Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Deltamethrin

MRID #: 427739-03

Matrix: Soil

Analysis: GC/ECD

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ANALYTICAL METHOD FOR THE DETERMINATION OF DELTAMETHRIN, AND DEGRADATES IN SOIL BY GAS CHROMATOGRAPHY

MRID # 42773903

CHEMALYSIS METHOD NO. CA004

SUBMITTED TO:

HOECHST-ROUSSEL AGRI-VET COMPANY
ROUTE 202-206
SOMERVILLE, NEW JERSEY
08876-1258

HRAV PROJECT NO.

90-0091

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900405

INITIATION DATE: July 10, 1990
~~INITIATION DATE: July 26, 1991~~

CONFIDENTIALITY STATEMENT

Analytical Method for the Determination of Deltametrin, Trans-Deltametrin and Degradates in Soil by Gas Chromatography

Good Laboratory Practice Statement

This method "Analytical Method for the Determination of Deltametrin, Trans-Deltametrin and Degradates in Soil by Gas Chromatography" was conducted according to EPA Good Laboratory Practice Standards, 40 CFR 160.

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7/26/91
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7/26/91
Date

Analytical Method for the Determination
of Deltametrin, Trans-Deltametrin and Degradates
in Soil by Gas Chromatography

Quality Assurance Monitoring Statement

This method has been audited, confirmed with the raw data and found to be compliance with the specifications for acceptance by Quality Assurance.

The following are dates on which the Quality Assurance unit conducted audits and the dates on which the findings of those audits were reported to management and the Study Director.

Type of Audit	Phase Audited	Audit Date	Date Reported to Study Director & Management
Data	Method Development	1-21-91	1-23-91
		1-29-91	1-31-91
		2-01-91	2-01-91
		2-28-91	3-01-91
		3-01-91	3-05-91
		3-06-91	3-14-91
		3-19-91	3-20-91
		3-24-91	4-09-91
		4-08-91	4-09-91
		4-09-91	4-09-91
		5-23-91	5-29-91

Quality Assurance Coordinator

Date

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1.0 INTRODUCTION

This report validates the method used for the determination of residues of deltamethrin, and its degradates trans-deltamethrin and decamethrinic Acid (Br_2CA) in soil. Analysis is by GC/ECD. The method sensitivity for deltamethrin and trans-deltamethrin is 0.002 ppm. The method sensitivity for decamethrinic acid is 0.010 ppm based on the lowest concentration standard analyzed The molecular structures of deltamethrin, trans-deltamethrin, decamethrinic acid and its pentafluorobenzyl ester derivative are presented in Figure 1.

Chemical Information

Deltamethrin, RU 22974

(1R,3R)3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid (S) alpha-cyano-(3-phenoxyphenyl) methyl ester

trans-Deltamethrin, RU 25979

(1R,3S)3-(2,2-dibromovinyl,-2,2-dimethylcyclopropanecarboxylic acid (S)-alpha-cyano-(3-phenoxyphenyl) methyl ester

Decamethrinic Acid, (Br_2CA), RU 23441

(1R-cis)-3-(2,2-dibromoethenyl)-2,2-dimethyl-cyclopropanecarboxylic acid

2.0 PRINCIPLE

Residues are extracted from soil with 1:1 hexane:acetone, filtered and aliquoted. An aliquot for the determination of deltamethrin and trans-deltamethrin is prepared by using a silica gel cartridge for clean-up. Another aliquot for the determination of decamethrinic acid is taken and derivatized using pentafluorobenzyl bromide (PFB-Br). The two final extracts are analyzed under different GC conditions.

3.0 EQUIPMENT

3.1 Round bottom flasks, 500 ml, 24/40 ground glass joints
3.2 Wide mouth bottles with teflon-lined caps, 500 ml
3.3 Volumetric flasks, 500 ml
3.4 Horizontal shaker
3.5 Buchner Funnels
3.6 Filtering Flasks
3.7 Whatman Glass Fiber Filters to fit Buchner Funnels
3.8 Rotary Evaporators
3.9 N_2-Evap analytical evaporator
3.10 Analytichem (Cat. No. 221834) silica gel cartridges with stopcocks (or equivalent)
3.11 Analytichem VAC-ELUT vacuum box for use with cartridges (or equivalent)

4.0 REAGENTS

4.1 Hexane, pesticide grade

4.2 Acetone, pesticide grade

4.3 Chloroform, pesticide grade

4.4 Ethyl ether, pesticide grade

4.5 Ethyl acetate, pesticide grade

4.6 K_2CO_3 (30%). Weigh 30 g K_2CO_3 in 100 ml DI water.

4.7 Pentafluorobenzyl bromide (5% in acetone). Weigh 5 g PFB-Br in 100 ml acetone. Prepare fresh monthly. PFB-Br is a lachrymator. Prepare and use under a hood.

