CHEVRON CHEMICAL COMPANY
ORTHO AGRICULTURAL CHEMICALS DIVISION
DEVELOPMENT RESEARCH DEPARTMENT
RICHMOND, CALIFORNIA

DETERMINATION OF FENPROPATHRIN AND DESPHENYLFENPROPATHRIN IN SOIL RESIDUE METHOD RM-22S-2

DATE: JULY 17, 1988
FILE NO: 740.01/DANITOL

INTRODUCTION

This method describes a procedure for the determination of fenpropathrin, [(RS)-α-cyano-3-phenoxybenzyl-2,2,3,3-tetramethylcyclopropanecarboxylate] and desphenylfenpropathrin, (α-cyano-3-hydroxybenzyl-2,2,3,3-tetramethylcyclopropanecarboxylate) in soil. Results of soil metabolism studies have shown that desphenylfenpropathrin is the major soil degradation product of fenpropathrin. This revision of method RM-22S-1 includes analysis for desphenylfenpropathrin previously described in a tentative method entitled "Method Used For The Determination of Desphenyl-Fenpropathrin In Soil," by J. C. Lai, dated May 20, 1986. In summary, the revised method involves extraction of residues with methanol/water, partitioning of residues into dichloromethane, C_{18} Sep Pak® cleanup and measurement by capillary column gas chromatography using a nitrogen/phosphorous specific flame ionization detector.

REAGENTS

Fenpropathrin - Reference Standard

Desphenylfenpropathrin - Reference Standard

Acetone - Pesticide Quality

Methanol - Pesticide Quality

Dichloromethane - Pesticide Quality

C_{18} Sep Pak® - Waters Associates, Inc., Milford, MA. Catalog No. 51900

Celite Analytical Filter-Aid

Sodium Sulfate - Anhydrous, granular, reagent grade, acetone washed and air-dried.

Sodium Chloride - Crystals, analytical grade, acetone-washed and air-dried.

EQUIPMENT

Omni-Mixer with adaptor for use with 1-pint Mason jars.

Rotary vacuum evaporators equipped with a heated water bath.

Buchner Funnels

Glass-fiber filter paper - Whatman GF/A

Separatory Funnels - 500 ml capacity, Teflon® stopcocks.

B-D Multifit syringe #2152 with Luer-lok, 10 cc capacity.

Gas Chromatograph (Varian Vista 6000 or equivalent) equipped with a split/splitless capillary column injection port, a Thermionic Specific Detector (TSD), a Varian 8000 autosampler and a Hewlett-Packard 3390A integrator:

Column:	30 m x 0.25 m ID methyl silicone (0.25 µ film thickness) capillary column (J&W Scientific, DB-1)
Carrier gas flow rate:	1.6 ml/min (He)
Split Ratio:	10:1
Injector temperature:	260°C
Column Oven Temperature:	
Initial:	200°C, hold 1.0 min
Rate:	10°C/min
Final:	250°C, hold for 8 minutes
Detector temperature:	300°C
Detector Gases	
Hydrogen:	4.5 ml/min
Air:	180 ml/min
Nitrogen (make-up):	40 ml/min

ANALYTICAL METHOD

All glassware should be rinsed with pesticide-quality acetone prior to use. The acetone-rinsed glassware should then be rinsed with the solvent to be used in that particular step of the procedure.

Extraction

Weigh out a 20 g sample of soil into a pint Mason jar. Fortify a control sample for recovery purposes with 1.0 ml of a 2.0 µg/ml acetone solution of fenpropathrin and desphenylfenpropathrin. Add 150 ml methanol/water (9/1, v/v) and blend on an Omni-mixer for five minutes. Add 1 teaspoon of Celite Analytical Filter-Aid to the sample and filter the extract through a Buchner funnel lined with a Whatman GF/A filter paper. Transfer the filter paper to the Mason jar and repeat the extraction and filtration steps once more using 100 ml of extraction solvent. Following filtration, rinse the filter cake with 50 ml of extraction solvent. Transfer the combined extract to a 500 graduated cylinder and dilute to 300 ml using deionized water.

