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Analysis of triallate residues in cereals and soil by gas chromatography with ion-trap detection

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ABSTRACT

Triallate residues in barley seedlings and soil samples were determined by gas chromatography with ion-trap detection. Soil was extracted with methanol on a mechanical shaker, and plants were extracted with acetonitrile in a Sorvall homogenizer. After evaporation of the organic solvents, the residue was dissolved in hexane, and plants extracts were cleaned-up on an alumina column. Gas chromatographic analysis was carried out using a BP-1 fused-silica capillary column with helium as carrier gas. To quantitate residues the total-ion chromatogram was obtained and then the selected-ion monitoring chromatograms were displayed at *m/z* 86 for triallate and at *m/z* 154 for the internal standard, methyl-(4-amino-2-chloro)-benzoate. The average recovery through the method from barley and soil samples was always higher than 80%. The limit of detection in the selected-ion mode was 0.01 mg/kg. Barley and soil samples treated with triallate were also analysed. A good agreement was observed between results obtained by this method and by gas chromatography with nitrogen–phosphorus detection.

INTRODUCTION

Triallate, *S*-2,3,3-trichloroallyldiisopropyl thiocarbamate, is a herbicide used to control wild oats in winter cereals. The determination of triallate residues has been usually carried out by gas chromatography (GC) with electron-capture detection [1–4] or alkali flame ionization detection [5], and recently by high-performance liquid chromatography [6].

Mass spectrometry (MS) is the most specific detection method that can be used in residue analysis, and today's small spectrometers, such as the ion-trap detector, are easy to handle. Therefore, GC with mass-selective detection is a valuable tool for the analysis of pesticide residues [7–9].

The aim of this work was to study the analysis of triallate residues, in soil and barley seedlings, by GC with ion-trap detection (ITD) and their quantitation using an internal standard, methyl-(4-amino-2-chloro)benzoate.

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EXPERIMENTAL

Instrumentation

A Perkin-Elmer 8500 gas chromatograph equipped with an ion-trap detector, ITD Finnigan, and a split–splitless injector for capillary columns was employed. A fused-silica capillary column, BP-1,12 m × 0.22 mm I.D. bonded phase 0.25 μm film thickness (Perkin-Elmer, Norwalk, CT, U.S.A.) was used with helium as carrier gas. Temperature settings were: injector, 270°C; detector, 300°C; column, 85 °C initial, held for 1 min, 30°C/min to 250°C, held for 5 min. A 2-μl volume was injected with the splitter closed for 1 min.

A Varian Aerograph 3700 equipped with an alkali flame-ionization detector and a glass column, 2 m × 6.35 mm I.D. (Sugelabor, Madrid, Spain) packed with 3% OV-17 on Chromosorb W HP (80–100 mesh) was used for GC determination with nitrogen–phosphorus detection (NPD) under the following conditions: injector temperature, 270°C; column temperature, 210°C; detector temperature, 300°C. Nitrogen was used as carrier gas at a flow-rate of 40 ml/min.

Mass spectrometric acquisition parameters

The transfer line temperature was 250°C. The scan parameters were: mass range, 40–310 daltons; scan-rate 0.5 s/scan, 2 μscans; radiofrequency (r.f.) voltage, 1.1 MHz and 0–7.5 kV; automatic gain control, from 78 μs to 25 ms. solvent delay, 3 min.

Materials

Triallate was obtained as reference standard, with 99.9% purity, from Monsanto (St. Louis, MO, U.S.A.). 4-Amino-2-chlorobenzoic acid was purchased from Sigma and esterified in our laboratory. All substances were dissolved in *n*-hexane (Merck, Darmstadt, F.R.G.).

