



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

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MEMORANDUM

DP Barcode: D263863

SUBJECT: Dithiopyr Method Evaluation-Report No. ECM0167S1-S4

FROM: Aubry E. Dupuy, Jr., Branch Chief *Aubry E. Dupuy, Jr.*  
OPP/BEAD/Environmental Chemistry Laboratory

TO: Kevin Costello (7507C)  
OPP/Environmental Fate and Effects Division  
Environmental Risk Branch

The BEAD/Environmental Chemistry Lab has performed an Environmental Chemistry Method Evaluation (ECME) on Dithiopyr and its metabolites in soil using the method, "Dithiopyr and Its Metabolites Soil Residue Analytical Method".

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 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

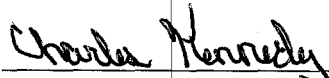
Environmental Chemistry Method Evaluation Report  
Dithiopyr and Its Metabolites Soil Residue Analytical Method

Report Number ECM0167S1-S4

Final Report

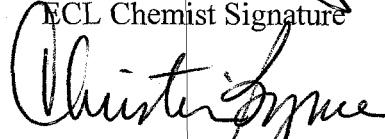
Environmental Chemistry Laboratory  
Biological and Economic Analysis Division

Prepared by: Charles Kennedy

  
ECL Chemist Signature

9/14/00  
Date

Reviewed by: Christian Byrne

  
ECL/QA Officer Signature

9/22/00  
Date

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Part 1

Summary and Conclusions

We have completed the Environmental Chemistry Method Evaluation (ECME) " Dithiopyr and Its Metabolites Soil Residue Analytical Method " MRID #445598-01. The method used to accomplish the analyses was submitted by Rohm and Haas Company in support of registration of Dithiopyr.

We established that the method could be used to monitor soil for the presence of Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 at an LOQ of 0.01 ppm and above.

Residues of Dithiopyr (RH-1664) and its three metabolites are extracted from the soil matrices by first shaking with 95% acetonitrile/0.2M HCL, and secondly with petroleum ether (PE). The PE phase containing the Dithiopyr is retained for further cleanup. The aqueous phase containing all the acidic metabolites are acidified, and then partitioned into diethyl ether (DE), followed by methylation with diazomethane. Water is added to the methylated solution, and methylated metabolites are extracted from the aqueous solution with PE. The extracts of the parent compound dithiopyr and the methylated metabolites are then combined and purified using a Florisil column. This combined extract is brought to final volume in isoctane. Quantitation is performed by gas-liquid chromatography using electron capture detection (GC/ECD).

In order to evaluate this method we fortified a soil matrix with Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 at 0.005 ppm (registrant's claimed LOD), 0.010 ppm (registrant's claimed LOQ), and 0.10 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 Dithiopyr (RH-1664), and its three metabolites at the LOQ and 10 x LOQ levels. Recoveries at the LOQ for RH-1664, RH-1765, RH-1766, and RH-3972 had RSDs equal to 4.1, 5.3, 4.4, and 1.6%, respectively. At 10 x LOQ the RSDs were equal to 2.9, 3.5, 4.9, and 5.7% respectively. The mean recoveries at 10 x LOQ for RH-1664 (93.0%), RH-1765, (85.5%), RH-1766, (83.8%), and RH-3972 (79.1%) were within the target range of 70% to 120%. Mean recoveries at the LOQ for RH-1664 (90.7%), RH-1765 (106.4%), RH-1766 (90.5%), and RH-3972 (76.7%) are all well within the target range. We found the recoveries and precision to be similar to those claimed by the registrant.

Part II

EPA Analytical Results

Results:

1. Dithiopyr (RH-1664)

Recovery Values for Soil Fortified at 0.005, 0.01, and 0.10 ppm in four replicates on Electron Capture GC Detector.

(3) Fortified (ppm)	(4) Found (ppm)	(5) Recovery %	(7) SD	(8) RSD %
Matrix Blk (1)	--	--	--	--
Sample#1-0.005 Sample#2-0.005 Sample#3-0.005 Sample#4-0.005 (2) Mean Recovery(6)	0.0039 0.0043 0.0042 0.0042 0.0042			
Sample#1-0.01 Sample#2-0.01 Sample#3-0.01 Sample#4-0.01  Mean Recovery	0.0094 0.0089 0.0086 0.0093 0.00928	94.3 88.7 86.4 93.2 90.7	3.8	4.1
Sample#1-0.10 Sample#2-0.10 Sample#3-0.10 Sample#4-0.10  Mean Recovery	0.0902 0.0963 0.0917 0.0938 0.093	90.2 96.3 91.7 93.8 93.0	2.7	2.9

Results:

2. Normal Monacid (RH-1765)

Recovery Values for Soil Fortified at 0.005, 0.01, and 0.10 ppm in four replicates on Electron Capture GC Detector.

