Estimation of *S*-2,3,3-Trichloroallyl *N*,*N*-Diisopropylthiolcarbamate (Triallate) Residues in Soil, Barley Straw, and Grain by Electron-Capture Gas Chromatography

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A gas chromatographic method for the determination of triallate is described. Samples are cold-extracted with a mixture of 2,2,4-trimethylpentane and isopropyl alcohol, after which the extract is shaken with water and the aqueous phase discarded. With soil extracts, aliquots of the 2,2,4-trimethylpentane layer are injected directly, but straw and grain extracts require further cleanup with Nuchar Attaclay. Recoveries at the 0.1- to 1.0-p.p.m. level are in excess of 90% with soil and barley grain and 80% with barley straw. The method is sensitive to 0.05 p.p.m.

Triallate (*S*-2,3,3-trichloroallyl *N*,*N*-diisopropylthiolcarbamate) is useful for the control of wild oats in a variety of crops. A gas chromatographic method (Desmoras *et al.*, 1963, 1964) for its determination in soils gives a recovery rate of 80 to 85%. The method described below uses a simple extraction and cleanup which produce a higher recovery with soils and is also suitable, with a slight modification, for use with barley straw and grain.

EXPERIMENTAL

Apparatus. Varian Aerograph 1520 gas chromatograph fitted with an electron-capture detector.

Reagents. All solvents were glass-distilled.

Extraction Procedure. SOIL. Moist soil samples from the field were crushed, mixed, and passed through a 10-mesh sieve. If necessary, the soil was allowed to air dry at 20° C. until a suitable physical condition for the manipulations was attained. Complete drying was avoided, however, as this caused loss of the herbicide. Moisture determinations were carried out on each soil. A 20-gram representative subsample was weighed into a 250-ml. stoppered conical flask. Fifty milliliters of mixed solvent (2,2,4-trimethylpentane and isopropanol, 2 to 1) were added; the slurry was shaken for 30 minutes on a wrist action shaker. After settling, the mixture was decanted and the supernatant liquid filtered through a fluted Whatman No. 1 paper. A 25-ml. aliquot of the filtrate was transferred by pipet into a 100-ml. separatory funnel and extracted with two 25-ml. portions of distilled water, the lower aqueous phase being discarded each time. Approximately 0.5 gram sodium chloride was added at each extraction to inhibit the formation of emulsions and to aid separation. After the second extraction, the remaining 2,2,4-trimethylpentane was run into a stoppered tube and shaken with anhydrous sodium sulfate. Aliquots of this solution were taken for gas chromatography.

STRAW AND GRAIN SAMPLES. Chopped straw samples and grain were milled to pass a 2-mm. screen. Ten grams of straw or 20 grams of grain from a representative subsample were weighed into a macerator jar. Sufficient mixed solvent to cover the sample (50 to 60 ml.) was added and the mixture blended for 3 minutes. The extract was filtered under vacuum through a 1/8-inch layer of Hyflo Supercel prepared in a 3-inch diameter sintered glass funnel. The residue was washed with 40 ml. of solvent, and residual solvent was pressed out with a small beaker. The filtrate was transferred to a 100-ml. graduated cylinder and made to volume with solvent. A 25-ml. aliquot was transferred by pipet into a 100-ml. separatory funnel and washed with two 25-ml. portions of distilled water as in the soil method. The 2,2,4-trimethylpentane layer was run into a stoppered tube, 0.5 gram of Nuchar Attaclay was added, and the mixture was shaken vigorously for 1 minute, then filtered immediately through a Whatman

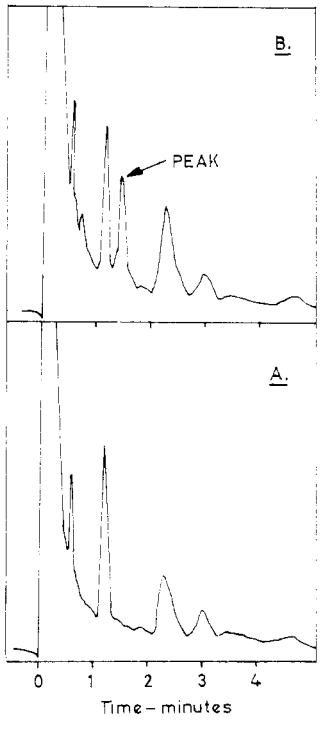

Figure 1. Chromatograms *A*, 3 mg. of control soil; *B*, 3 mg. of control soil fortified with 0.1 p.p.m. triallate

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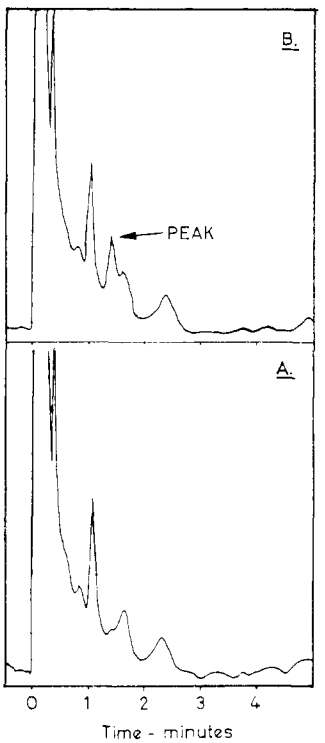