4.8 Silica gel, 5% deactivated. Dry silica overnight. Weigh out 95 g and add 5 ml water. Shake for several hours.

4.9 Sodium hydroxyide, 0.1 N. Weigh 4 g sodium hydroxide pellets into 1000 ml volumetric flask. Bring to volume with DI water.

4.10 Deltamethrin, trans-Deltamethrin, Decamethrinic Acid and the Penta-FluoroBenzyl Ester of Decamethrinic Acid analytical standards are available from Hoechst-Roussel Agri-Vet Co., Route 202-206, Somerville, NJ 08876-1258.

5. PROCEDURE

5.1 Standard Preparation

Deltamethrin Stock Solution (RU 22974) - Weigh 100.0 mg deltamethrin into a 100 ml volumetric flask. Bring to volume with acetone.

Transfer 1.0 ml of stock solution into a 100 ml volumetric. Bring to volume with hexane. The concentration of this solution is 10.0 ug/ml.

trans-Deltamethrin Stock Solution (RU 26979) - Weigh 100 mg trans-deltamethrin into a 100 ml volumetric flask. Bring to volume with acetone.

Transfer 1.0 ml stock solution into a 100 ml flask. Bring to volume in hexane. The concentration of this solution is 10.0 ug/ml.

Decamethrinic Acid Stock Solution (RU 31441) - Weigh 100 mg decamethrinic acid into a 100 ml volumetric flask. Bring to volume with acetone.

Transfer 1.0 ml stock solution into a 100 ml flask. Bring to volume with acetone. The concentration of this solution is 10.0 ug/ml.

Decamethrinic Acid PFB, Ester (RU 91-2668) - Weigh 100 mg decamethrinic acid PFB ester into a 100 ml volumetric flask. Bring to volume with acetone.

Transfer 1.0 ml stock solution into a 100 ml flask. Bring to volume with hexane.

Standards for GC Analysis - Prepare appropriate dilutions for a mixture of deltamethrin and trans-deltamethrin at 0.20 ug/ml, 0.10 ug/ml, 0.05 ug/ml, 0.02 ug/ml and 0.01 ug/ml in hexane.

Prepare appropriate dilutions of the derivatized standard at 0.20 ug/ml, 0.10 ug/ml, 0.05 ug/ml, 0.02 ug/ml and 0.01 ug/ml in hexane:ether:acetone 98:1:1 (v:v:v).

5.2 Sample Fortification

Control soil samples are fortified at 0.002 ppm, and 0.10 ppm with deltamethrin and trans-deltamethrin. Control samples are fortified at 0.01 ppm and 0.10 ppm with decamethrinic acid.

5.3 Sample Extraction Clean-Up

5.3.1. Weigh 40.0 grams of soil into a 500 ml bottle.
5.3.2. Add 300 ml of 1:1 hexane:acetone. Shake on horizontal shaker for 1 hour.
5.3.3. Suction filter through a glass fiber filter to remove soil. Rinse filter with 1:1 hexane:acetone. Quantitatively transfer to a 500 ml volumetric flask and bring to volume with 1:1 hexane:acetone. Split filtrate into two 250 ml aliquots into two 500 ml round bottom flasks and evaporate to near dryness by rotary evaporation at 40-45°C.

5.4 Deltamethrin and trans-Deltamethrin Clean-Up

5.4.1. Rinse and condition a silica gel SPE cartridge (Analytichem LR01304) with 10 ml chloroform followed by 10 ml of hexane.
5.4.2. Rinse the flask, step 5.3.3., with 10 ml of hexane and transfer quantitatively to column. Repeat with another 10 ml portion of hexane.
5.4.3. Using a vacuum box and stopcock, control the drip rate to 1-2 ml/min. Rinse the column with 10 ml hexane. Do not allow the column to go dry. Discard the hexane.
5.4.4. Add 5 ml of chloroform to the silica gel column reservoir and collect the eluate in a graduated test tube.
5.4.5. Concentrate the sample to near dryness using an N_2-Evap at a temperature of 35-40°C.
5.4.6. Bring sample to final volume of 2.0 ml with hexane. Transfer 1.0 ml into two GC vials for GC/ECD analysis. This fraction contains deltamethrin and trans-deltamethrin.