(3) Fortified (ppm)	(4) Found (ppm)	(5) Recovery %	(7) SD	(8) RSD %
*Matrix Blk (1)	0.00135	-	-	-
Sample#1-0.005 Sample#2-0.005 Sample#3-0.005 Sample#4-0.005 (2) Mean Recovery(6)	0.00593 0.00662 0.00605 0.00509 0.00592			
Sample#1-0.01 Sample#2-0.01 Sample#3-0.01 Sample#4-0.01 Mean Recovery	0.0103 0.0114 0.0106 0.0102 0.0106	102.7 114.5 106.1 102.3 106.4	5.6	5.3
Sample#1-0.10 Sample#2-0.10 Sample#3-0.10 Sample#4-0.10 Mean Recovery	0.0830 0.0898 0.0853 0.0840 0.0855	83.0 89.8 85.3 84.0 85.5	3.0	3.5

\*Matrix background for RH-1765 (0.0013455 ppm) has been subtracted out for recovery.

Results:

3. Reverse Monoacid (RH-1766)

Recovery Values for Soil Fortified at 0.005, 0.01, and 0.10 ppm in four replicates on Electron Capture GC Detector.

(3) Fortified (ppm)	(4) Found (ppm)	(5) Recovery (%)	(7) SD	(8) RSD %
Matrix Blk (1)	—	—	—	—
Sample#1-0.005 Sample#2-0.005 Sample#3-0.005 Sample#4-0.005 (2) Mean Recovery(6)	0.0041 0.0044 0.0041 0.0038 0.0041			
Sample#1-0.01 Sample#2-0.01 Sample#3-0.01 Sample#4-0.01 Mean Recovery	0.00873 0.00960 0.00909 0.00876 0.00905	87.3 96.0 90.9 87.6 90.5	4.0	4.4
Sample#1-0.10 Sample#2-0.10 Sample#3-0.10 Sample#4-0.10 Mean Recovery	0.0795 0.0894 0.0833 0.0828 0.838	79.5 89.4 83.3 82.8 83.8	4.1	4.9



Results:

4. Diacid (RH-3972)

Recovery Values for Soil Fortified at 0.005, 0.01, and 0.1 ppm in four replication on Electron  
 Capture GC Detector.

(3) Fortified (ppm)	(4) Found (ppm)	(5) Recovery %	(7) SD	(8) RSD %
Matrix Blk (1)	-	-	-	-
Sample#1-0.005 Sample#2-0.005 Sample#3-0.005 Sample#4-0.005 (2) Mean Recovery(6)	0.00199 0.00292 0.00229 0.0024 0.0024			
Sample#1-0.01 Sample#2-0.01 Sample#3-0.01 Sample#4-0.01 Mean Recovery	0.0078 0.0075 0.0077 0.0077 0.0077	78.0 75.0 77.2 76.5 76.7	1.3	1.6
Sample#1-0.10 Sample#2-0.10 Sample#3-0.10 Sample#4-0.10 Mean Recovery	0.0739 0.0849 0.0784 0.0790 0.0791	73.9 84.9 78.4 79.0 79.1	4.5	5.7

Notes:

(1) Limit of Detection (LOD), equivalent to 0.005 ppm in soil sample.

Limit of Quantitation (LOQ), equivalent to 0.010 ppm in soil sample.

The LOD and LOQ were determined by ECL as a 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 0.005, 0.010, and 0.10 ppm.

(3) Fortified (ppm) = Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 Fortification Levels.

(4) Found (ppm) = Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 Recovery Levels in Terms of Concentration.

(5) Recovery % = Percent Recovery of Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 as referred to in the Calculation Section.

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

(7) SD = Standard Deviation of % Recovery of Four Replicate Samples of Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972.

(8) RSD = Relative Standard Deviation of % Recovery of Four Replicate Samples of Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972.

Part III

Experimental Details

General description of method:

**Step 1. Extraction**

Weigh 10 g of soil in a 200 mL Teflon® sample bottle. Fortification should be made at this time. Add 50 mL of 95% acetonitrile/0.2 M HCL and shake for 15 minutes on a linear reciprocating shaker. Filter sample into a 250 mL filtering flask, then wash sample bottle and soil filter with 2 x 25 mL of 95% acetonitrile/0.2M HCL and add to filtrate. Transfer the sample into a 300 mL pear shaped flask and concentrate the sample to about 3 mL using a rotary evaporator (approximately

35°C) under pressure.

### **Step 2. Partition**

Transfer the concentrated sample to a 500 mL separatory funnel. Rinse the pear shaped flask with 2 x 25 mL of 0.02M NaOH. Add 2 mL of 1 M NaOH by pipette, 20 mL of saturated NaCl solution and 50 mL of petroleum ether (PE) to the separatory funnel. Shake for 2 minutes and then allow phases to separate for approximately 10 minutes. The PE (upper) phase contains the parent Dithiopyr (RH-1664), and the aqueous (lower) phase contains the acidic metabolites. Drain the aqueous phase to a second separatory funnel. Add 2 mL of 6 M HCL by pipette and 50 mL of diethyl ether (DE) to the separatory funnel containing the metabolites (aqueous phase). Shake for 2 minutes and allow the phases to separate, then transfer upper phase to a 100 mL pear-shaped flask.

