B97-47

Attachment 1

423571-04

STUDY TITLE: Residue Analytical Method for the Determination of Bifenthrin and 4'-Hydroxy Bifenthrin in/on Corn Matrices

TEST SUBSTANCES: Bifenthrin and 4'-hydroxy bifenthrin

DATA REQUIREMENT: Pesticide Assessment Guidelines Subdivision O, 171-4: Residue Analytical Method

AUTHOR: James E. Ridler

STUDY DATES:

Study Initiated:	September 1988
Experiment Terminated:	March 1991
Study Completed:	May 1992

PERFORMING LABORATORY: FMC Corporation
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Residue Chemistry
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STUDY NUMBERS: 182COF87R3-1
182COF88R1-3

Non-Proprietary Information
FMC Corporation Authorizes the Release or Use of This Method by Federal and State Agencies

FMC CORPORATION

STATEMENT OF NO DATA CONFIDENTIALITY CLAIMS

No claim of confidentiality is made for any information contained in this study on the basis of its falling within the scope of FIFRA 10(d)(1)(A), (B), or (C).

Company: FMC Corporation

RF Cook
Ronald F. Cook
Manager, Residue Chemistry
COMPANY AGENT

18 May 92
Date

GOOD LABORATORY PRACTICES STATEMENT

To the best of my knowledge, the study reported herein (Study Numbers 182COF87R3-1 and 182COF88R1-1, "Residue Analytical Method for the Determination of Bifenthrin and 4'-Hydroxy Bifenthrin in/on Corn Matrices," FMC Corporation, Agricultural Chemical Group, P-2550M) was initiated in accordance with, conducted and reported in compliance with the Good Laboratory Practices Standards set forth in Title 40, Part 160 of the Code of Federal Regulations of the United States of America.

James E. Ridler — May 18, 1992
James E. Ridler
Residue Data Chemist
STUDY DIRECTOR

R. F. Cook — 18 May 92
Ronald F. Cook
Manager, Residue Chemistry
SPONSOR

Eunice M. Cuirle — 18 May, 1992
Eunice M. Cuirle
Manager, Product Development and Registration
SUBMITTER

QUALITY ASSURANCE STATEMENT

It is the intent of FMC Corporation that all studies sponsored by or conducted by our facility shall be of the highest quality and meet or exceed the criteria promulgated by the EPA to assure the quality and integrity of the data generated. Studies 182COF87R3-1 and 182COF88R1-1 reported herein was inspected by the FMC ACG Research and Development Quality Assurance Unit and findings submitted to the Study Director, and signed by the Manager of Residue Chemistry and the Director of Developmental Chemistry on the following dates:

INSPECTION DATES	DATE SUBMITTED TO STUDY DIRECTOR	DATE SIGNED BY MANAGEMENT	DATE SIGNED BY DIRECTOR
2/13/90	2/20/90	2/21/90	2/23/90
7/10/90	7/10/90	7/11/90	7/20/90

FMC ACG Research and Development Quality Assurance Unit audited the raw data, all records, and the report. The report was found to be an accurate reflection of the study and the data generated. All raw data will be maintained by FMC Corporation, P.O. Box 8, Princeton, NJ 08543, in the Quality Assurance Archives.

M S Barge

Maureen Barge
Group Leader

5/18/92
Date

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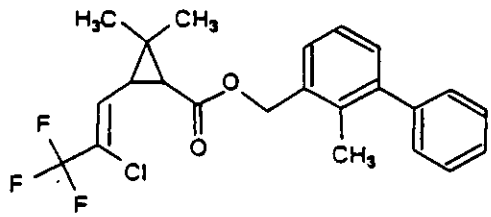
I. INTRODUCTION

Bifenthrin, the active ingredient in Capture® 2EC insecticide/miticide, is currently being developed by FMC Corporation for the control of several foliar pests on a variety of crops, one of which is field corn. The active ingredient in Capture 2 EC has the chemical name [2-methyl-(1,1'-biphenyl)-3-yl]methyl-3-(2-chloro-3,3,3,-trifluoro-1-propenyl)-2,2-dimethylcyclopropane carboxylate, is code numbered FMC 54800, and has the common name bifenthrin. The chemical structure is as follows:



BIFENTHRIN

The objective of this report is to describe the analytical method for the determination of bifenthrin and its possible crop metabolite, 4'-hydroxy bifenthrin residues in corn matrices (grain, silage, and stover). This was accomplished by modifying existing methodology to produce one method for the analysis of both compounds.

The assay method reported herein for bifenthrin and 4'-hydroxy bifenthrin on grain, silage, and stover utilized a solvent extraction, a partitioning step, two Florisil® column clean-ups and quantitation by a gas chromatograph equipped with a capillary column and an electron capture detector.

The analytical method for both compounds was practiced to a limit of quantitation (LOQ) of 0.05 ppm for grain, 0.1 ppm for silage and 0.5 ppm for stover. The limit of detection (LOD) was set at 0.01 ppm for grain, 0.02 ppm for silage and 0.2 ppm for stover.

Capture® is a registered trademark of FMC Corporation.

II. SUMMARY

The analysis for bifenthrin and 4'-hydroxy bifenthrin in/on field corn was accomplished using a single analytical procedure. Previous corn analyses involved separate analytical methods for bifenthrin and 4'-hydroxy bifenthrin. The analytical method established for this study combined the two methods into one method which consists of an acetone blend, a liquid/liquid partition, a Florisil column clean-up, and a solid phase (Florisil) clean-up, which produces a bifenthrin fraction and a separate 4'-hydroxy fraction. Quantitation is performed by separate injections of each solution.

Final sample solutions for each matrix are quantitated using a gas chromatograph equipped with a Megabore, capillary column and an electron capture detector. The determination of method recovery is based on an external standard calibration.

The method is practiced at a limit of quantitation of 0.05 ppm for corn grain and with a limit of detection at 0.01 ppm for both analytes. However, the LOQs are 0.1 and 0.5 ppm, with LODs at 0.02 and 0.2 ppm for corn silage and stover, respectively. The average method recovery for bifenthrin using the three corn matrices was 78% which included a range from 57% to 111%. For 4'-hydroxy bifenthrin, the average method recovery using the corn matrices was 83% with a range from 63 to 106%.

III. SUMMARY TABLES AND GRAPHICS

A. Summary of Method Recoveries

TABLE 1

SUMMARY OF BIFENTHRIN METHOD RECOVERIES IN FIELD CORN MATRICES

MATRIX	FORTIFICATION LEVEL (PPM)	NUMBER OF ANALYSES	RECOVERY RANGE (%)	AVERAGE RECOVERY (%)
Grain	0.05	5	63.0 - 100.0	82.7
	0.10	6	80.0 - 111.0	90.2
	0.25	1	NA[a]	69.6
		Overall Grain Recovery		85
		Standard Deviation		±15
				n=12
Silage	0.10	1	NA	80.0
	0.20	1	NA	80.5
	0.25	1	NA	81.6
	0.50	5	66.2 - 79.4	71.9
	1.0	2	57.4 - 64.6	61.0
	5.0	1	NA	69.9
	10	1	NA	67.4
		Overall Silage Recovery		72
		Standard Deviation		± 8
				n=12
Stover	0.5	2	72.0 - 78.6	75.3
	1.0	5	73.0 - 81.5	76.5
	2.0	3	72.4 - 79.0	76.3
	5.0	1	NA	78.8
	10	1	NA	77.2
	20	1	NA	80.2
		Overall Stover Recovery		77
		Standard Deviation		± 3
				n=13
		Overall Corn Recovery		77.9%
		Standard Deviation		±10.8%
		Number of Analyses		37