5.5 Decamethrinic Acid Partition and Clean-Up

5.5.1. Quantitatively transfer residue from step 5.3.3. to a 250 ml separatory funnel with 20 ml of 0.1 N NaOH.

5.5.2. Add 20 ml ethyl ether. Shake for 1 minute with venting. Discard ethyl ether.

5.5.3. Add 20 ml ethyl ether. Shake for 1 minute with venting. Discard ethyl ether.

5.5.4. Add 10 ml of 0.5 N HCl followed by 20 ml ethyl ether.

5.5.5. Shake for 1 minute with venting. Collect ethyl ether in a 500 ml round bottom flask.

5.5.6. Add 20 ml ethyl ether. Shake for 1 minute with venting. Collect ethyl ether in the 500 ml round bottom flask.

5.5.7. Evaporate the sample by rotary evaporation at 40-45°C.

5.5.8. Add 100 ml acetone, 1 ml of PFB-Br (5% in acetone) and 300 ul of 30% K_2CO_3.

5.5.9. Reflux gently for 3 hours.

5.5.10. Evaporate the sample by rotary evaporation at 40-45°C.

5.5.11. Add 250 ml ether, 2 ml DI water and 10 ml ethyl acetate. Swirl vigorously.

5.5.12. Filter through 12g anhydrous sodium sulfate prewashed with ether.

5.5.13. Evaporate sample to near dryness by rotary evaporation at 40-45°C.

5.5.14. Bring sample to final volume of 10 ml in a glass scintillation vial with hexane:ether:acetone (98:1:1).

5.5.15. Freeze all samples until analysis.

5.6. Analysis Conditions

Analysis by Gas Chromatography for deltamethrin and trans-deltamethrin is accomplished using the following column and conditions:

Instrument: HP 5890 GC with Autosampler

Column: DB-1, 30 m x 0.322 mm, film thickness 0.25 um

Injector: 200°C, splitless, purge on at 1.0 min., 20 ml/min

Detector: Electron Capture, 325°C, make-up argon/methane, 30 ml/min.

Temp Program: 100°C for 1 min.
20°C/min.
230°C for 12 min.

10°C/min.
250°C for 5 min.

Carrier Gas: Helium, 5 ml/min.

Inj. Vol: 2 uL

Under these conditions, approximate retention times are as follows:

cis-deltamethrin	19.1 min.
trans-deltamethrin	19.5 min.

Analysis by Gas Chromatography for Br_2CA is accomplished using the following column and conditions:

Instrument: HP 5890 GC, with Autosampler

Column: DB-1, 30 m x 0.322 mm, film thickness 0.25 um

Injector: 200°C, splitness, purge on at 1 min.

Temp Program:
100°C for 1 min.
20°C/min.
230°C for 10 min.
10°C/min.
250°C for 5 min.

Carrier Gas: Helium, 5 ml/min.

Inj. Vol: 2 uL

Under these conditions, approximate retention time is as follows:

penta-fluorobenzyl ester of decamethrinic acid: 16.6 minutes

GC conditions my be changed to produce similar results.

Typical standardization data for deltamethrin, trans-deltamethrin and decametrinic acid PFB ester aree shown in Tables 1 and 2. Recovery data for fortified soil are presented in Table 3. Typical chromatograms for standards, control soil and fortified control soil are depicted in Figures 3-5.

Sensitivity

The method is sensitive to 0.002 ppm for deltamethrin and trans-deltamethrin and to 0.010 ppm for decamethrinic acid PFB ester based on the lowest concentration standard analyzed.

5.7 Calculationn of Residues

$$\text{mg injected} = \frac{W \times V2\ V4}{V1 \times V3 \times DF}$$

where W = 40.0 grams sample
V1 = 500 ml initial volume
V2 = 250 ml aliquot volume
V3 = 2.0 mL or 10.0 final volume
V4 = 2 uL injected
DF = Dilution Factor

$$\text{ppm, residue} = \frac{\text{ng from curve}}{\text{mg injected}}$$

Field samples are corrected for soil moisture such that ppm, residue (dry weight basis)

$$= \frac{\text{ppm, residue} \times 100}{(100 - \% \text{ Moisture})}$$

5.8. Time Requirements

A trained analyst can complete the extraction of a set of 10-12 samples in 12 hours. A flowchart of the extraction procedures (Figure 2) indicates possible stopping points during extraction.

6.0 References

EN-CAS Method No. ENC-7/89
Maguire, R. James, et al. J. Agric. Food Chem., Vol 37, Nov. 4, 1989.

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Table 1. Typical Standardization Data for Deltamethrin, trans-Deltamethrin and Decamethrinic Acid PFB Ester.

