

5/8/00

129032



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF PESTICIDE PROGRAMS
ENVIRONMENTAL CHEMISTRY LABORATORY
BUILDING 1105—JOHN C. STENNIS SPACE CENTER
STENNIS SPACE CENTER, MISSISSIPPI 39529-6000
TELEPHONE (228) 688-3216 FACSIMILE (228) 688-3536

May 8, 2000

MEMORANDUM

DP Barcode: 258718

SUBJECT: Pyriproxyfen Method Evaluation-Report No. ECM0155S1-S2

FROM: *Aubry E Dupuy, Jr.*
Aubry E. Dupuy, Jr., Branch Chief
OPP/BEAD/Environmental Chemistry LaboratoryTO: Thuy Nguyen
OPP/Environmental Fate and Effects Division (7507C)
Environmental Risk BranchJohn Jordan
OPP/Environmental Fate and Effects Division (7507C)
Environmental Risk Branch

The BEAD/Environmental Chemistry Lab has performed an Environmental Chemistry Method Evaluation (ECME) on Pyriproxyfen in soil using the method, "Determination of Pyriproxyfen and PYPAC Residues in Soil and Soil Sediment".

The attached method evaluation report includes three parts:

Part I: Summary and Conclusions

In this section any problems encountered with the method and how they were handled are discussed. ECL's opinion of how well the method performed is also presented.

Part II: Analytical Results

In this section the individual results of each sample at each spiking level of each analyte is listed. The arithmetical means and descriptive statistics for each spiking level are also presented here.

Part III: Experimental Details

In this section any modification(s) that were made to the method, along with instrument parameters, spiking levels, example calculations, representative samples



2032012

and standard chromatograms and standard curves are listed and/or discussed.

If you have questions concerning this report, please contact Charles Kennedy at (228) 688-2443 or Aubry Dupuy at (228) 688-3212.

cc: Christian Byrne, QA Officer
BEAD/ECL

Charles Kennedy
BEAD/ECL

Environmental Chemistry Method Evaluation Report

Determination of Pyriproxyfen and PYPAC in Soil and Soil Sediment Method RM-33S-1-6

Report Number ECM0155S1-S2

Final Report

Environmental Chemistry Laboratory
Biological and Economic Analysis Division

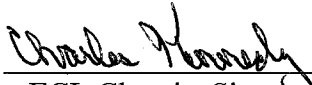
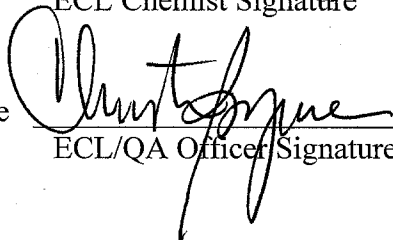
Prepared by: Charles Kennedy	 ECL Chemist Signature	<u>4/17/00</u> Date
Reviewed by: Christian Byrne	 ECL/QA Officer Signature	<u>5/2/00</u> Date

TABLE of CONTENTS

Part I Summary and Conclusions -----	Page 3
Part II Analytical Results -----	Page 4
Part III Experimental Details -----	Page 6
Appendix A: Structure of Pyriproxyfen -----	Page 36
Structure of PYPAC -----	Page 36
Appendix B: Soil Characterization -----	Page 37

Part I

Summary and Conclusions

We have completed the Environmental Chemistry Method Evaluation (ECME) "Determination of Pyriproxyfen and PYPAC Residues in Soil and Soil Sediment Method RM-33S-1-6". The method used to accomplish the analyses was submitted by Valent U.S.A. Corporation in support of registration MRID No. 440369-16.

We at ECL established that the method could be used to monitor soil for the presence of Pyriproxyfen and its degradate, PYPAC, at LOQ of 0.02 ppm and above.

Pyriproxyfen and its degradate, PYPAC, were extracted from soil. Before analysis the degradate, PYPAC, was methylated to PYPAC-Methyl ester using methyl iodide. Two separate extracts were analyzed by gas chromatography (GC), using an nitrogen phosphorus detector.

In order to evaluate this method we fortified a soil matrix with Pyriproxyfen and PYPAC at 0.01 ppm (registrant's claimed LOD), 0.02 ppm (registrant's claimed LOQ), and 0.2 ppm (10 x LOQ). All samples were extracted and analyzed in replicates of four at each fortification level. We found the precision to be well within our target limits of $\leq 20\%$ relative standard deviation (RSD) for Pyriproxyfen and its degradate at the LOQ and 10 x LOQ levels. No statistics were calculated at the LOD. Pyriproxyfen, and PYPAC had RSD's equal to 4.2%, and 3.7%, respectively, at the LOQ of 0.02 ppm and 5.6%, and 2.2%, respectively, at 0.2 ppm. The mean recoveries of Pyriproxyfen and PYPAC at 0.2 ppm (98.2%, and 94.1%, respectively) and at 0.02 ppm (97.5%, and 100.6% respectively) are also within our target range of 70% to 120%. We found the recoveries and precision to be similar to those claimed by the registrant.

Part II

EPA Analytical Results

Results:

1. Pyriproxyfen

Recovery Values for Soil Fortified at 0.01, 0.02, and 0.2 ppm in four replicates on Nitrogen Phosphorus GC Detector.

(3) Fortified (ppm)	(4) Recovery (ppm)	(5) Recovery %	(7) SD	(8) RSD %
Matrix Blk (1)	—	—	—	—
Sample#1-0.01 Sample#2-0.01 Sample#3-0.01 Sample#4-0.01 (2) Mean Recovery (6)	0.0079 0.0095 0.0087 0.0098 0.0090			
Sample#1-0.02 Sample#2-0.02 Sample#3-0.02 Sample#4-0.02 Mean Recovery	0.0202 0.0187 0.0189 0.0202 0.0195	101.0 93.5 94.5 101.0 97.5	4.06	4.17
Sample#1-0.2 Sample#2-0.2 Sample#3-0.2 Sample#4-0.2 Mean Recovery	0.1991 0.2019 0.1801 0.2044 0.1964	99.5 101.0 90.0 102.2 98.2	5.54	5.64

Part II

Results:

2. PYPAC (*PYPAC Me)

Recovery Values for Soil Fortified at 0.01, 0.02, and 0.2 ppm in four replicates on Nitrogen Phosphorus GC Detector.

(3) Fortified (ppm)	(4) Recovery (ppm)	(5) Recovery %	(7) SD	(8) RSD %
Matrix Blk (1)	--	--	--	--
Sample#1-0.01 Sample#2-0.01 Sample#3-0.01 Sample#4-0.01 (2)	0.0111 0.0109 0.0102 0.0108			
Mean Recovery (6)	0.0108			
Sample#1-0.02 Sample#2-0.02 Sample#3-0.02 Sample#4-0.02	0.0197 0.0203 0.0211 0.0194	98.3 101.6 105.5 97.2	3.73	3.71
Mean Recovery	0.0201	100.6		
Sample#1-0.2 Sample#2-0.2 Sample#3-0.2 Sample#4-0.2	0.1855 0.1927 0.1841 0.1909	92.7 96.3 92.1 95.4	2.06	2.19
Mean Recovery	0.1883	94.1		

*The molecular weight factor ($167/181 = 0.923$) to convert PYPAC-Me to PYPAC.. For example, if Sample#1-0.02 (PYPAC-Me) had a recovery value of 0.0213 ppm, then 0.923 times 0.0213 ppm equals a recovery value of 0.0197 ppm for PYPAC.

Notes:

(1) Limit of Detection (LOD), equivalent to 0.01 ppm in soil sample.

Limit of Quantitation (LOQ), equivalent to 0.02 ppm in soil sample.

The LOD and LOQ were determined by 3:1 signal to noise ratio and 10:1 signal-to-noise ratio, respectively.

(2) The four values (Sample#1, Sample#2, Sample#3, Sample#4) are replicate soil samples at each of three concentration levels of 0.01, 0.02, and 0.2 ppm.

(3) Fortified (ppm) = Pyriproxyfen, and PYPAC Fortification Levels.

(4) Recovery (ppm) = Pyriproxyfen, and PYPAC Recovery Levels in Terms of Concentration.

(5) Recovery % = Percent Recovery of Pyriproxyfen, and PYPAC as referred to in the Calculation Section.

(6) Mean Recovery = Average Percent Recovery of Sample#1, Sample#2, Sample#3 and Sample#4.

(7) SD = Standard Deviation of Percent Recovery of Four Replicate Samples of Pyriproxyfen, and PYPAC.

(8) RSD = Relative Standard Deviation of Percent Recovery of Four Replicate Samples of Pyriproxyfen and PYPAC.

Part III

Experimental Details

General description of method:

This method determines residues of Pyriproxyfen and one of its metabolites, PYPAC, in soil and soil sediment. Pyriproxyfen and PYPAC are simultaneously extracted from soil using methanol/0.1 N NaOH but are separated by partitioning with dichloromethane. The Pyriproxyfen, which is extracted into the dichloromethane phase, is cleaned-up with alumina column

chromatography and analyzed by gas chromatography using a nitrogen-phosphorus specific detector (NPD-Analytical Procedures #1). The basic aqueous phase, containing the PYPAC, is acidified and extracted with ethyl acetate and methylated with methyl iodide. After cleanup by silica gel solid phase extraction, the sample extract is analyzed by gas chromatography using a NPD (Analytical Procedures #2).

Extraction (Analytical Procedures #1)

Weigh 20 grams of soil into a French square bottle (1 pint). At this point, control samples to be used for method recoveries are fortified with Pyriproxyfen and PYPAC. Add 40 mL of methanol/0.1 N NaOH (4:1, v/v) to the sample and place on a linear shaker for 15 minutes at high speed.

Filter the sample into a 500 mL filter flask using a 9 cm Buchner funnel and 9 cm Whatman GF/A glass fiber filter paper. Rinse the bottle with 20 mL of extraction solvent and add to the Buchner funnel. Transfer the filter cake back into the French bottle and re-extract with 40 mL of methanol/0.1 N NaOH (4:1, v/v). Filter as above, combining this extract with the first extract. Rinse the French bottle with 20 mL of extraction solvent and add to the Buchner funnel.

Transfer the combined filtrates to a 500 mL round-bottom flask. Rinse the filter flask with two 20 mL portions of methanol/0.1 N NaOH (4:1, v/v) and add to the 500 mL round-bottom flask. Evaporate to approximately 20 mL using a rotary-evaporator and water bath set to <40°C.

Dichloromethane/Water Partitioning

Add 100 mL of deionized water treated with 1 gram of sodium sulfate to the round-bottom flask and swirl. Transfer the sample to a 500 mL separatory funnel, add 1 mL of Hastings-Sendroy buffer, and adjust the pH to 7 with 1 M phosphoric acid. Add 100 mL of dichloromethane to the separatory funnel using portions of this dichloromethane to rinse the round-bottom flask. Shake for approximately 1 minute and drain the lower dichloromethane layer through a 10 cm filter funnel containing approximately 50 grams of sodium sulfate, suspended on a glass wool plug, into a 500 mL round-bottom flask.

Add 100 mL of dichloromethane to the separatory funnel and partition as above. Drain the lower dichloromethane layer through the filter funnel containing the sodium sulfate into the 500 mL round-bottom flask containing the first extract. Rinse the sodium sulfate with two 10 mL of dichloromethane. Save the upper aqueous layer for PYPAC analysis. Evaporate the combined dichloromethane layers, containing the Pyriproxyfen residues, to dryness using a rotary-evaporator and water bath set to <40°C.

Alumina Column Cleanup

Place a glass wool plug at the bottom of the glass chromatography column. Close the column stopcock and add 25 mL of hexane:ethyl acetate (10:1, v/v) to the column. Measure 10 mL of alumina in a 10 mL graduated cylinder and slowly add to the column while gently tapping the side of the column. Rinse the alumina down the column wall with hexane:ethyl acetate (10:1, v/v). Measure 1-3 mL of sodium sulfate in the 10 mL graduated cylinder and add to the top of the column. Open the column stopcock and allow the solvent to drain to the top of the column. Discard the eluant.

Add 3 mL of hexane-ethyl acetate (10:1, v/v) to the round-bottom flask containing the sample extract. Swirl and sonicate for 15 seconds to dissolve the residue and transfer to the top of the column using a Pasteur pipet. Rinse the flask with three 3 mL portions of hexane:ethyl acetate (10:1, v/v) and transfer each rinse to the top of the column. Drain the solvent to the top of the sodium sulfate layer after each rinse. Discard this eluant (a total of 12 mL).

Place a 100 mL round-bottom flask under the column and elute the Pyriproxyfen with 28 mL of hexane:ethyl acetate (10:1, v/v). Evaporate the eluate to dryness using a rotary-evaporator and water bath set to $<40^{\circ}\text{C}$. Add 2 mL of toluene to the flask containing the dried sample residue. Swirl and sonicate for 15 seconds to completely dissolve the residue. Transfer the extract to a screw cap vial using a Pasteur pipet and store at $\leq 0^{\circ}\text{C}$ until GC analysis.

Extraction (Analytical Procedures #2)

Add 3 mL of 1 N HCL to the aqueous phase in the separatory funnel containing the PYPAC residues from the dichloromethane/water partitioning step, (Analytical Procedures #1). Stopper the funnel and shake gently to mix completely.

Add 100 mL of ethyl acetate to the separatory funnel and shake for approximately one minute. Drain the lower aqueous layer into the original 500 mL round-bottom flask. Pour the upper ethyl acetate layer into a clean 500 mL round-bottom flask through a 10 cm filter funnel containing approximately 20 grams of sodium sulfate, suspended on a plug of glass wool.

Return the aqueous phase to the separatory funnel, add 200 mL of ethyl acetate and partition as above. Discard the lower aqueous layer. Pour the upper ethyl acetate layer through the 10 cm filter funnel containing the sodium sulfate into the 500 mL round-bottom flask containing the first extract.

