Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Trifluralin

MRID #: 155978

Matrix: Soil/Water

Analysis: GC/ECD

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APPENDIX H

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DETERMINATION OF TRIFLURALIN IN AGRICULTURAL SOIL, HYDROSOIL, AND WATER

AM-AA-CA-R084-AB-755

Trifluralin is extracted from soil with acetonitrile:water, 99:1 and from hydrosoil with methanol. Water samples are extracted with dichloromethane. The trifluralin is purified by Florisil column chromatography and measured by gas chromatography using an electron capture detector.

Reagents

1. Methanol, reagent grade
2. Sodium chloride, 10 percent
3. Dichloromethane, redistilled
4. Acetonitrile, reagent grade
5. Sodium sulfate, reagent grade, anhydrous
6. Hexane, reagent grade
7. Toluene, redistilled
8. Florisil, 100-200 mesh, deactivated and standardized (see Section H under Procedure)
9. Decane, Eastman Organic Chemicals No. 2405, redistilled
10. Trifluralin Standard Solution, 50 mcg/ml - Accurately weigh 10 mg of trifluralin reference standard. Transfer the standard to a 200-ml volumetric flask and bring to the mark with toluene. This solution is stable for 6 months when refrigerated, and protected from light and solvent evaporation.
11. Keeper solvent, 1 percent decane in dichloromethane

Apparatus

1. Sample blending equipment
2. Gyratory shaker, or equivalent
3. Chromatographic columns, 14 mm i.d. x 250 mm length, equipped with stopcock
4. Rinco evaporator, or equivalent
5. Gas Chromatograph equipped with electron capture detector.
6. Whatman filter paper GF/F 0.7 µm, 5.5 cm

Procedure

A. Preparation of Standard Solutions and Standard Curve

1. Prepare standard solutions in methanol for fortifying recovery samples at the following concentrations:

a: Soil - 5.0 mcg/ml
b. Hydrosoil - 0.05 mcg/ml
c. Water - 0.125 mcg/ml

2. Prepare standard solutions in toluene over the range of 0.01 to 0.3 mcg/ml for the standard curve.

B. Preparation of Sample

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

2. Hydrosoil samples should be mixed until homogeneous. Then remove about a 20-gram sample, accurately weigh, and determine the loss on drying (LOD) in a 105°C oven.

C. Extraction of Soils

1. Weigh a 50 g sample of soil into a pint mason jar.

2. Add 100 ml of 99:1 (v/v) acetonitrile:water.

3. Blend for 15 minutes using a gyratory platform shaker. Normally an oscillating speed of 300 rpm is sufficient to assure complete movement of the sample.

4. Allow solid particles to separate and transfer by pipette a 10-ml aliquot of the clear supernatant extract into a 125-ml boiling flask. When extracts remain turbid, filter a portion through Whatman No. 1 filter paper and transfer exactly 10 ml to a 125-ml boiling flask.

5. Add 30 ml acetonitrile to the boiling flask.

6. Evaporate the acetonitrile:water to a volume of 3-5 ml on a Rinco rotary evaporator and a 40-45°C water bath.

7. Add 25 ml of 1 percent decane in dichloromethane to the extracts.

8. Remove the dichloromethane with a Rinco evaporator and a 40-45°C water bath. A very small portion of decane will remain in the flask after all the dichloromethane has been evaporated.

9. Proceed to purification Section F

D. Extraction of Hydrosoils

1. Mix the hydrosoil sample until it is homogeneous.

2. Weigh into a quart mason jar a sample that is equivalent to 50 gram of dry soil. This may be calculated using the following equation.

$$\text{Sample Weight (gram)} = \frac{50}{100 - \text{LOD}} \times 100$$

3. Add methanol to bring the total liquid volume to 250 ml. The amount of methanol to be added may be calculated using the following equation:

Volume of Methanol (ml) = 250 - (Sample wt. - 50)

4. Cap the jar with aluminum foil and mix for 30 minutes on a gyratory platform shaker. Normally, an oscillating speed of 300 rpm will result in complete movement of the sample.

5. Allow solid particles to settle and transfer a 125-ml portion of extract to a 500-ml separatory funnel.

NOTE: If the solids do not settle, filter the mixture using S and S No. 588 filter paper. Certrifugation may be necessary to separate the liquid and solid fractions.

