INTRODUCTION:

BROOT pesticide is a 1:4 mixture of 2,3,5-trimethylphenyl methylcarbamate and 3,4,5-trimethylphenyl methyl carbamate isomers. The common name for BROOT is trimethacarb. The analytical method presented here allows the simultaneous quantification of 2,3,5-trimethacarb (2,3,5-TMC) and 3,4,5-trimethacarb (3,4,5-TMC) in soil. This method was developed to analyze soil samples from a field soil dissipation study currently being conducted at Union Carbide research stations in Clayton, NC, Newton, IA, and Manteca, CA.

Trimethacarb residues are extracted from soil samples with an acetone/water/phosphoric acid mixture. After filtration, acetone is evaporated from the extraction mixture and the trimethacarb is partitioned into dichloromethane. The dichloromethane extract is evaporated to dryness and then dissolved in a suitable volume of ethyl acetate before quantification of TMC residues by capillary gas chromatography.

Apparatus:

a) Hewlett-Packard 5880A gas chromatograph (Hewlett-Packard, Avondale, PA) equipped with a Hewlett-Packard 19320 capillary inlet system and a nitrogen-phosphorus detector.

b) Lab-Line Junior Orbit Shaker (Lab-Line Instruments, Inc., Melrose Park, Illinois).

c) Polypropylene animal-watering bottles with screw-cap, 250 mL capacity, cat. no. 02-893B. (Fisher Scientific, Pittsburgh, PA).

d) Beckman TJ-6 Tabletop Centrifuge (Beckman Instruments, Palo Alto, CA)

e) Buchner funnels, 43 mm plate diameter.

f) Whatman #1 filter paper, 4.25 cm diameter.

g) Side-arm filter flasks, 500 mL.

h) Separatory funnels, 250 mL.

i) Plastic funnels, 100 mm top diameter.

j) Erlenmeyer flasks, 250 mL.

k) BLUE-M Stabil-Therm oven.
(General Signal, Blue Island, IL 60406)

l) Disposable aluminum weighing dishes, 57 mm diameter (Fisher Scientific, Pittsburgh, PA)

Reagents:

a) Acetone, glass distilled (MCB Reagents, E. M. Industries, Gibbstown, N.J.).

b) Water, HPLC grade or purified by a Milli-Q water purification system (Millipore Corporation, Bedford, MA), or equivalent.

c) Phosphoric acid, 85%, analytical reagent. (Mallinckrodt, Inc., Paris, KY).

d) Hyflo-Supercel filter aid (Johns-Manville, Denver, CO).

e) Dichlormethane, glass distilled (MCB Reagents, E. M. Industries, Gibbstown, N. J.).

f) Anhydrous sodium sulfate (Mallinckrodt, Inc., Paris, KY)

g) Ethyl acetate, glass distilled (MCB Reagents, E. M. Industries, Gibbstown, N. J.).

h) 2,3,5-trimethylphenyl methylcarbamate analytical standard.

i) 3,4,5-trimethylphenyl methylcarbamate analytical standard.

j) Extracting Solvent :700 mL acetone + 300 mL water + 5 mL 85% phosphoric acid.

Standard Solutions:

a) Weigh 0.0500 grams 2,3,5-trimethylphenyl methylcarbamate and 0.0500 grams 3,4,5-trimethylphenyl methylcarbamate into a 100 mL volumetric flask and dilute to the mark with acetone. This solution contains 500 µg/mL of each trimethacarb isomer.

b) Make appropriate dilutions of solution a) with acetone to obtain "spiking solutions" containing 50.0, 10.0, 5.00, 2.50, 1.00, and 0.500 µg/mL of each trimethacarb isomer in acetone.

c) Dilute 1.00 mL of solution a) to 50.0 mL with ethyl acetate. This solution contains 10.0 µg/mL of each trimethacarb isomer.

d) Make appropriate dilutions of solution c) with ethyl acetate to obtain chromatographic standards containing 1.00, 0.500, 0.200, and 0.100 µg/mL of each trimethacarb isomer in ethyl acetate. Use pure ethyl acetate for the 0 µg/mL chromatographic trimethacarb standard.

Procedure:

1. Air-dry each sample overnight at room temperature on a clean piece of plastic, aluminum foil, or plastic-coated paper.

2. Pick out and discard grass, rocks, sticks and roots from the dried soil and break up any soil lumps with a spatula. Sieve the soil using a screen with 2 mm openings (U.S. Sieve mesh No. 10). Mix well and subsample for analysis.

3. Weigh 50 grams of soil into an 8 ounce plastic animal-watering bottle.

4. Fortification of samples for determination of recoveries should be done at this point.

5. Add 50 mL of extracting solvent to the plastic bottle and shake on the orbit shaker at 300 rpm for 5 minutes.

6. Centrifuge for 5 minutes at 2000 rpm.

7. Filter the supernatant liquid by suction through a Buchner funnel containing a thin bed of Hyflo-Supercel on a 4.25 cm circle of Whatman #1 filter paper. Collect the filtrate in a 500 mL side-arm flask.

8. Add 50 mL of extracting solvent to the soil that remains in the plastic bottle. Shake the bottle vigorously to break up the soil clump, then place the bottle on the orbit shaker for 5 minutes at 300 rpm.