Methylation

Evaporate the combined ethyl acetate layers to approximately 5 mL using a rotary-evaporator and water bath set to $<30^{\circ}\text{C}$. Transfer the extract to a 50 mL round-bottom flask using three 5 mL portions of acetone and a Pasteur pipet. Evaporate the acetone just to dryness using a rotary-evaporator.

Remove the flask from the evaporator and transfer the extract to a 5 mL reaction vial using three 1 mL portions of acetone and a Pasteur pipet. Evaporate to approximately 1 mL using the N-Evap and a gentle stream of nitrogen.

Add 50 μL of TBAH followed by 100 μL of methyl iodide to the reaction vial. Cap the vial and vortex briefly, and heat to $45\text{-}50^{\circ}\text{C}$ in a dry bath for 2 hours. At the end of the reaction period, remove the vial and cool to room temperature. Add 50 μL of 1-octanol to the vial, vortex briefly, and carefully evaporate the acetone to approximately 0.3 mL under a extremely gentle stream of nitrogen. Add 1 mL of hexane:ethyl acetate (5:2, v/v) and vortex for 15 seconds.

Silica Gel SPE Cleanup

Attach a Bakerbond SPE® silica gel disposable column to the vacuum manifold. Pre-condition the column with 10 mL of hexane at a flow rate of < 5 mL/minute.

Place a 10 mL collection tube under the column. Transfer the sample extract to the column and collect until the solvent reaches the top of the packing. Use no vacuum during the sample application and elution steps; use a gravity flow only. Rinse the reaction vial with three 1 mL portions of hexane:ethyl acetate (5:2, v/v) and transfer each portion to the column. Dilute the extract to volume with hexane:ethyl acetate (5:2, v/v) before GC analysis.

Table 1 (page 10) summarizes the retention times observed for the HP 6890 gas chromatograph with an NPD detector.

The chemical structures of Pyriproxyfen, PYPAC, and PYPAC Methyl ester are shown in Appendix A.

Modification to method:

No modification necessary

Sources of analytical reference standards:

Pyriproxyfen and its degradate analytical standards were obtained from Valent U.S.A. Corporation, 1333 N. California Blvd., Walnut Creek, CA. Inc., Telephone (925) 280-2028.

1. Pyriproxyfen: Lot# AS-1723b, 100% purity, Expiration Date: 02/17/2000
2. PYPAC: Lot# AS-1725b, 99.8% purity, *Expiration Date: 10/10/99
*The Analytical Reference Standard PYPAC Lot# AS1725b characterization was certified again October 25, 1999. 99.4% purity, Expiration Date: 10/14/2000
3. PYPAC Methyl ester: Lot# A-1729c, 99.7% purity, Expiration Date: 10/27/2000

Source of sample matrix:

The soil (Batch 3A) used was obtained from Iowa State University and was characterized by A&L Analytical Laboratories. A copy of the characterization report is included in Appendix B.

Instrumentation for quantitation (listed only if different from that listed in method)

Hewlett Packard 6890 ChemStation with Auto Injector and GC NPD.

Instrumentation for confirmation: Not applicable.

Relative retention parameters for the present evaluation:

Table 1

Analyte	Chemical Abstracts Registry No.	Retention Time (minutes)
Pyriproxyfen	V-Arc-767	4.7
PYPAC, Methyl ester	V-Arc-730	5.0

Notes on analytical procedures:

ECL found the method to work well for Pyriproxyfen, and its degradate PYPAC (PYPAC Methyl ester). ECL observed a very good linear relationship between concentration versus detector response and used a standard linear regression curve for all calculations.

Comments:

Completion of a set (seven samples) required 37 man hours over a course of 6 days to complete setup, extraction, partition, methylation, SPE cleanup, alumina cleanup, and 5 hours for GC analysis and data analysis for Pyriproxyfen and PYPAC Methyl ester (PYPAC).

(a) Calibration

The HP 6890 EC gas chromatograph was calibrated with Pyriproxyfen at concentrations of 0.1 µg/mL, 0.2 µg/mL, 0.6 µg/mL and 2.0 µg/mL. PYPAC Methyl ester (PYPAC) was calibrated at concentrations of 0.02 µg/mL, 0.04 µg/mL, 0.12 µg/mL and 0.4 µg/mL. The correlation coefficients were 0.99998 (Pyriproxyfen), and 0.99978 (PYPAC Methyl ester).

(b) Calculation Curve

1. Standard Curve

A standard curve was constructed by linear regression analysis of concentration of external standard (µg/mL) versus peak height count for each analyte. The recovery concentration of the analyte (µg/mL) in fortified soil was determined from the linear regression equation for the analyte. The calibration curve is constructed using the concentration on the X-axis and the response (peak height) on the Y-axis. The regression equation is: $Y = mX + b$

Where: Y = peak height count
X = concentration of extract
m = slope of calibration curve
b = Y-intercept

2. Calculation of Analytes in Samples

- a. Pyriproxyfen, and its degradate calibration curve were used to calculate the concentration of Pyriproxyfen and its degradate in each fortified sample extract using the regression equations calculated from the standards which are analyzed as part of the analytical set.

$$X(\text{conc. of analyte}) = \frac{(\text{Peak Height of Sample}) - (\text{y intercept})}{\text{Slope}}$$

(in extract)

- b. Then to find the concentration of the analyte in the sample use the formula:

$$\text{Conc. in Sample} = X [V/W]$$

where: X = conc. of analyte in sample extract (µg/mL)
V = final volume of extract (2 mL for Pyriproxyfen at LOD, LOQ, and at 10 x LOQ)
(10 mL for PYPAC Methyl ester (PYPAC) at LOD, LOQ,
10 x LOQ)
W = weight of sample extracted (20 g)

3. Example Calculation

To manually calculate the concentration of Pyriproxyfen, and PYPAC in a soil sample, use the calibration curve equation to find the concentration of analyte in the sample extract. Then apply the formula in Section b-2 to find the concentration of analyte in the sample.

Sample: Run#1 @ 0.02 ppm for Pyriproxyfen

Calibration curve equation is $Y = 11.75190X + 6.34901e-3$

Peak Height of Pyriproxyfen is 2.38059

Sample wt. is 20.0 g, final vol. is 2 mL

Substitute for Y, $2.38 = 11.75X + 0.0063$

$$X = (2.38 - 0.0063)/11.75$$

$$X = 0.2020 \mu\text{g/mL}$$

$$\text{Conc. in sample: } X = \frac{0.2020 \mu\text{g}}{\text{mL}} \left[\frac{2 \text{ mL}}{20 \text{ g}} \right] = \frac{0.0202 \mu\text{g}}{\text{g}} \text{ or } 0.0202 \text{ ppm}$$

$$\text{Percent recovery: } \frac{0.0202 \text{ ppm}}{0.02 \text{ ppm}} \times 100 = 101.0\%$$

Sample: Run#1 @ 0.02 ppm for PYPAC (PYPAC Methyl ester)

Calibration curve equation is $Y = 26.79038X - 1.83253e-1$

Peak Height of PYPAC is 0.957779

Sample wt. is 20.0 g, final vol. is 10 mL

Substitute for Y, $0.9578 = 26.79X - 0.1833$

$$X = (0.958 + 0.1833)/26.79$$

$$X = 0.0426 \text{ ng/mL}$$

$$\text{Conc. in sample } X = \frac{0.0426 \text{ ng}}{\text{mL}} \left[\frac{10 \text{ mL}}{20 \text{ g}} \right] [*0.923] = \frac{0.0197 \text{ ng}}{\text{g}} \text{ or } 0.0197 \text{ ppm}$$

$$\text{Percent recovery: } \frac{0.0197 \text{ ppm}}{0.02 \text{ ppm}} \times 100 = 98.3\%$$

*To find the ppm of PYPAC in the methylated extracts (total PYPAC Methyl ester ppm in methylated extract) times (molecular weight conversion 0.923) = PYPAC in ppm.

Chromatograms and Linear Regression Curves

A. Pyriproxyfen Calibration Standard Analyzed by GC NPD at 0.1 $\mu\text{g/mL}$, 0.2 $\mu\text{g/mL}$, 0.6 $\mu\text{g/mL}$, and 2.0 $\mu\text{g/mL}$.

A-1: 0.1 $\mu\text{g/mL}$ (equivalent to 0.01 ppm in soil)

A-2: 0.2 $\mu\text{g/mL}$ (equivalent to 0.02 ppm in soil)

A-3: 0.6 $\mu\text{g/mL}$ (equivalent to 0.06 ppm in soil)

A-4: 2.0 $\mu\text{g/mL}$ (equivalent to 0.2 ppm in soil)

B. PYPAC (PYPAC Methyl ester) Calibration Standard Analyzed by GC NPD at 0.02 $\mu\text{g/mL}$, 0.04 $\mu\text{g/mL}$, 0.12 $\mu\text{g/mL}$, and 0.4 $\mu\text{g/mL}$.

B-1: 0.02 $\mu\text{g/mL}$ (equivalent to 0.01 ppm in soil)

B-2: 0.04 $\mu\text{g/mL}$ (equivalent to 0.02 ppm in soil)

B-3: 0.12 $\mu\text{g/mL}$ (equivalent to 0.06 ppm in soil)

B-4: 0.4 $\mu\text{g/mL}$ (equivalent to 0.2 ppm in soil)

C. Linear Regression Curve for Pyriproxyfen at 0.1 $\mu\text{g/mL}$ (0.01 ppm), 0.2 $\mu\text{g/mL}$ (0.02 ppm), 0.6 $\mu\text{g/mL}$ (0.06 ppm), and 2.0 $\mu\text{g/mL}$ (0.2 ppm).

D. Linear Regression Curve for PYPAC (PYPAC Methyl ester) 0.02 $\mu\text{g/mL}$ (0.01 ppm), 0.04 $\mu\text{g/mL}$ (0.02 ppm), 0.12 $\mu\text{g/mL}$ (0.06 ppm), and 0.4 $\mu\text{g/mL}$ (0.2 ppm)

E. Pyriproxyfen Fortification at 0.01 ppm (0.1 $\mu\text{g/mL}$) Analyzed by GC NPD.

E-1: Matrix Blank.

E-2: Pyriproxyfen Sample #1 Fortified Soil.

F. Pyriproxyfen Fortification at 0.02 ppm (0.2 $\mu\text{g/mL}$) Analyzed by GC NPD.

F-1: Matrix Blank.

F-2: Pyriproxyfen Sample #1 Fortified Soil.

G. Pyriproxyfen Fortification at 0.2 ppm (2.0 $\mu\text{g/mL}$) Analyzed by GC NPD.

G-1: Matrix Blank.

G-2: Pyriproxyfen Sample #1 Fortified Soil.

H. PYPAC (PYPAC Me ester) Fortification at 0.01 ppm (0.02 $\mu\text{g/mL}$) Analyzed by GC NPD

H-1: Matrix Blank

H-2: PYPAC Sample #1

I. PYPAC (PYPAC Me ester) Fortification at 0.02 ppm (0.04 $\mu\text{g/mL}$) Analyzed by GC NPD.

I-1: Matrix Blank

I-2: PYPAC Sample #1

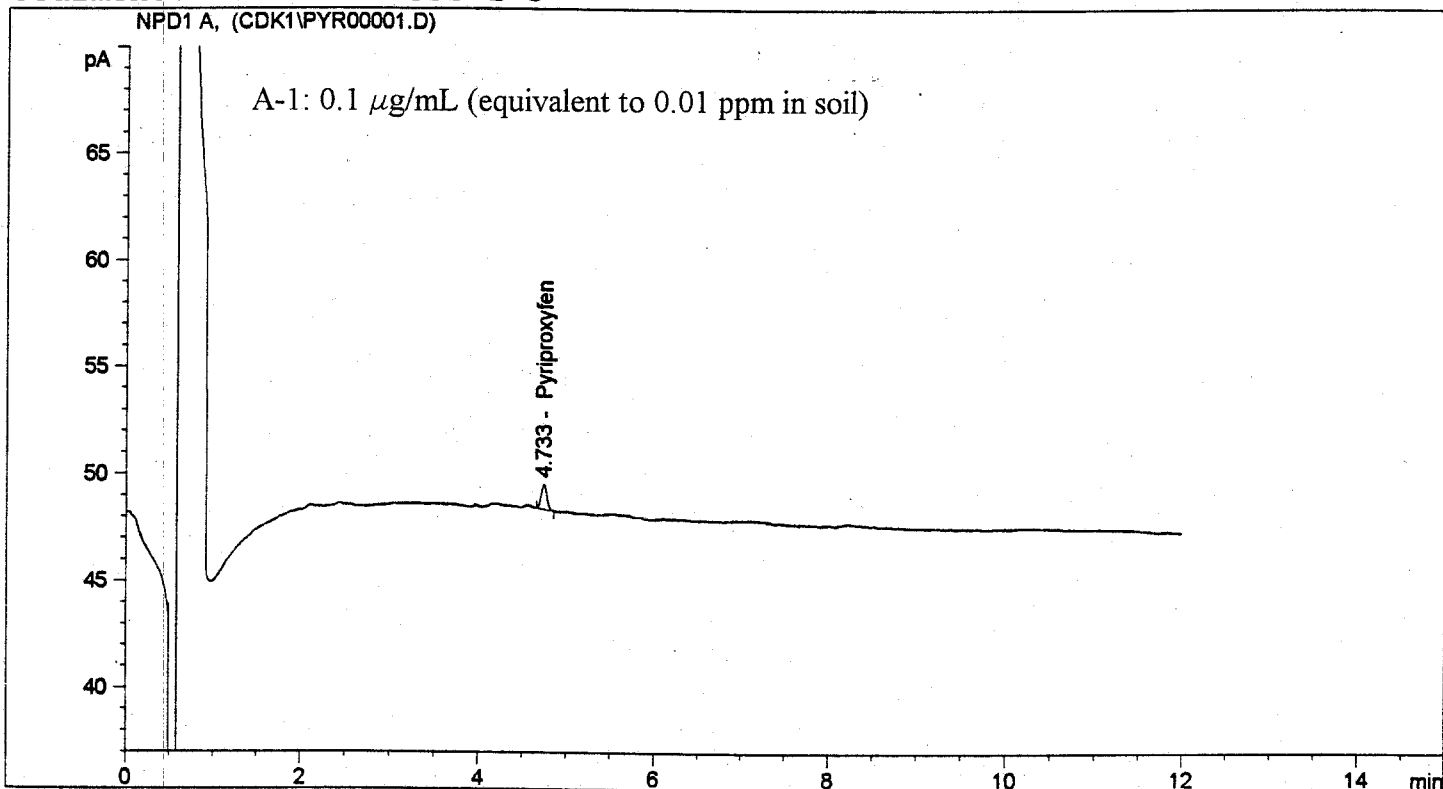
J. PYPAC (PYPAC Me ester) Fortification at 0.2 ppm (0.4 $\mu\text{g/mL}$) Analyzed by GC NPD.