Procedure

Soil (10 g) was extracted twice with 40 ml of methanol on a mechanical shaker for 1 h. Barley seedlings were extracted twice with 40 ml of acetonitrile in a Sorvall homogenizer. The organic solvents were removed under vacuum on a rotary evaporator, and the residue was dissolved in 1–5 ml of hexane. Plant extracts were cleaned-up on an alumina column (6 g), and triallate was eluted with 5 ml of hexane–10% diethyl ether. The fraction was concentrated, brought to volume with hexane, and analysed by GC.

RESULTS AND DISCUSSION

Fig. 1 shows the total-ion chromatogram obtained with 2 ng of triallate and 10 ng of the internal standard. The mass spectrum of triallate achieved with a concentration close to 1 ng per peak approaches the limit of detection with cyclic

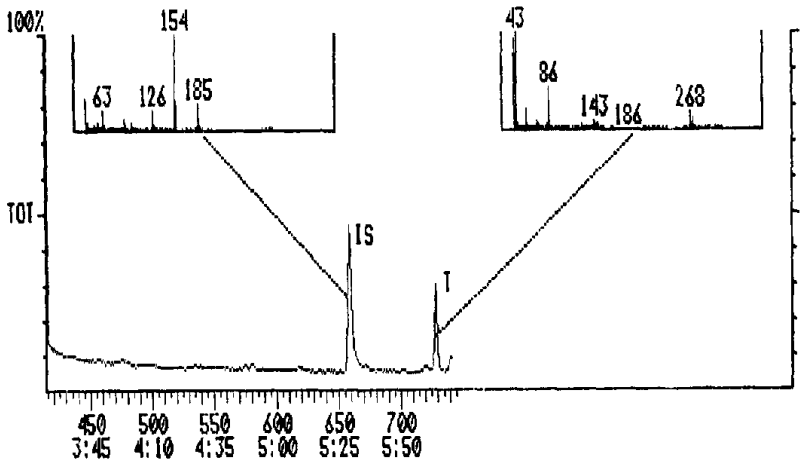

Fig. 1. Total-ion chromatogram of the internal standard (IS) and triallate (T) with their mass spectra. A 10-ng amount of I.S. and 2 ng of T were injected.

scanning, and it displays a higher proportion of lower masses, in comparison with spectra obtained at higher concentrations. Nevertheless, the spectrum can be reliably recognized by means of the best fit search in the NBS library among 42 000 compounds.

The triallate residues were quantified by selecting the m/z 86 ion for triallate and m/z 154 ion for the internal standard, after acquisition of the total-ion chromatogram of the sample (Fig. 2). The ratio of the areas of these selected ions was obtained for each sample and compared with the ratio found for mixtures of

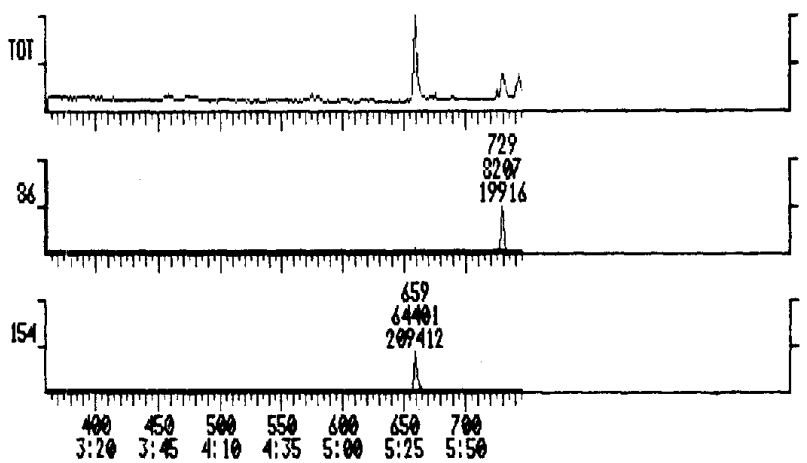

Fig. 2. Total-ion and SIM chromatograms of barley seedling extract. The sample was spiked with 0.2 mg/kg triallate and 2 mg/kg I.S. Retention time in scans, height and peak area are reported at m/z 86 for triallate and m/z 154 for the I.S.