### **Step 3. Methylation**

Reduce the volume of metabolites in DE extract to 5 mL using a rotary evaporator. Transfer this concentrated DE extract to a 50 mL conical graduated centrifuge tube. Rinse the pear-shape flask twice with 10 mL DE, and combine in the centrifuge tube. Reduce the DE extract volume to 1 mL under a gentle stream of nitrogen. Add 1 mL of diazomethane to the extract, stopper and mix gently using a vortex mixer. Let the methylation reaction proceed for 20 minutes at room temperature.

After the methylation is complete, add 1 mL of methanol to the reaction mixture and evaporate to about 0.5 mL under a gentle stream of nitrogen. Add 4 mL of water and 10 mL of PE to the centrifuge tube. Using a pasteur pipette, thoroughly mix the liquid phases by gently drawing the liquid up and down. Allow the phases to separate and then transfer the PE (upper) phase to a column packed with 20g of Na<sub>2</sub>SO<sub>4</sub> and collect the eluate in a 100 mL pear-shaped flask. Repeat the PE extraction by adding another 10 mL of PE to the aqueous phase remaining in the centrifuge tube. Stopper the centrifuge tube, shake for 1 minute and transfer the second PE extract to the Na<sub>2</sub>SO<sub>4</sub> column and collect the eluate in the same 100 mL pear-shaped flask. Pass the PE fraction containing the parent compound RH-1664 (retained from the first partition in the initial separatory funnel) through the same Na<sub>2</sub>SO<sub>4</sub> column and combine with the metabolites in the same 100 mL pear-shaped flask. Reduce the volume of this combined extract to 10 mL by rotary evaporation at 30°C.

#### **Step 4. Florisil Column Cleanup**

Fill a 2 x 30 cm chromatography column with PE. Add 15 g of Florisil and top with Na<sub>2</sub>SO<sub>4</sub>. Drain the PE just to the top of the bed of Florisil and load sample. Rinse the column with 30 mL of 5% DE in PE. Elute the sample into a 100 mL pear-shaped flask using 50 mL of 50% DE in PE. Add 5 mL of isooctane to the flask and reduce the volume to less than 5 mL using rotary evaporation at 30°C. Transfer the sample to a 15 mL graduated test tube. Rinse the flask twice with 2 mL of isooctane, add the rinses to the test tube, and adjust the final volume to 10 mL with isooctane.

Table 1 (page 11) summarizes the retention times observed for the HP 6890 gas chromatograph with an electron capture detector.

The structural formula of Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 are shown in Appendix A.

#### **Modification to method:**

No modification necessary

#### **Sources of analytical reference standards:**

Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 analytical standards was obtained from Rohm and Hass Research Laboratories, 727 Norristown Road, P.O. Box 904, Spring House, PA 19477-0904. Telephone: (215)-619-5164. Fax (215) 641-7857

1. Dithiopyr (RH-101664), Lot # PIT-9001-1444-A, 99.9% purity, Expiration Date: 01/27/05.
2. RH-131765, Lot#PIT-9101-2666-A, 99.8% purity, Expiration Date: 06/06/01.
3. RH-131766, Lot#PIT-9101-2665-A, 92.5% purity, Expiration Date: 10/19/02.
4. RH-133972, Lot#CMT-4352C, 99.5% purity, Expiration Date: 02/25/01.

#### **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 GC System with on column Auto Injector and Electron Capture Detector.

Instrumentation for confirmation: Not applicable.

Relative retention parameters for the present evaluation:

Table 1

Analyte	Chemical Abstracts Registry No.	Retention Time (Minutes)
Dithiopyr (RH-1664)	PIT-9001-1444-A	17.6
Normal Monoacid (RH-1765)	PIT-9101-2666-A	14.4
Reverse Monoacid (RH-1766)	PIT-9101-2665-A	14.7
Diacid (RH-3972)	CMT-4352C	12.4

Notes on analytical procedures:

ECL found the method to work well for Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972. Some interference was observed in the control Matrix Blank and Solvent Blank at the retention time of RH-1765. This value was subtracted out so final recovery values could be determined as stated in the method.

Comments:

Completion of a large analysis set (eighteen samples) required 7 days for weighing, spiking, and extraction, and approximately 12 hours for GC analysis and data collection.

(a) Calibration

The HP 6890 EC gas chromatograph was calibrated with Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 standards at concentrations of 5.0 ng/mL, 10.0 ng/mL, 50.0 ng/mL and 100.0 ng/mL. The correlation coefficients were 0.99998 (RH-1664), 1.00000 (RH-1765), 0.99998 (RH-1766), and 0.99968 (RH-3972).