J-1: Matrix Blank

J-2: PYPAC Sample #1

A. Pyriproxyfen Calibration Standard Analyzed by GC NPD at 0.1 $\mu\text{g/mL}$, 0.2 $\mu\text{g/mL}$, 0.6 $\mu\text{g/mL}$, and 2.0 $\mu\text{g/mL}$.

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



External Standard Report

Sorted By : Signal
 Calib. Data Modified : Friday, November 19, 1999 7:01:25 AM
 Multiplier : 1.0000
 Dilution : 1.0000

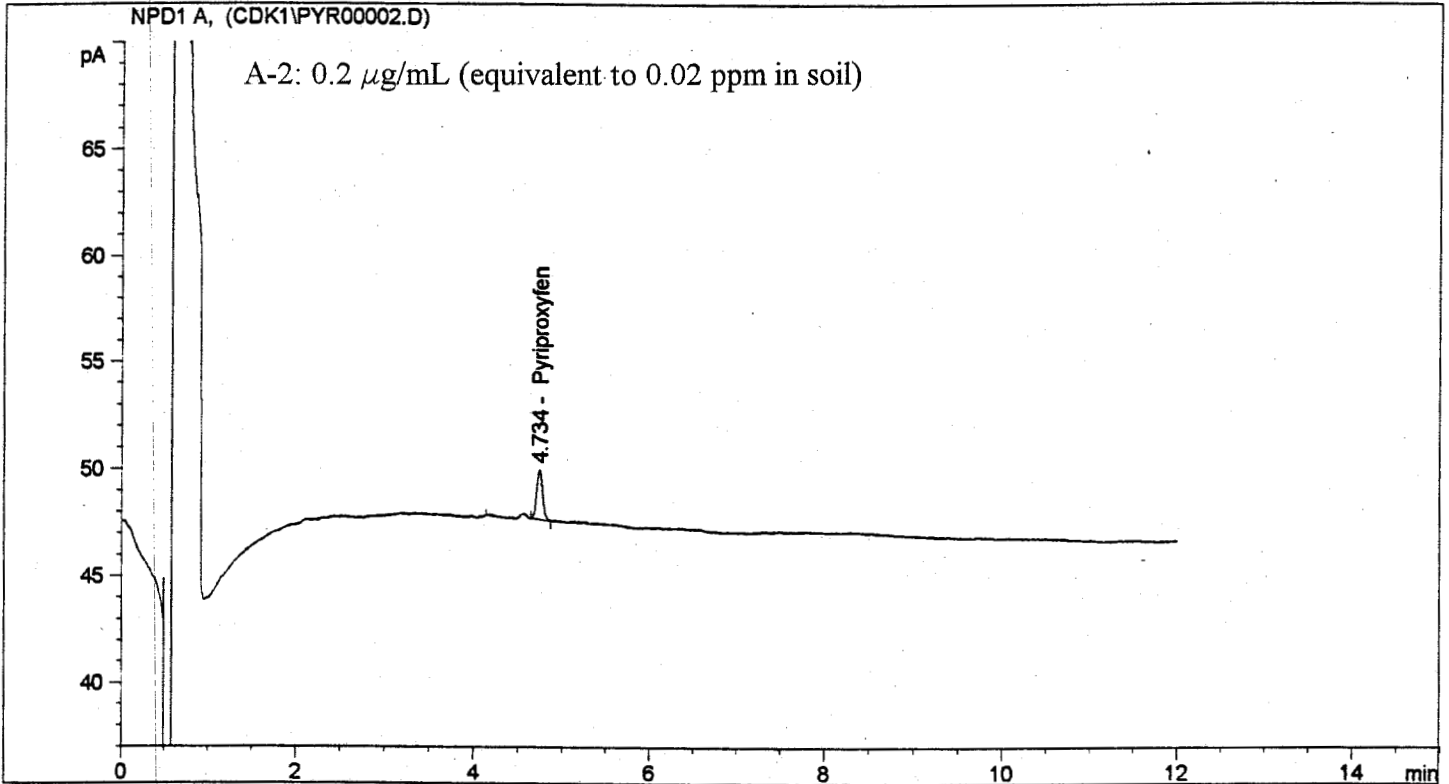
Signal 1: NPD1 A,

RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
4.733	BP	1.15444	8.46247e-2	9.76942e-2		Pyriproxyfen

Totals : 9.76942e-2

Results obtained with enhanced integrator!

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Friday, November 19, 1999 7:01:25 AM
 Multiplier : 1.0000
 Dilution : 1.0000

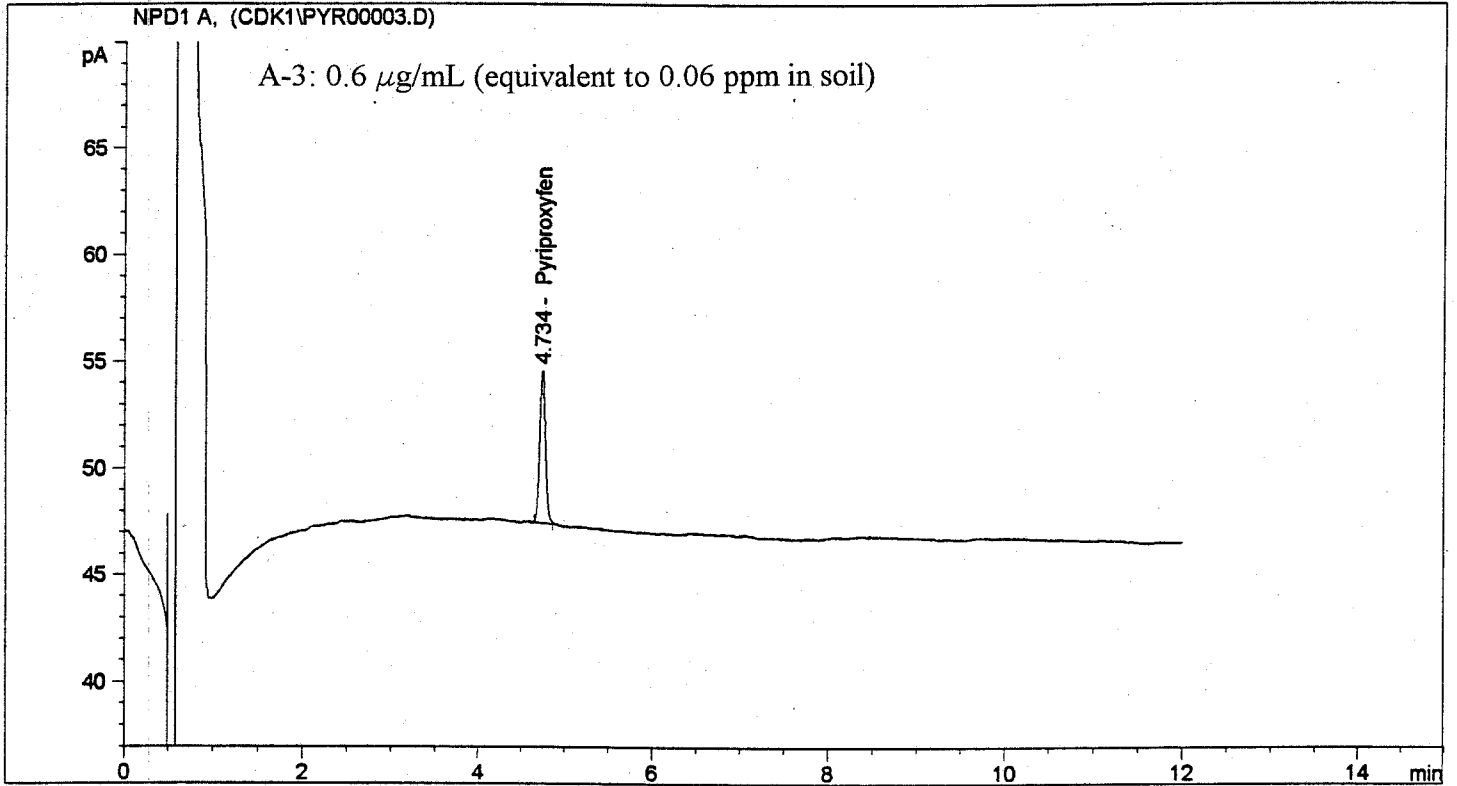
Signal 1: NPD1 A,

RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
4.734	PP	2.31593	8.48594e-2	1.96529e-1		Pyriproxyfen

Totals : 1.96529e-1

Results obtained with enhanced integrator!

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Friday, November 19, 1999 7:01:25 AM
 Multiplier : 1.0000
 Dilution : 1.0000

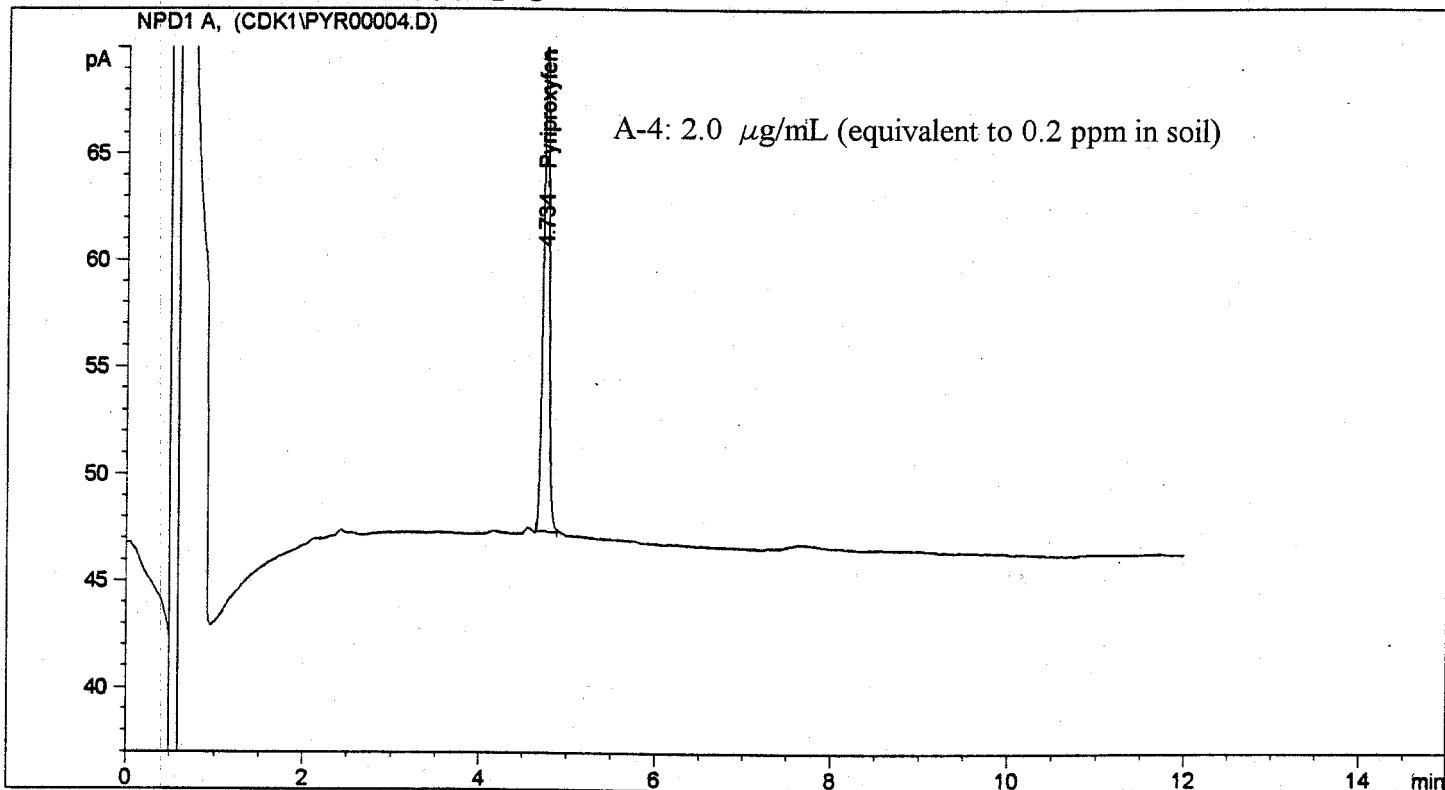
Signal 1: NPD1 A,

RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
4.734	BB	7.14671	8.50171e-2	6.07592e-1		Pyriproxyfen

Totals : 6.07592e-1

Results obtained with enhanced integrator!