Partition

Transfer a 150 ml aliquot of the well-mixed extract to a 500 ml separatory funnel and add 150 ml of deionized water and 10 g of sodium chloride. Partition the extract with 50 ml of dichloromethane. Filter the dichloromethane extract through sodium sulfate into a roundbottom flask. Repeat the partition and filtration steps with one additional 50 ml portions of dichloromethane. Rinse the sodium sulfate cake with 50 ml of dichloromethane. Evaporate the extract to dryness in a 25°C water bath and redissolve the sample in 5 ml of methanol.

C_{18} Sep Pak® Cleanup

Prewash the Sep Pak® with two 10 ml portions of methanol. Transfer the sample to the cartridge and elute into a 50-ml roundbottom flask. Complete the elution with an additional 5 ml of methanol. Evporate the combined eluates and redissolve the sample in a 2.0 ml of ethyl acetate.

MEASUREMENT

The linearity of the gas chromatography system should be checked daily by analyzing mixed standards of fenpropathrin plus desphenylfenpropathrin with concentrations of 0.05, 0.25, 0.5 and 1.0 µg/ml. Response factors should have a coefficient of variation of ±5% or less.

Inject 1.0-2.0 µl of reference standard solution (0.5 µg/ml fenpropathrin and desphenylfenpropathrin in ethyl acetate) into the gas chromatograph. Inject the same volume of sample extract. If required, dilute the sample extracts with additional ethyl acetate to obtain peaks within the linear range of the instrument. Sequence of analysis should be standard, standard, fortified sample, sample, standard, sample, sample, standard ....

CALCULATION

$$\text{ppm} = \frac{\text{Peak Area (Sample)}}{\text{Ave. Peak Area (Std.)}} \times 0.5\ \mu\text{g/ml} \times \frac{2.0\ \text{ml}}{10\ \text{g}} \times 2 \times \text{Dilution Factor}$$

LIMIT OF DETECTION

The limit of detection is approximately 0.01 ppm for both fenpropathrin and desphenylfenpropathrin for a 20 g soil sample analyzed using the described procedure.

NOTES:

1. A fortified control sample must be analyzed concurrently with each set of samples.

2. Method recovery for fortified samples must be between 70 - 120% to be acceptable. All samples analyzed concurrently with a fortified sample which does not have an acceptable method recovery must be reanalyzed.

A. L. HAMADA

G. H. FUJIE

Reviewed By:

GHF:gt

cc: G. O. Breault
Residue Laboratory
R&D Files

CHEVRON CHEMICAL COMPANY
ORTHO AGRICULTURAL CHEMICALS DIVISION
RESIDUE CHEMISTRY LABORATORY
RICHMOND, CALIFORNIA

DETERMINATION OF FENPROPATHRIN AND
TWO METABOLITES IN SOIL
RESIDUE METHOD RM-22S-3

DATE: MAY 30 , 1989
FILE NO: 740.01/DANITOL

INTRODUCTION

This method describes a procedure for the determination of fenpropathrin, [(RS)-α-cyano-3-phenoxybenzyl-2,2,3,3-tetramethylcyclopropane carboxylate], desphenylfenpropathrin, (α-cyano-3-hydroxybenzyl-2,2,3,3-tetramethylcyclopropane carboxylate) and 4'-OH-fenpropathrin, (α-cyano-3-[4-hydroxyphenoxy]benzyl-2,2,3,3-tetramethylcyclopropane carboxylate) in soil. Soil metabolism studies have shown that desphenylfenpropathrin and 4'-OH-fenpropathrin are major degradation products of fenpropathrin. This revision of method RM-22S-2 allows the simultaneous analysis for all three moieties and incorporates a new cleanup procedure developed by Sumitomo Chemical Company for the analysis of the two degradates (Ref. 1 and 2). In summary the revised method involves extraction with methanol/0.1N HCl, partitioning of residues into dichloromethane, Florisil column cleanup and measurement by gas chromatography using a nitrogen/phosphorous flame ionization detector.