(b) Calculation Curve

1. Standard Curve

A standard curve was constructed by linear regression analysis of concentration of external standard (ng/mL) versus peak height for Dithiopyr (RH-1764) and its three metabolites. The recovery concentration of the analyte (ng/g) in fortified soil was determined from the linear regression equation for the analyte. The calibration curve is constructed using the concentration (ng/ml) 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 Analyte in Samples

a. Dithiopyr (RH-1664), and its three metabolite calibration curve were used to calculate the concentration of Dithiopyr (RH-1664) and its metabolites in each fortified sample extract using the regression equation 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 ( $\mu\text{g/mL}$ )  
V = final volume of extract (10 mL)  
W = weight of sample extracted (10 g)

3. Example Calculation

To manually calculate the concentration of Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 in a soil, use the calibration curve equation to find the concentration of analyte in the sample extract. Then apply the formula in Section 2-b to find the concentration of analyte in the sample.

**Sample: Sample#1 @ 0.010 ppm for Dithiopr (RH-1664)**

Calibration curve equation is  $Y = 17.88683X + 13.06521$

Peak Height Count of RH-1664 is 188.89928

Sample wt. is 10.0 g, final vol. is 10 mL

Substitute for Y,  $181.82669 = 17.89X + 13.07$

$$X = (181.83 - 13.07)/17.89$$

$$X = 9.43 \text{ ng/mL}$$

$$\text{Conc. in sample} = \frac{9.43 \text{ ng}}{\text{mL}} \times \frac{10 \text{ mL}}{10 \text{ g}} \times \frac{1 \mu\text{g}}{1000 \text{ ng}} = \frac{0.00943 \mu\text{g}}{\text{g}} \text{ or } 0.00943 \text{ ppm}$$

$$\text{Percent recovery} = \frac{0.00943 \text{ ppm}}{0.010 \text{ ppm}} \times 100 = 94.3\%$$

Chromatograms and Linear Regression Curves

A. Calibration Standards Analyzed by GC at 5.0 ng/mL, 10.0 ng/mL, 50.0 ng/mL, and 100.0 ng/mL.

A-1: 5.0 ng/mL (equivalent to MDL in soil)

A-2: 10.0 ng/mL (equivalent to LOQ in soil)

A-3: 50.0 ng/mL

A-4: 100.0 ng/mL (equivalent to 10 x LOQ in soil)

B. Linear Regression Curves for Dithiopyr (RH-1664) and three metabolites.

B-1: Linear Regression Curves for Dithiopyr (RH1664), RH-1765, RH-1766, and RH-3972 at 5.0 ng/mL (MDL), 10.0 ng/mL (LOQ), 50.0 ng/mL, and 100.0 ng/mL (10 x LOQ).

C. Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 Fortification at 0.005 ppm (MDL) Analyzed by Electron Capture GC.

C-1: Matrix Blank

C-2: Dithiopyr (RH-1664) and Three Metabolites Sample #4 Fortified Soil.

D. Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 Fortification at 0.01 ppm (LOQ)  
Analyzed by Electron Capture GC.

D-1: Matrix Blank.

D-2: Dithiopyr (RH-1664) and Three Metabolites Sample #2 Fortified Soil.

E. Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 Fortification at 0.10 ppm (10 x  
LOQ) Analyzed by Electron Capture GC.

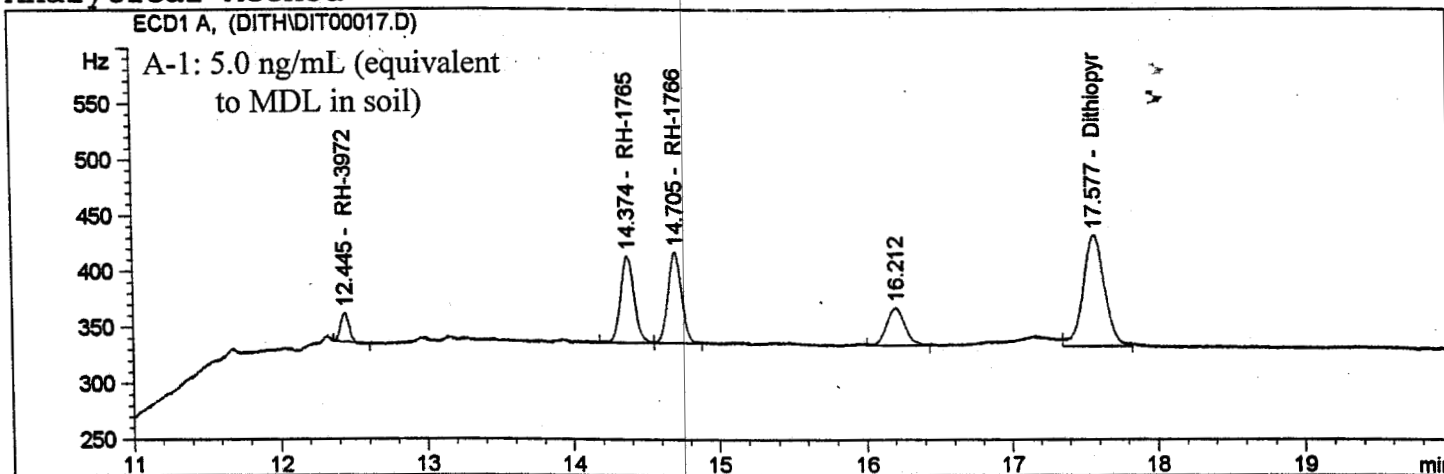
E-1: Matrix Blank.