Figure 2. Chromatograms *A*, 1.5 mg. of control straw; *B*, 1.5 mg. of control straw fortified with 0.1 p.p.m. triallate

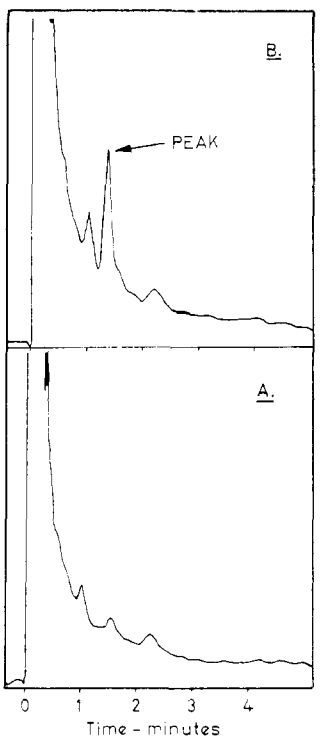

Figure 3. Chromatograms *A*, 3 mg. of control grain; *B*, 3 mg. of control grain fortified with 0.1 p.p.m. triallate

No. 1 paper into a stoppered tube. Aliquots of this solution were taken for gas chromatography.

Gas Chromatography. A 5-foot × 1/8-inch glass column was packed with 5% DC 11 on 60- to 80-mesh acid-washed Chromosorb W. The injector port was packed with glass wool arranged so that on injection of a sample, the tip of the needle just penetrated the glass wool.

Operating Conditions

Injector temperature	210° C.
Column temperature	180° C.
Detector temperature	200° C.
Gas flow rate	100 ml. per minute of oxygen-free nitrogen
Sensitivity	× 1
Attenuation	8
Chart speed	30 inches per hour

The calibration curve of log peak height *vs.* log nanograms triallate was linear over the range 0.05 to 1.0 ng. The final 2,2,4-trimethylpentane solutions were diluted where necessary so that the standard injection volume of 5 μl. had a triallate concentration within the calibration range.

RESULTS AND DISCUSSION

Figures 1 to 3 show chromatograms obtained from control samples and controls fortified with 0.1 p.p.m. of triallate. The samples were fortified by adding solutions of

Table I. Recovery of Triallate from Soil and Crops

	Added, P.P.M.	Found, P.P.M.[a]	Recovery, % Av.	Recovery, % S.D.	No. of Detns.
Begbroke soil (Sandy loam)	0	0.026[b]	...	...	10
	0.1	0.107	107	6.6	10
	0.5	0.49	98	8.8	10
	1.0	1.02	102	2.3	10
Barley straw (Variety Vada)	0	0.045	...	...	6
	0.1	0.083	83	7.8	6
	0.5	0.43	86	6.1	6
	1.0	0.86	86	7.4	6
Barley grain	0	0.019	...	...	6
	0.1	0.100	100	2.3	6
	0.5	0.45	90	5.1	6
	1.0	0.96	96	6.7	6

[a] Corrected for blank values.
[b] Standard deviation for blank samples was 0.004 p.p.m. for soil and 0.002 p.p.m. for straw and grain.

triallate in 2,2,4-trimethylpentane to the crops and soil before extraction. Recovery experiments were carried out at three different levels, and the results are presented in Table I. Bates (1964) has suggested that the limit of detection of a method should be taken as $2s/\sqrt{n}$ where s is the standard deviation of the control samples, and n is the number of replicate determinations on the treated samples. On this basis, assuming $n = 2$, the limit of detection for soil, straw, and grain is 0.006, 0.003, and 0.003 p.p.m., respectively. In practice, the limits 0.05 p.p.m. for straw and 0.025 p.p.m. for soil and grain were arbitrarily chosen for routine use.

After 10 to 15 injections, examination of the glass wool packed in the injector showed that a considerable amount of coextracted material was held up by it. This probably contributed to making these analyses practicable without the need for more stringent cleanup techniques by prolonging column life and lengthening the intervals between detector cleaning.

Triallate is a relatively volatile herbicide and throughout this work all soil determinations were made on wet soil. The moisture content of the soils varied between 13 and 16% with a mean of 14.6%. Earlier work in this laboratory showed that air drying of soil samples to constant weight at 20° C. caused a loss of triallate. The mean percentage loss was 28% with a range of 19 to 42%. Therefore, all soil samples must be analyzed immediately after sampling or be deep frozen until analyzed.

Using the method described, no detectable residues of triallate were found in barley straw or grain harvested from plots that had received a pre-emergence application of 1.5 pounds per acre of triallate.

LITERATURE CITED

Bates, J. A. R., *Chem. Ind. (London)* **1964,** p. 1591.
Desmoras, J., Jacquet, P., Laurent, M., Vertalier, S., *Compt. Rend. 2e Conf. Com. Franc. Mauv. Herbes (COLUMA)* **1963, 1964,** pp. 179-88.

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