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Note

High-performance liquid chromatographic determination of triallate residues in soils

A. PEÑA HERAS and F. SÁNCHEZ-RASERO*
Estación Experimental del Zaidín, U.E.I. de Química Analítica, Profesor Albareda, 1, 18008-Granada (Spain)
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Triallate is the ISO common name for *S*-2,3,3-trichloroallyl diisopropyl-thiocarbamate. It is a soil-applied herbicide for the control of weeds in dycotyledons and a variety of other crops, particularly, wild oats in barley, lentils and peas. Its residues in soil have been determined by gas–liquid chromatography with electron capture detection[1–3].

This paper describes a simple high-performance liquid chromatographic (HPLC) method, using Sep-Pak C_{18} cartridges[4] for sample preparation. The study has been carried out at the 1-ppm level since, for soil persistence research (breakdown rates and phytotoxicity), lower levels are generally superfluous. Various ways are suggested for work at the 0.1-ppm level with this method.

EXPERIMENTAL

Apparatus

A Hewlett-Packard 1084B high-performance liquid chromatograph equipped with a microprocessor, electronic integrator, 79875A variable-wavelength detector (190–600 nm), automatic variable-volume injector, etc., as described previously[5], was used. The column (Hewlett-Packard 79918A) was 200 mm × 4.6 mm. I.D., stainless steel, packed with LiChrosorb RP-8 (10 μm).

The filters (Millipore, Bedford, MA, U.S.A.) used were Type HAWP for water, EHWP for methanol and FHLP for acetonitrile, pore size 0.5 μm. Sep-Pak C_{18} cartridges (Waters Associates, Milford, MA, U.S.A.) were used.

Soils

All soil samples were air-dried at room temperature and passed through a 2-mm sieve. Some properties of the sieved soils are shown in Table I.

Herbicide

Triallate, reference standard, purity, 99.6%, was obtained from Monsanto (St. Louis, MO, U.S.A.). A stock solution was prepared containing 15 μg per ml of methanol.

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TABLE I

SOME PROPERTIES OF THE SOILS

Soil type	*pH*	*Clay (%)*	*Silt (%)*	*Sand (%)*	*Organic matter (%)*
Clay loam	7.8	44.2	54.2	0.7	3.0
Loamy sand	7.8	11.1	21.8	67.1	1.2
Sandy loam	7.9	6.7	5.5	87.8	0.1

Soil fortification and extraction procedure

A 1-ml volume of the stock solution was added to 15 g of soil. After thorough mixing, the sample was extracted twice with 50-ml portions of methanol by shaking mechanically for 30 min, then centrifuged at 1865 *g* for 20 min and the supernatant filtered through a Whatman No. 1 filter-paper. Finally, the centrifuge-tube and filter were washed twice with 10-ml portions of methanol. A 10-ml volume of water was added to the combined extracts and, after mixing, concentrated to about 10 ml under reduced pressure on a water-bath at 45°C.

Clean-up procedure

A Sep-Pak C_{18} cartridge was activated with 5 ml acetonitrile, then flushed with 10 ml water. The concentrated extract was passed through the Sep-Pak at a constant flow-rate with the aid of a peristaltic pump. The cartridge was then washed with 14 ml water and the triallate was eluted with 5 ml of acetonitrile.

Chromatography

The chromatographic conditions were as follows: eluent, acetonitrile–water (60:40), flow-rate 1.8 ml/min; column temperature, 40°C; wavelength, 215 *vs.* 430 nm; attenuation, 2^4; slope sensitivity, 0.15. Aliquots (25 μl) of the solution eluted from the Sep-Pak were injected into the chromatograph and their peak areas compared with those obtained from a standard solution prepared from 1 ml of the herbicide stock solution and treated exactly like the sample but without soil.

RESULTS AND DISCUSSION

Some preliminary tests were carried out to choose the extraction solvent system, the quantity of water to be added to the methanolic extract before concentrating, the water-bath temperature for that concentration procedure and the volume of acetonitrile required to elute the Sep-Pak cartridge. The homogeneity of these cartridges was tested as well.

Extraction solvent

Methanol, acetone, methanol–acetone (1/3) and methanol–acetone (3:1) were compared. Similar recoveries were obtained in the four cases and methanol was chosen because it produced the clearest extracts. Cotterill[6] also found that methanol was the most efficient solvent system in comparison with chloroform and acetonitrile.

Quantity of water

Volumes of 4, 6, 8, 10, 12 and 14 ml water were added to six methanolic soil extracts, all of them prepared in the described manner, before concentrating. The recoveries were 22, 49, 83, 81, 79 and 67%, respectively. A volume of 10 ml was chosen which corresponded to the optimum recovery.

