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Electron-Capture Gas Chromatographic Determination of Diflubenzuron and Permethrin in Soil and Water

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An electron-capture gas chromatographic method is described for the determination of diflubenzuron in the presence of permethrin in soil and water. Diflubenzuron is derivatized to *N*-(4-chlorophenyl)-trifluoroacetamide by using trifluoroacetic anhydride with trimethylamine as a catalyst. Permethrin remains unchanged by the derivatization reaction. Mean recoveries for soil and water at two fortification levels were 87%, 92%, and 94% for diflubenzuron, *cis*-permethrin, and *trans*-permethrin, respectively.

The insect growth regulator diflubenzuron [Dimilin, *N*-[[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide] cannot be analyzed directly by electron-capture gas chromatography (ECGC) because the compound either decomposes or irreversibly adsorbs on GC columns commonly used for pesticide analyses (Corley et al., 1974). As a result, high-performance liquid chromatography (HPLC) methods were developed and successfully used to determine residues of diflubenzuron in water (Schaefer and Dupras, 1976), soil and plants (Schaefer and Dupras, 1977; Mansager et al., 1979), manure (Oehler and Holman, 1975), and fish (DiPrima et al., 1978; Schaefer et al., 1979). However, because GC offers the possibility of higher sensitivity, several derivitization procedures involving the formation of a thermally stable diflubenzuron derivative, easily detectable by ECGC, have been developed. DiPrima (1976) reported the determination of diflubenzuron in aquatic vegetation by hydrolyzing the extracted diflubenzuron to 4-chloroaniline and derivatizing with heptafluorobutyric anhydride to form *N*-(4-chlorophenyl)-heptafluorobutyramide, which is easily detectable by ECGC. A similar method (DiPrima, 1977) was reported for soil and sediment. Worobey and Webster (1977, 1978) reported the determination of diflubenzuron as its trifluoroacetyl derivative. Their method involved the direct derivatization of diflubenzuron with trifluoroacetic anhydride to form *N*-(4-chlorophenyl)trifluoroacetamide. Cleavage of diflubenzuron occurred during the reaction,

eliminating the need for a separate hydrolysis step. DeMilo et al. (1978) were able to similarly derivatize diflubenzuron with trifluoroacetic anhydride but added pyridine as a catalyst to obtain quantitative conversion. However, we found none of the aforementioned ECGC procedures satisfactory for reasons to be mentioned later.

The synthetic pyrethroid insecticide permethrin [3-phenoxybenzyl(±)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] can be analyzed directly and easily by ECGC, as was reported recently by Fujie and Fullmer (1978) for permethrin residues in plant, animal, and soil matrices and by Carroll et al. (1981) for permethrin residues on cotton plants and in soil and water. Permethrin, however, readily undergoes ester cleavage to 3-phenoxybenzyl alcohol and the dichlorovinyl acids, which is the basis of a derivatization procedure reported by George and McDonough (1975).

This paper presents the results of our efforts to develop a more satisfactory ECGC analytical procedure for diflubenzuron residues in water and soil, because of anticipated field studies involving both diflubenzuron and permethrin in agricultural runoff. In order to shorten analysis time, we also wanted to be able to determine permethrin directly on the same GC column used for derivatized diflubenzuron, since it was highly probable that both diflubenzuron and permethrin would be present together in the same runoff samples.

EXPERIMENTAL SECTION

Apparatus. A Micro Tek Model DSS-162 gas chromatograph, upgraded with a solid-state temperature programmer and dual-channel electrometer and equipped with a high-temperature ⁶³Ni electron capture detector and a Hewlett-Packard Model 3388A plotting integrator was employed for isothermal analyses. A glass column, 1.2 m long × 6 mm o.d. × 4 mm i.d. and packed with 3% SP2401 on 100-120-mesh Supelcoport, was used at 120 °C for

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derivatized diflubenzuron and at 200 °C for *cis*- and *trans*-permethrin. The carrier gas (filter-dried N₂, 99.995% minimum purity) flow rate was 90 mL/min for both derivatized diflubenzuron and *cis*- and *trans*-permethrin. The detector and inlet temperatures were 270 and 245 °C, respectively. A Tracor Model 565 gas chromatograph equipped with a high-temperature ⁶³Ni electron capture detector and a Hewlett-Packard Model 3390A plotting integrator was employed for temperature-programmed analyses. The column packing and carrier gas were as described previously except that the column was 2-mm i.d. The column oven was programmed from 105 to 210 °C at 21 °C/min. The detector and inlet temperatures were 350 and 240 °C, respectively.

