operated at 300°) was used. The glass column (1.5 m × 6.0 mm O.D.) was packed with 10% of OV-1 on Chromosorb G-HP (80–100 mesh), and the carrier gas was argon containing 5% of methane at a flow-rate of 40 ml/min. With a column temperature of 190° the retention times for dichlobenil, trifluralin, dinitramine and triallate were 0.95, 2.85, 4.5 and 5.0 min, respectively.

Chromatographic standards were prepared by adding 20 or 200 μl of the mixed herbicide solution to 100 ml of *n*-hexane, to give solutions containing 0.01 or 0.10 ng of the four chemicals per μl. The concentrations of the various herbicides present in the samples were calculated by comparing the sample peak heights with those of the appropriate standard.

RESULTS AND DISCUSSION

Typical gas chromatograms obtained from the standard solution containing 0.01 ng/μl of each herbicide, and from Jameson sandy loam fortified at the level of 0.05 ppm, indicated (see Fig. 1) that the 10% OV-1 column gave a good resolution of the individual herbicides; although resolution between dinitramine and triallate was not complete, adequate quantitative measurements could be made. Recoveries of the four herbicides from treated soils (see Table II) were all greater than 90%, and reproducibility was excellent. Separate experiments showed that no interfering sub-

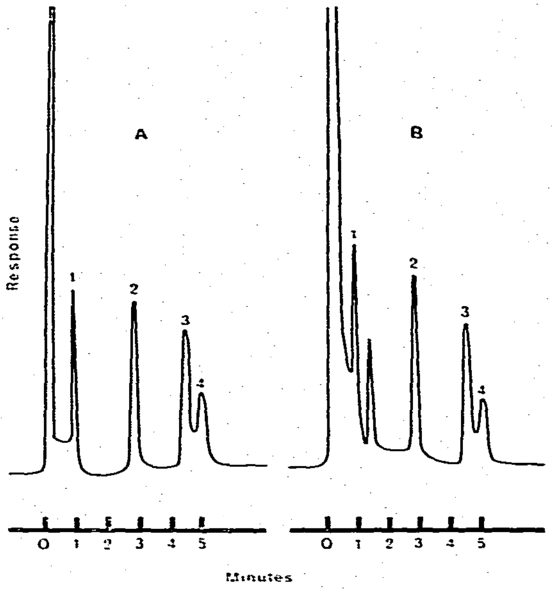

Fig. 1. Chromatogram of (A) 4 μl of standard solution containing 0.04 ng of dichlobenil (1), trifluralin (2), dinitramine (3), and triallate (4); and (B) Jameson sandy loam fortified with 0.05 ppm of the four herbicides.

stances were detected in any of the untreated soils, even at the high attenuations required for the analysis of the lower concentrations of herbicides in the soils.

The soil samples were frozen for 8 weeks before analysis, as it is the practice in this laboratory to air-dry field soils containing herbicide residues to constant weight at room temperature and then to store them at −5° while awaiting extraction and analysis.

A mixture (2:1) of benzene and isopropanol has been used for the extraction dichlobenil[8], triallate[9] and trifluralin[10] from soils. For dinitramine, this solvent mixture gave recoveries of less than 50% from all three soil types. Acetonitrile–water (9:1)

TABLE II

RECOVERY OF DICHLOBENIL, TRIFLURALIN, DINITRAMINE AND TRIALLATE FROM FORTIFIED SOILS

Soil	*Amount added (ppm)*	*Recovery (%)*[*]			
		Dichlobenil	*Trifluralin*	*Dinitramine*	*Triallate*
Regina heavy clay	0.05	92 ± 5	96 ± 5	96 ± 8	96 ± 6
	0.5	93 ± 1	104 ± 4	106 ± 4	101 ± 3
Jameson sandy loam	0.05	92 ± 9	92 ± 11	93 ± 9	95 ± 5
	0.5	93 ± 2	106 ± 4	107 ± 4	100 ± 1
Melfort silty clay	0.05	94 ± 5	106 ± 12	90 ± 8	112 ± 12
	0.5	97 ± 3	101 ± 3	102 ± 3	105 ± 4

[*] Mean and standard deviation from four determinations.

was finally selected as extracting solvent with excellent results (see Fig. 1 and Table II).

The proposed procedure for the recovery of triallate at the level of 0.5 ppm from the three soils was compared with methods using benzene and isopropanol[9] or trimethylpentane and isopropanol[11] as extractants. The last two solvent systems gave recoveries of less than 60% from dry soils. However, recoveries were almost 100%, and thus comparable to those obtained by using aqueous acetonitrile, when the soils were moistened to the wilting point and equilibrated overnight before extraction. Thus, an advantage to using acetonitrile as extracting solvent is that samples containing triallate do not have to be moistened with water before extraction[12].

With the present procedure, residues of dichlobenil, dinitramine, triallate and trifluralin (singly, or in the presence of each other) can be detected in a variety of soils simply, rapidly and accurately at levels down to 0.05 ppm. The herbicide recoveries obtained (see Table II) are also comparable to, or better than, those attained by using methods[8,13-16] outlined for their individual analyses.

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