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Friday, November 19, 1999 7:01:25 AM
 Multiplier : 1.0000
 Dilution : 1.0000

Signal 1: NPD1 A,

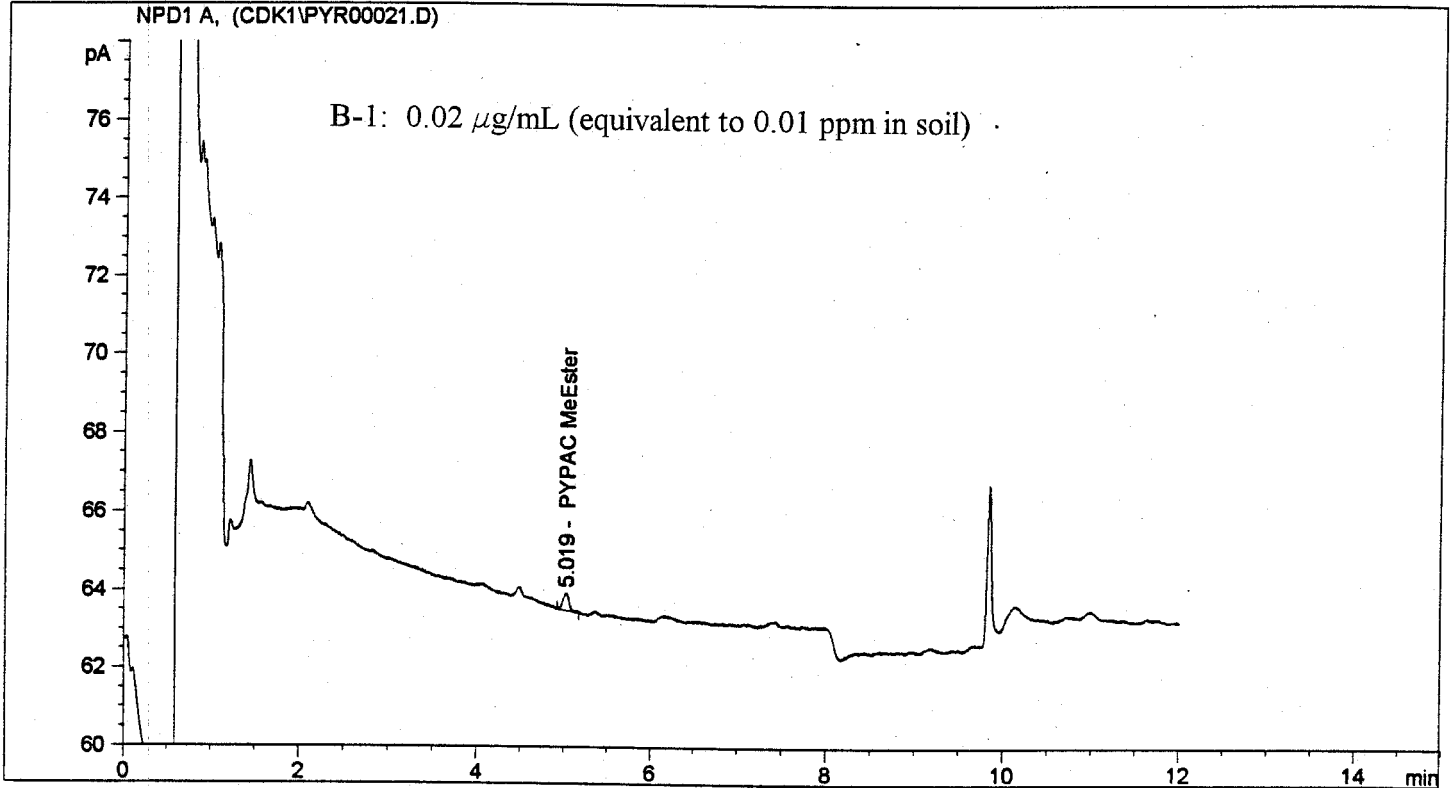
RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
4.734	BB	23.48881	8.50697e-2	1.99818		Pyriproxyfen

Totals : 1.99818

Results obtained with enhanced integrator!

B. PYPAC (PYPAC Methyl ester) Calibration Standard Analyzed by GC NPD at 0.02 $\mu\text{g/mL}$,
 0.04 $\mu\text{g/mL}$, 0.12 $\mu\text{g/mL}$, and 0.4 $\mu\text{g/mL}$.

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil
 Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Monday, November 22, 1999 8:37:21 AM
 Multiplier : 1.0000
 Dilution : 1.0000

Signal 1: NPD1 A,

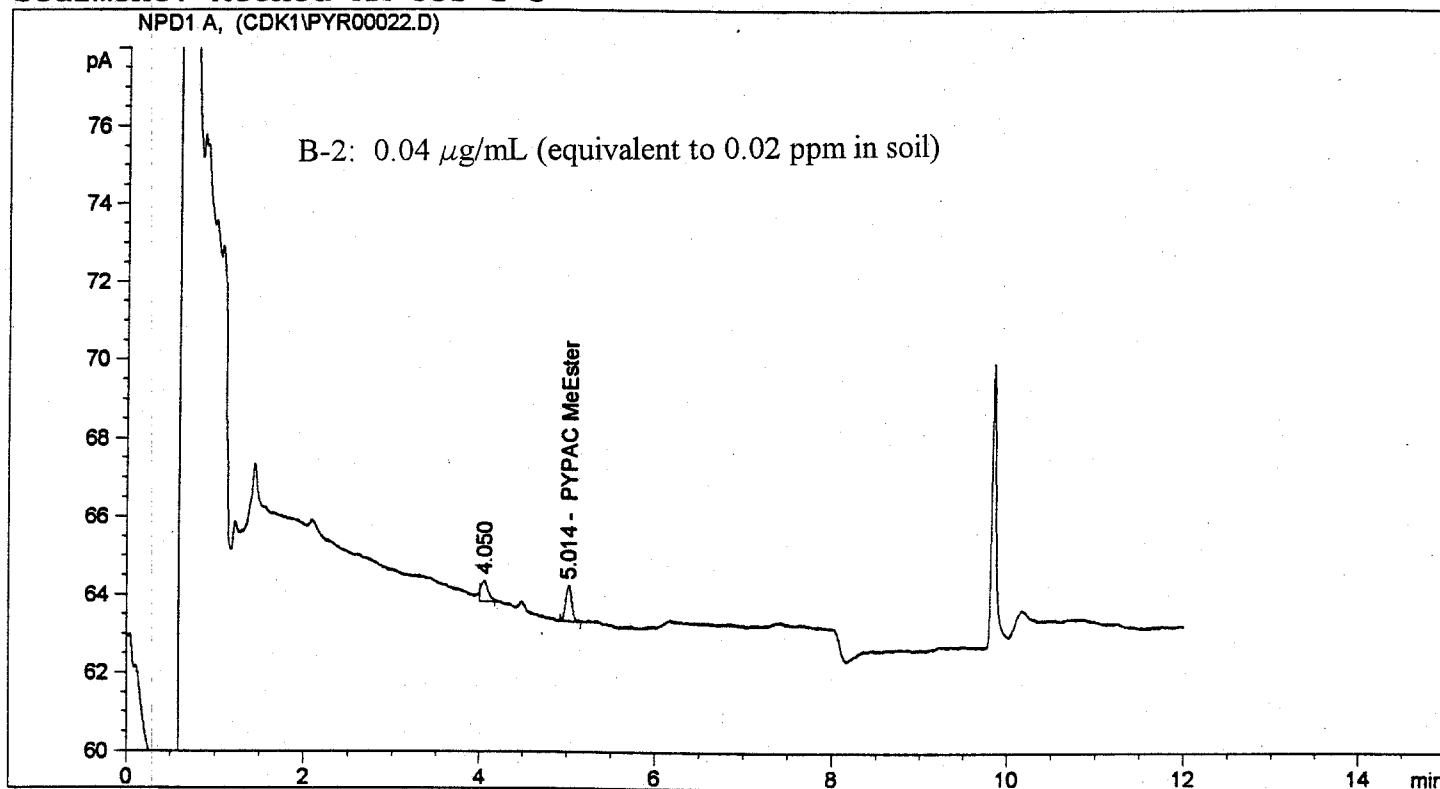
RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
5.019	PB	4.36287e-1	5.30052e-2	2.31255e-2		PYPAC MeEster

Totals : 2.31255e-2

Results obtained with enhanced integrator!

=====

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Monday, November 22, 1999 8:37:21 AM
 Multiplier : 1.0000
 Dilution : 1.0000

Signal 1: NPD1 A,

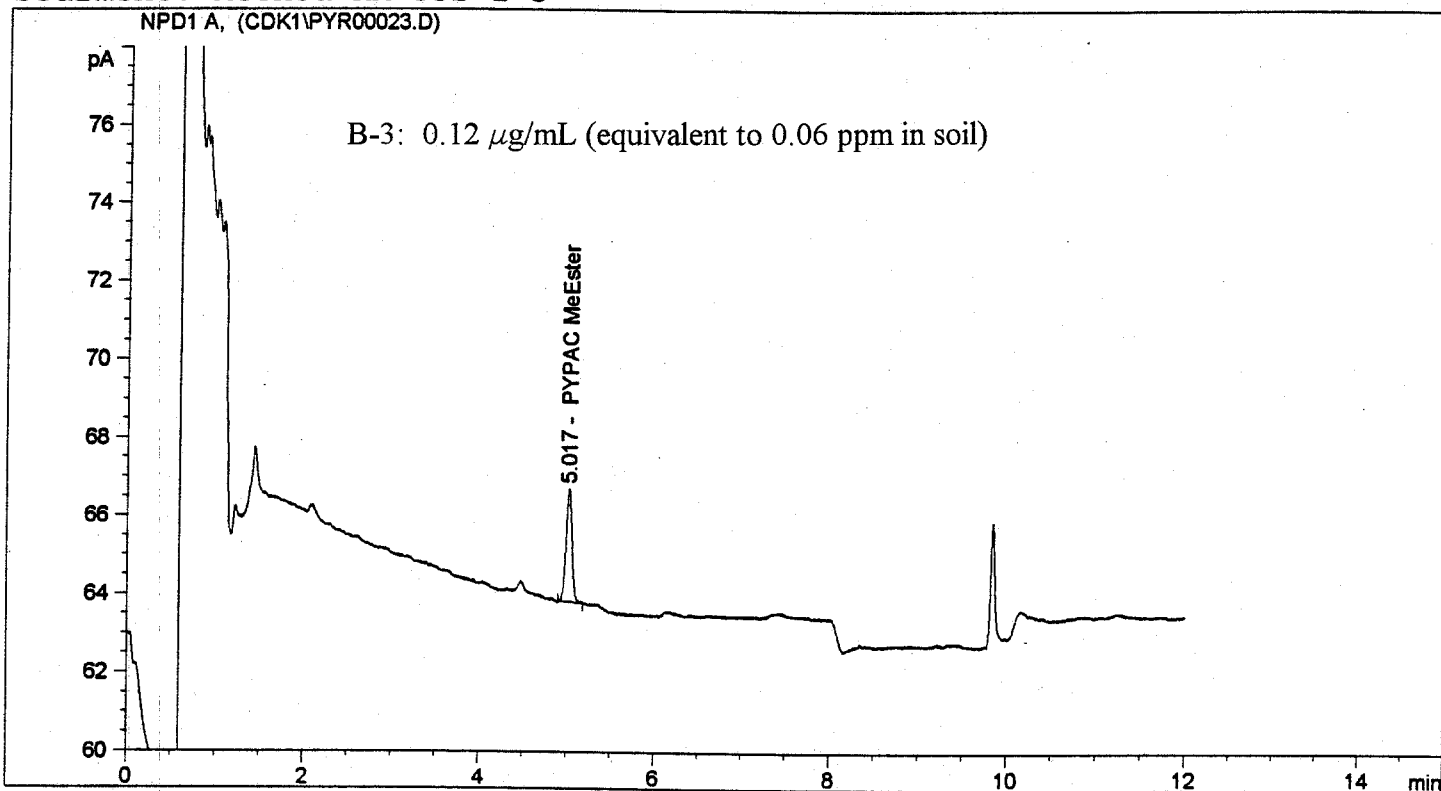
RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
5.014	PP	9.12284e-1	4.48248e-2	4.08929e-2		PYPAC MeEster

Totals : 4.08929e-2

Results obtained with enhanced integrator!