[a] = Not Applicable

TABLE 2

SUMMARY OF
4'-HYDROXY BIFENTHRIN METHOD RECOVERIES
IN FIELD CORN MATRICES

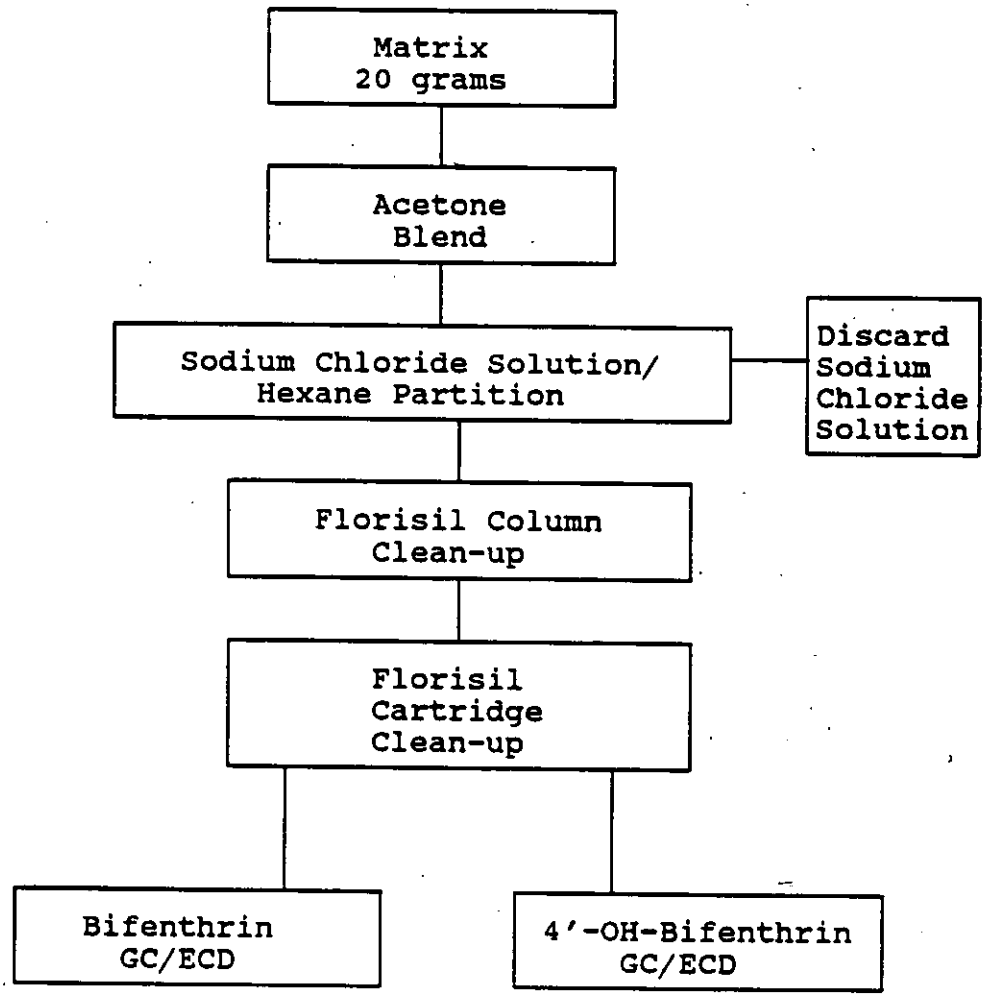
MATRIX	FORTIFICATION LEVEL (ppm)	NUMBER OF ANALYSES	RECOVERY RANGE (%)	AVERAGE RECOVERY (%)
Grain	0.05	6	74.0 - 106.0	90.3
	0.10	6	65.0 - 105.0	85.6
			Overall Grain Recovery	88
			Standard Deviation	±15
				n=12
Silage	0.10	1	NA[a/]	71.0
	0.20	1	NA	76.0
	0.25	1	NA	72.8
	0.50	5	63.0 - 78.0	73.2
	1.0	2	68.0 - 75.0	71.5
	5.0	1	NA	92.4
			Overall Silage Recovery	75
			Standard Deviation	± 8
				n=11
Stover	0.5	3	76.6 - 96.0	87.7
	1.0	6	66.8 - 101.5	87.3
	2.0	3	76.2 - 78.7	77.1
			Overall Stover Recovery	85
			Standard Deviation	±11
				n=12
			Overall Corn Recovery	82.7%
			Standard Deviation	±12.5%
			Number of Analyses	35

[a/] = Not Applicable

B. Method Flow Scheme

FIGURE 1

**METHOD FLOW SCHEME FOR
BIFENTHRIN AND 4'-HYDROXY BIFENTHRIN
IN FIELD CORN GRAIN, SILAGE AND STOVER**



IV. MATERIALS AND STUDY DESIGN

A. Test Substances

Bifenthrin is the common name of the active ingredient in Capture 2EC. It has the chemical name [2-methyl (1,1'-biphenyl)-3-yl-methyl-3-(2-chloro-3,3,3,-trifluoro-1-propenyl)-2,2-dimethyl-cyclopropane carboxylate (see Section X, Table 3 for structure), code number of FMC 54800, and a CAS Number 82657-04-3. Capture 2 EC is an emulsified concentrate containing two pounds of active ingredient per gallon. It is manufactured by FMC Corporation and has the EPA Registration Number 279-3069.

A potential crop metabolite of bifenthrin, 4'-hydroxy bifenthrin, was also analyzed for this study. Its chemical name is [2-methyl-(4'-hydroxy-1,1'-biphenyl)-3-yl]-methyl-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethyl-cyclopropane carboxylate and has a code number FMC 78128 (see Section X, Table 3 for structure).

B. Test Commodities

Corn is a member of the cereal grain crop group. Field corn grain, silage, and stover are used as animal feed.

For sample processing, corn grain should be frozen with liquid nitrogen and finely ground in a Thomas-Wiley® mill. Silage and stover samples should also be processed with liquid nitrogen and chopped with a large Hobart® cutter/mixer.

All the samples should be maintained frozen (ca. -18°C) during shipping and storage to insure sample integrity.

C. Study Design and Procedures

Fortification is accomplished by adding a known amount of bifenthrin and/or 4'-hydroxy bifenthrin standard in hexane solution directly onto the control sample matrix by syringe or pipette.

After fortification, sample containers should be left open at room temperature to allow the hexane to evaporate.

The fortified samples should be carried through the method as part of an assay set with the control sample to determine the method recovery.

D. Analytical Standards

The purity of the bifenthrin and 4'-hydroxy bifenthrin analytical standards was determined before preparing the standard solution. A stock solution of 1000 ng/μL was prepared by dissolving the appropriate amount of the above analytical standard in hexane (Section X, Table 4). Working solutions in concentrations from 0.1 to 100 ng/μL were prepared by appropriate dilutions of the stock solution in hexane. Working solutions were used for fortification, injection standard, and instrument linearity calibration. Stock and working solutions were stored in volumetric containers in a refrigerator/freezer unit to insure maintenance of proper concentrations. Bifenthrin and 4'-hydroxy bifenthrin have shown a pattern of stability as an analytical standard or in stock and working solutions.

E. Equipment

Analytical balance
Beaker, 400 mL
Capillary column, SPB-1 or equivalent
Centrifuge tube, 13 mL
Concentrator tip, for Kuderna-Danish
Chromatographic column, 12 mm (i.d.) X 240 mm long with 250 mL reservoir
Cylinder, graduated, various sizes
Filter paper, 11 cm Whatman 934-AH
Flask, Erlenmeyer, 250 mL
Flask, Suction, 500 mL
Funnel, 11 cm, Buchner
Gas Chromatograph, Hewlett-Packard equipped with an Electron Capture Detector
Glass wool
Kuderna-Danish evaporator
N-Evap evaporator

Pipet, disposable
Snyder column
Steam bath
Syringe, various sizes
Tube, capped, 25 X 150 mm, VWR
Tube, uncapped, 25 X 150 mm, VWR
Vacuum manifold, Supelco
Vial, injection, 2 mL
Vial cap, double-faced Teflon/silicone, Supelco
Virtis®, homogenizer
Vortex mixer, VWR

F. Reagents and Standards

Acetone, Resi-analyzed
Analytical standards, Bifenthrin, Residue Inventory Number 198, 97.9% purity; 4' hydroxy bifenthrin, Residue Inventory Number 221, 99.0% purity, FMC Corporation, Princeton, NJ
Cyclohexane, Resi-analyzed
Ethyl acetate, Resi-analyzed
Florisil®, 100/200 mesh
Florisil®, Solid phase extraction cartridge
Hexane, Resi-analyzed
Methanol, Resi-analyzed
Methyl-t-butyl ether (MTBE), Omni-Solv, E.M. Science
Sodium chloride
Sodium sulfate, anhydrous, reagent grade
Water, distilled

Equivalent equipment and reagents may be used if the materials listed in this report are not available.

V. ANALYTICAL PROCEDURE

A. Residue Method

The analytical method for the determination of bifenthrin and 4'-hydroxy bifenthrin in/on field corn matrices (grain, silage, and stover) includes the following steps:

Extraction - A 20 gram subsample is weighed into a 400 mL beaker and blended for 5 minutes with 200 mL of acetone.

The sample is filtered through a Buchner funnel lined with Whatman GF/A glass fiber filter paper into a 500 mL suction flask. The beaker and filter cake are rinsed with 2 X 20 mL of acetone and the rinses are added to the filtrate. The filtrate is transferred to a graduated cylinder and the volume adjusted to 250 mL. A 1 gram sample aliquot (12.5 mL) is transferred to a 25 X 150 mm capped tube and concentrated down to approximately 1 mL on a nitrogen evaporator.

Partition - Ten mL of 5% sodium chloride in water solution is added to the 1 mL sample. The sample is then partitioned with 10 mL of hexane for one minute, pulsing every 15 seconds. Two additional 10 mL hexane partitions are then performed. After each partition the hexane layer is removed and transferred to a 25 X 150 mm uncapped tube. The hexane solution (~ 30 mL) is concentrated on a nitrogen evaporator to approximately 10 mL.