E-2: Dithiopyr (RH-1664) and Three Metabolites Sample #1 Fortified Soil.



A. Calibration Standards Analyzed by GC at 5.0 ng/mL, 10.0 ng/mL, 50.0 ng/mL, and 100.0 ng/mL.

ECM0167S1-S4: Study Title-" Dithiopyr and Its Metabolites Soil Residue Analytical Method"



=====  
 External Standard Report  
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 Dilution : 1.0000

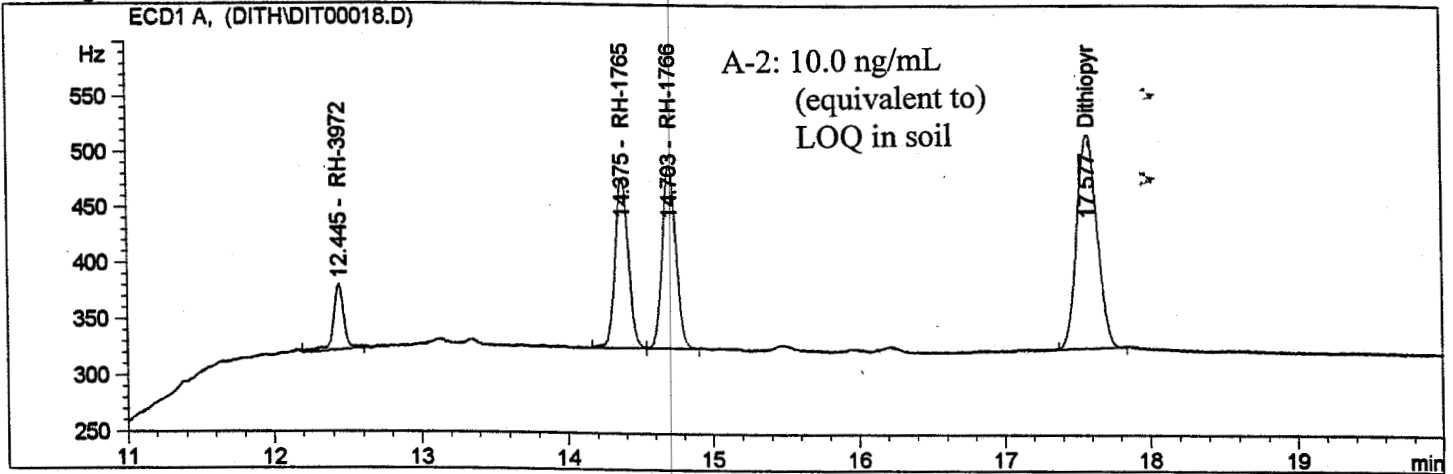
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RetTime [min]	Type	Height [Hz]	Amt/Height	Amount [ng/ml]	Grp	Name
12.445	VP	25.64422	1.49017e-1	3.82142		RH-3972
14.374	PV	77.79535	5.97912e-2	4.65148		RH-1765
14.705	VB	81.70155	5.64296e-2	4.61039		RH-1766
17.577	VV	99.83089	4.85903e-2	4.85081		Dithiopyr

Totals : 17.93410

Results obtained with enhanced integrator!  
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ECM0167S1-S4: Study Title-" Dithiopyr and Its Metabolites Soil Residue Analytical Method"



External Standard Report

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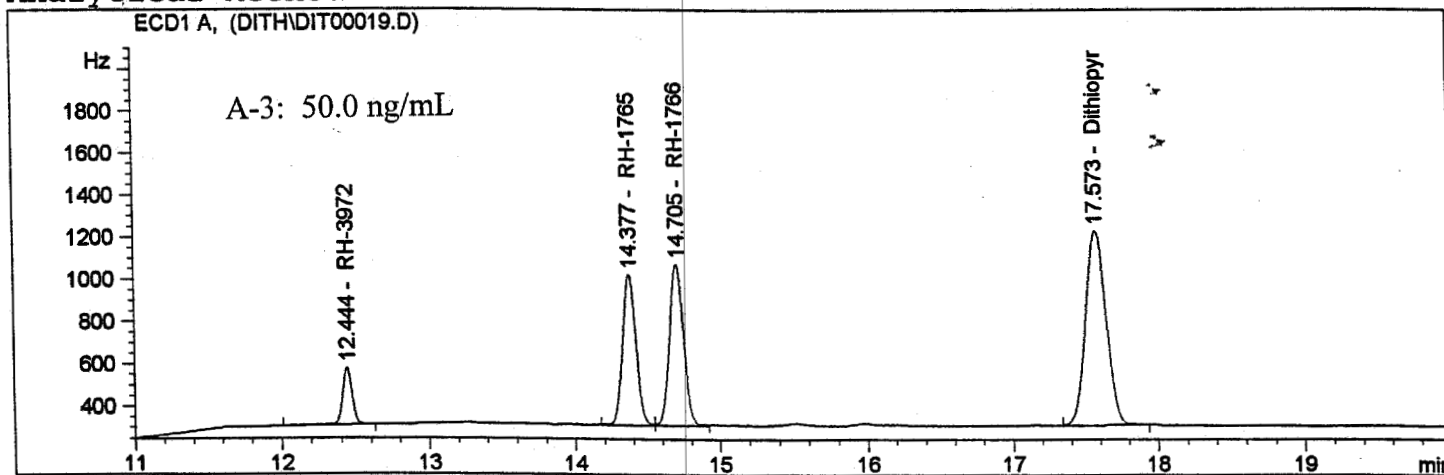
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RetTime [min]	Type	Height [Hz]	Amt/Height	Amount [ng/ml]	Grp	Name
12.445	VB	58.07712	1.76846e-1	10.27072		RH-3972
14.375	BP	152.37086	6.61070e-2	10.07278		RH-1765
14.703	VB	164.36098	6.20272e-2	10.19485		RH-1766
17.577	BB	190.20511	5.20668e-2	9.90337		Dithiopyr