TABLE I

RECOVERY OF TRIALLATE ADDED TO SOIL AND BARLEY SEEDLINGS

Sample	Added (mg/kg)	Recovery (mean ± S.D., $n=5$) (%)	
		ITD	NPD
Soil	0.2	91.4±9.1	90.0±7.1
	1.0	89.3±9.5	91.6±8.6
	2.0	92.4±7.3	93.0±6.0
Barley	0.2	85.3±7.6	86.3±8.5
	1.0	89.8±7.4	95.3±4.6
	2.0	87.8±4.0	89.4±6.6

triallate and the internal standard of known concentration. The detector response was linear from 1 to at least 6 μg/ml triallate, which represents 2–12 ng of substance per peak.

Table I shows the herbicide recovery via the analytical method from barley seedlings and soil samples spiked before extraction by addition of 0.2–2 mg/kg herbicide. The average recovery was always higher than 80%, with a relative standard deviation equal to or less than 9%. These samples were also analysed by the GC–NPD method (Table I). The recoveries are nearly the same as those obtained by GC–ITD, with an average difference within the 95% confidence interval, $d=0.0012 < \mu=0.08$, indicating the equivalence of the methods [10].

The detection limit of the GC–ITD method with cyclic scanning was near 0.1 mg of triallate per kg fresh weight, based on a 10-g sample. This limit can be improved to 0.01 mg/kg using selected-ion monitoring (SIM). Fig. 3 shows the

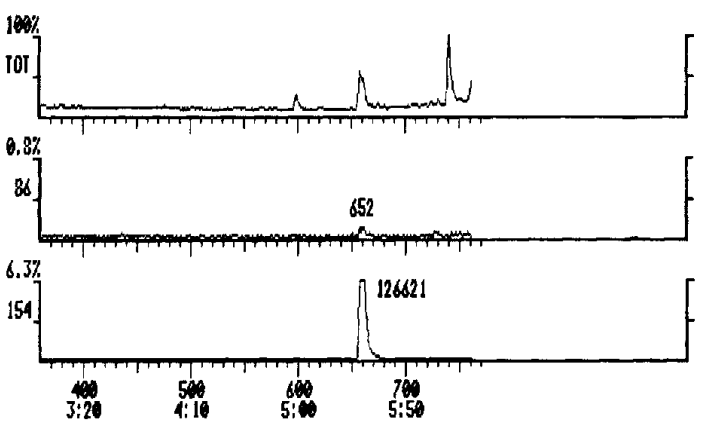

Fig. 3. Total-ion and SIM chromatograms of an untreated soil extract. The sample was spiked with 1 mg/kg I.S. Peak areas are shown at *m/z* 154 for the I.S. and *m/z* 86 for the highest background peak.