Florisil Column Procedure - The glass chromatographic column is plugged with glass wool and filled with 100 mL of hexane. Fifteen grams of deactivated Florisil (3% water by weight) is slowly added. The Florisil is allowed to settle and capped with a 0.5 inch layer of anhydrous sodium sulfate. The 10 mL hexane solution is quantitatively transferred to the Florisil column. The tube is rinsed 2 X 2 mL of hexane and each rinse is added to the column. One hundred mL of hexane is added to the column and allowed to elute to waste.

The bifenthrin and 4'-hydroxy bifenthrin are eluted off the column with 100 mL of 60/39/1 (v/v/v) hexane/methyl-t-butyl-ether/methanol. The eluant is collected in a Kuderna-Danish evaporator fitted with a 10 mL concentrator tip and concentrated on a steam bath to approximately 10 mL. The 10 mL sample is concentrated on a nitrogen evaporator to approximately 1 mL.

Florisil Prep Sep Cartridge - Florisil Prep Sep extraction cartridges are attached to a vacuum manifold and conditioned with 10 mL of acetone, 2 X 10 mL of hexane and an additional 5 mL of hexane.

The sample extract is transferred to the cartridge with a disposable pipet and slowly eluted through the cartridge. The tip is rinsed with 2 X 1 mL of cyclohexane. Each rinse is added to the column and slowly eluted. The bifenthrin is collected off the cartridge with 5 mL of 10% (v/v) ethyl acetate in hexane. The eluant is collected slowly in a 13 mL graduated centrifuge tube. Next, the 4'-hydroxy bifenthrin is slowly eluted off the cartridge with 10 mL of 60/39/1 (v/v/v) hexane/methyl-t-butyl ether/methanol.

The eluant containing the 4'-hydroxy bifenthrin is collected in another 13 mL centrifuge tube. The separate bifenthrin and 4'-hydroxy bifenthrin extracts are concentrated on a nitrogen evaporator to 0.5 mL volume. The samples are adjusted to 5 mL with hexane and concentrated to final volume depending on the matrix (0.5 mL for grain, 1 mL for silage, and 5 mL for stover).

Each sample is transferred to a vial which is sealed with a double-faced Teflon/silicone cap for injection on the gas chromatograph. Quantitation is performed by separate injection for bifenthrin and 4'-hydroxy bifenthrin.

B. Instrumentation

Bifenthrin and 4'-hydroxy bifenthrin residues are determined by a Hewlett-Packard 5880A gas chromatograph equipped with an electron capture detector, a HP autosampler, and a HP integrator. Equivalent gas chromatograph, integrator, data acquisition system, and autosampler may be used. Section XII, Appendix A1 shows one example of the operating conditions. The chromatographic conditions can be modified or optimized for best resolution and detection sensitivity.

C. Method Validation and Quality Control

The analytical method recovery is determined by the results from the fortified control samples. The control sample should be analyzed to assure that no bifenthrin, 4'-hydroxy bifenthrin or any interferences are present.

D. Method of Calculation

The magnitude of bifenthrin and/or 4'-hydroxy bifenthrin in each sample is determined by an external standard calibration method. A run standard is injected at the beginning of every set and subsequently after every two sample solutions. The amount of bifenthrin and/or 4'-hydroxy bifenthrin is quantitated from the detector response transmitted to the integrator. The response as peak area (or peak height) is calculated as nanogram (ng) of analyte based on the injection of run standards.

The nanogram value reported is calculated by comparing the area units of the sample to the area units of the calibrated run standard using the following formula:

$$\text{ng of analyte in sample} = \frac{\text{area units (sample)}}{\text{area units (standard)}} \times \text{ng injected (standard)}$$

Results of each analysis are reported on a ppm ($\mu g/g$) basis by using the following formula:

$$\text{compound content ppm } (\mu g/g) = \frac{\text{ng of analyte in sample}}{\text{mg of sample injected}}$$

Method recovery is then obtained by comparing the bifenthrin and/or 4'-hydroxy bifenthrin content recovered from the sample to the initial fortification level.

$$\text{method recovery (\%)} = \frac{\text{compound content (ppm)}}{\text{fortification level (ppm)}} \times 100$$

If there was background in a control sample, it was subtracted from the fortified control sample prior to determination of method recovery.

E. Interferences

1. **Sample Matrices** - For a few of the control samples for silage (2) and stover (3), a response (peak area, a bump on the front or back of the peak of interest when determining method recovery) interfered with the peak of interest or produced erroneous resolution of the peak due to tailing.

   In all instances, peak height integration resolved this problem.

2. **Other Pesticides** - No interference due to other pesticides was observed or analyzed for this study.

3. **Solvents and Labware** - No interference was observed from solvents and labware.

F. Confirmatory Techniques

No other confirmatory techniques were used for this study.

G. Time Required for Analysis

This analytical procedure requires approximately eight hours. During this time, one person can complete a set of eight samples from initial weighing until gas chromatographic measurement.

H. Modifications or Potential Problems

The instrument integration using peak area was done automatically based on an external standard calibration. However, due to poor resolution (peak tailing or a bump on the front or back of the peak of interest when determining method recovery) in some of the silage and stover control samples, peak heights were used to manually calculate these residue data. In addition, some method recovery values for grain and stover were manually calculated by peak height due to poor peak area integration by the instrument.

This method has been successfully validated for 4'-hydroxy bifenthrin in corn grain by an independent laboratory (Section XI. Reference 3). The following comments were recommended by the independent laboratory.

1) Gentle heating and/or sonication may be required to completely dissolve the 4'-hydroxy bifenthrin in hexane while preparing the 1000 ng/uL stock solution.

2) The size and/or manufacturer of the Florisil SPE cartridge used in the sample clean-up needs to be specified. The independent laboratory used a Sep-Pak cartridge from Waters and these cartridges are only available in one size.

3) The Florisil Column used in sample clean-up (especially if the method is being run for the first time or a new lot of Florisil is being used) should be profiled prior to sample introduction.

4) During GC analysis, the response of the analyte declined as more sample matrix was introduced to the system. To prevent the decline in sensitivity from effecting the quantitation of 4'-hydroxy bifenthrin, the analyst should keep the injection volume at 1 uL if possible and maintain the GC system daily by a) removing 20 to 30 cm from the inlet end of the column, b) replacing the septa, and c) inspecting the injection liner for residue and cleaning or replacing the injection liner if it is dirty.

VI. STORAGE STABILITY

Bifenthrin and 4'-hydroxy bifenthrin analytical standards are assayed on a regular basis for percent purity. Both standards have a proven pattern of stability. A stock solution (1000 µg/mL) is prepared in hexane and is remade on an annual basis, as needed. Fresh dilute solutions are prepared at suitable concentrations on a monthly basis. All solutions should be stored in volumetric containers in a refrigerator/freezer unit and have a proven stability for their respective storage periods.

VII. RESULTS AND DISCUSSION

A. Accuracy and Precision

The accuracy and the precision of the analytical method are determined by the average recovery and standard deviation of the results from the fortified control samples. Tables 1 and 2 in Section III present the average method recovery and standard deviation for each matrix. The average method recovery for bifenthrin was 78% and 83% for 4'-hydroxy bifenthrin. The standard deviation for both compounds is 11 and 13%, respectively. The individual method recovery data for each matrix can be found in Section X, Tables 5 to 9.

B. Limits of Detection and Quantitation

The method is practiced at a limit of quantitation (LOQ) of 0.05 ppm for corn grain and with a limit of detection (LOD) at 0.01 ppm. The LOQs are 0.1 and 0.5 ppm, with LODs at 0.02 and 0.2 ppm for corn silage and stover, respectively. The method recovery values for this study ranged from 0.05 ppm to 0.25 ppm for grain, 0.1 ppm to 10 ppm for silage and 0.1 ppm to 5 ppm for stover.

C. Ruggedness Testing

This method has been practiced for the determination of bifenthrin and 4'-hydroxy bifenthrin residues on corn matrices (grain, silage, and stover). It was developed from two separate analytical methods (one for bifenthrin and one for 4'-hydroxy bifenthrin) into one method for the analysis of both compounds.

The standard deviation for bifenthrin is 11% and for 4'-hydroxy bifenthrin, 13%. These results indicate that this method is reliable and accurate based on the number of fortifications (n=37 for bifenthrin and n=35 for 4'-hydroxy bifenthrin) and the wide range of fortification levels (0.05 to 10 ppm).

D. Limitations

Preventive maintenance of the gas chromatograph system (changing septa, removing a portion of the inlet end of the column and inspecting the column liner) should be done on a routine basis in order to prevent instrument and integration problems.

VIII. CONCLUSION

The analytical method for the determination of bifenthrin and 4'-hydroxy bifenthrin in corn matrices consists of an acetone blend, a liquid/liquid partition, a Florisil column clean-up, and a solid phase extraction (Florisil) clean-up. The method is reliable as evidenced by the successful validation of this method by an independent laboratory. It also consumes small volumes of solvents as compared to previous methodology. The method recovery ranges from 57 to 111%, with standard deviation ranging from 11 to 13% depending on the matrix and compound analyzed.