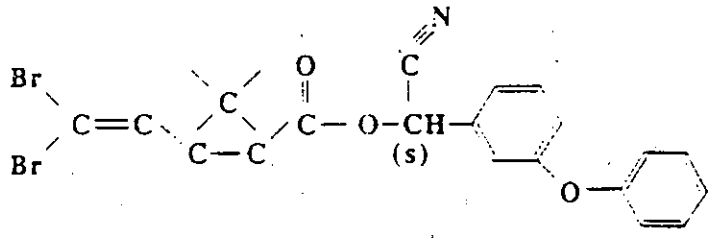
Standard Conc.	Peak Height	ng Injected	Regression Parameters
	Deltamethrin		
0.01 ug/ml	1592	0.02	Corr. coeff (r) 0.9920
0.01 ug/ml	1457	0.02	y intercept (b) 899.7
0.02 ug/ml	2869	0.04	slope (m) 42202.2
0.05 ug/ml	5415	0.10	
0.05 ug/ml	4433	0.10	
0.10 ug/ml	10818	0.20	
0.10 ug/ml	8777	0.20	
0.20 ug/ml	17415	0.40	
	trans-Deltametrin		
0.01 ug/ml	1091	0.02	Corr. coeff (r) 0.9931
0.01 ug/ml	1303	0.02	y intercept (b) 641.0
0.02 ug/ml	2668	0.04	slope (m) 41756.6
0.05 ug/ml	5201	0.10	
0.05 ug/ml	4275	0.10	
0.10 ug/ml	10262	0.20	
0.10 ug/ml	8377	0.20	
0.20 ug/ml	17048	0.40	
	Decamethrinic Acid PFB Ester		
0.01 ug/ml	1383	0.01	Corr. coeff (r) 0.9905
0.01 ug/ml	4761	0.02	y intercept (b) -4205
0.02 ug/ml	4633	0.02	slope (m) 408918
0.05 ug/ml	18109	0.05	
0.10 ug/ml	28297	0.10	
0.10 ug/ml	36819	0.10	
0.20 ug/ml	81020	0.20	

Table 2. Recovery Data for Soil Fortified with Deltamethrin, trans-Deltamethrin and Decamethrinic Acid.

Depth	Fortification Level	Replicate	Percent Recovery	Average
		Deltamethrin		
0-6"	0.002 ppm	1	115	100
		2	89	
		3	96	
	0.020 ppm	1	107	89
		2	84	
		3	76	
		trans-Deltamethrin		
0-6"	0.002 ppm	1	94	81
		2	72	
		3	76	
	0.020 ppm	1	103	102
		2	103	
		3	101	
		Decamethrinic Acid PFB Ester		
0-12"	0.010 ppm	1	104	93
		2	84	
		3	90	
	0.100 ppm	1	96	95
		2	88	
		3	101	
	0.500 ppm	1	114	106
		2	91	
		3	113	

STUDY #

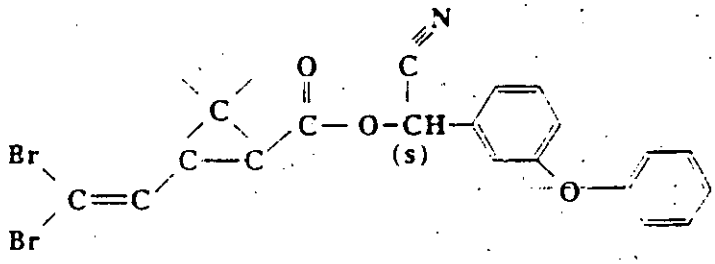
Figure 1: Chemical Structures (1 of 2)



DELTAMETHRIN

RU 22974

(1R,3R)3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid (S)-alpha-cyano-(3-phenoxyphenyl) methyl ester

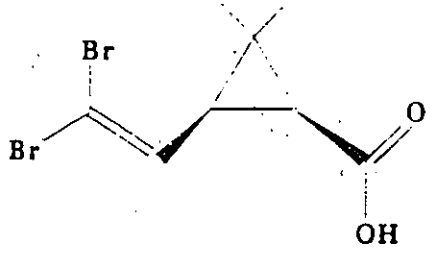


trans-DELTAMETHRIN

RU 26979

(1R,3S)3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid (S)-alpha-cyano-(3-phenoxyphenyl) methyl ester

Figure 1: Chemical Structures (2 of 2)

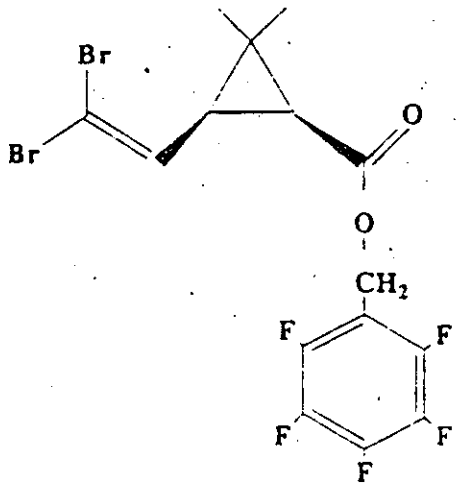


DECAMETHRINIC ACID

(BR_2CA)

RU 23441

(1R-cis)-3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropane-carboxylic acid



DECAMETHRINIC ACID PFB ESTER

Pentafluorobenzyl ester of (1R-cis)-3-(2,2-dibromoethenyl)-2,2-dimethyl-cyclopropanecarboxylic acid

Figure 2: Sample Preparation Scheme (1 of 2)

40.0 grams of soil

Add 300 ml of 1:1 hexane:acetone (pesticide grade).