=====

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Monday, November 22, 1999 8:37:21 AM
 Multiplier : 1.0000
 Dilution : 1.0000

Signal 1: NPD1 A,

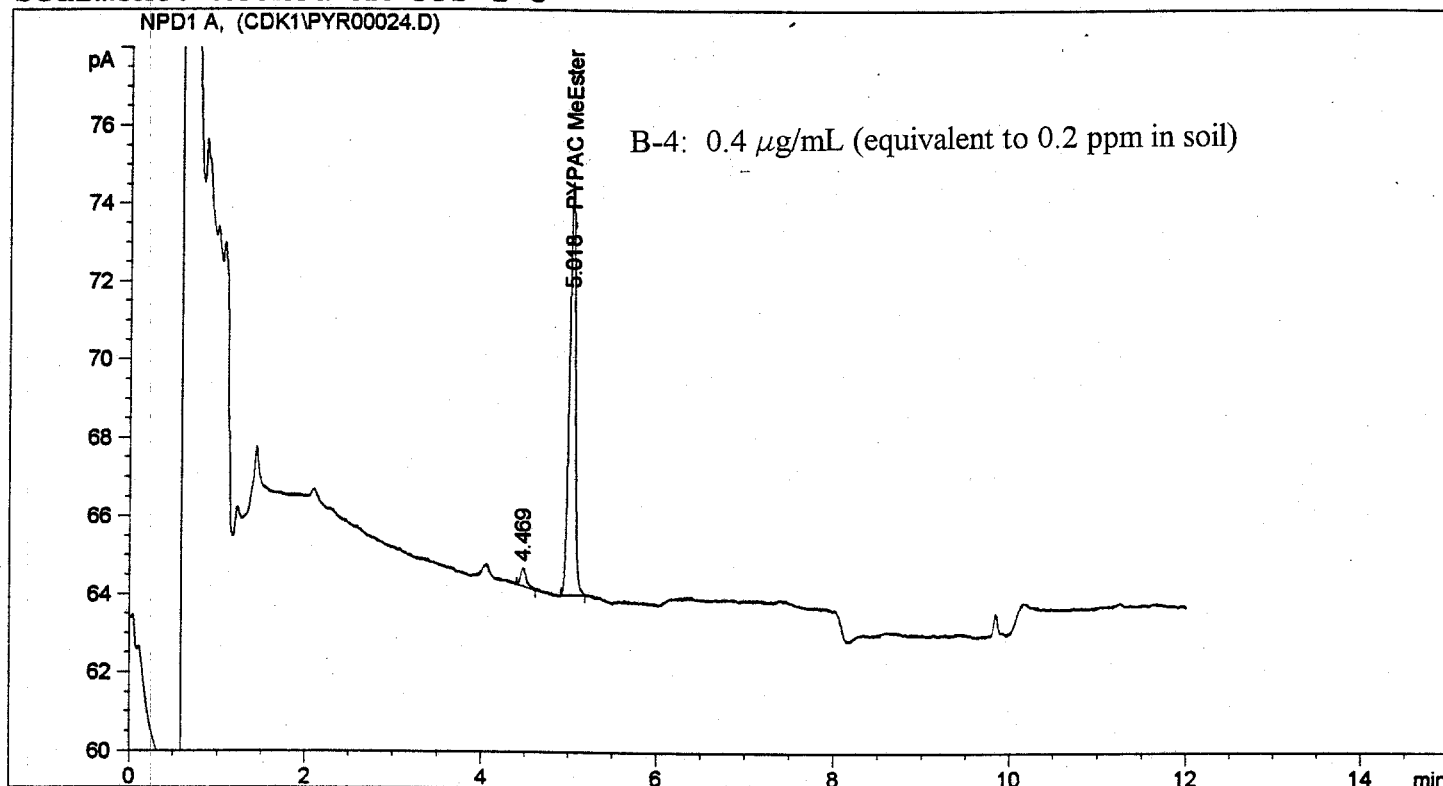
RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
5.017	PP	2.88720	3.96960e-2	1.14610e-1		PYPAC MeEster

Totals : 1.14610e-1

Results obtained with enhanced integrator!

=====

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Monday, November 22, 1999 8:37:21 AM
 Multiplier : 1.0000
 Dilution : 1.0000

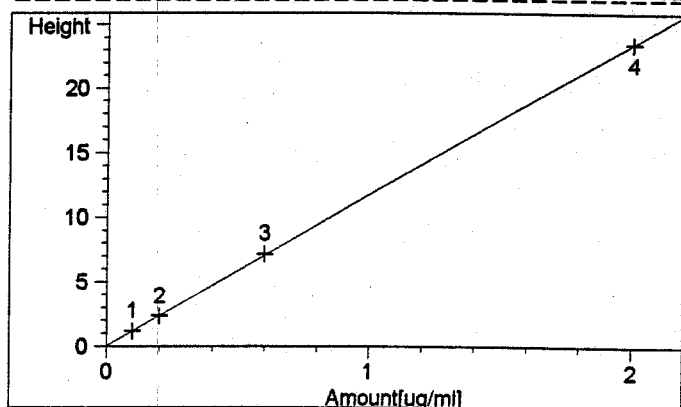
Signal 1: NPD1 A,

RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
5.018	BB	10.56964	3.79740e-2	4.01371e-1		PYPAC MeEster

Totals : 4.01371e-1

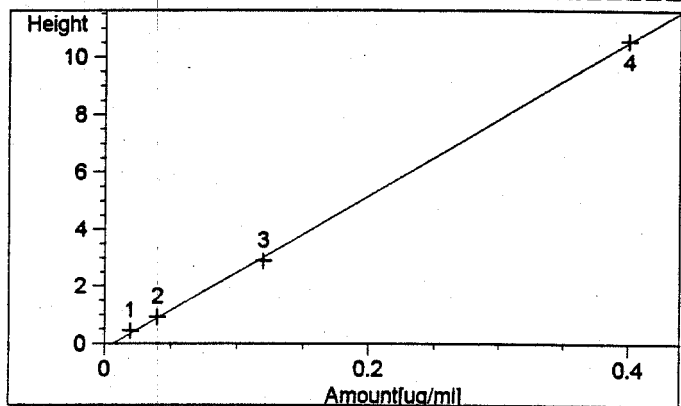
Results obtained with enhanced integrator!
 =====

C. Linear Regression Curve for Pyriproxyfen at 0.1 $\mu\text{g/mL}$ (0.01 ppm), 0.2 $\mu\text{g/mL}$ (0.02 ppm), 0.6 $\mu\text{g/mL}$ (0.06 ppm), and 2.0 $\mu\text{g/mL}$ (0.2 ppm).



Pyriproxyfen at exp. RT: 4.734
NPD1 A,
Correlation: 0.99998
Residual Std. Dev.: 0.07354
Formula: $y = mx + b$
m: 11.75190
b: 6.34901e-3
x: Amount [$\mu\text{g/mL}$]
y: Height

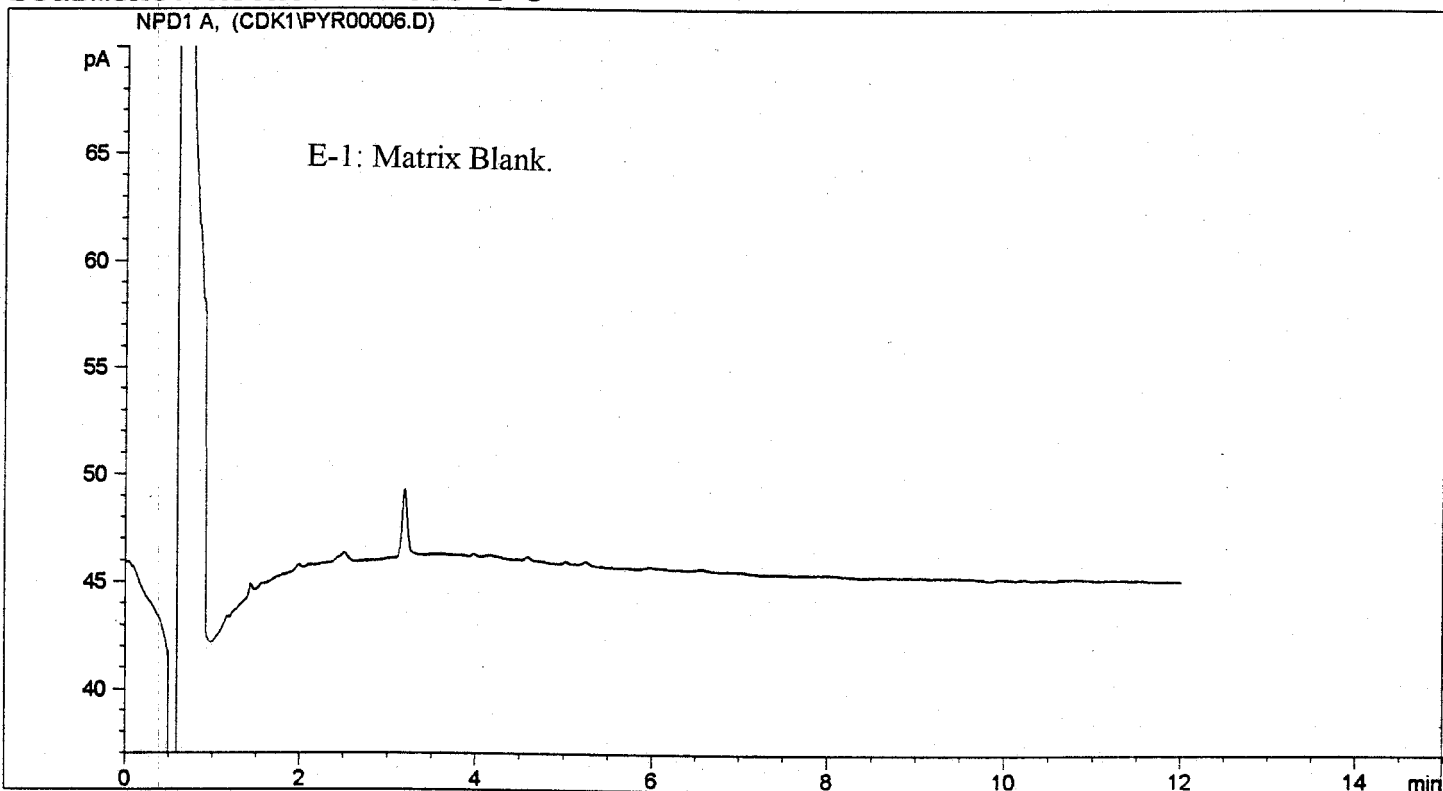
D. Linear Regression Curve for PYPAC (PYPAC Methyl ester) 0.02 $\mu\text{g/mL}$ (0.01 ppm), 0.04 $\mu\text{g/mL}$ (0.02 ppm), 0.12 $\mu\text{g/mL}$ (0.06 ppm), and 0.4 $\mu\text{g/mL}$ (0.2 ppm)



PYPAC MeEster at exp. RT: 5.018
NPD1 A,
Correlation: 0.99978
Residual Std. Dev.: 0.12203
Formula: $y = mx + b$
m: 26.79038
b: -1.83253e-1
x: Amount [$\mu\text{g/mL}$]
y: Height

E. Pyriproxyfen Fortification at 0.01 ppm (0.1 µg/mL) Analyzed by GC NPD.

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



External Standard Report

Sorted By : Signal
 Calib. Data Modified : Friday, November 19, 1999 7:01:25 AM
 Multiplier : 1.0000
 Dilution : 1.0000

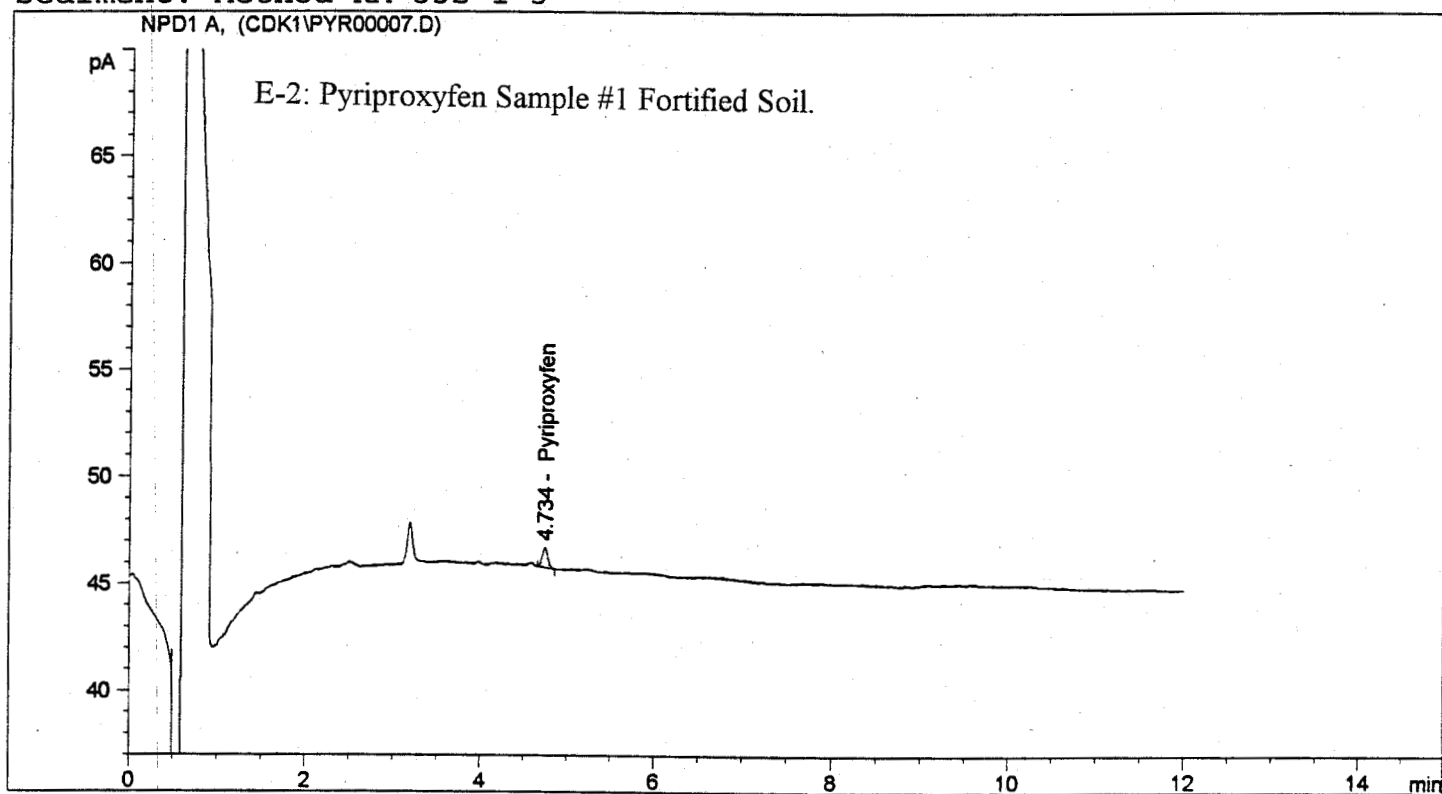
Signal 1: NPD1 A,

RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
4.734	-	-	-	-	-	Pyriproxyfen

Totals : 0.00000

Results obtained with enhanced integrator!