All the equipment needed to perform the analysis, e.g., gas chromatograph with electron capture detector, is readily available in most residue analytical laboratories. An experienced residue analyst following the procedure exactly as written, and being aware of the possible potential problems, should not experience interference problems and should obtain adequate recoveries.

IX. CERTIFICATION

We, the undersigned, hereby declare that this study was performed under our supervision according to the procedures herein described, and that this report provides a true and accurate record of the results obtained.

James E. Ridler
Residue Data Chemist
AUTHOR/STUDY DIRECTOR

May 18, 1992
Date

Ronald F. Cook
Manager, Residue Chemistry
SUPERVISOR

18 May 92
Date

ADDITIONAL STUDY PERSONNEL:

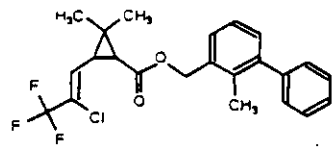
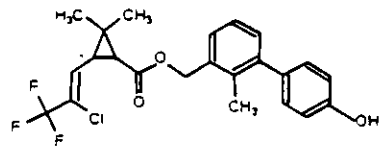
William D. Nagel, Chemist
Dave Baffuto, Laboratory Technician

X. TABLES AND FIGURES

A. Test and Reference Substances

TABLE 3

ANALYTICAL STANDARDS

COMPOUND	CHEMICAL NAME	FMC NUMBER	INVENTORY NUMBER	PERCENT PURITY	STRUCTURE
Bifenthrin	[2-methyl (1,1'-biphenyl) -3-yl]-methyl-3-(2-chloro -3,3,3-trifluoro- 1-propenyl)-2,2-dimethyl- cyclopropanecarboxylate	54800	198	97.9	
4'-Hydroxy Bifenthrin	[2-methyl-(4'-hydroxy- 1,1'-biphenyl)-3-yl]- methyl-3-(2-chloro- 3,3,3-trifluoro-1- propenyl)-2,2-dimethyl- cyclopropanecarboxylate	78128	A-41 221	97.1 99.0	

B. Reference Solutions

TABLE 4

REFERENCE SOLUTIONS

COMPOUND	SOLVENT OF SOLUTIONS	CONCENTRATION OF SOLUTION (ng/ul)	STANDARD SOLUTION INDEX NUMBER	DATE PREPARED
Bifenthrin [a/]	Hexane	1000	347	3/6/90
	Hexane	100	347-16	5/1/90
	Hexane	100	347-23	5/29/90
	Hexane	1000	358	7/30/90
	Hexane	100	358-1	7/30/90
	Hexane	100	358-8	8/30/90
	Hexane	100	358-15	9/28/90
	Hexane	100	358-22	10/29/90
4'-Hydroxy bifenthrin [a/]	Ethyl Acetate	1000	349	3/6/90
	Hexane	100	349-22	5/1/90
	Hexane	100	349-31	5/29/90
	Ethyl Acetate	1000	354	7/3/90
	Hexane	100	354-1	7/3/90
	Hexane	100	354-12	8/3/90
	Hexane	100	354-21	8/31/90
	Ethyl Acetate	1000	384	9/19/90
	Hexane	100	384-3	9/28/90
	Hexane	100	384-12	10/29/90
	Hexane	100	384-19	11/29/90

[a/] = All subsequent dilutions were prepared on a monthly basis

C. Method Recovery Data

TABLE 5

METHOD RECOVERIES OF BIFENTHRIN AND 4'-HYDROXY BIFENTHRIN FROM LABORATORY-FORTIFIED CORN GRAIN SAMPLES

COMPOUND	SAMPLE IDENTIFICATION	SET IDENTIFICATION	FORTIFICATION LEVEL (ppm)	RECOVERED AMOUNT (ppm)	PERCENT RECOVERY	DATE ANALYZED
Bifenthrin	CRF87-5-C	1R	0.05	0.0315	63.0	6/14/90
	87104-1-2	2R2	0.05	0.0330	66.0	6/22/90
	87SFT-152-C	3	0.05	0.0433	86.6	6/11/90
	87JJK-7-4	24	0.05	0.0490	98.0	10/25/90
	87RSP-64-CD	29	0.05	0.0500	100.0	11/15/90
				Average	82.7	
				Standard Deviation	±17	n = 5
	87JJK-4-C	1R	0.1	0.0953	95.3	6/14/90
	87HLG-21-C	2R2	0.1	0.0883	88.3	6/22/90
	PRD581-C	3	0.1	0.0810	81.0	6/11/90
	88CMS-8-C	4	0.1	0.1110	111.0	6/15/90
	EVG87-18AD	5	0.1	0.0853	85.3	6/19/90
	87HLG-18C	18	0.1	0.0800	80.0	9/26/90
				Average	90.2	
				Standard Deviation	±12	n = 6
	88RSP-50-C	4	0.25	0.1740	69.6	6/18/90
4'-Hydroxy Bifenthrin	CRF87-5-C	1R	0.05	0.0503	106.0	6/14/90
	87HLG-21-C	2R	0.05	0.0370	74.0	6/14/90
	87SFT-152-C	3	0.05	0.0408	81.6	6/12/90
	87JJK-8-4	18	0.05	0.0480	96.0	9/27/90
	87RSP-64-CD	29	0.05	0.0410	82.0	11/19/90
	87HLG-21-C	31	0.05	0.0510	102.0	12/17/90
				Average	90.3	
				Standard Deviation	±13	n = 6
	87JJK-4-C	1R	0.1	0.1050	105.0	6/14/90
	87HLG-21-C	2R	0.1	0.0718	71.8	6/14/90
	PRD-581-C	3	0.1	0.0735	73.5	6/12/90
	88CMS-8-C	4	0.1	0.0650	65.0	6/18/90
	EVG87-18AD	5	0.1	0.0930	93.0	6/21/90
	87HLG-18C	18	0.1	0.1050	105.0	9/27/90
				Average	85.6	
				Standard Deviation	±18	n = 6

TABLE 6

METHOD RECOVERIES OF BIFENTHRIN FROM LABORATORY-FORTIFIED CORN SILAGE SAMPLES

COMPOUND	SAMPLE IDENTIFICATION	SET IDENTIFICATION	FORTIFICATION LEVEL (ppm)	RECOVERED AMOUNT (ppm)	PERCENT RECOVERY	DATE ANALYZED
Bifenthrin	87JJK-8-2	20	0.10	0.800	80.0	10/3/90
	87HLG-16-C	21R	0.20	0.161	80.5	10/12/90
	88CMS-7-C	27	0.25	0.204	81.6	11/9/90
	87CRF-4-C	20	0.50	0.341	68.2	10/3/90
	87104-1-1	21	0.50	0.356	71.2	10/4/90
	87SFT-151-C	26	0.50	0.331	66.2	11/6/90
	87JJK-7-2	28	0.50	0.372	74.4	11/12/90
	87RSP-43-C	30	0.50	0.397	79.4	11/20/90
				Average	71.9	
				Standard Deviation	±5 n = 5	
	88RSP-24-C	26	1.0	0.574	57.4	11/6/90
	EVG87-16A-Dup	30R	1.0	0.646	64.6	11/26/90
				Average	61.0	
	87HLG-19-C	25	5.0	3.493	69.9	11/5/90
	88CMS-7-C	24	10	6.735	67.4	10/25/90

TABLE 7

METHOD RECOVERIES OF 4'-HYDROXY BIFENTHRIN FROM LABORATORY-FORTIFIED CORN SILAGE SAMPLES

COMPOUND	SAMPLE IDENTIFICATION	SET IDENTIFICATION	FORTIFICATION LEVEL (ppm)	RECOVERED AMOUNT (ppm)	PERCENT RECOVERY	DATE ANALYZED
4'-Hydroxy Bifenthrin	87JJK-8-2	20	0.10	0.710	71.0	10/5/90
	87HLG-16-C	21	0.20	0.152	76.0	10/5/90
	88CMS-7-C	27	0.25	0.182	72.8	11/8/90
	87CRF-4-C	20	0.50	0.389	77.8	10/5/90
	87104-1-1	21R2	0.50	0.350	70.0	10/30/90
	87SFT-151-C	26	0.50	0.387	77.4	11/6/90
	87JJK-7-2	28	0.50	0.390	78.0	11/12/90
	87RSP-43-C	30	0.50	0.315	63.0	11/20/90
				Average	73.2	
				Standard Deviation	±7 n = 5	
	88RSP-24-C	26	1.0	0.750	75.0	11/8/90
	EVG87-16A-Dup	30R	1.0	0.680	68.0	11/27/90
				Average	71.5	
	87HLG-19-C	25	5.0	4.619	92.4	11/7/90