6. Add 100 ml of deionized water and 50 ml 10 percent saline solution to the separatory funnel.

7. Extract with three 40-ml portions of dichloromethane and combine the extracts in a 250-ml boiling flask. If phase separation is not clearly defined, the extracts may be filtered through sodium sulfate granules. If sodium sulfate is used, following the filtration, wash the sodium sulfate bed with dichloromethane and collect the wash in the boiling flask. Do not allow water into the flask containing the dichloromethane extracts.

8. Add 10 ml decane keeper solvent to the flask containing the dichloromethane extracts.

9. Evaporate the dichloromethane using a Rinco rotary evaporator and a 40-45°C water bath. The 0.1-ml decane will remain in the flask after all the dichloromethane has been evaporated.

10. Proceed to Purification, Section F.

E. Extraction of Water Samples

1. Shake sample well and transfer a 100-ml aliquot to a 250-ml separatory funnel.

2. Vacuum filter about 125 ml of the water sample through a Whatman GF/F 0.7 µm filter paper 5.5 cm in diameter. Transfer a 100-ml aliquot of this filtrate to a 250-ml separatory funnel.

3. Extract the filtrate with two 30-ml portions of dichloromethane and combine the extracts in a 125-ml boiling flask. If phase separation is not clearly defined, the extracts may be filtered through sodium sulfate granules. If sodium sulfate is used, following the filtration, wash the sodium sulfate bed with dichloromethane and collect the wash in the boiling flask. Do not allow water into the flask containing the dichloromethane extract.

4. Add 10-ml decane keeper solvent to the flask containing the dichloromethane extracts.

5. Evaporate the dichloromethane using a Rinco rotary evaporator and a 40-45°C water bath. The 0.1-ml decane will remain in the flask after all the dichloromethane has evaporated.

6. Proceed to Purification, Section F.

F. Purification

1. Prepare a Florisil column for each sample as follows:

   a. Place a pledget of glass wool into the bottom of a 14 mm i.d. glass chromatographic column. Add 15-ml hexane and tap the glass wool pledget with a stirring rod to eliminate air bubbles.

   b. Add 10 ± 0.5 ml of standardized Florisil through a funnel. Add 5-10 ml hexane and stir with a rod. Rinse sides of column with additional hexane.

      NOTE: See Section H, Standardization of Florisil, for preparation of adsorbant.

      NOTE: The Florisil must be added to columns in a reproducible manner to obtain a consistant elution pattern for all samples within a set.

   c. After the Florisil has settled, add about 1.5 cm of anhydrous sodium sulfate, layering it carefully to avoid disturbance of the level Florisil surface. Rinse sides of the column with hexane.

   d. Drain the hexane down to the sudium sulfate surface prior to adding the sample.

2. Transfer the residue from Sections C, D, or E to the column using 2 x 5-ml portions of hexane. Allow each addition of hexane to pass through the adsorbant at a flow rate of 3-5 ml per minute. Rinse the sides of the column with an additional 5 ml of hexane.

3. Wash the column with 10 ml of hexane. Discard the eluate to this point.

4. Pass 70 ml hexane through the column and collect in a 125-ml boiling flask.

   NOTE: The above describes column parameters utilized in the author's laboratory. There is lot-to-lot variability in activation of Florisil, and each lot should be standardized as described in Section H.

5. Add 10 ml decane keeper solvent to the column eluants.

6. Evaporate the hexane by rotary vacuum evaporation. The 0.1-ml decane will remain in the flask.

7. Dissolve the residue in the flask in the appropriate volume of toluene, mix thoroughly and proceed with the gas chromatographic measurement.

   Soil Samples - 5.0 ml
   Hydrosoil Samples - 0.9 ml
   Water Samples - 0.9 ml

G. Standard Recovery and Control Sample

1. Soil - A standard recovery sample of 0.1 ppm may be run with soil samples which have control material available. System recoveries (all reagents without soil) which simulate the 0.1 ppm recovery are used when control soil is unavailable. The standard recovery sample is prepared by adding 5.0 mcg of trifluralin standard to 50 g of control soil.