REAGENTS

Fenpropathrin - Reference Standard

Desphenylfenpropathrin - Reference Standard

4'-OH-fenpropathrin - Reference Standard

Acetone - Pesticide Quality

Methanol - Pesticide Quality

Dichloromethane - Pesticide Quality

Hexanes - Pesticide quality

Ethyl Acetate - Pesticide quality

Hydrochloric Acid - 0.1 N

Celite Analytical Filter-Aid

Sodium Sulfate - Anhydrous, granular, reagent grade, acetone washed and air-dried.

Sodium Chloride - 5% aqueous solution (50 g/liter of water)

Florisil - Activated at 1200°F, mix 3 parts by weight of 60-100 mesh with 2 parts 100-200 mesh. Heat overnight at 110°C prior to deactivation with 10% water (See Note 2).

EQUIPMENT

Omni-Mixer with adaptor for use with 1-pint Mason jars.

Rotary vacuum evaporators equipped with a heated water bath.

Buchner Funnels

Glass-fiber filter paper - Whatman GF/A

Separatory Funnels - 1000 ml, Teflon® stopcocks

Liquid Chromatography Column - 300 x 22 mm, Supelco # 6-4760

Gas Chromatograph (Hewlett-Packard 5890A or equivalent) equipped with both a packed column and a split/splitless capillary injection port, a nitrogen/phosphorous flame ionization detector, a HP-7673A autosampler and a HP-3392A integrator.

Column A: 15 m x 0.53 mm ID 5% phenyl-methyl silicone (1.5 µm film) megabore column (J&W Scientific; DB-5)

Column B: 15 m x 0.53 mm 50% phenyl-methyl silicone (1.0 µm film) megabore column (J&W Scientific; DB-17)

Injector:	Packed column with megabore adaptor
Carrier gas flow rate:	30 ml/min (He)
Auxillary gas flow rate:	0-15 ml/min (He)
Detector gases:	
Hydrogen:	3.5 ml/min
Air:	90-120 ml/min
Injector temperature:	260-280°C
Detector Temperature:	260-300°C

Column Oven Temperatures:	Column A	Column B
Initial:	150°C, hold 1.0 min	200°C hold 2.0 min
Rate:	20°C/min	12°C 1.0 min
Final:	270°C, hold for 1 min	260°C, hold for 2 min
Desphenylfenpropathrin:	4.1 min	2.8
Fenpropathrin:	5.7 min	5.2
4'-OH-fenpropathrin:	6.9 min	7.9 min
	(Figure 1)	(Figure 2)

The above parameters serve only as a guide for chromatography of the soil samples. Changes to the operating parameters may be made to optimize the chromatography for a particular instrument or soil matrix.

ANALYTICAL METHOD

All glassware should be rinsed with pesticide-quality acetone prior to use. The acetone-rinsed glassware should then be rinsed with the solvent to be used in that particular step of the procedure.

Extraction

Weigh out a 20 g sample of soil into a pint Mason jar. Fortify a control sample for recovery purposes with 1.0 ml of a 2.0 µg/ml acetone solution of *fenpropathrin, desphenylfenpropathrin* and 4'-OH-fenpropathrin. Add 100 ml methanol/0.1N HCl (8/2,v/v) and blend on an Omni-mixer for five minutes. Add 1 teaspoon of Celite Analytical Filter-Aid to the sample and filter the extract through a Buchner funnel lined with a Whatman GF/A filter paper. Transfer the filter cake to the Mason jar and repeat the extraction and filtration steps once more using 100 ml of extraction solvent. Following filtration, rinse the filter cake with 50 ml of extraction solvent.

Partition

Transfer the combined extracts to a 1000 ml separatory funnel and add 250 ml of 5% aqueous NaCl solution. Partition the extract with 100 ml of dichloromethane. Filter the dichloromethane extract through sodium sulfate into a roundbottom flask. Repeat the partition and filtration steps with one additional 100 ml portion of dichloromethane. Rinse the sodium sulfate cake with 50 ml of dichloromethane. Evaporate the combined extract to dryness in a 25°C water bath using the rotary vacuum evaporator. Redissolve the sample in 3 ml of hexane/ethyl acetate (3/1, v/v).