TABLE 8

METHOD RECOVERIES OF BIFENTHRIN FROM LABORATORY-FORTIFIED CORN STOVER SAMPLES

COMPOUND	SAMPLE IDENTIFICATION	SET IDENTIFICATION	FORTIFICATION LEVEL (ppm)	RECOVERED AMOUNT (ppm)	PERCENT RECOVERY	DATE ANALYZED
Bifenthrin	87RSP-65-C	12R	0.5	0.360	72.0	8/29/90
	87CRF-6-C	15	0.5	0.393	78.6	9/6/90
				Average	75.3	
	87SFT-153-C	12	1.0	0.815	81.5	8/23/90
	87JJK-7-6	13	1.0	0.730	73.0	8/29/90
	EVG87-17-A	14	1.0	0.732	73.2	9/4/90
	87104-1-3	15	1.0	0.755	75.5	9/6/90
	87JJK-8-6	16	1.0	0.792	79.2	9/13/90
				Average	76.5	
				Standard Deviation	±4	n = 5
	87HLG-17-C	13	2.0	1.542	77.1	8/29/90
	87HLG-20-C	16	2.0	1.448	72.4	9/13/90
	88RSP-49-C	17	2.0	1.580	79.0	9/17/90
				Average	76.2	
				Standard Deviation	±3	n = 3
	PRD-581-C	14	5.0	3.940	78.8	9/4/90
	88CMS-9-C	17	10	7.717	77.2	9/17/90
	87HLG-20-C	24	20	16.04	80.2	10/31/90

TABLE 9

METHOD RECOVERIES OF 4'-HYDROXY BIFENTHRIN FROM LABORATORY-FORTIFIED CORN STOVER SAMPLES

COMPOUND	SAMPLE IDENTIFICATION	SET IDENTIFICATION	FORTIFICATION LEVEL (ppm)	RECOVERED AMOUNT (ppm)	PERCENT RECOVERY	DATE ANALYZED
4'-Hydroxy Bifenthrin	87RSP-65-C	12	0.5	0.480	96.0	8/24/90
	PRD-581-C	14	0.5	0.453	90.6	9/7/90
	87CRF-6-C	15	0.5	0.383	76.6	9/6/90
				Average	87.7	
				Standard Deviation	±10 n = 3	
	87SFT-153-C	12	1.0	1.015	101.5	8/24/90
	87JJK-7-6	13	1.0	0.823	82.3	8/30/90
	EVG87-17-A	14	1.0	0.853	85.3	9/7/90
	87104-1-3	15	1.0	0.668	66.8	9/7/90
	87JJK-8-6	16	1.0	0.895	89.5	9/14/90
	88CMS-9-C	17	1.0	0.985	98.5	9/18/90
				Average	87.3	
				Standard Deviation	±12 n = 6	
	87HLG-17-C	13	2.0	1.530	76.5	8/30/90
	87HLG-20-C	16	2.0	1.573	78.7	9/18/90
	88RSP-49-C	17	2.0	1.523	76.2	9/18/90
				Average	77.1	
				Standard Deviation	±1 n = 3	

XI. REFERENCES

1. Akkari, KH, "Analytical Method for the Determination of 4'-OH-Bifenthrin in/on Field Corn," FMC Corporation, ACG, Princeton, NJ, P-1694M, May 1987, MRID #402579-04.

2. Ridler, JE, "Magnitude of the Residue of Bifenthrin and 4'-Hydroxy Bifenthrin in/on Field Corn," FMC Corporation, ACG, Princeton, NJ, P-2550, March 1991.

3. Morris, AD and Winkler, DA, "Independent Method Validation Ruggedness Trial For 4' Hydroxy-Bifenthrin in Corn Grain Using FMC Corporation Method P-2550M, Residue Analytical Method for the Determination of Bifenthrin and 4' Hydroxy-Bifenthrin in/on Corn Matrices," EN-CAS Analytical Laboratories, Winston-Salem, NC 27107, PC-0170, April 1992.

XII. APPENDICES

A1. Instrument Parameters (Bifenthrin)

GC/ECD*

COLUMN:	SPB-1, methyl silicone, 15 m x 0.53 um
INLET:	Direct Injection (250°C)
OVEN TEMPERATURE:	
Initial Temp:	235°C
Run Time:	10 minutes
Post Run Temp:	280°C
Hold Time	10 minutes
DETECTOR TEMPERATURE:	350°C
GAS FLOW RATE:	He, carrier, ~5 mL/min Ar/CH_4, make-up, ~35 mL/min
RETENTION TIME:	~4.3 minutes

* Equivalent GC and GC columns can be used to determine bifenthrin residue. Chromatographic conditions can be modified or optimized for best detection sensitivity.

A2. Instrument Parameters (4'-hydroxy bifenthrin)

GC/ECD*

COLUMN:	SPB-1, methyl silicone, 15 m x 0.53 um
INLET:	Direct Injection (250°C)
OVEN TEMPERATURE:	
Initial Temp:	255°C
Run Time:	10 minutes
Post Run Temp:	280°C
Hold Time	10 minutes
DETECTOR TEMPERATURE:	350°C
GAS FLOW RATE:	He, carrier, ~5 mL/min Ar/CH_4, make-up, ~35 mL/min
RETENTION TIME:	~4.8 minutes

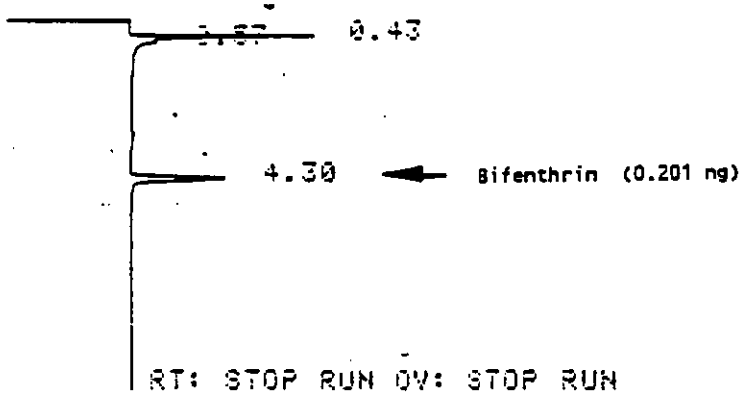
* Equivalent GC and GC columns can be used to determine 4'-hydroxy bifenthrin residue. Chromatographic conditions can be modified or optimized for best detection sensitivity.

B. Chromatograms

FIGURE NUMBER	DESCRIPTION	AMOUNT INJECTED
2	Standard, Bifenthrin	0.20 ng
3	Corn Grain, Control	4 mg
4	Corn Grain, Fortified	4 mg
5	Corn Silage, Control	2 mg
6	Corn Silage, Fortified	2 mg
7	Corn Stover, Control	0.4 mg
8	Corn Stover, Fortified	0.4 mg
9	Standard, Bifenthrin	0.40 ng
10	Standard, 4-Hydroxy bifenthrin	0.20 ng
11	Corn Grain, Control	4 mg
12	Corn Grain, Fortified	4 mg
13	Corn Silage, Control	2 mg
14	Corn Silage, Fortified	2 mg
15	Corn Stover, Control	0.4 mg
16	Corn Stover, Fortified	0.4 mg
17	Standard, 4'-Hydroxy bifenthrin	0.40 ng

FIGURE 2

STANDARD 347-29
BIFENTHRIN
SET 1
2 uL, 0.1 ng/uL INJECTED

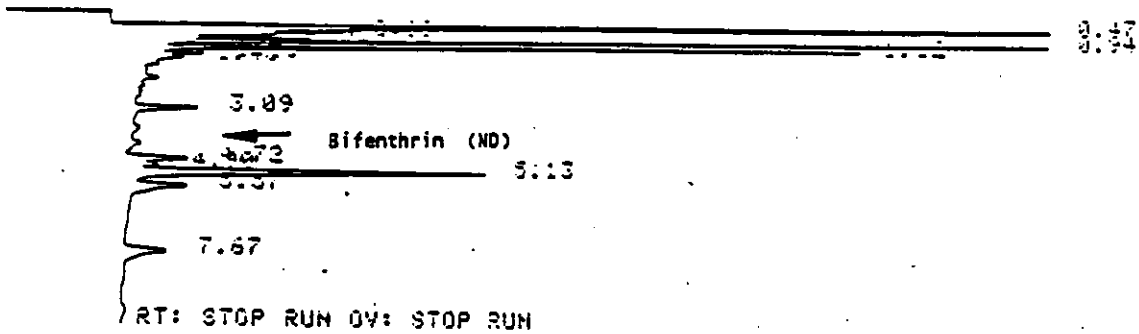


[hp] 5880A SAMPLER INJECTION @ 09:49 JUN 14, 1990
SAMPLE # : ID CODE :
4 0.1-347-29
54800
ESTD

RT	AREA	TYPE	CAL	AMOUNT	NAME
4.30	1029.10	BB	1	0.201	54800

FIGURE 3

CORN GRAIN, CONTROL
PRD-383-87-JJK-8-4
SET 1 SAMPLE 5; HP 5880
2 uL, 4 mg INJECTED



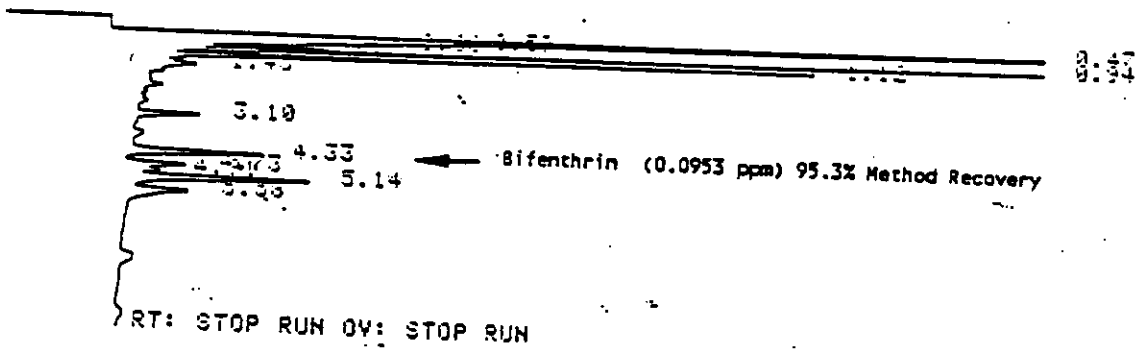
[HP] 5880A SAMPLER INJECTION @ 11:38 JUN 14, 1990
SAMPLE # : ID CODE :
8 5.2.500
METHOD ABORTED
AREA %

