

Estimation of *S*-2,3-Dichloroallyl *N,N*-Diisopropylthiolcarbamate (Diallate) Residues in Soils by Electron-Capture Gas Chromatography

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A simple method is described for the gas chromatographic determination of diallate residues in soils using an electron-capture detector. Recoveries

of 86 to 97% are obtained from clay and loam soils treated at the 0.5- to 5.0-p.p.m. level.

Diallate (*cis*- and *trans*-*S*-2,3-dichloroallyl *N,N*-diisopropylthiolcarbamate) is used extensively on the Canadian prairies and elsewhere for the control of wild oats in cereals and other crops. A bioassay method has been developed (Banting, 1967) for the estimation of diallate residues in soil using oat seedlings (*Avena sativa* var. Rodney) as the test species. The bioassay technique has the disadvantage of being time-consuming as well as non-specific and so the following simple analytical method, based on electron-capture gas chromatography, was developed. This procedure gives excellent recoveries from both clay and loam soils with the minimum of cleanup.

EXPERIMENTAL

Apparatus. The gas chromatograph used was a Varian 204-2C equipped with glass-lined injector ports and electron-capture detector operated at 70 volts in a d.c. mode. The 7-foot \times 1/8-inch o.d. glass column was packed with 5% SE-30 on 80- to 100-mesh Chromasorb W (regular) and connected directly to the detector base.

Oxygen-free nitrogen was the carrier gas at a flow rate of 50 ml. per minute. Injector temperature was 230° C., column temperature 160° C., and detector temperature 200° C. Under these conditions diallate had a retention time of 1.5 minutes.

Reagents. All solvents were glass-distilled and obtained from Burdick & Jackson Laboratories, Inc., Muskegan, Mich.

Extraction Procedure. Field samples were crushed and sieved to pass a 2-mm. sieve and their moisture contents determined. In general, a soil moisture intermediate between the wilting point and the field capacity of the soil type under investigation was satisfactory for reproducible herbicide extractions. If necessary, the soil was allowed to air-dry at 20° C., or distilled water was added, until a suitable physical condition was obtained. As diallate is rather volatile, drying could not be effected at an elevated temperature. Twenty-gram samples were weighed into 125-ml. glass-stoppered flasks to which 40 ml. of benzene and 20 ml. of 2-propanol were

added. The flasks were then shaken for 30 minutes on a wrist-action shaker, and after settling 30-ml. aliquots of the supernatant liquid were pipetted into 250-ml. separatory funnels and shaken twice with 25-ml. portions of 3% sodium carbonate solution to remove the 2-propanol and the acidic impurities. The pale yellow benzene layer was run into a small stoppered flask and dried over anhydrous sodium carbonate. Further cleanup was achieved by the addition of 0.2 gram of Nuchar Attaclay to the flasks, followed by shaking for 1 minute. After settling, 5- μ l. aliquots of the colorless benzene solution were injected directly into the injection port of the gas chromatograph.

The calibration curve of peak heights *vs.* nanograms of diallate injected was linear over the range of 0.2 to 10 ng.

RESULTS AND DISCUSSION

In all recovery experiments, 20-gram samples of sieved, dry Regina heavy clay and Oxbow-Weyburn loam were fortified by the addition of the required amount of diallate in 50 μ l. of hexane. After thorough mixing, water was added until a suitable moisture level was obtained, and the samples were allowed to equilibrate for 24 hours prior to analysis.

Typical gas chromatograms obtained from control samples of Oxbow-Weyburn loam and samples fortified with 0.5-p.p.m. diallate are shown Figure 1. Diallate is a mixture of *cis* and *trans* isomers (Harman and D'Amico, 1967) which have different boiling points and vapor pressures; however, under the stated operating conditions of the gas chromatograph there was no separation of the two isomers (Figure 1). Even when the column temperature was lowered to 140° C. no resolution of the single peak was observed.

In recovery experiments carried out at herbicide concen-

Table I. Recovery of Diallate from Soils

Sample	Determinations	Added, P.P.M.	Found, P.P.M.	Recovery, %	Std. Dev.
Regina heavy clay	6	5.0	4.7	94	4.3
		1.0	0.97	97	3.8
Oxbow-Weyburn loam	6	1.0	0.90	90	3.8
		0.50	0.43	86	8.6

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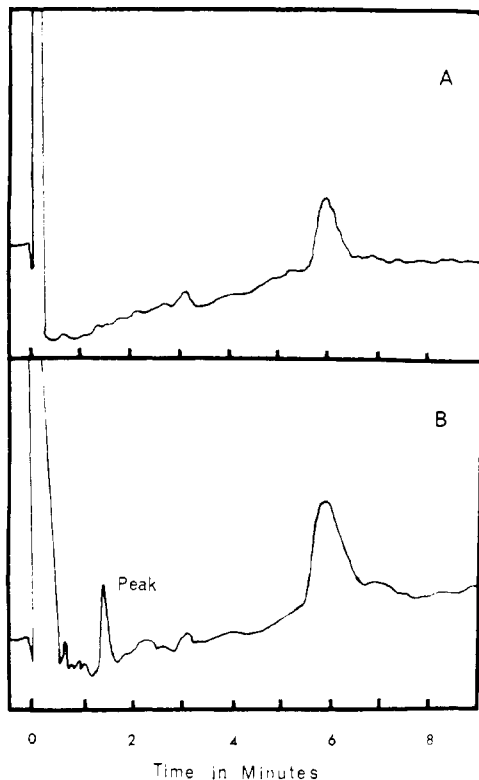


Figure 1. Gas chromatogram of Oxbow-Weyburn loam

- A. 20 grams of control sample
- B. 20 grams of control sample fortified with 0.5-p.p.m. diallate

trations of 0.5, 1.0, and 5.0 p.p.m. (Table I) excellent recoveries were obtained from both soils at all levels. Regina heavy clay has a 4% organic matter content and Oxbow-Weyburn loam, 6.5%; the higher value for the latter may account for the slightly lower diallate recoveries.

Lower herbicide recoveries were noted from fortified dry soils, and a certain minimum amount of moisture appears to be necessary for good extraction of the residues. The wilting points for Regina heavy clay and Oxbow-Weyburn loam are 20 and 12%, respectively. As long as the moisture content of the soils was at, or above, the wilting points, reproducible diallate recoveries were obtained.

Using the method described, diallate can be detected with accuracy at the 0.5-p.p.m. level, though with care it should be possible to detect residues at lower levels. Diallate is therefore not as sensitive to electron-capture detection as the closely related chlorinated analog triallate (*S*-2,3,3-trichloroallyl *N,N*-diisopropylthiolcarbamate), for which a sensitivity of 0.025 p.p.m. in soils has been reported (McKone and Hance, 1967). This increased sensitivity for triallate must be due largely to the additional chlorine atom.

ACKNOWLEDGMENT

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