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Friday, November 19, 1999 7:01:25 AM
 Multiplier : 1.0000
 Dilution : 1.0000

Signal 1: NPD1 A,

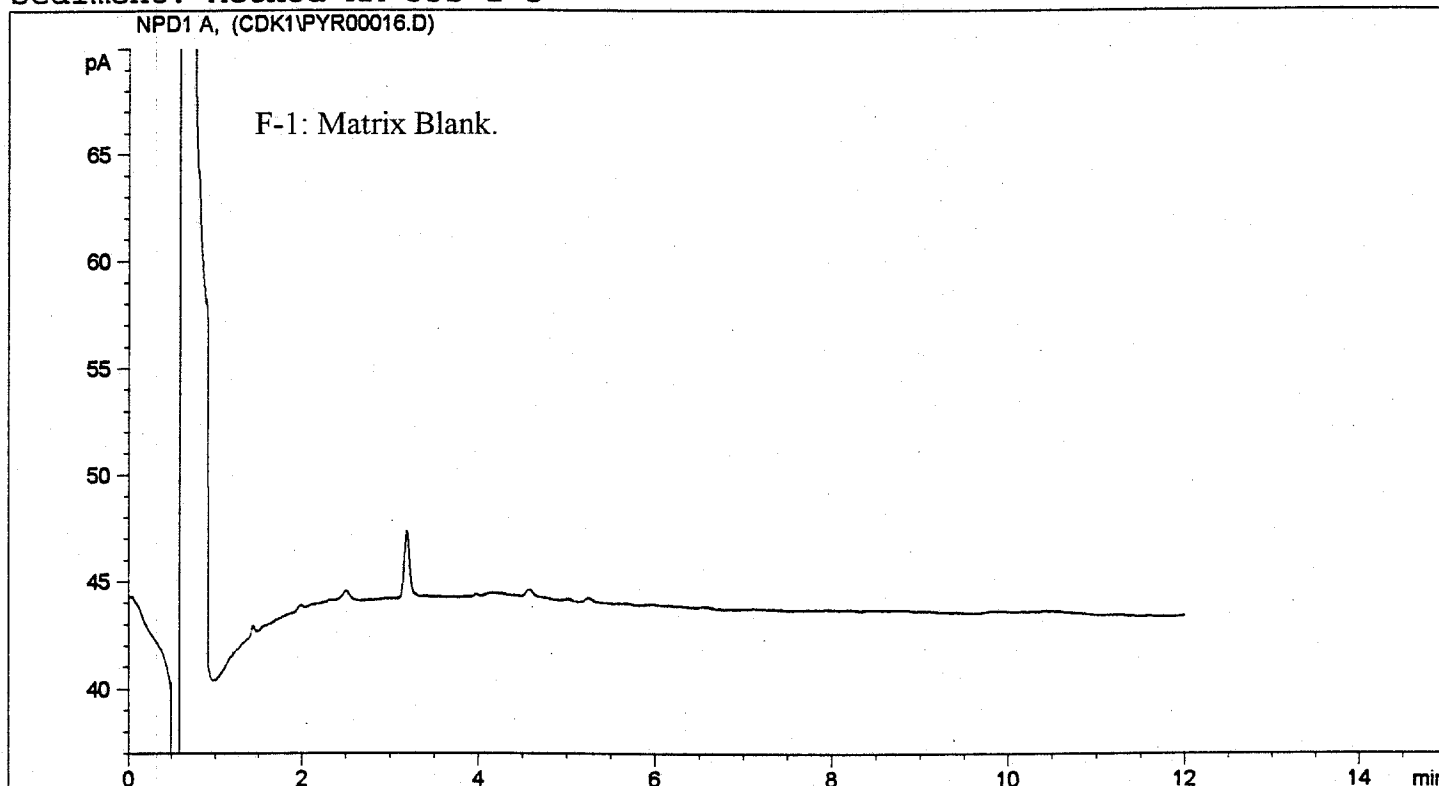
RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
4.734	PB	9.33327e-1	8.45138e-2	7.88790e-2		Pyriproxyfen

Totals : 7.88790e-2

Results obtained with enhanced integrator!

F. Pyriproxyfen Fortification at 0.02 ppm (0.2 µg/mL) Analyzed by GC NPD.

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Friday, November 19, 1999 7:01:25 AM
 Multiplier : 1.0000
 Dilution : 1.0000

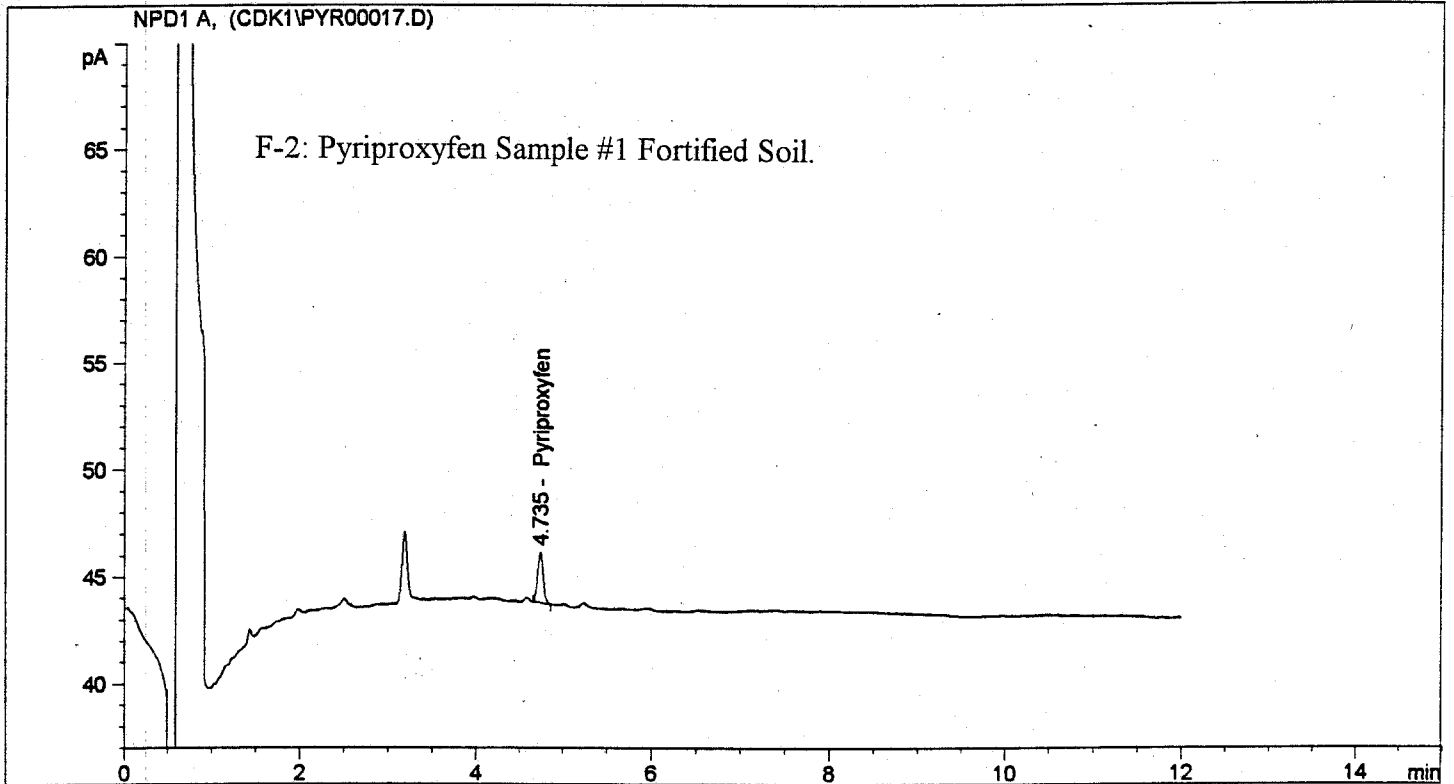
Signal 1: NPD1 A,

RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
4.734	-	-	-	-	-	Pyriproxyfen

Totals : 0.00000

Results obtained with enhanced integrator!

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Friday, November 19, 1999 7:01:25 AM
 Multiplier : 1.0000
 Dilution : 1.0000

Signal 1: NPD1 A,

RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
4.735	PB	2.38059	8.48657e-2	2.02030e-1		Pyriproxyfen

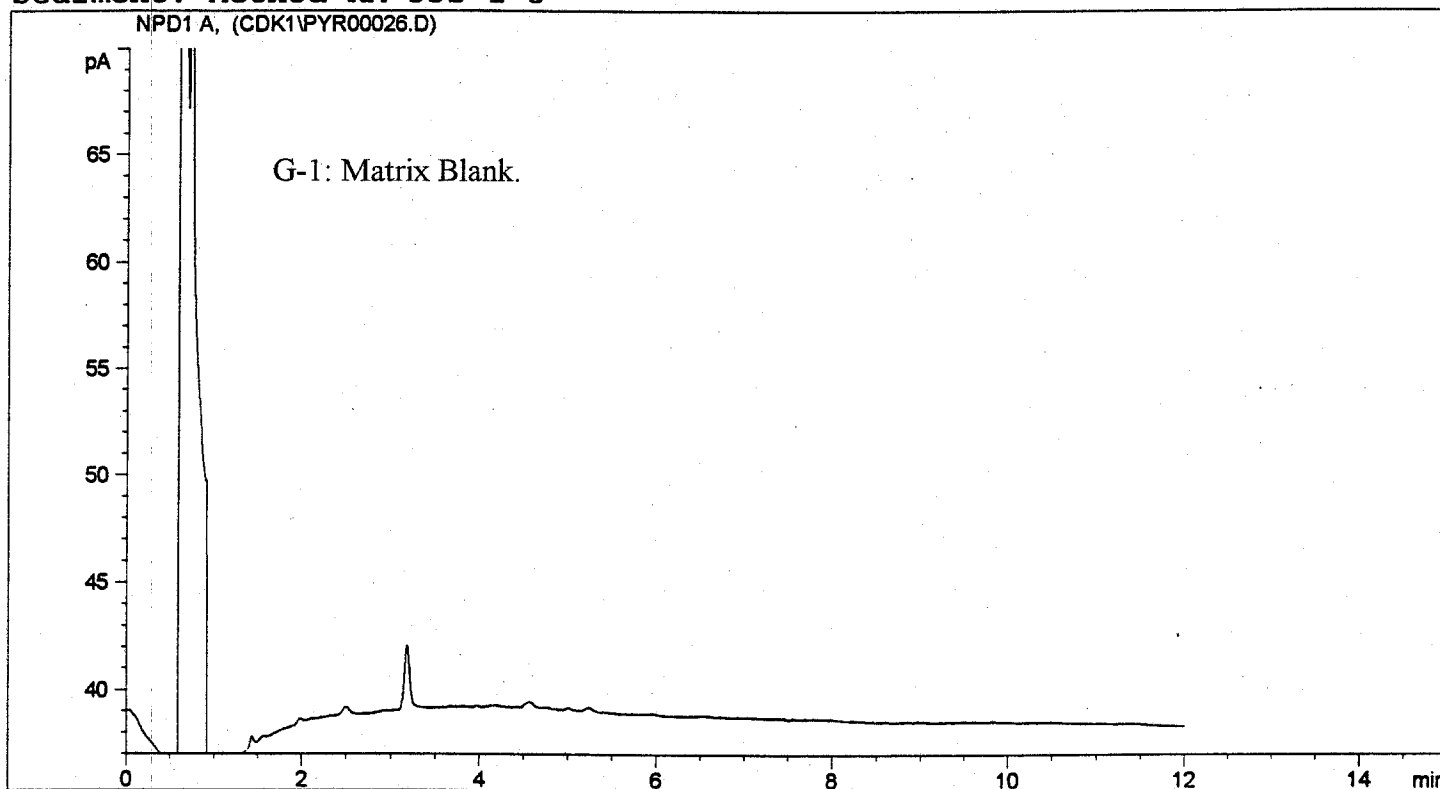
Totals : 2.02030e-1

Results obtained with enhanced integrator!

=====

G. Pyriproxyfen Fortification at 0.2 ppm (2.0 µg/mL) Analyzed by GC NPD.

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Friday, November 19, 1999 7:01:25 AM
 Multiplier : 1.0000
 Dilution : 1.0000

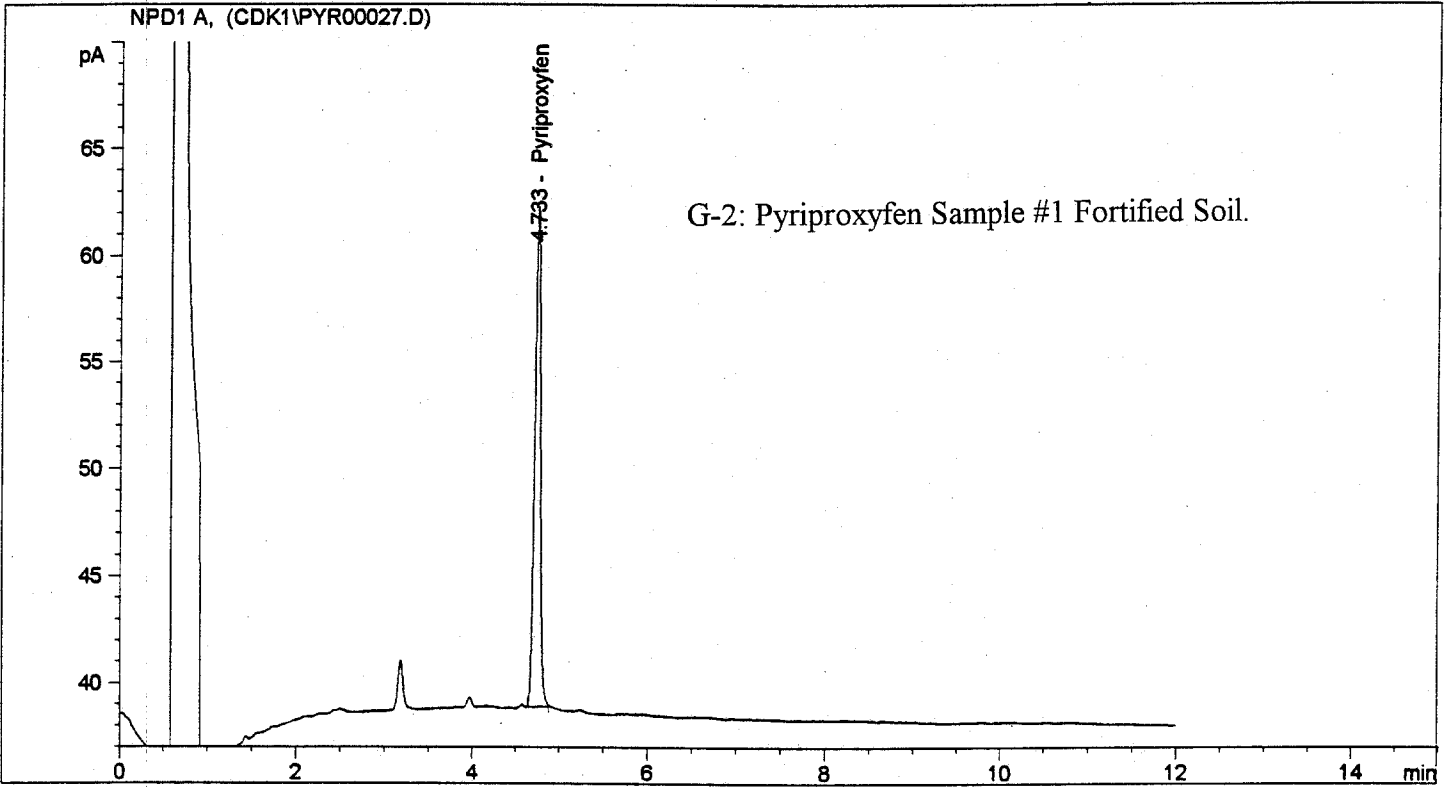
Signal 1: NPD1 A,

RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
4.734	-	-	-	-	-	Pyriproxyfen

Totals : 0.00000

Results obtained with enhanced integrator!