Reagents. All solvents were pesticide grade (all glass distilled). Trifluoroacetic anhydride (99+%) was obtained from Pierce Chemical Co., Rockford, IL; 4-chloroaniline (mp 71–73 °C), NaCl (reagent, crystals), and anhydrous Na₂SO₄ (reagent, granular) were from MCB, Baton Rouge, LA; Florisil (60–100 mesh) was from Fisher Scientific, Houston, TX; trimethylamine (anhydrous, 99+%) was from Matheson, East Rutherford, NJ. Analytical-grade diflubenzuron (99.5%, mp 229–232 °C) and *N*-(4-chlorophenyl)heptafluorobutyramide (98+%, mp 92–97 °C) were provided by Thompson-Hayward Chemical Co., Kansas City, KS.

Synthesis of Reference Compounds. *N*-(4-Chlorophenyl)trifluoroacetamide (C₈H₅ClF₃NO). Add 3.1 g of trifluoroacetic anhydride slowly to 30 mL of benzene containing 1.3 g of 4-chloroaniline and 3.0 g of trimethylamine. Heat the mixture for 30 min on a water bath at 50–55 °C. Allow it to cool, quantitatively transfer it to a separatory funnel, wash it with 30 mL of aqueous 5% NH₄OH solution, drain the aqueous phase and discard, and dry the benzene phase by dripping through anhydrous Na₂SO₄. Evaporate the phase to dryness under a gentle stream of dry air and recrystallize the residue from benzene: mp 124–125 °C [lit. mp 123–124 °C (Stauffer, 1972)]. Anal. Calcd for C₈H₅ClF₃NO: C, 42.97; H, 2.25; N, 6.27. Found: C, 42.91; H, 2.17; N, 6.26.

***N*-(4-Chlorophenyl)heptafluorobutyramide (C₁₀H₅ClF₇NO).** Use 6.2 g of heptafluorobutyric anhydride and proceed as described for the trifluoroacetyl derivative. Recrystallize it from ethanol: mp 96–98 °C (Thompson-Hayward standard mp 92–97 °C). Anal. Calcd for C₁₀H₅ClF₇NO: C, 37.12; H, 1.56; N, 4.33. Found: C, 36.97; H, 1.48; N, 4.33.

Extraction and Derivatization Procedure. Soil. Sonify (Branson Model J-17A sonifier cell disruptor) 10 g of air-dry soil in a 225-mL wide-mouth bottle for 3 min with 200 mL of 1:1 hexane–ethyl acetate. Filter the extract, quantitatively transfer it to a separatory funnel, wash it once with 200 mL of warm H₂O (about 60 °C), drain and discard the H₂O washing, dry the organic phase over anhydrous Na₂SO₄, and evaporate it almost to dryness (<0.5 mL) under dry air. Take it up in 5 mL of benzene in a 15-mL glass-stoppered centrifuge tube, add 100 μL of trifluoroacetic anhydride and 100 μL of trimethylamine solution (0.5 M in benzene), and heat the mixture in a tightly stoppered centrifuge tube for 30 min on a water bath at 50–55 °C. Allow it to cool, quantitatively transfer it to a separatory funnel, wash it once with 15 mL of aqueous 5% NH₄OH and once with 15 mL of H₂O, drain and discard the washings, and dry the benzene phase over anhydrous Na₂SO₄. Bring the phase to a suitable volume for ECGC analysis. This procedure takes about 2.5 h.

Water. Add 5 g of NaCl and 100 mL of ethyl acetate to 100 mL of water sample and stir it on a magnetic stirrer

for 1 h. Quantitatively transfer to separatory funnel, drain and discard the aqueous layer, wash it once with 100 mL of warm H₂O, discard the washing, and dry the ethyl acetate layer over anhydrous Na₂SO₄. Evaporate the layer almost to dryness under dry air and derivatize as described previously for soil. This procedure takes about 3 h.

Cleanup Procedure. Prewash an all-glass chromatographic column (40 cm × 20 mm i.d. with a coarse porosity fritted disk at the bottom), containing 15 g of deactivated Florisil and topped by 10 g of anhydrous Na₂SO₄, with 50 mL of hexane, allow it to drain, and discard the hexane eluant. Prepare deactivated Florisil (5% moisture) by adding 5 mL of distilled water to 100 g of activated Florisil (heated overnight at 135 °C). Quantitatively add the benzene solution (concentrated to 5 mL) from the derivatization procedure to the deactivated Florisil column followed by 90 mL of 9:1 hexane–ethyl ether, collect the entire eluant; and concentrate it to a suitable volume for ECGC analysis. When needed, this procedure takes about 1 h.

Safety Precautions. Benzene is a possible carcinogen and trifluoroacetic and heptafluorobutyric anhydrides are strong skin and eye irritants. Proper protective clothing should be worn at all times when working with these compounds. All procedures should be conducted in a properly functioning fume hood.