Florisil Column Cleanup

Close the stopcock on the liquid chromatography column, plug with a wad of glass wool and add 50 ml of hexane/ethyl acetate (3/1, v/v). Weigh out 15 g of deactivated Florisil and add slowly to the column to avoid air bubbles within the bed. Allow the Florisil to settle, then cap with approximately 1-inch of sodium sulfate. Drain the solvent layer to the top of the sodium sulfate bed.

Transfer the concentrated sample extract to the column with three 3-ml rinses of mixed solvent. Allow each portion to drain to the top of the sodium sulfate layer before adding the next rinse portion. Following the last rinse, add 10 ml of mixed solvent to the column and elute. Discard all column eluates. Place a 100-ml roundbottom flask under the column and elute the sample with 55 ml of hexane/ethyl acetate (3/1, v/v). Evaporate the extract to dryness and redissolve in 2.0 ml of ethyl acetate.

MEASUREMENT

The linearity of the gas chromatographic system should be checked daily by analyzing mixed standards of fenpropathrin, desphenylfenpropathrin and 4'-OH-fenpropathrin. A concentration range of 0.1, 0.5, 1.0 and 2.0 µg/ml is recommended. The mean of the response factors (integration counts/std. conc.) should have a coefficient of variation of ±10% or less. Variance from this requirement must be approved by supervisory personnel.

Inject 1.0-4.0 µl of reference standard solution (1.0 µg/ml fenpropathrin, desphenylfenpropathrin and 4'-OH-fenpropathrin) into the gas chromatograph. Inject the same volume of sample extract. As required, dilute the sample extracts with ethyl acetate to obtain peaks within the linear range of the instrument. A suggested sequence of analysis is standard, sample, sample, standard, sample, sample, standard. . . . The coefficient of variation of the mean of the standards should be ±10% or less. Variance from this requirement must be approved by supervisory personnel.

CALCULATION

$$PPM = \frac{\text{Integration CTS. (Sample)}}{\text{Ave. Integration CTS. (Std.)}} \times 1\ \mu g/ml \times \frac{2.0\ ml}{20\ g} \times \text{Dilution Factor}$$

$$\% \text{ Recovery} = \frac{\text{PPM Fortified - PPM Control}}{\text{PPM Fortification}} \times 100$$

LIMIT OF DETECTION

The limit of detection is approximately 0.01 ppm for fenpropathrin, desphenylfenpropathrin and 4'-OH-fenpropathrin for a 20 g soil sample analyzed using the described procedure.

NOTES:

1. A fortified control sample must be analyzed concurrently with each set of samples. Method recovery must be between 70-120% to be acceptable. All samples analyzed concurrently with a fortified sample that does not have an acceptable method recovery must be reanalyzed or the requirement waived by supervisory personnel.

2. Preparation of Deactivated Florisil

Weigh out 2 kg of activated Florisil and transfer to a plastic screw-capped jar. Add 200 ml deionized water and mix well. Allow the deactivated Florisil to sit overnight in the capped jar. Prior to use, verify the activity of the Florisil by analyzing a mixed 10 µg standard. Recovery must be 90% or greater for all three compounds.

3. Gas Chromatography Alternatives

Due to the complexity of multiple component analysis, two gas chromatography columns of different polarity are described in the analytical method. If matrix interference cannot be separated on either column for all three components simultaneously, split analyses may be used to analyze for one or more components on one column and the second and/or third component on the alternate column. If a matrix interference cannot be separated on either column, then narrow-bore capillary column chromatography may be used if linearity and reproducibility requirements of the method are satisfied.

REFERENCES

1. Onishi, et. al., Report No. ER-MT08911, "Residue Analytical Method for 4'-OH-fenpropathrin, One of the Metabolites of Fenpropathrin, in Soil," May 12, 1989.

2. Onishi, et. al., Report No. ER-MT-8912, "Residue Analytical Method for Desphenyl-fenpropathrin, One of the Metabolites of Fenpropathrin, in Soil," May 12, 1989.

A. L. HAMADA

G. H. FUJIE

Reviewed By:

GHF:gt

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