RT	AREA	TYPE	AREA %
0.47	36775.50	BV	51.563
0.66	1279.12	VV	2.141
0.85	559.60	BV	0.937
0.94	5192.96	VP	8.694
1.12	4289.68	PV	7.182
1.33	275.47	VV	0.461
1.45	290.59	VP	0.486
3.09	732.87	PV	1.227
4.72	945.41	PV	1.583
4.90	483.28	VV	0.809
5.13	6369.66	VV	10.664
5.57	1496.33	VV	2.505
7.67	1040.55	BB	1.742

REDUCED TO 85% OF ORIGINAL

FIGURE 4

CORN GRAIN, FORTIFIED CONTROL
PRD-383-87-JJK-4
SET 1 SAMPLE 6; HP 5880
2 uL, 4 mg INJECTED



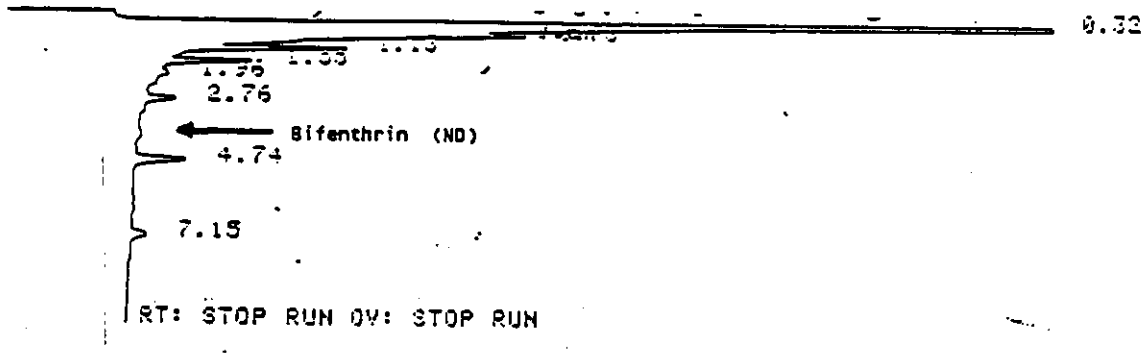
HP 5880A SAMPLER INJECTION @ 12:05 JUN 14, 1990
SAMPLE # : ID CODE :
9 6.2.500
54800
ESTD

RT	AREA	TYPE	CAL	AMOUNT	NAME
4.33	1952.96	BP	1	0.381	54800

REDUCED TO 85% OF ORIGINAL

FIGURE 5

CORN SILAGE, CONTROL
PRE-313-88-CMS-7-C
SET 27 SAMPLE 137
2uL, 2 mg INJECTED



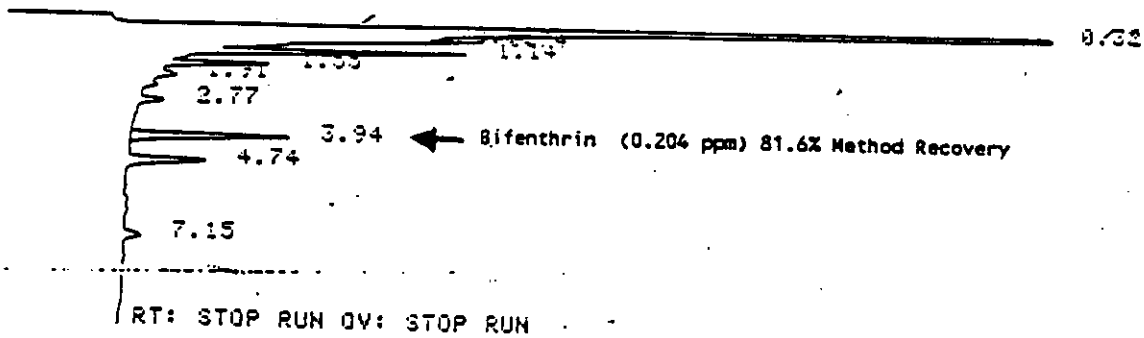
[hp] 5880A SAMPLER INJECTION @ 16:15 NOV 9, 1990
SAMPLE # : ID CODE :
2 137.2.1000
METHOD ABORTED
AREA %

RT	AREA	TYPE	AREA %
0.32	231947.00	BV	81.726
0.67	10870.70	VV	3.830
0.73	21052.00	VV	7.413
1.13	6752.57	BP	2.379
1.55	4302.22	PP	1.516
1.96	835.07	PP	0.294
2.76	1941.34	PP	0.684
4.74	4318.51	PP	1.522
7.15	1791.94	VP	0.631

REDUCED TO 85% OF ORIGINAL

FIGURE 6

CORN SILAGE, FORTIFIED CONTROL
PRE-313-88-CMS-7-C
SET 27 SAMPLE 138
2uL, 2 mg INJECTED



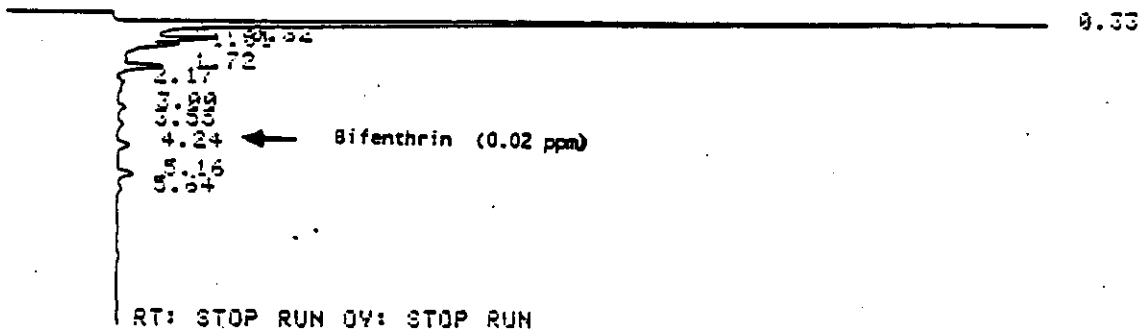
[hp] 5880A SAMPLER INJECTION @ 16:42 NOV 9, 1990
SAMPLE # : ID CODE :
3 138.2.1000
54800
ESTD

RT	HEIGHT	TYPE	CAL	AMOUNT	NAME
3.94	1417.60	HH	1	0.502	54800

REDUCED TO 85% OF ORIGINAL

FIGURE 7

CORN STOVER, CONTROL
PRD-541-87-SFT-153-C
SET 12 SAMPLE 21
2 uL, 0.4 mg INJECTED



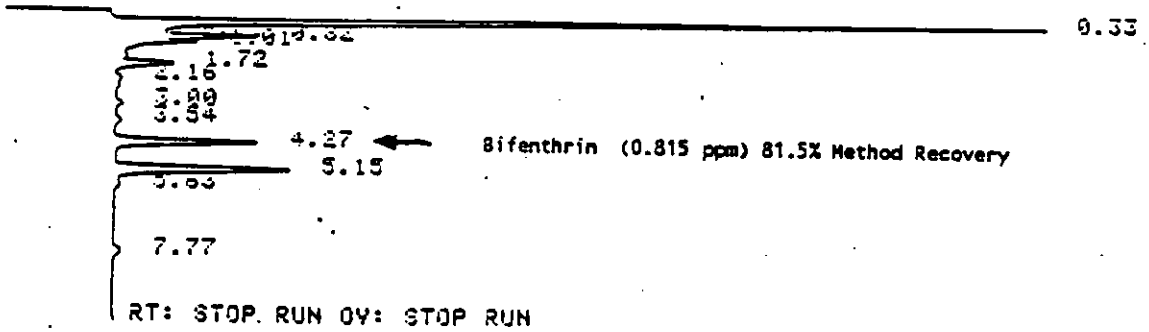
[hp] 5880A SAMPLER INJECTION @ 17:14 AUG 23, 1990
SAMPLE # : ID CODE :
8 21.2.5000
54000
ESTD