Shake on a horizontal shaker for 1 hour.

Suction filter through a glass fiber filter (Whatman GF/C) to remove soil. Rinse extraction bottle and filter with 1:1 hexane:acetone.

Transfer filtrate quantitatively to a 500 ml volumetric flask and bring to volume with 1:1 hexane:acetone.**

cis/trans Deltamethrin Clean-up

Evaporate 250 ml aliquot to near dryness by rotary evaporation at 40-45 C.

Condition a silica gel SPE cartridge with 10 ml chloroform followed by 10 ml hexane.

Transfer residue with 10 ml of hexane to column

Control the drip rate through column at 1-2 ml/min.

Rinse flask with 10 ml of hexane and quantitatively transfer to column.

Rinse the column with 10 ml hexane. Discard the hexane.

Add 5.0 ml chloroform to column resevoir and collect the eluate in a graduated test tube.**

**Stopping point
Refrigerate sample.

Br_2CA Partition

Evaporate 250 ml aliquot to near dryness by rotary evaporation at 40-45 C.

Transfer to a 250 ml separatory funnel with 20 ml 0 0.1 N NaOH.

Add 20 ml ethyl ether. Shake for 1 minute with venting. Discard ethyl ether.

Add 20 ml ethyl ether. Shake for 1 minute with venting. Discard ethyl ether.

Add 10 ml of 0.5 N HCl followed by 20 ml ethyl ether.

Shake for 1 minute with venting and collect ethyl ether.

Add 20 ml ethyl ether. Shake for one minute with venting and collect ethyl ether.

Figure 2: Sample Preparation Scheme (2 of 2)

cis/trans Deltamethrin Cleanup (cont.)

Concentrate to dryness under nitrogen at 35-40 C.

↓

Dissolve in hexane to final volume of 2.0 ml.

↓

Freeze samples.

Br_2CA Partition (cont.)

Evaporate by rotary evaporation at 40-45 C.

↓

Add 100 ml acetone. Set up acetone control and 0.20 ug/ml standard.**

↓

Add 1.0 ml of PFB-Br (5 % acetone) and 300 ul of 30 % K_2CO_3.

↓

Reflux gently for 3 hrs

↓

Evaporate by rotary evaporation at 40-45 C.

↓

Add 250 ml ether, 2 ml water and 10 ml ethyl acetate. Swirl vigorously.

↓

Filter through 12 g anhydrous sodium sulfate prewashed with ether.

↓

Evaporate to near dryness by rotary evaporation at 40-45 C.

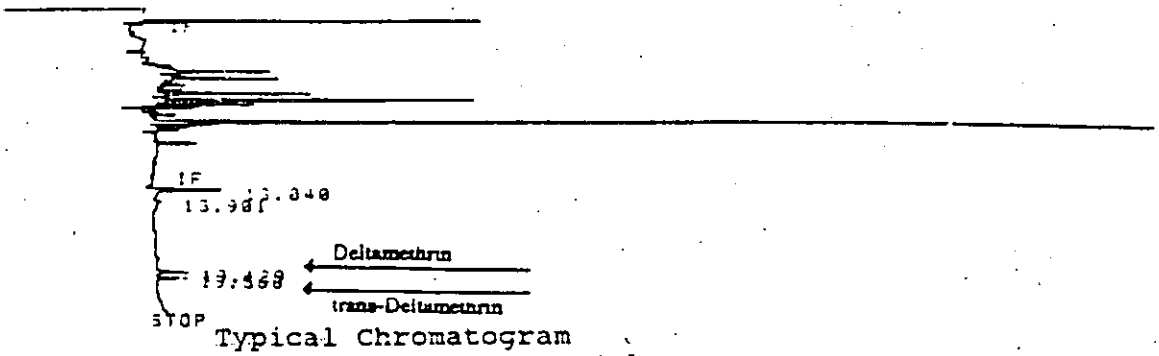
↓

Bring sample to final volume of 10 ml with hexane:ether:acetone (98:1:1 v:v:v).

↓

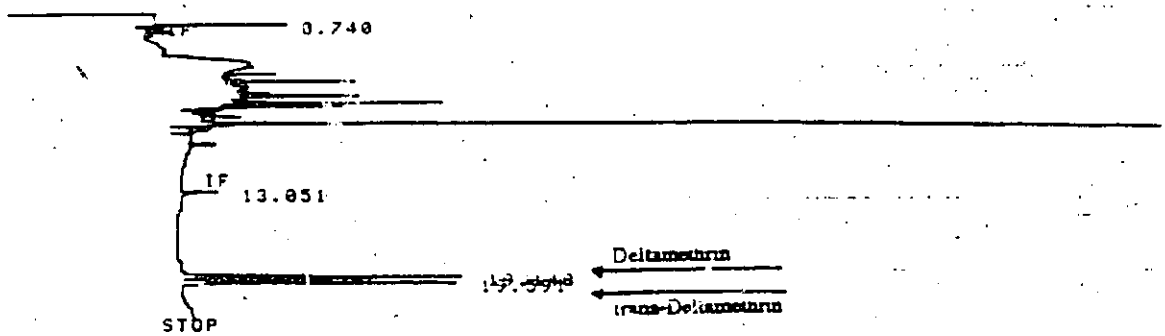
Freeze samples.