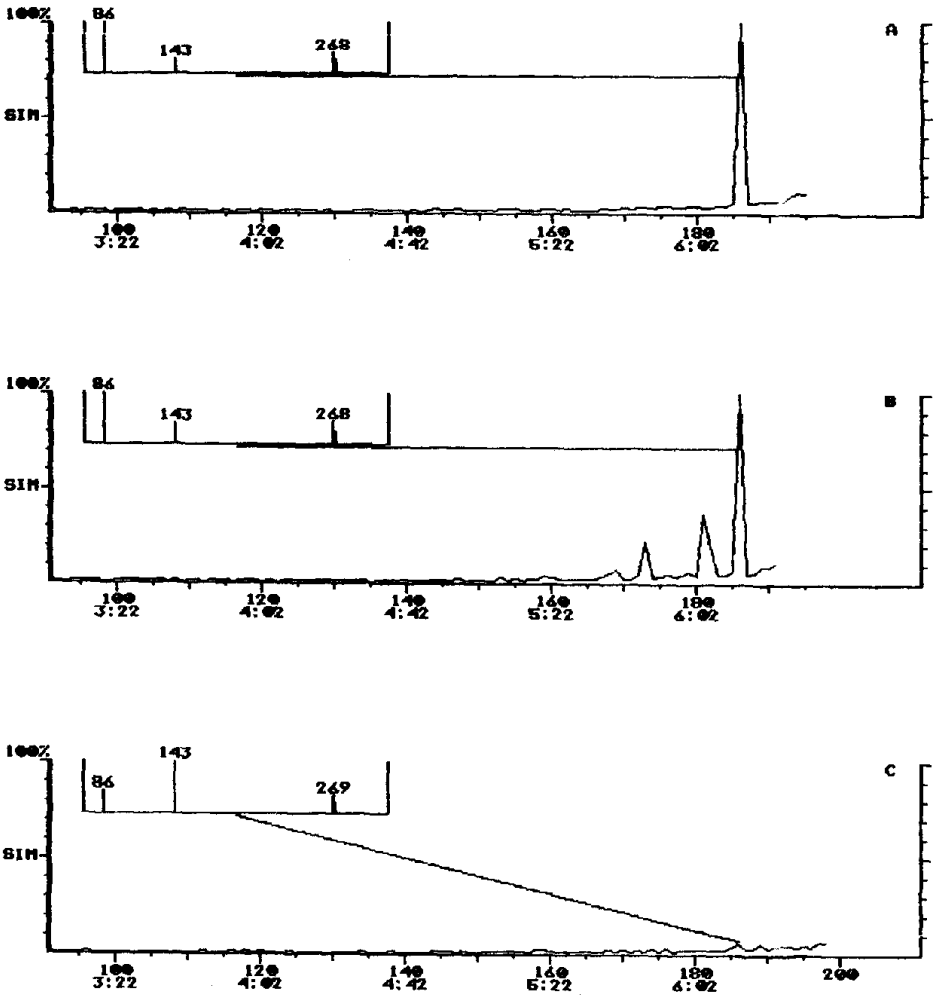

Fig. 4. MID chromatograms obtained at *m/z* 86, 143 and 268–270. (A) Standard, 0.5 μg/ml; (B) treated soil sample, 0.07 mg/kg fresh weight; (C) untreated soil sample.

TABLE II

TRIALLATE RESIDUES FOUND IN SOIL AND BARLEY SAMPLES

Sample	Found (mean ± % R.S.D., $n = 3$) (mg/kg)	
	ITD	NPD
Soil	0.07 ± 5.7	0.08 ± 5.0
Barley	1.35 ± 3.7	1.20 ± 4.2
Barley	0.96 ± 2.4	0.97 ± 4.1

total and SIM chromatograms of an untreated soil sample spiked with 1 mg/kg internal standard (I.S.). The area of the I.S. peak was 126 621, and that of the highest peak of the background observed at *m/z* 86 was 652, which should correspond to a concentration of triallate lower than 0.01 mg/kg.

Fig. 4 shows multiple-ion detection (MID) chromatograms of a treated soil sample containing 0.07 mg/kg triallate compared with an untreated soil. The selected ions *m/z* 86,143 and 268–270 allowed the recognition of triallate, in the NBS library search, at the level found in the treated sample. The area of the peak at the retention time of triallate in the untreated soil sample is equivalent to a concentration of 0.005 mg/kg triallate, with ions that have a relative abundance different from that obtained with triallate.

Several samples of barley seedlings and soil treated with triallate were also analysed by GC–ITD and GC–NPD. Table II shows the mean of three determinations and their relative standard deviations. Although different chromatographic columns and conditions were employed with each technique, the results show good agreement.

CONCLUSIONS

The results presented in this paper demonstrate that the GC–ITD method can be used to determine triallate residues in soil and barley seedlings down to 0.01 mg/kg. The values obtained with this method are similar to those determined by GC–NPD.

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