Journal of Chromatography, 262 (1983) 328–330
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 15,773

Note

Simplified heptafluorobutyrylation of linuron and its metabolite 3,4-dichloroaniline

B. L. WOROBEY

Food Research Division, Bureau of Chemical Safety, Food Directorate, Health Protection Branch, Ottawa, Ontario K1A 0L2 (Canada)

(Received February 11th, 1983)

The use of derivatization techniques in the gas–liquid chromatographic (GLC) analysis of pesticides is widely accepted. Functional group transformations are usually employed: (a) to produce a more thermally stable compound (*e.g.* mono- and disubstituted phenylureas), (b) to form a more detector-sensitive derivative (especially for the electron-capture detector, ECD), and (c) for confirmation purposes.

N-Perfluoroacylation can fulfill all the above criteria. Several publications have described the N-perfluoroacylation of insecticidal carbamates[1,2,6] and ureas[3], and herbicidal ureas[2,4–6]. Recently, a screening program was initiated for halogenated anilines and their parent compounds and N-heptafluorobutyryl derivatives were prepared for the analysis of linuron and its metabolite, 3,4-dichloroaniline, in carrot samples. Since monitoring laboratories are sometimes concerned about implementing derivative procedures because of the time required for preparation, a simplified method was investigated to reduce the time required.

EXPERIMENTAL

Reagents and Chemicals

All solvents were residue-free glass-distilled grade. Heptafluorobutyric anhydride (HFBA) was used as received from Pierce. Linuron (N-methyl-N-methoxy-N′-(3,4-dichlorophenylurea)) was obtained from Agriculture Canada and assayed at 99.7% purity. 3,4-Dichloroaniline (3,4-DCA) was from Aldrich (98%) and recrystallized from hexane–methanol (9:1) after hot filtration through Norit A decolourizing carbon. Standards were prepared in acetonitrile.

Sodium carbonate (Baker analyzed grade) was used to prepare a 0.1 *M* aqueous solution (distilled water).

Gas chromatography

Chromatograph: Tracor MT220 with a Microtek ^{63}Ni ECD; column: 1% 1240 DA on 100–120 Supelcoport (Supelco), 1.23 m × 4 mm I.D.), nitrogen flow-rate 100 ml/min at detector, temperatures: column 175°C, detector 305°C, injector 190°C.