Figure 3: Representative Chromatograms of Deltamethrin and trans-Deltamethrin (1 of 2)



Typical Chromatogram
GC Standard: 0.01 ug/ml
Deltamethrin and trans-Deltamethrin

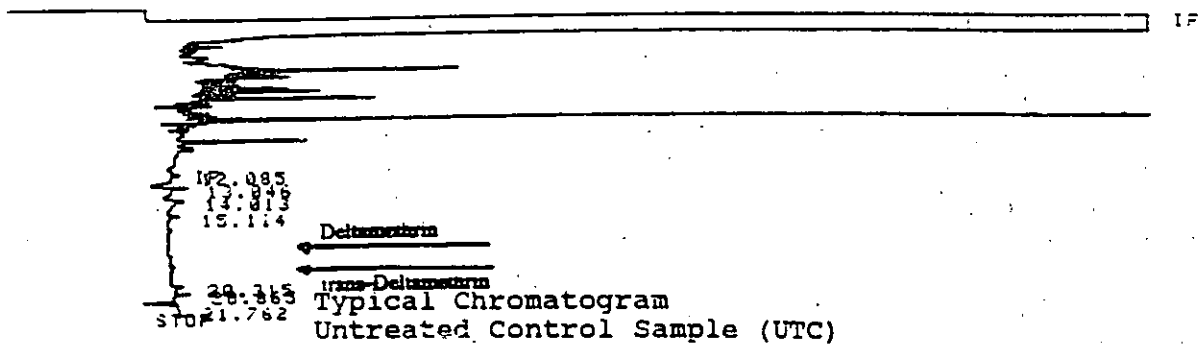
0.02 ng injected, GC run #590, dated 07/23/90



Typical Chromatogram
GC Standard: 0.20 ug/ml
Deltamethrin and trans-Deltamethrin

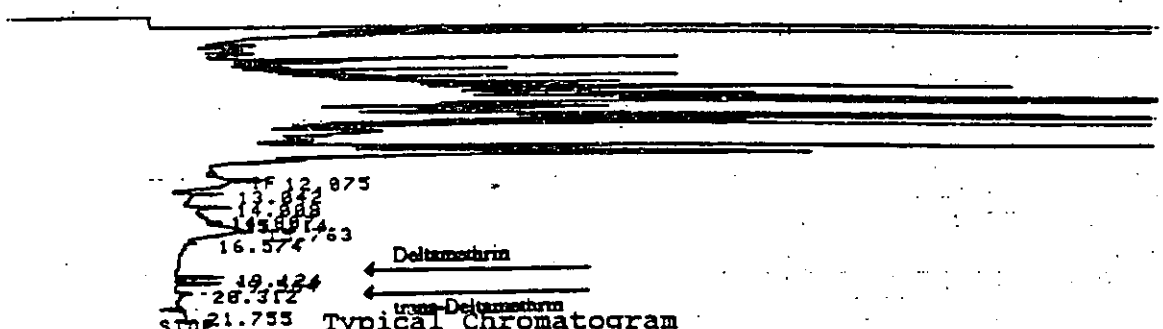
0.40 ng injected, GC run #586, dated 07/23/90

Figure 3:-- Representati : Chromatograms of Deltamethrin and trans-Delta rin (2 of 2)



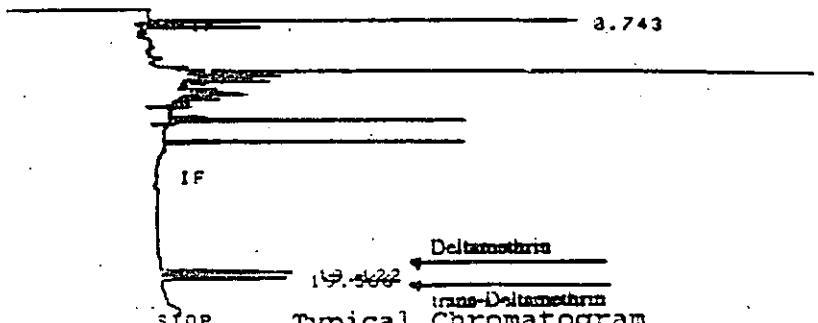
Typical Chromatogram
Untreated Control Sample (UTC)