Totals : 40.44172

Results obtained with enhanced integrator!

ECM0167S1-S4: Study Title-" Dithiopyr and Its Metabolites Soil Residue Analytical Method"



External Standard Report

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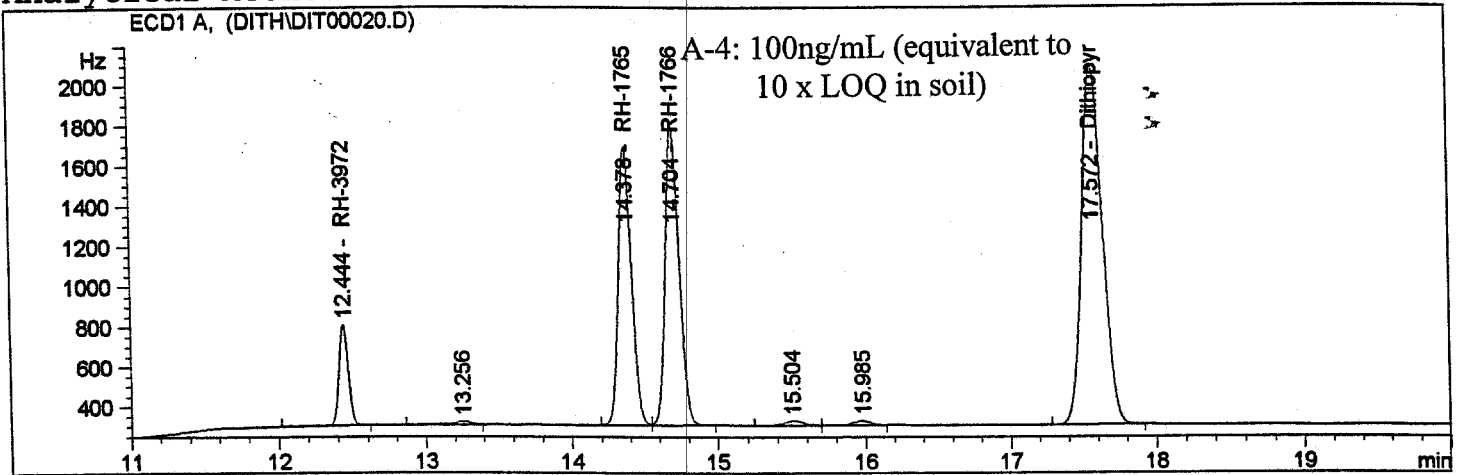
Signal 1: ECD1 A,

RetTime [min]	Type	Height [Hz]	Amt/Height	Amount [ng/ml]	Grp	Name
12.444	BB	267.57083	1.94074e-1	51.92864		RH-3972
14.377	VV	708.91785	7.12793e-2	50.53120		RH-1765
14.705	VV	759.30963	6.63623e-2	50.38953		RH-1766
17.573	BB	915.58759	5.51093e-2	50.45738		Dithiopyr

Totals : 203.30675

Results obtained with enhanced integrator!

ECM0167S1-S4: Study Title-" Dithiopyr and Its Metabolites Soil Residue Analytical Method"



External Standard Report

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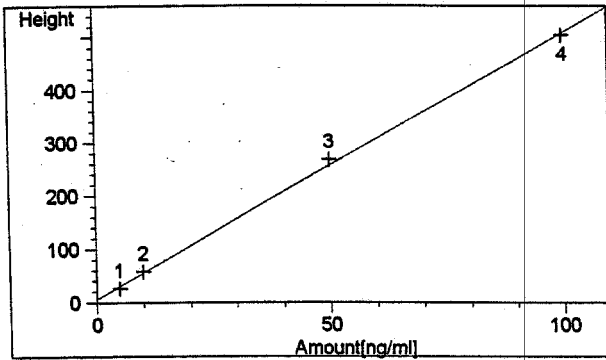
Signal 1: ECD1 A,