2. Hydrosoil - Two standard recovery samples of 0.001 ppm are run with hydrosoil samples when control material is available. Two system recoveries (all reagents without hydrosoil) which simulate the 0.001 ppm recovery are used when control hydrosoil is unavailable. A system blank is run with each sample set.

3. Water - A system blank and two recoveries at the 0.0005 ppm level for filtered water are assayed with each set. The system recoveries are prepared by adding 0.125 mcg of trifluralin standard to 250 ml of control or tap water. The entire volume is filtered and then two 100-ml aliquots are taken for use as filtered recoveries.

Recovery and control samples of soil, hydrosoil, and water are assayed exactly as experimental samples.

H. Standardization of Florisil

1. The Florisil as received must be deactivated prior to use by the addition of distilled water. Determine the loss on drying of the adsorbent as received (normally 1-2 percent). Add sufficient distilled water to an appropriate amount of Florisil to give a total moisture content of 8.0 percent. After addition of the water, stir gently with a rod to break up lumps. Tumble the Florisil for 1 hour in a closed container and allow to stand for 2 hours prior to use.

2. Determination of the column parameters.

   a. Prepare a Florisil column as described in step F., 1. under Procedure.

   b. Add 4 ml of 50 mcg/ml trifluralin standard solution to a 125-ml evaporating flask. Add 20 ml of acetonitrile and evaporate just to dryness on rotary evaporator.

   c. Dissolve in 5-ml hexane and proceed with the chromatography.

   d. Observe the yellow trifluralin band as it moves down the column and measure the volume of forerun to discard and the amount of eluate to collect for that particular lot of Florisil. To insure complete elution, collect an additional 10 to 15 ml of hexane after the color is eluted from the column.

3. To quantitatively check the elution of trifluralin, a known amount of standard may be chromatographed using the visable parameters defined in Step H, 2. The hexane eluate is evaporated and brought to the appropriate volume with toluene for exact measurement by gas chromatography.

I. Gas Chromatography

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

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

Oven Temperature - 190°C

Injection Block Temerature - 250°C

Detector Temperature - 300°C

Electrometer - Attenuate to provide 30 percent of full scale deflection from the injection of 0.4 ng of Trifluralin standard solution. The retention time for trifluralin is about 4.5 minutes.

The preferred column for the detection and measurement of trifluralin is 5 percent Carbowax 20M. However 5 percent XE-60, 5 percent W-98, or ULTRA-BOND 100/120 mesh* may also be used.

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

J. Calculations

1. Recoveries

$$\text{percent recovery} = \frac{\text{mcg/ml (from std. curve)} \times SV \times AF \times 100}{\text{mcg fortified}}$$

Where:

SV = sample volume - 5.0 ml for soil
1.0 ml for hydrosoil
1.0 ml for water

AF = aliquot factor - 10 for soil
2 for hydrosoil
1 for water

2. Parts Per Million

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

Where:

DF = dilution factor (1.0 unless sample is diluted)

Discussion

This procedure has been modified to allow detection at the 0.0005 ppm level in water. In this laboratory the procedure yields recoveries in excess of 85 percent for soils, 75 percent for hydrosoils, and 75 percent for filtered water. The assay sensitivity is potentially 0.02 ppm for soils, 0.001 ppm for hydrosoil and 0.0005 ppm for water.

Decane is added prior to each complete evaporation to reduce volatility losses of trifluralin. The immediate removal of the evaporating flask from vacuum just at dryness is required if decane is not used as a keeper solvent.

* 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.

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It is recommended that prior to the use of a new lot of decane that exactly 4.9 ml of 0.1 mcg/ml trifluralin standard solution in toluene be added to a boiling flask containing 0.1 ml of decane. This solution should be injected into the gas chromatograph and the peak compared to that of a 0.1 mcg/ml standard solution without decane. A slight quenching effect (>5 percent) has been observed due to the impurities in some lots of decane. When this occurs a second and sometimes a third distillation may be necessary to totally remove all those impurities.

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

These precautions should be observed in the analysis for trifluralin.

1. All evaporations should be performed by thin-film rotary vacuum evaporation to prevent loss of the compound. Use of a current of air for evaporation must be avoided.

2. Trifluralin is photolabile and exposure to light, especially sunlight, should be minimized.

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