20 mg injected, GC run #591, dated 07/23/90



Typical Chromatogram
0.002 ppm Deltamethrin and
trans-Deltamethrin Fortification
(91 % Recovery)

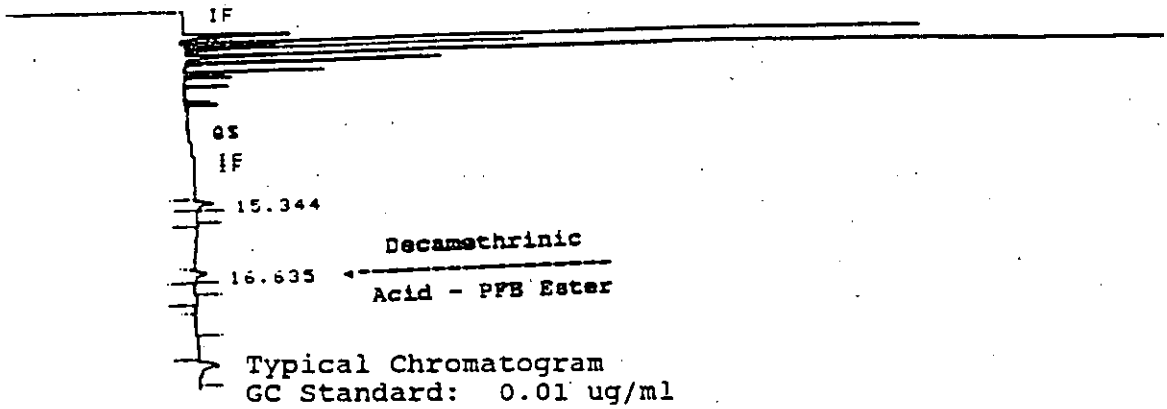
20 mg injected, GC run #592, dated 07/23/90



Typical Chromatogram
0.10 ppm Deltamethrin and
trans-Deltamethrin Fortification
(88% Recovery)

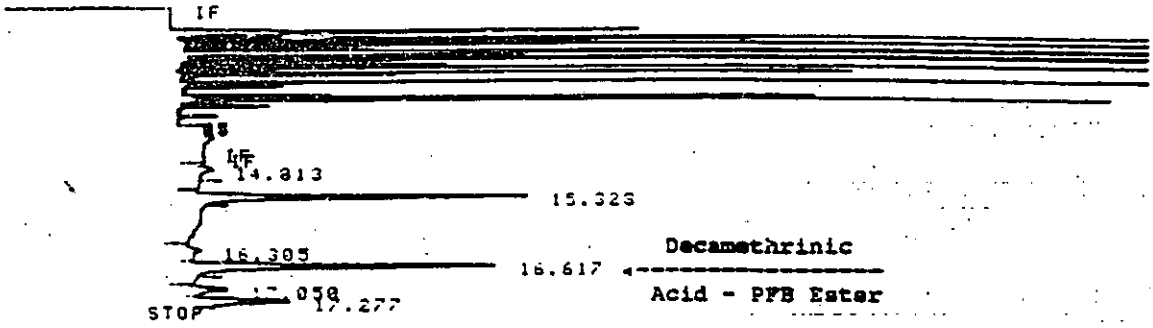
STUDY #: 0 mg injected, GC run #593, dated 07/23/90

Figure 4: Representative Chromatograms of Decamethrinic Acid PFB Ester (1 of 2)



Typical Chromatogram
GC Standard: 0.01 ug/ml
Decamethrinic Acid PFB Ester

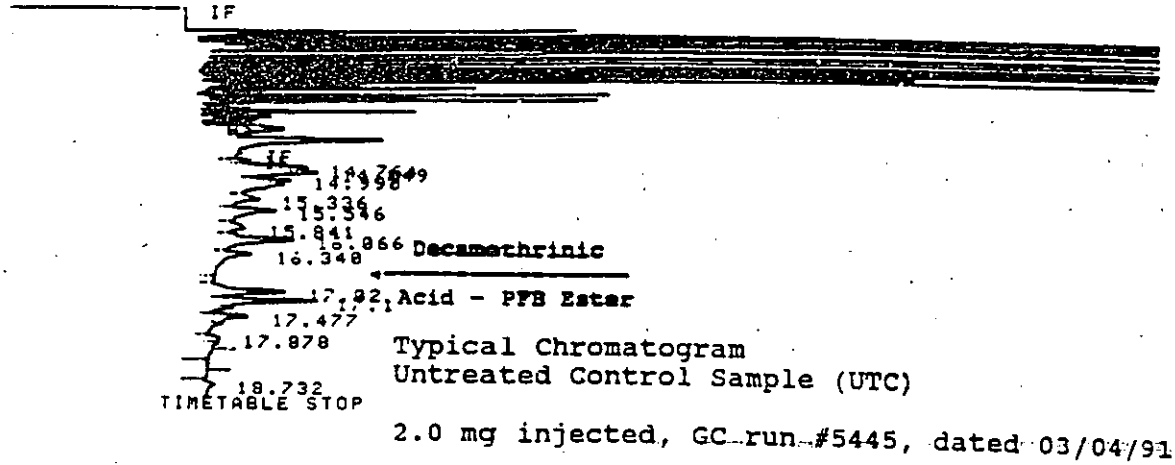
0.01 ng injected, GC run #5443, dated 03/04/91