Method

The derivatization procedure is as follows: 1.0 ml of a 7.7 μg/ml acetonitrile

0021-9673/83/$03.00

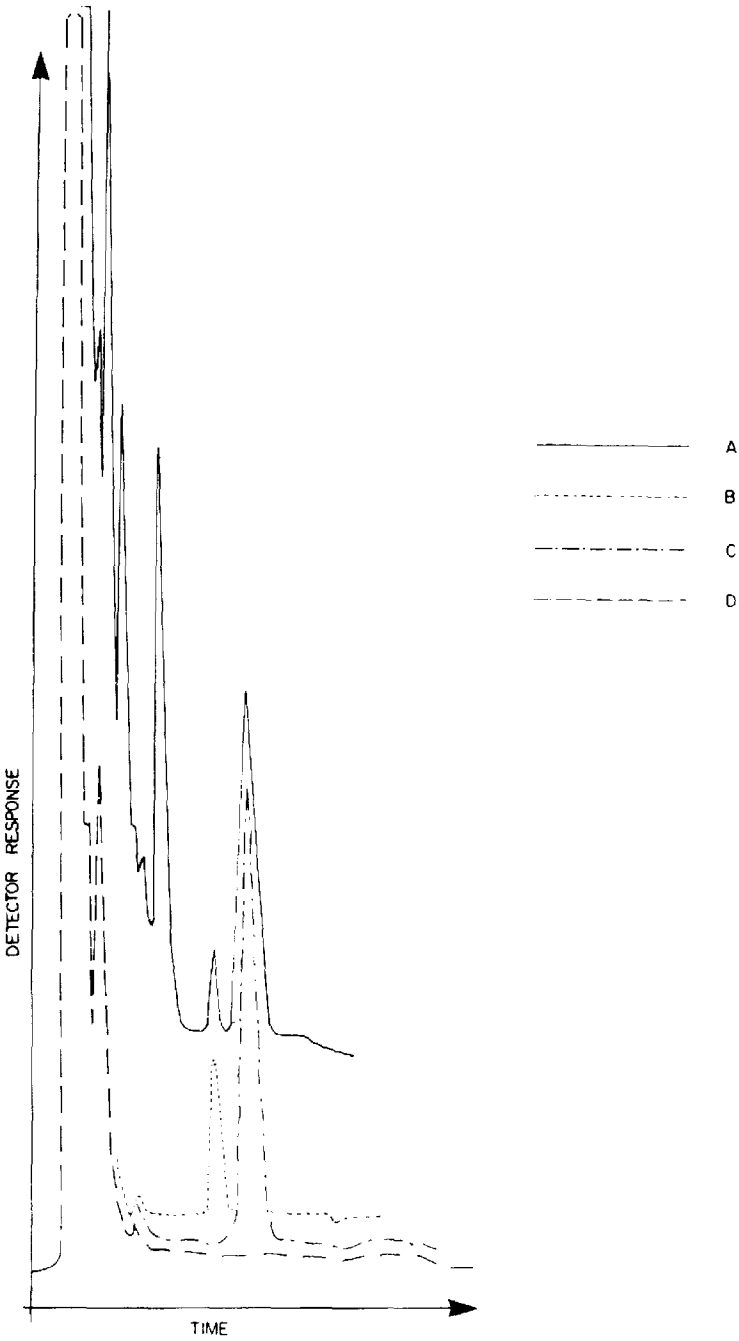

Fig. 1. GLC- ECD chromatograms of: (A) derivatized carrot extract, (B) 0.004 ng 3,4-DCA-HFB derivative, (C) 0.128 ng linuron-HFB derivative, (D) 1 μl derivatized reagent blank; electrometer setting $8 \cdot 10^{-10}$ A f.s.d.

linuron or 3,4-DCA solution and 0.1 ml HFBA were added to a 5-ml ground glass-stoppered centrifuge tube, mixed in a vortex mixer, and incubated at 60°C in a water bath for 15 min. Two ml 0.1 *M* Na_2CO_3 was added, mixed in a vortex mixer, and extracted with 3 × 1.0 ml hexane, by mixing in a vortex mixer. Hexane layers were transferred with a Pasteur pipette into a 5-ml graduated glass-stoppered centrifuge tube, the volume was reduced under nitrogen to 1 ml and injected into the GLC–ECD system.

RESULTS AND DISCUSSION

The N-heptafluorobutyryl derivative of linuron and 3,4-dichloroaniline had retention times of 3 min and 2.5 min, respectively; and the derivatized reagent blank was free from interferences (Fig. 1B, C and D). Fig. 1A illustrates a chromatogram of derivatized carrot extract, chromatograms of other carrot extracts showed no peaks at 2.5 or 3 min. ECD response was 35% f.s.d. (0.128 ng) and 10% f.s.d. (0.004 ng) for derivatized linuron and 3,4-DCA respectively.

The simplified derivatization method had several advantages over other methods. The advantages are: (a) simplification, (b) less time required, and (c) higher yields. Extraction of the derivative with 2 × 1 ml hexane resulted in *ca.* 50% greater recovery at 0.05 μg/ml *vs.* a single 1 ml or 2 ml partitioning. At 0.4 μg/ml, recoveries with 1 ml were equal to a 2 × 1 ml hexane partition.

The yield (*ca.* 100%) and precision (mean deviation ±3%) of the proposed method were optimal as evidenced by comparable peak areas per ng injected for 0.1 ml of a 77 μg/ml *versus* 1.0 ml of a 7.7 μg/ml linuron standards derivatized. No unreacted linuron or 3,4-dichloroaniline was detected. The derivatization of toluene-based standards resulted in *ca.* 50% lower yields *vs.* standards prepared in acetonitrile. Derivative formation maybe enhanced in acetonitrile *vs.* toluene because of the higher dipole moment and dielectric constant of the former; these physicochemical properties probably facilitate the ionization of HFBA (see mechanism, Worobey and Webster[3]) resulting in higher yields within the time reported. The addition of 0.1 *M* Na_2CO_3 to the reaction mixture removed a late GLC eluting co-extractive peak.

The modified method therefore, expedites analysis while at the same time maximizes yields; sensitivity is excellent permitting a better confirmation of residues, cleaner chromatograms (dilution of co-extractives), and more accurate quantitation of these compounds in environmental or food matrices. The method may logically be employed for any halogenated anilines, phenylureas, and phenylcarbamates for which N-heptafluorobutyrylation or N-perfluoroacylation has been shown to be successful.

ACKNOWLEDGEMENT

The author greatfully acknowledges the careful technical assistance of Ms. L. Panopio.

REFERENCES

1 E. D. Magallona, *Residue Rev.*, 56 (1975) 1.
2 W. P. Cochrane, *J. Chromatogr. Sci.*, 13 (1975) 246.
3 B. L. Worobey and G. R. B. Webster. *J. Chromatogr.*, 153 (1978) 423.
4 W. P. Cochrane and R. Purkayastha, *Toxicol. Environ. Chem. Rev.*, 1 (1973) 137.
5 D. G. Saunders and L. E. Vanatta, *Anal. Chem.*, 46 (1977) 1319.
6 J. F. Lawrence and J. J. Ryan, *J. Chromatogr.*, 130 (1977) 97.