RetTime [min]	Type	Height [Hz]	Amt/Height	Amount [ng/ml]	Grp	Name
12.444	BB	504.73251	1.96319e-1	99.08834		RH-3972
14.378	BV	1385.89771	7.19711e-2	99.74455		RH-1765
14.704	VP	1490.74475	6.69499e-2	99.80523		RH-1766
17.572	PB	1797.96350	5.55008e-2	99.78843		Dithiopyr

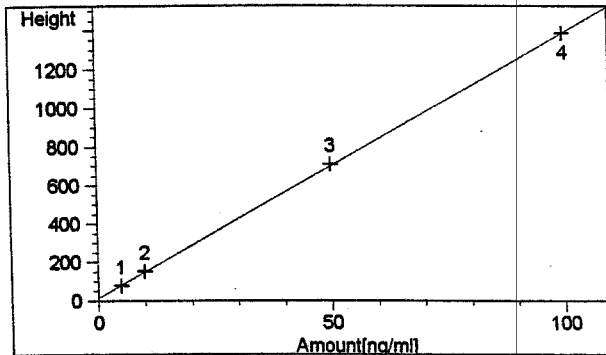
Totals : 398.42655

Results obtained with enhanced integrator!

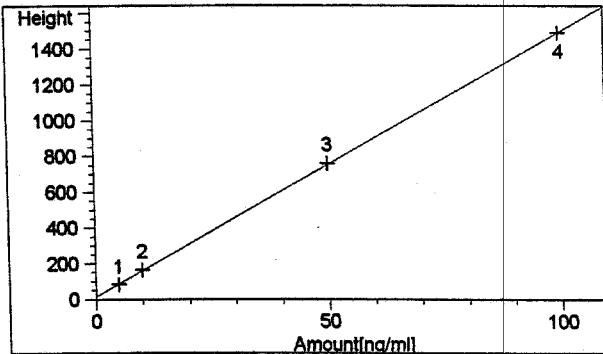
B-1: Linear Regression Curves for Dithiopyr (RH1664), RH-1765, RH-1766, and RH-3972 at 5.0 ng/mL (MDL), 10.0 ng/mL (LOQ), 50.0 ng/mL, and 100.0 ng/mL (10 x LOQ).



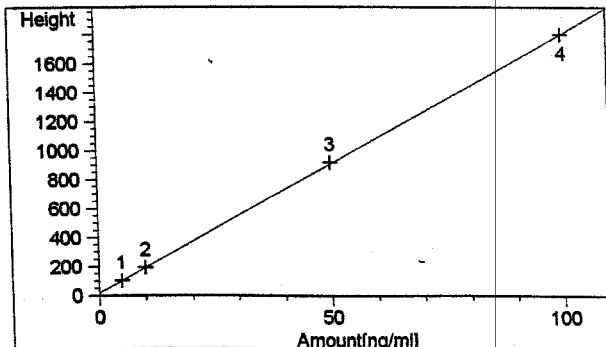
RH-3972 at exp. RT: 12.444  
ECD1 A,  
Correlation: 0.99951  
Residual Std. Dev.: 8.47362  
Formula:  $y = mx + b$   
m: 5.02891  
b: 6.42665  
x: Amount [ng/ml]  
y: Height



RH-1765 at exp. RT: 14.378  
ECD1 A,  
Correlation: 0.99996  
Residual Std. Dev.: 6.69818  
Formula:  $y = mx + b$   
m: 13.75602  
b: 13.80955  
x: Amount [ng/ml]  
y: Height



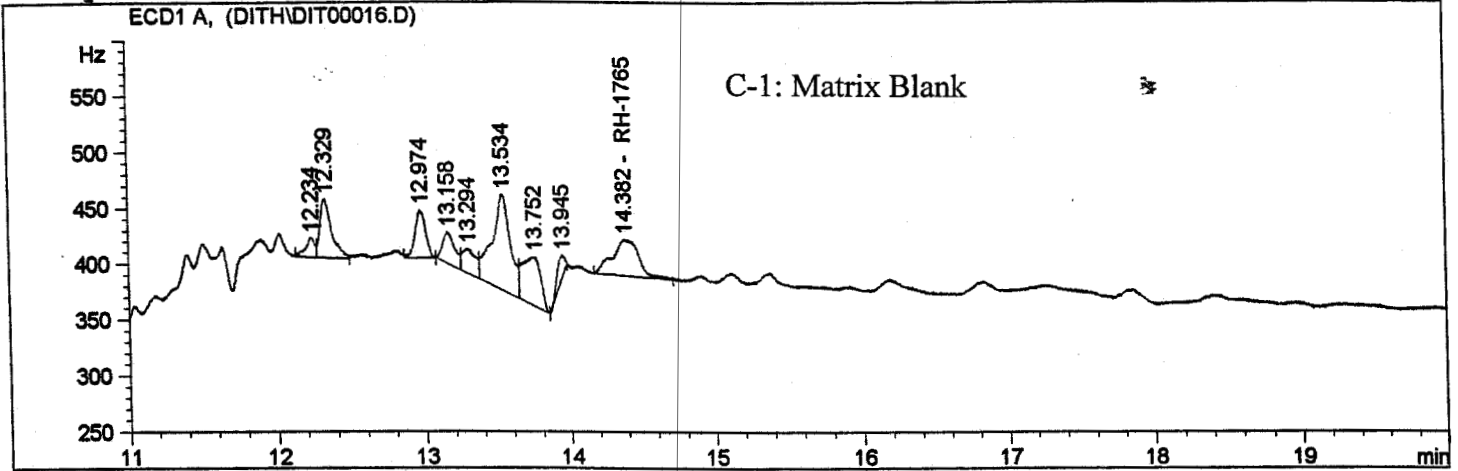
RH-1766 at exp. RT: 14.704  
ECD1 A,  
Correlation: 0.99997  
Residual Std. Dev.: 6.44712  
Formula:  $y = mx + b$   
m: 14.80168  
b: 13.46010  
x: Amount [ng/ml]  
y: Height