Typical Chromatogram
GC Standard: 0.10 ug/ml
Decamethrinic Acid PFB Ester

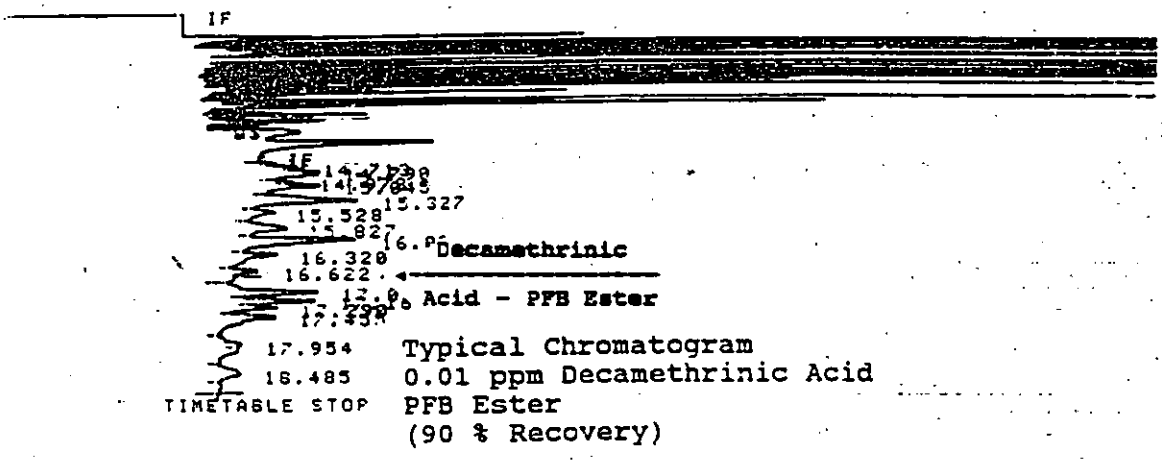
0.10 ng injected, GC run #5463, dated 03/05/91

Figure 4:— Representative Chromatograms of Decamethrinic Acid PFB Ester (2 of 2)



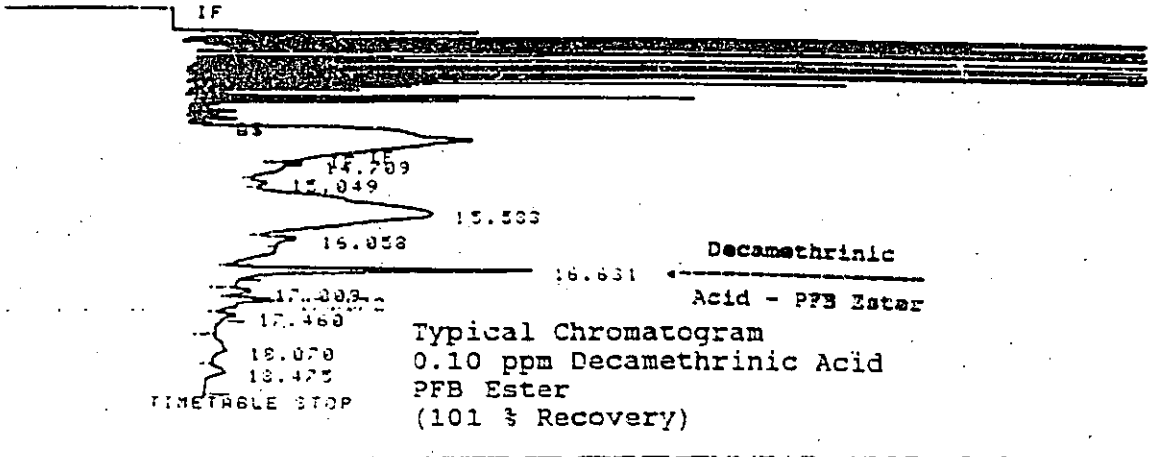
Typical Chromatogram
Untreated Control Sample (UTC)

2.0 mg injected, GC run #5445, dated 03/04/91



Typical Chromatogram
0.01 ppm Decamethrinic Acid
PFB Ester
(90 % Recovery)

2.0 mg injected, GC run #5460, dated 03/04/91



Typical Chromatogram
0.10 ppm Decamethrinic Acid
PFB Ester
(101 % Recovery)

1.0 mg injected, GC run #5453, dated 03/04/