9. Filter the supernatant through the same filter that was used in step 7, combining the filtrate in the same flask from step 7.

10. Repeat steps 8 and 9 once more.

11. Evaporate acetone from the combined extracts using a gentle stream of air in a 40°C water bath. Remove the flask from the water bath when acetone vapors are no longer detected.

12. Using a 250 mL separatory funnel, partition trimethacarb residues into three 50 mL portions of dichloromethane.

13. Pass the dichloromethane extracts through a cotton-stoppered plastic funnel containing 100 grams of anhydrous sodium sulfate, collecting the combined extracts in a 250 mL Erlenmeyer flask. Rinse the sodium sulfate with an additional 20 mL portion of dichloromethane and add the rinse to the combined dichloromethane extracts.

14. Evaporate the combined dichloromethane extracts to dryness in a 40°C water bath under a gentle stream of air. Remove the flask from the water bath immediately after attaining dryness.

15. Pipet 5.00 mL ethyl acetate into the flask and swirl to dissolve the residue.

16. Inject 1 µL of the ethyl acetate solution into the gas chromatograph.

17. Use ethyl acetate to make appropriate dilutions of the final ethyl acetate solution if the peak(s) are larger than those in the highest chromatographic standard.

18. Gas Chromatographic Conditions:

    Column: 15 meter x 0.32 mm ID. fused silica capillary column coated with a 0.25 µm film of DB-1701 (J & W Scientific, Rancho Cordova, CA).

    Carrier: 14 psi Helium (~6 mL/min)
    Split flow = 15 mL/min
    Injection Temperature = 200°C
    Detector Temperature = 300 °C
    Column Temperature = 155°C (Isothermal)

    Use the splitless insert but operate in the split mode. Glass wool and normal GC packings in the split insert promote the decomposition of trimethacarb. Under these conditions the retention time for 2,3,5-trimethacarb is approximately 1.8 minutes while the retention time for 3,4,5-trimethacarb is approximately 2.5 minutes.

19. Determination of soil moisture: Weigh an empty aluminum weighing pan to the nearest 0.01 gram and record this weight. Place 20-30 grams of air dried soil from step 2 into the pan and record the combined weight of the pan and soil. Place the pan and soil in an oven at 105°C for twelve hours. Place the pan and soil in a desiccator until the sample returns to room temperature. Weigh the soil and pan and record this weight.

Quantification: Soil Moisture:

The amount of moisture in the air-dried soil is calculated by subtracting the combined weight of soil and aluminum weighing dish after oven-drying from the combined weight of soil and aluminum weighing dish before oven-drying. The moisture is then expressed as a fractional amount of the dry (oven-dried) soil weight.

$$M = \text{Factor Soil Moisture Correction} = \frac{W-D}{D-P}$$

where:

W = weight of air-dried soil plus weighing pan
D = weight of oven-dried soil plus weighing pan
P = weight of weighing pan

Quantification: Concentration of Trimethacarb in Soil:

Prepare a calibration line for each trimethacarb isomer by plotting the peak height for the isomer versus the concentration (in µg/mL) of the isomer in the chromatographic standard solution. The concentration of each trimethacarb isomer in a soil sample extract is determined from its peak height and the slope and intercept of its respective calibration line.

$$A = \text{conc. of trimethacarb isomer in the injected sample (in µg/mL)} = \frac{(\text{Peak Height})-(\text{Intercept})}{(\text{Slope})}$$

This equation is valid only if the volume of sample extract injected into the gas chromatograph (1 µL) is equal to the volume of chromatographic standard injected into the gas chromatograph (1 µL) during preparation of the calibration line.

Calculate the concentration of each trimethacarb isomer (in parts-per-million) in the original soil sample, on a dry weight basis, using the following equation:

$$\text{Concentration of trimethacarb isomer in soil sample (ppm)} = \frac{100\ AV\ (M + 1)}{RS}$$

Where:

V = final volume of ethyl acetate (in mL)
R = percent recovery (determined from fortified samples)
S = weight of air-dried soil used in step 3.
M = Soil Moisture Correction Factor.

DISCUSSION:

Some important aspects of the method merit emphasis here.

The first critical steps in the method are air-drying and mixing the soil. Since air-dried soil is easier to mix than moist soil, the air-drying step helps to ensure that a representative analytical subsample is obtained from the original soil sample. Results from a separate experiment have shown no loss of either TMC isomer from soil during air-drying.

Second, the choice of extraction solvent was based on work by Andrawes and Blanton (Ref. 1). They showed that an acetone/water/phosphoric acid mixture was effective in the extraction of strongly adsorbed TMC from soil.

Third, successful gas chromatography of TMC requires careful attention to temperature and active sites within the chromatographic system. Injection port temperature was selected to minimize thermal decomposition while still providing rapid vaporization of the sample. The injection port liner should not be packed with glass wool or normal GC packing materials. These packings provide a large hot surface area and promote TMC decomposition. Whereas TMC decomposes on regular gas chromatographic packings, it can be chromatographed intact on inert fused silica capillary columns.

Although the nitrogen-phosphorus detector provides sensitive, selective detection for TMC, the response of the detector may drift with time. Therefore standards should be chromatographed fairly often and interspersed among samples.

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Attachments: Tables 1 - 4
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