Water-bath temperature

The recoveries at 35, 45 and 55°C were 57, 76 and 45%, respectively. It seems likely that a decomposition takes place at 55°C due to the high temperature, as well as at 35°C because of the very long time (45 *vs.* 12 min) necessary to concentrate to about 10 ml.

Volume of acetonitrile

Volumes of 2 and 5 ml were assayed, the respective recoveries being 81 and 88%. The latter volume was chosen because of the higher recovery, but it is evident that 2 ml could also be used if greater sensitivity is desired.

Homogeneity of cartridges

Five parallel experiments were carried out. Aliquots of the same concentrated methanolic soil extract were pased through five different Sep-Pak cartridges, the recoveries being, respectively 63.9, 65.0, 62.9, 60.4 and 62.7% ($\bar{x}$ = 62.9%; relative standard deviation s_r = 2.7). The close agreement of the recoveries is proof of the cartridges' homogeneity.

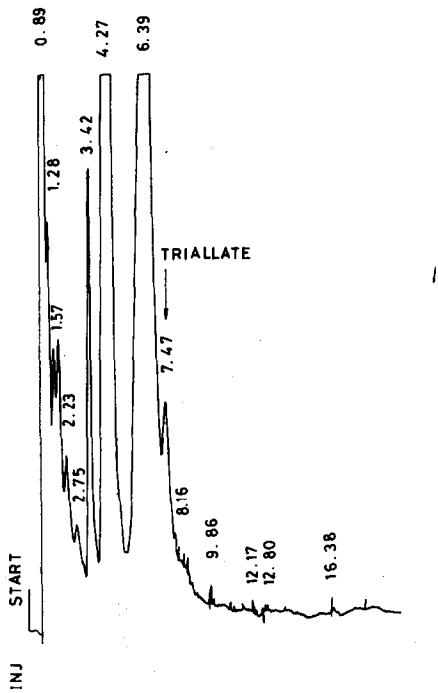

Fig. 1. Chromatogram of a clay loam soil fortified with 1 ppm of triallate, without Sep-Pak clean-up.

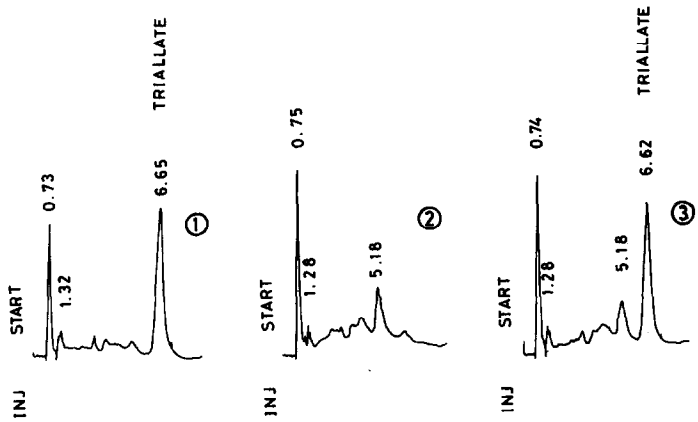

Fig. 2. Typical chromatogram of (1) a standard solution, (2) unfortified and (3) fortified clay loam soil, after Sep-Pak purification.

Triallate was found to have an absorption maximum at 208 nm. Nevertheless, a wavelength of 215 nm was chosen for the measurements, in order to avoid interferences from the eluent.

The chromatogram shown in Fig. 1, obtained from a fortified soil sample without clean-up by Sep-Pak, indicates the necessity of following a purification procedure in order to eliminate most coextracted extraneous soil constituents.

Fig. 2 shows typical chromatograms of a standard solution (a), unfortified (b) and fortified soil extracts (c), all after Sep-Pak purification. The baselines are flat enough to allow adequate quantitative measurements of the triallate peaks. It is evident that peaks with only half these heights could also be measured with good precision.

Triallate recoveries, from the different soils, expressed as the means of three determinations, with their corresponding confidence limits at $P < 0.05$, were: clay loam, 80.4 ± 1.71%, $s_r = 1.34$; loamy sand, 93.3 ± 1.84%, $s_r = 0.79$; and sandy loam, 90.0 ± 2.45%, $s_r = 1.70$. These results are comparable to, or better than, those obtained by Grou *et al.*[7] in the determination of some carbamate pesticides by HPLC.

If necessary, it would be possible to work at the 0.1-ppm level with this method by means of the isolated or simultaneous use of the following alternatives: lower peak height, Sep-Pak elution with 2 ml acetonitrile and greater injection volume since, according to Hanks and Colvin[8], up to one-third the elution volume of the peak of interest can be injected with little or no effect on column performance. Nevertheless, the effect of the difference between the solvent and mobile phase should be taken into account.

The results obtained, with greater recoveries from the loamy sand and the sandy loam soils, are in accord with those of other authors in the sense that either the organic[9,10] or the clay[11] contents are responsible for soil herbicide retention.

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