Agricultural Analytical Chemistry
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Methods are routinely revised.
Interested parties may receive revisions
by request to the above address.

DETERMINATION OF BENEFIN IN SOIL BY SOLID PHASE EXTRACTION

AM-AA-CA-R125-AA-755

Benefin[1] is extracted from soil with 99:1 acetonitrile:water, and an aliquot is diluted with deionized (DI) water to a maximum acetonitrile content of 50%. Benefin is purified by C18 solid phase extraction and then measured by gas chromatography using electron capture detection.

REAGENTS

1. Acetonitrile, reagent grade
2. Toluene, pesticide grade
3. Methanol, reagent grade

APPARATUS

1. Sample grinding and blending equipment
2. Gyratory shaker
3. C18 Solid Phase Extraction Cartridge, Waters or equivalent
4. Solid Phase Extraction System
5. Gas Chromatograph equipped with an electron capture detector
6. Vortex mixer

PROCEDURE

A. Preparation of Standard Solutions and Standard Curve

1. Benefin Stock Standard Solution, 50 µg/mL - Accurately weigh 10 mg of benefin reference standard. Transfer the standard to a 200-mL volumetric flask and dilute to volume with toluene. This solution is stable for 6 months when refrigerated and protected from light and solvent evaporation.

2. Prepare a standard solution at a concentration of 10.0 µg/mL in methanol (MeOH) for fortifying the recovery samples. This solution is prepared from the Benefin Stock Standard Solution.

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[1]N-Butyl-N-ethyl-2,6-dinitro-4-(trifluoromethyl)-benzenamine

3. Prepare standard solutions in toluene over the range of 0.01 µg/mL to 0.3 µg/mL for obtaining a standard curve.

B. Preparation of Sample

Soil should be mixed in a suitable blender. Add a known weight of dry silica (approximately equal to the sample weight) if the soil is too moist to flow freely.

C. Extraction of Soils

1. Weigh a 90-g sample of soil into a pint Mason jar. If sand has been added, weigh a sample equivalent to 90 g of soil.

2. Add 100 mL of 99:1 acetonitrile:water.

3. Shake for 15 minutes using a gyratory platform shaker. An oscillating speed of 300 rpm is usually sufficient to ensure complete extraction.

4. Allow solid particles to separate, and transfer by pipette a 5.0-mL aliquot of the clear supernatant extract into a 25-mL scintillation vial. When extracts remain turbid, filter a portion through Whatman No. 1 filter paper and transfer exactly 5.0 mL to a 25-mL scintillation vial.

5. Add 5.0 mL of deionized water to the scintillation vial and vortically mix.

D. Purification

1. Condition the C18 cartridge by adding 5 mL of methanol and pulling through the cartridge with vacuum. Repeat the procedure with a 5-mL volume of deionized water. Discard the eluate.

2. Transfer the 10-mL diluted sample aliquot to the conditioned C18 cartridge and pull through under vacuum. Discard the eluate.

3. Elute the benefin from the C18 cartridge with 5.0 mL of toluene into a test tube.

4. Vortically mix the toluene eluant and allow to set for 15 minutes.

5. Transfer a portion of the toluene to a GC vial, and cap the vial for gas chromatographic analysis.

E. Standard Recovery

1. A standard recovery sample of 0.11 ppm may be assayed with soil samples which have control material available. System recoveries (all reagents without soil) which simulate the 0.11 ppm recovery are used when control soil is unavailable. The standard recovery sample is prepared by adding 10.0 µg of the benefin fortification standard to 90 g of control soil, and assaying as an experimental sample.

F. Gas Chromatography

Gas Chromatograph - Hewlett-Packard Model 5713A equipped with Ni-63 electron capture detector, or an equivalent GC system.

Column - 120 cm x 2 mm i.d., glass, packed with 5% Carbowax 20M on Chromosorb W-HP 80/100 mesh

Oven Temperature - 190°C

Injection Block Temperature - 250°C

Detector Temperature - 300°C

Carrier Gas - 90% Argon, 10% Methane

Flow Rate - 60 mL/min, or adjusted to give optimum peak shape

Electrometer - Attenuate to provide 30% of full scale deflection (approximately 7-7.5 cm) from the injection of 0.4 ng of benefin standard solution. The retention time for benefin is about 4.2 minutes.

The preferred column for the detection and measurement of benefin is 5% Carbowax 20M. However, 5% XE-60, 5% W-98, ULTRA-BOND™ 100/120 mesh,* 50% Phenylmethyl Megabore (0.53 mm i.d. x 10 m), or Megabore DB-5 (0.53 mm i.d. x 15 m) may also be used.

NOTE: The above conditions are only intended as guidelines. Actual conditions may vary from one laboratory to another.

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* ULTRA-BOND™: Commercially available from Alltech Associates. May be produced in the laboratory as described by W. A. Aue, C. R. Hastings, and S. Kapila, Analytical Chemistry, Vol. 45 (April, 1973) 725-728.

G. Calculations

1. Recoveries

$$\text{Percent recovery} = \frac{\mu g/mL \text{ (from std. curve)} \times SV \times AF \times 100}{\mu g \text{ fortified}}$$

Where:

SV = sample volume (5.0 mL for soil)

AF = aliquot factor (20 for soil)

2. Parts Per Million

$$ppm = \frac{\mu g/mL \times SV \times DF \times AF \times 100}{\text{sample wt. (g)} \times \text{percent recovery}}$$

Where:

DF = dilution factor (1.0 unless sample is diluted)

3. Pounds Per Acre (LB/A):

LB/A = ppm x WT x CF

Where:

WT = total weight (kg) of soil sample collected, including any sand added prior to mixing

CF = conversion factor for converting residues in ppm to LB/A, and:

$$CF = \frac{4.395}{r^2 \times N}$$

r = inside radius (inches) of the tip of the soil sampler probe

N = number of soil subsamples collected and composited into a single sample

H. Discussion

This procedure was developed to increase assay efficiency and to handle the large quantity of benefin soil samples which are analyzed. The solid phase extraction eliminated both a florisil column step and two evaporations from a previous procedure (AM-AA-CA-R027-AA-755).

Reference Notebook: WY3

This extraction procedure has been used on most soil types which are present throughout the U.S. with little difficulty from binding problems. This procedure was developed to quantitate only benefin because no major soil metabolites exist at levels high enough to be quantitated by this procedure.

The sample results must always be adjusted for either the system recovery or the spiked soil recovery because a positive bias is present in all recovery data observed. This is a result of using immiscible solvents in the solid phase extraction procedure. The void volume of this system is 0.5 mL; therefore, when the sample is eluted with 5.0 mL of toluene, the first 0.5 mL is an immiscible solvent which results in an actual final sample volume of 4.5 mL. By always adjusting results for the recovery obtained with the run, this is corrected during the calculation of the final result.

Interference from ethalfluralin and trifluralin can be eliminated with the use of alternate gas chromatographic columns. Five percent Carbowax 20M yields near-baseline separation for ethalfluralin and benefin. Benefin can be separated from trifluralin on an ULTRA-BOND™ 100/120 mesh column.

Benefin is photosensitive and exposure to light, especially sunlight, should be minimized.

METHOD HISTORY

R125-AA: Prepared by D. W. Yordy, O. D. Decker, S. E. Fisher (1/88)

LITERATURE CITED

Decker, O. D. and Griggs, R. D., "Determination of Benefin in Agricultural Crops and Soil", AM-AA-CA-R027-AA-755, Lilly Research Laboratories, 1980.

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