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



External Standard Report

Sorted By : Signal
 Calib. Data Modified : Friday, November 19, 1999 7:01:25 AM
 Multiplier : 1.0000
 Dilution : 1.0000

Signal 1: NPD1 A,

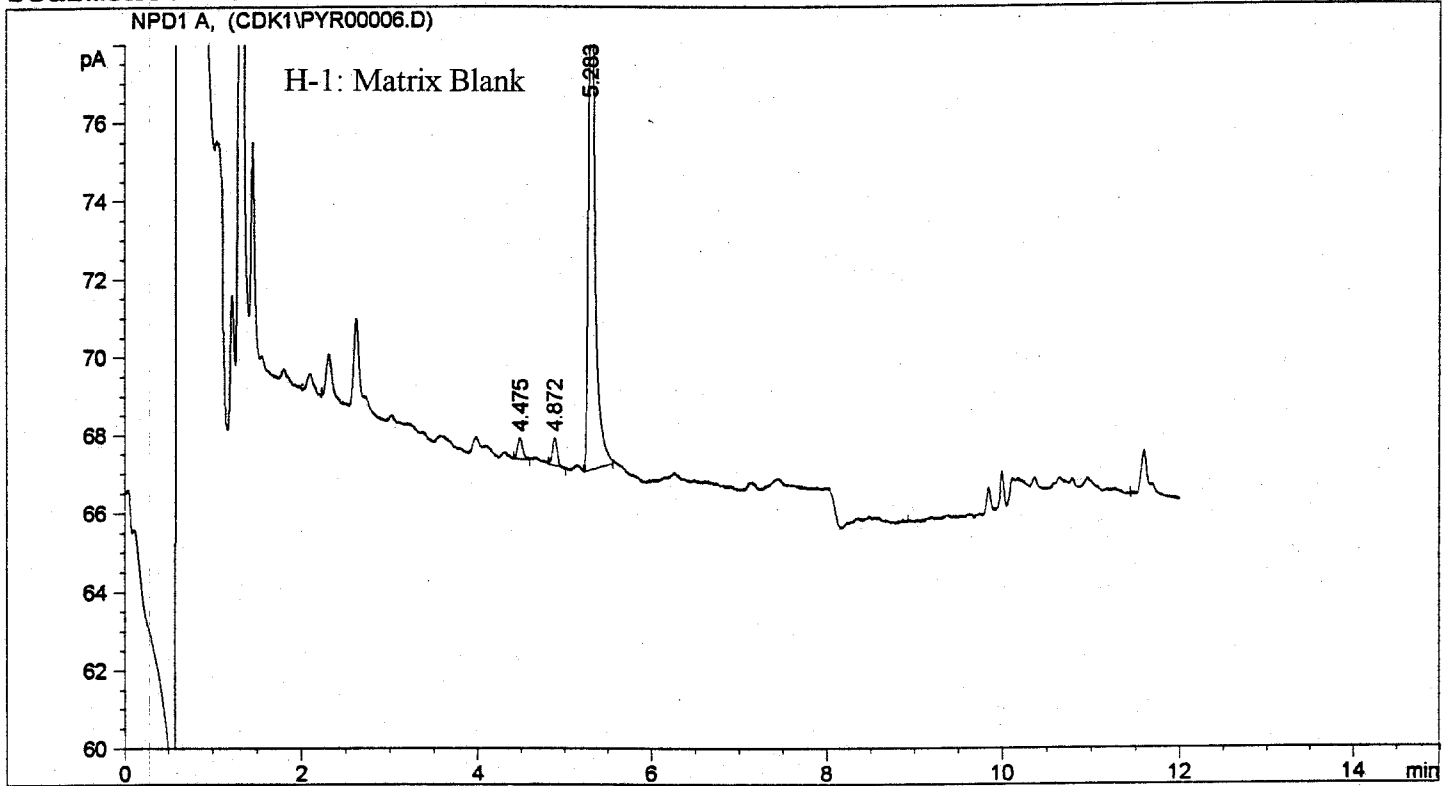
RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
4.733	BB	23.40135	8.50696e-2	1.99074		Pyriproxyfen

Totals : 1.99074

Results obtained with enhanced integrator!

H. PYPAC (PYPAC Me ester) Fortification at 0.01 ppm (0.02 µg/mL) Analyzed by GC NPD

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Monday, November 22, 1999 8:37:21 AM
 Multiplier : 1.0000
 Dilution : 1.0000

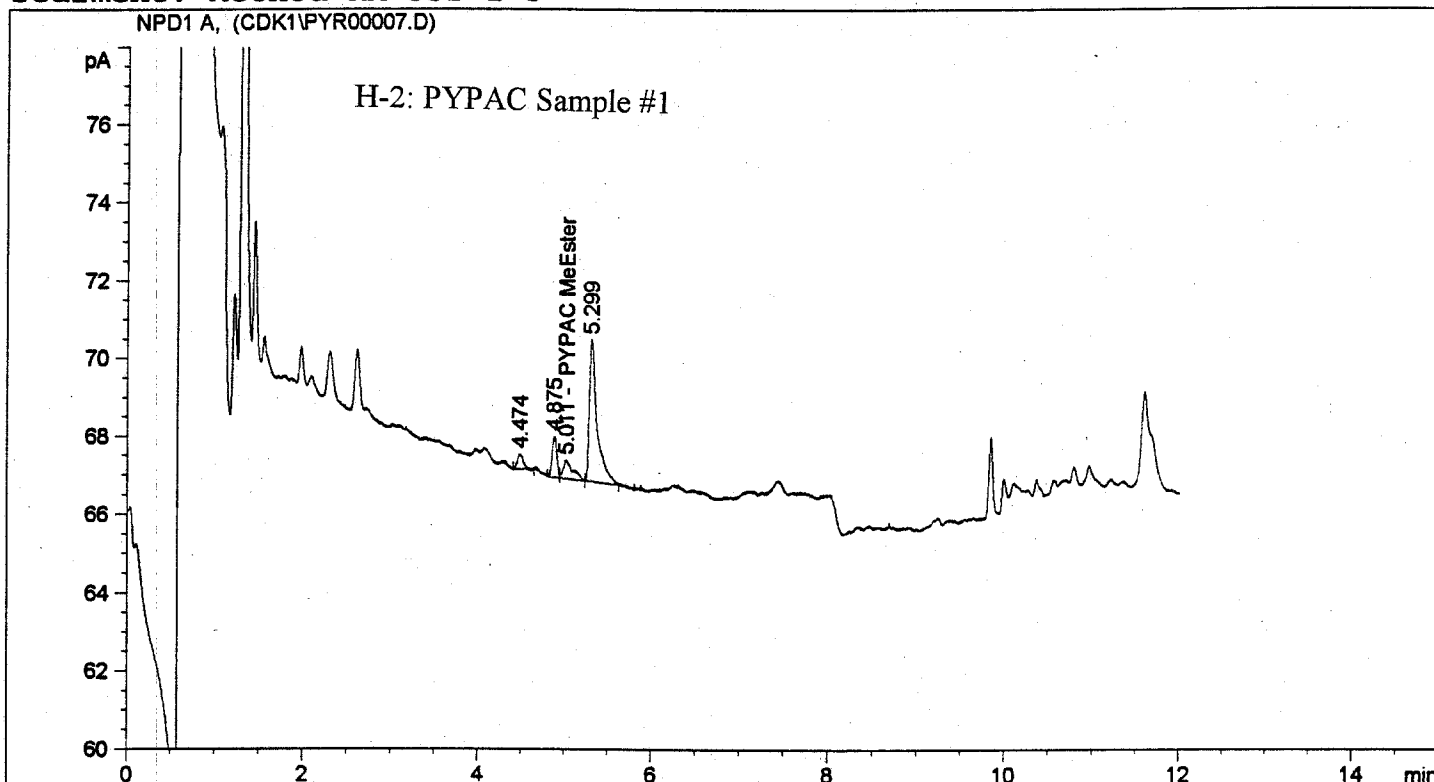
Signal 1: NPD1 A,

RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
5.018	-	-	-	-	-	PYPAC MeEster

Totals : 0.00000

Results obtained with enhanced integrator!

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Monday, November 22, 1999 8:37:21 AM
 Multiplier : 1.0000
 Dilution : 1.0000

Signal 1: NPD1 A,

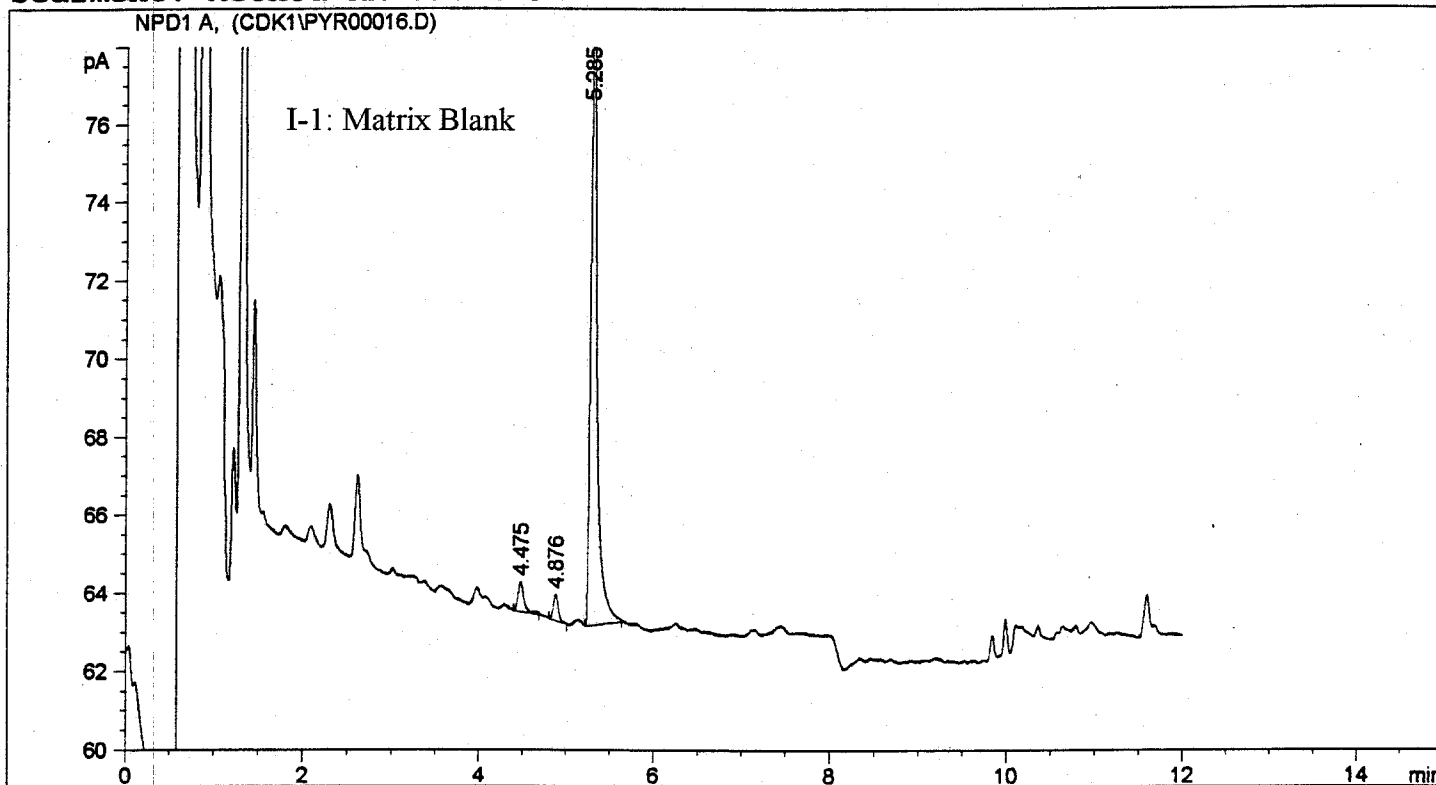
RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
5.011	VV	4.61330e-1	5.21541e-2	2.40603e-2		PYPAC MeEster

Totals : 2.40603e-2

Results obtained with enhanced integrator!