RT	AREA	TYPE	CAL	AMOUNT	NAME
4.24	1295.60	PH	1	4.7338E-02	54000

REDUCED TO 85% OF ORIGINAL

FIGURE 8

CORN STOVER, FORTIFIED CONTROL
PRD-541-87-SFT-153-C
SET 12 SAMPLE 22
2 uL, 0.4 mg INJECTED



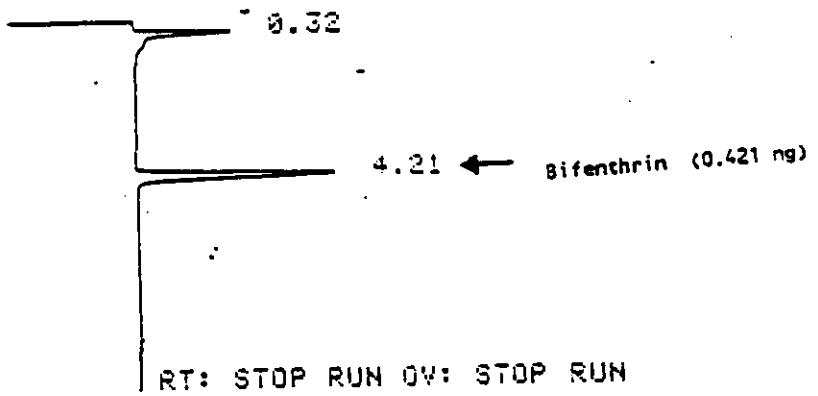
Chp1 5880A SAMPLER INJECTION @ 17:41 AUG 23, 1990
SAMPLE # : ID CODE :
9 22.2.5000
54800
ESTD

RT	AREA	TYPE	CAL	AMOUNT	NAME
4.27	10927.70	PV	1	0.370	54800

REDUCED TO 85% OF ORIGINAL

FIGURE 9

STANDARD 358-6
BIFENTHRIN
SET 12
2 uL, 0.2 ng/uL INJECTED



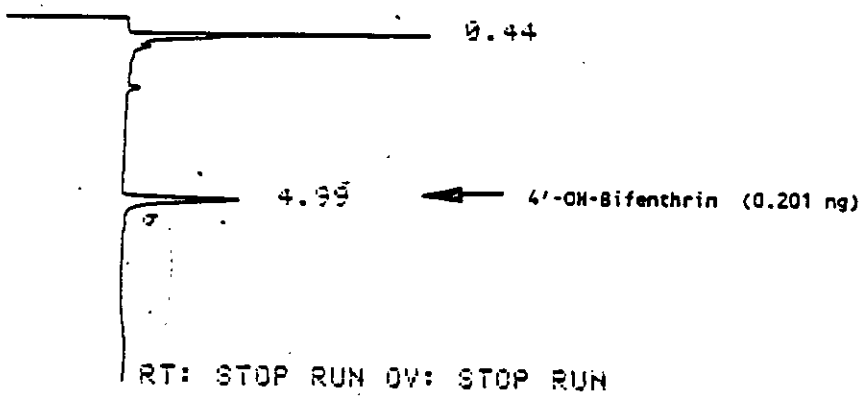
[hp] 5880A SAMPLER INJECTION @ 19:57 AUG 23, 1990
SAMPLE # : ID CODE :
14 358-6-0.4

54800
ESTD

RT	AREA	TYPE	CAL	AMOUNT	NAME
4.21	12415.10	BB	1	0.421	54800

FIGURE 10

STANDARD 349-37
4'-OH-BIFENTHRIN
SET 1
2 uL, 0.1 ng/ul INJECTED

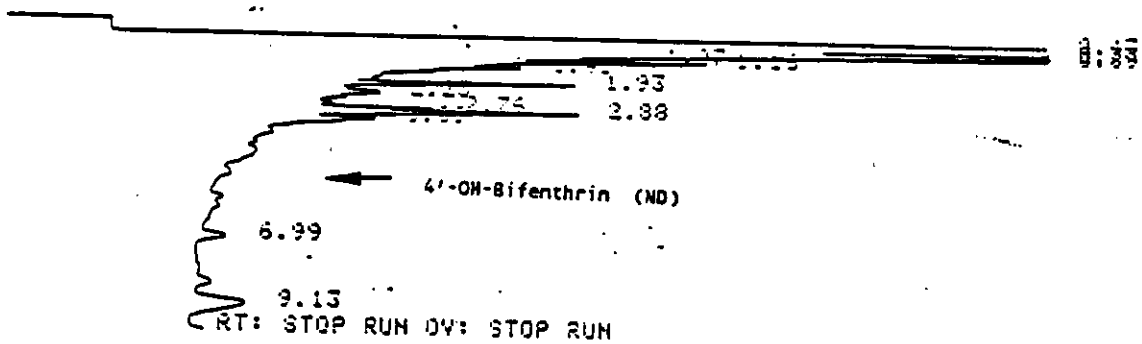


[hp] 5880A SAMPLER INJECTION @ 20:03 JUN 14, 1990
SAMPLE # : ID CODE :
10 0.1-349-37
4-54800
ESTD

RT	AREA	TYPE	CAL	AMOUNT	NAME
4.99	484.30	BH	1	0.201	4-54800

FIGURE 11

CORN GRAIN, CONTROL
PRD-383-87-JJK-8-4
SET 1 SAMPLE 5
2 uL, 4 mg INJECTED



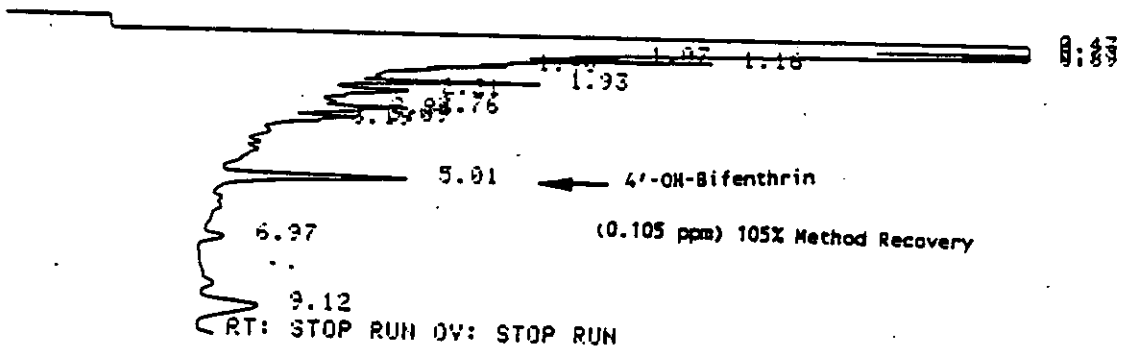
Knpl 5880A SAMPLER INJECTION @ 19:09 JUN 14, 1999
SAMPLE # : ID CODE :
3 5.2.500
METHOD ABORTED
AREA %

RT	AREA	TYPE	AREA %
0.47	30283.70	BV	48.487
0.77	14022.10	VV	22.451
0.89	4149.89	VV	6.644
1.07	1326.98	VV	2.125
1.16	3016.92	VV	4.830
1.41	1304.13	VV	2.088
1.93	1626.09	VV	2.604
2.25	1295.63	VV	2.074
2.76	914.84	VV	1.465
2.88	1824.46	VV	2.921
3.09	1966.94	VV	3.149
6.99	157.49	BP	0.252
9.13	568.42	BB	0.910

REDUCED TO 85% OF ORIGINAL

FIGURE 12

CORN GRAIN, FORTIFIED CONTROL
PRD-383-87-JJK-4-C
SET 1 SAMPLE 6
2 uL, 4 mg INJECTED



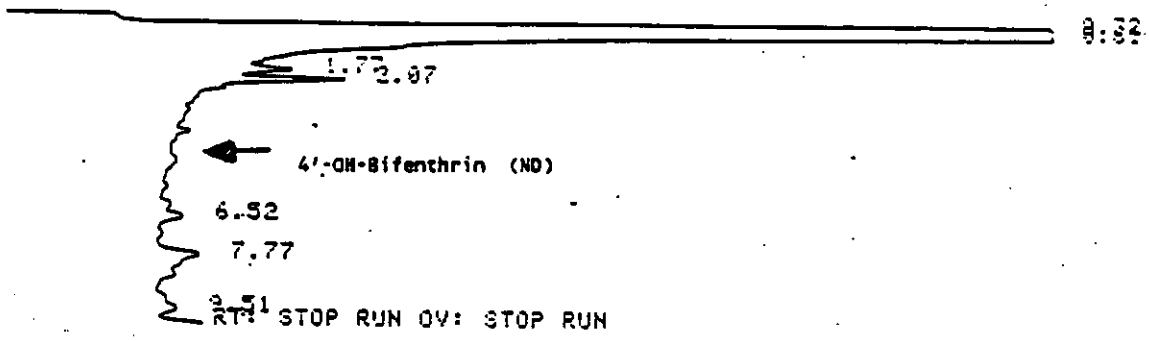
[hp] 5880A SAMPLER INJECTION @ 13:36 JUN 14, 1990
SAMPLE # : ID CODE :
9 6.2.500
4-54300
ESTD