RESULTS AND DISCUSSION

Numerous attempts were made to derivatize diflubenzuron by carefully following published procedures, but no one method proved satisfactory. The procedure of DiPrima (1976, 1977) called for a 12-h acid hydrolysis step to convert diflubenzuron to 4-chloroaniline, which is then reacted for 3 h with heptafluorobutyric anhydride to form *N*-(4-chlorophenyl)heptafluorobutyramide for determination by ECGC. We found this procedure too lengthy and obtained a derivatization efficiency of only 74.4 ± 4.1% in the range of 1–10 μg of diflubenzuron. The derivatization procedure of Worobey and Webster (1977), although considerably shorter (30-min reaction time) and more direct (i.e., no hydrolysis step), also proved inefficient with a conversion of only 61.9 ± 2.0% in the 1–10 μg of diflubenzuron range. Extending the reaction time to 1 h did not improve the derivatization efficiency. The very similar procedure of DeMilo et al. (1978), but using pyridine as a catalyst, was also found to be unsuitable because of an irremovable interference (probably pyridine) in the gas chromatogram.

The derivatization procedure which we found to be very efficient was similar to that of DeMilo et al. (1978) but with trimethylamine substituted for pyridine as a catalyst. Acylations of amines using trimethylamine as a catalyst are usually quantitative within a few minutes, and trimethylamine (if incompletely removed) does not cause disturbances in the gas chromatogram when electron capture detection is used (Pierce Chemical Co., 1981). We also determined that with this procedure, permethrin could be quantitatively coextracted with diflubenzuron but remained unchanged by the derivatization reaction. This eliminated the need for a separate analytical procedure for permethrin residues occurring in the same samples as diflubenzuron residues.

Table I shows the results obtained with this method using water and soil fortified with diflubenzuron and permethrin. The recovery values for diflubenzuron averaged about 87% overall. This was slightly less than we had hoped for but was better than we could achieve following published procedures. The limit of quantitative detection was 0.05 ng for diflubenzuron and 0.10 ng each

Table I. Percent Recovery of Diflubenzuron and Permethrin from Soil and Water

| fortification level, ppm | recovery, % ^a | | |
|--------------------------|--------------------------|------------------------|--------------------------|
| | diflubenzuron | <i>cis</i> -permethrin | <i>trans</i> -permethrin |
| water | | | |
| 0.01 | 85.9 ± 3.6 | 92.9 ± 3.8 | 94.1 ± 2.6 |
| 0.10 | 89.4 ± 2.3 | — ^b | — |
| soil | | | |
| 0.10 | 84.8 ± 3.2 | 89.5 ± 4.4 | 91.7 ± 1.2 |
| 1.00 | 91.2 ± 1.8 | 93.3 ± 5.9 | 96.8 ± 4.9 |

^a Means of six replicates. Three replicates were determined by isothermal ECGC and three by temperature-programmed ECGC. ^b Not determined because the permethrin water solubility is 0.07 ± 0.02 ppm.

for *cis*- and *trans*-permethrin. Cleanup on deactivated florasil was required for the lower fortification level for both soil and water. The warm water washing used in the extraction procedures for soil and water was necessary to remove the diflubenzuron metabolites, (4-chlorophenyl)urea and 4-chloroaniline, which would probably be present in environmental samples. These metabolites, if not removed, would also be derivatized to *N*-(4-chlorophenyl)trifluoroacetamide. Brief studies with soil fortified at the 0.10-ppm level and water fortified at the 0.01-ppm level with both diflubenzuron metabolites revealed only non-measurable traces of the trifluoroacetyl derivative on the gas chromatograms. The warm water washing could have contributed to the <90% recovery values obtained for diflubenzuron. Although the diflubenzuron standard was kept refrigerated at all times except when in actual use, slight deterioration to (4-chlorophenyl)urea and 4-chloroaniline prior to the fortification of soil and water could have still occurred. This may also have contributed to the <90% recoveries.

This method was developed out of necessity because of unsatisfactory results obtained with published procedures. It was also developed by trial and error using "bits and pieces" of these same published procedures. This method thus represents just another example of the constant need to modify established procedures to suit a particular situation. Other researchers may perhaps have to make re-

finements of our work for their own purposes.

Registry No. *N*-(4-Chlorophenyl)trifluoroacetamide, 404-25-1; *N*-(4-chlorophenyl)heptafluorobutyramide, 79497-98-6; diflubenzuron, 35367-38-5; *cis*-permethrin, 61949-76-6; *trans*-permethrin, 61949-77-7; permethrin, 52645-53-1; trifluoroacetic anhydride, 407-25-0.

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