I. PYPAC (PYPAC Me ester) Fortification at 0.02 ppm (0.04 µg/mL) Analyzed by GC NPD.

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Monday, November 22, 1999 8:37:21 AM
 Multiplier : 1.0000
 Dilution : 1.0000

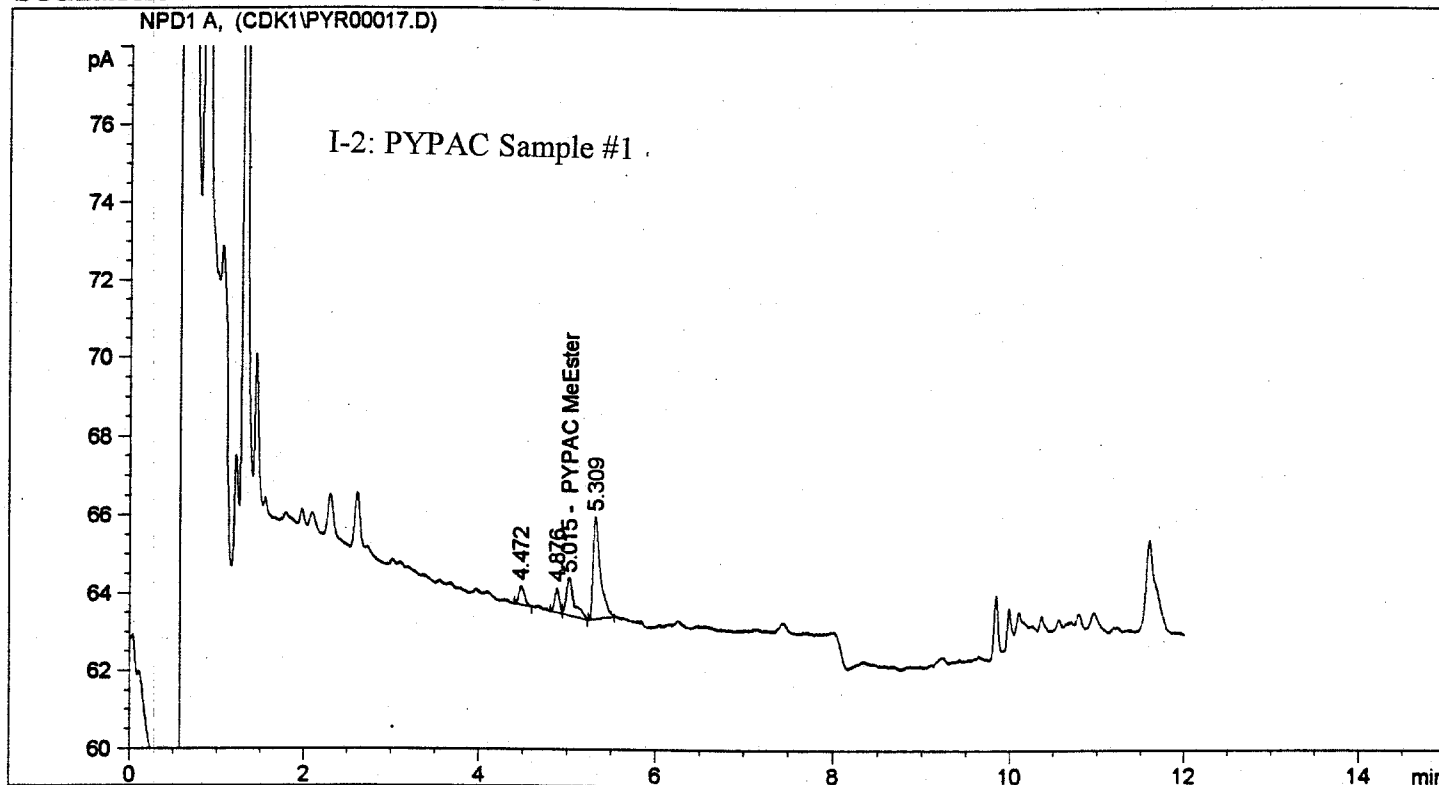
Signal 1: NPD1 A,

RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
5.018		-	-	-		PYPAC MeEster

Totals : 0.00000

Results obtained with enhanced integrator!
 1 Warnings or Errors :

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Monday, November 22, 1999 8:37:21 AM
 Multiplier : 1.0000
 Dilution : 1.0000

Signal 1: NPD1 A,

RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
5.015	VB	9.57779e-1	4.44686e-2	4.25911e-2		PYPAC MeEster

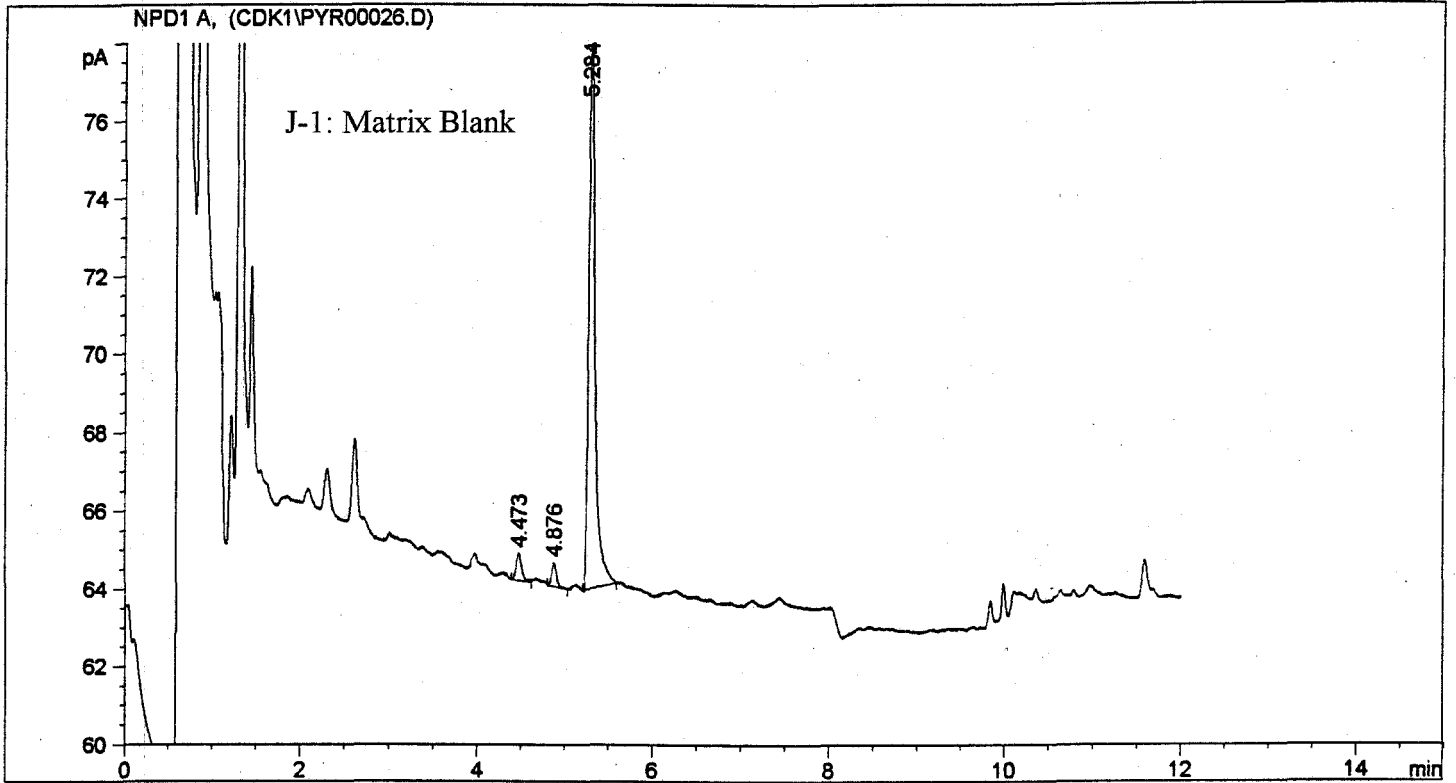
Totals : 4.25911e-2

Results obtained with enhanced integrator!

=====

J. PYPAC (PYPAC Me ester) Fortification at 0.2 ppm (0.4 µg/mL) Analyzed by GC NPD.

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Monday, November 22, 1999 8:37:21 AM
 Multiplier : 1.0000
 Dilution : 1.0000

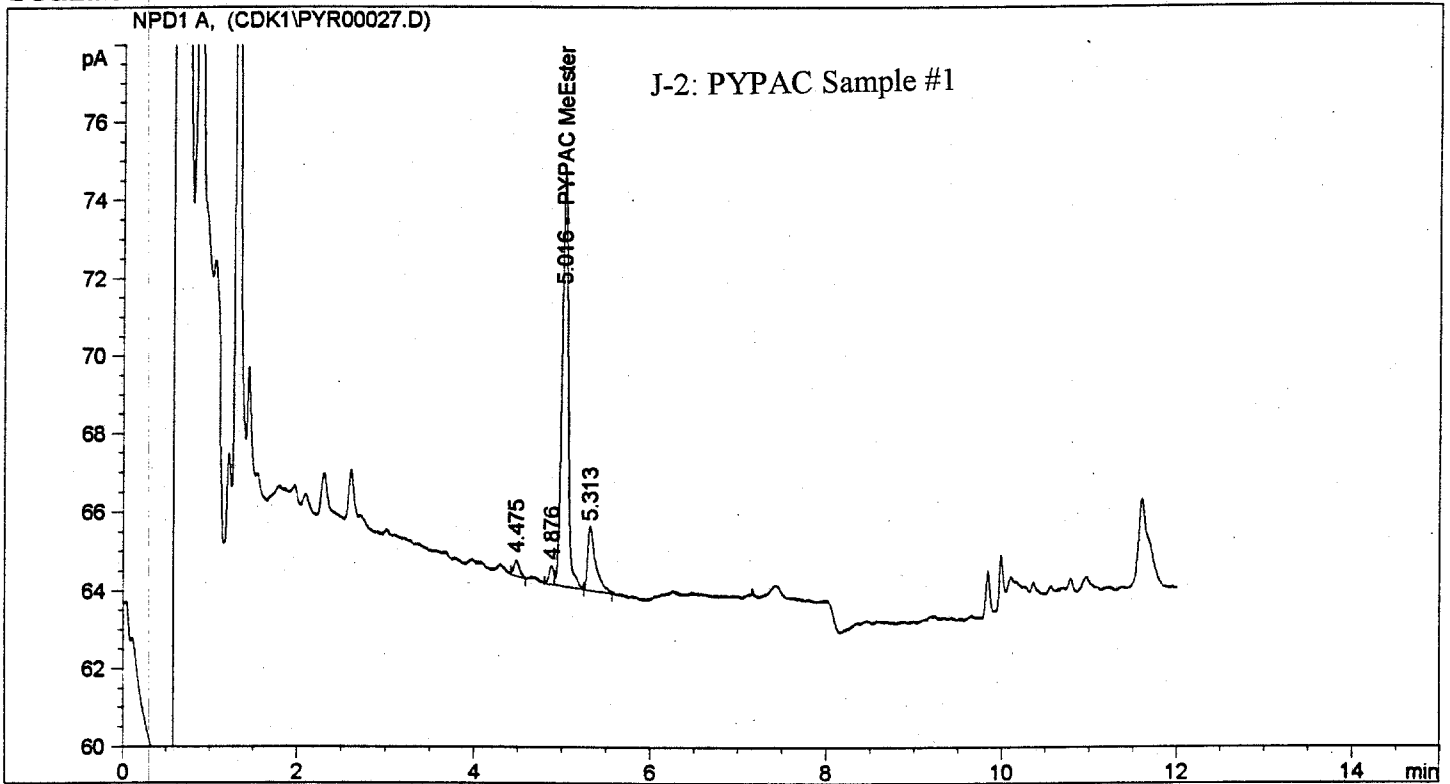
Signal 1: NPD1 A,

RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
5.018	-	-	-	-	-	PYPAC MeEster

Totals : 0.00000

Results obtained with enhanced integrator!
 1 Warnings or Errors :

Determination Of Pyriproxyfen and PYPAC Residues In Soil And Soil
 Sediment. Method RM-33S-1-5



=====
 External Standard Report
 =====

Sorted By : Signal
 Calib. Data Modified : Monday, November 22, 1999 8:37:21 AM
 Multiplier : 1.0000
 Dilution : 1.0000

Signal 1: NPD1 A,

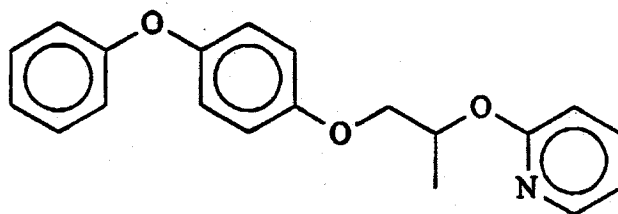
RetTime [min]	Type	Height [pA]	Amt/Height	Amount [ug/ml]	Grp	Name
5.016	VV	10.58386	3.79731e-2	4.01902e-1		PYPAC MeEster

Totals : 4.01902e-1

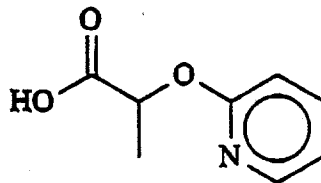
Results obtained with enhanced integrator!
 =====

APPENDIX A:

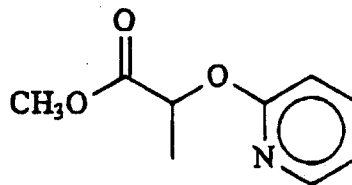
STRUCTURE OF PYRIPROXYFEN AND ITS DEGRADATE METABOLITE PYPAC



Pyriproxyfen



PYPAC



PYPAC-Methyl