RT	AREA	TYPE	CAL	AMOUNT	NAME
5.01	1013.63	PB	1	0.420	4-54300

REDUCED TO 85% OF ORIGINAL

FIGURE 13

CORN SILAGE, CONTROL
PRD-355-87-JJK-8-2
SET 20 SAMPLE 81
2 uL, 2 mg INJECTED



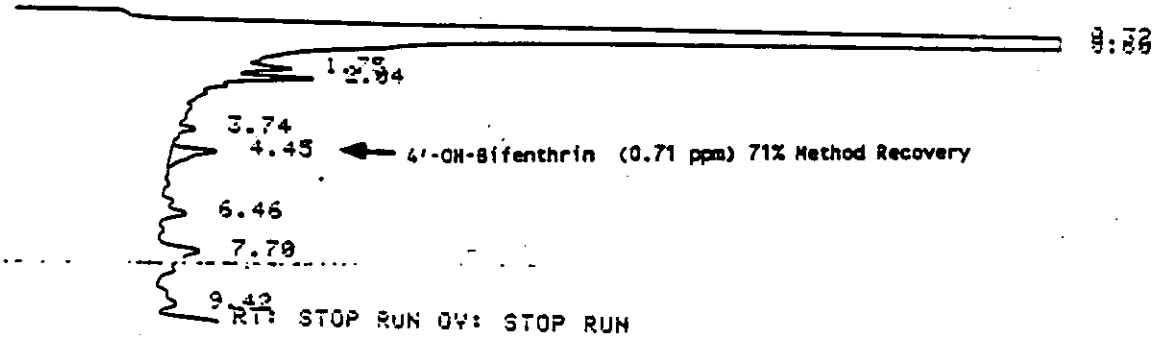
[hp] 5880A SAMPLER INJECTION @ 11:04 OCT 5, 1990
SAMPLE # : ID CODE :
2 81.2.1000
METHOD ABORTED
AREA %

RT	AREA	TYPE	AREA %
0.32	137095.00	BV	68.769
0.61	49365.70	VS	24.762
1.77	1933.23	PV	0.970
2.07	3892.83	VP	1.953
6.52	1170.12	VP	0.587
7.77	4327.57	PH	2.171
9.51	1572.47	HH	0.789

REDUCED TO 85% OF ORIGINAL

FIGURE 14

CORN SILAGE, FORTIFIED CONTROL
PRD-355-87-JJK-8-2
SET 20 SAMPLE 82
2 ul, 2 mg INJECTED



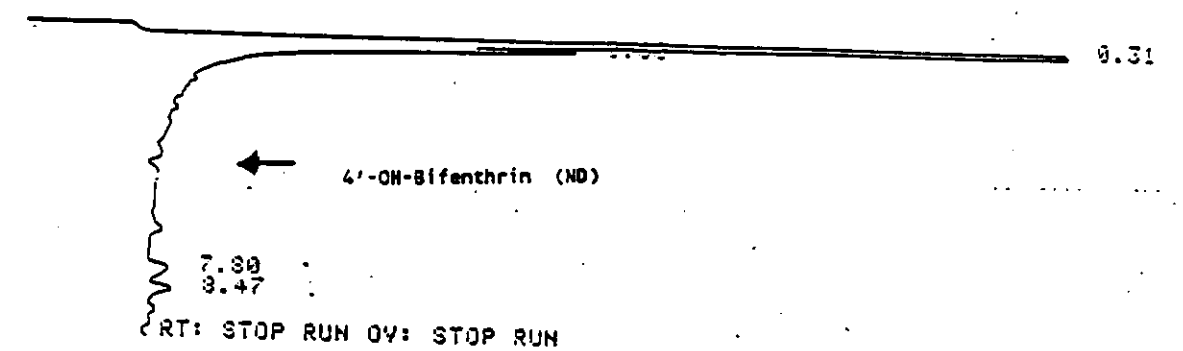
[hp] 5890A SAMPLER INJECTION @ 11:31 OCT 5, 1990
SAMPLE # : ID CODE :
3 82.2.1000
4-54300
ESTD

RT	HEIGHT	TYPE	CAL	AMOUNT	NAME
4.45	184.41	BP	1	0.142	4-54300

REDUCED TO 85% OF ORIGINAL

FIGURE 15

CORN STOVER, CONTROL
PRD-602-EVG-87-17A
SET 14 SAMPLE 37
2 uL, 0.4 mg INJECTED



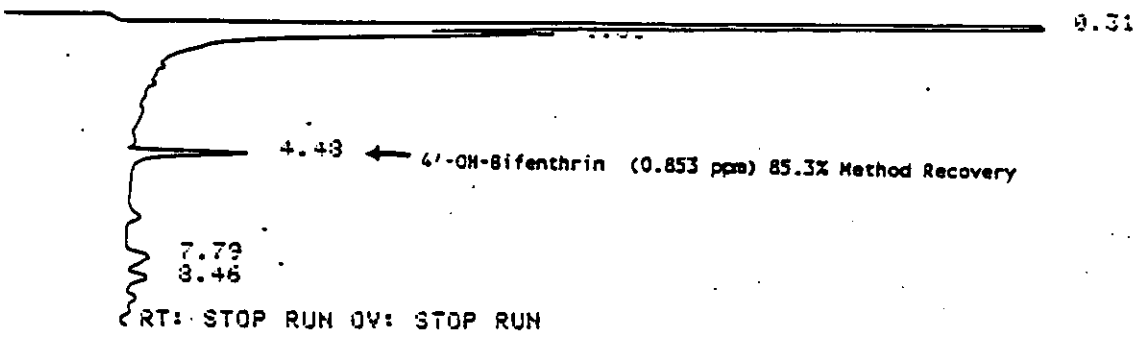
[hp] 5890A SAMPLER INJECTION @ 16:56 SEP 7, 1990
SAMPLE # : ID CODE :
8 37 A 2.5000
METHOD ABORTED
AREA %

RT	AREA	TYPE	AREA %
0.31	56110.30	BH	68.991
0.60	19351.60	HH	23.794
7.30	3319.25	HH	4.081
8.47	2549.15	HH	3.134

REDUCED TO 85% OF ORIGINAL

FIGURE 16

CORN STOVER, FORTIFIED CONTROL
PRD-602-EVG-87-17A
SET 14 SAMPLE 38
2 uL, 0.4 mg INJECTED



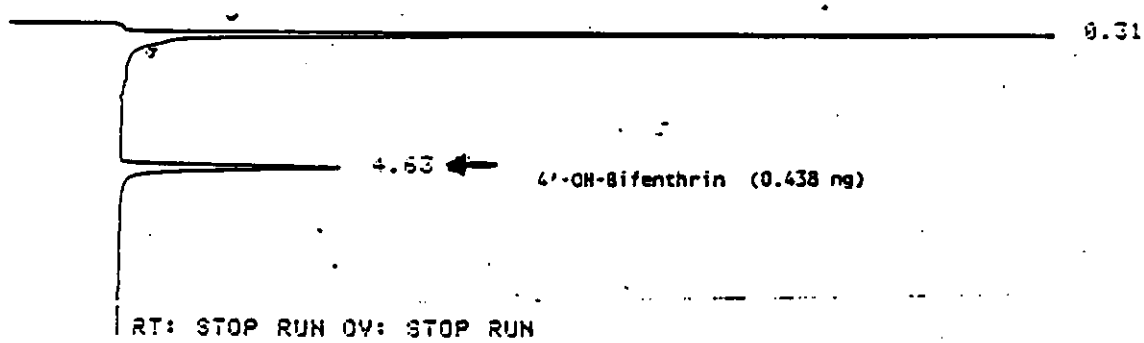
[hp] 5880A SAMPLER INJECTION @ 17:23 SEP 7, 1990
SAMPLE # : ID CODE :
9 38 A 2.5000
4-54300
ESTD

RT	AREA	TYPE	CAL	AMOUNT	NAME
4.43	2731.24	BV	1	0.341	4-54300

REDUCED TO 85% OF ORIGINAL

FIGURE 17

STANDARD 354-17
4'-OH-BIFENTHRIN
SET 12
2uL, 0.2 ng/uL INJECTED



OUT OF PAPER
[hp] 5880A SAMPLER INJECTION @ 19:56 AUG 24, 1990
SAMPLE # : ID CODE :
14 354-17-0.4
4-54300
ESTD

RT	AREA	TYPE	CAL	AMOUNT	NAME
4.63	4650.12	BB	1	9.433	4-54300

REDUCED TO 85% OF ORIGINAL