Dithiopyr at exp. RT: 17.572  
ECD1 A,  
Correlation: 0.99998  
Residual Std. Dev.: 6.75866  
Formula:  $y = mx + b$   
m: 17.88683  
b: 13.06521  
x: Amount [ng/ml]  
y: Height

C. Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 Fortification at 0.005 ppm Analyzed by Electron Capture GC.

ECM0167S1-S4: Study Title-" Dithiopyr and Its Metabolites Soil Residue Analytical Method"



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

Sorted By : Signal  
 Calib. Data Modified : 09/11/2000 2:32:17 PM  
 Multiplier : 1.0000  
 Dilution : 1.0000

Signal 1: ECD1 A,

RetTime [min]	Type	Height [Hz]	Amt/Height	Amount [ng/ml]	Grp	Name
12.444		-	-	-		RH-3972
14.382	VB	32.31815	4.16327e-2	1.34549		RH-1765
14.704		-	-	-		RH-1766
17.572		-	-	-		Dithiopyr

Totals : 1.34549

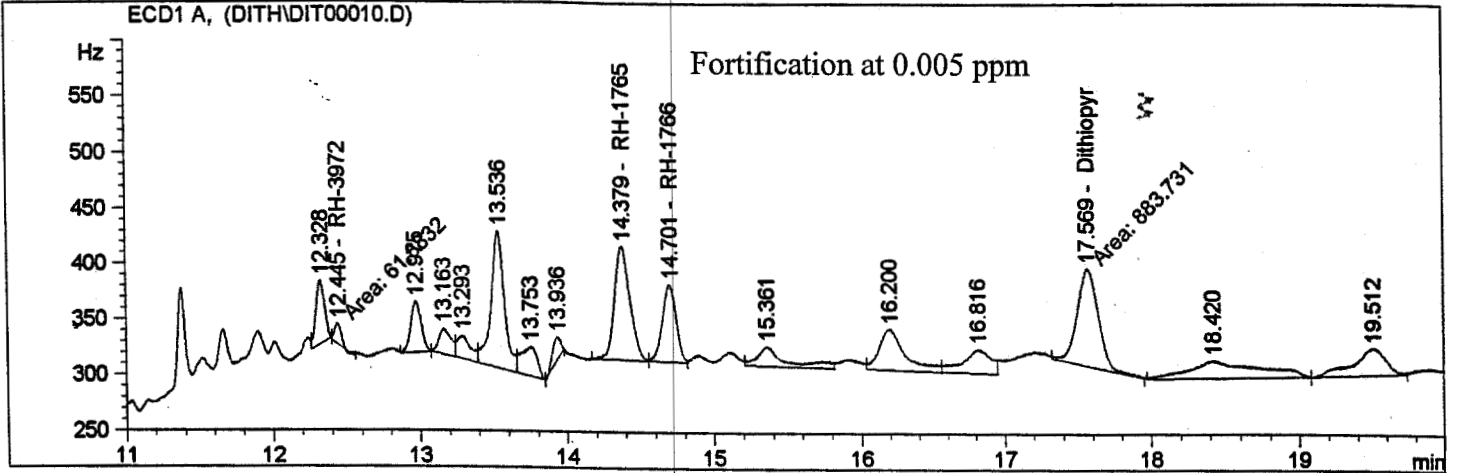
Results obtained with enhanced integrator!  
 1 Warnings or Errors :

Warning : Calibrated compound(s) not found

=====

C-2: Dithiopyr (RH-1664) and Three Metabolites Sample #4 Fortified Soil.

ECM0167S1-S4: Study Title-" Dithiopyr and Its Metabolites Soil Residue Analytical Method"



External Standard Report

Sorted By : Signal  
 Calib. Data Modified : 09/11/2000 2:32:17 PM  
 Multiplier : 1.0000  
 Dilution : 1.0000

Signal 1: ECD1 A,

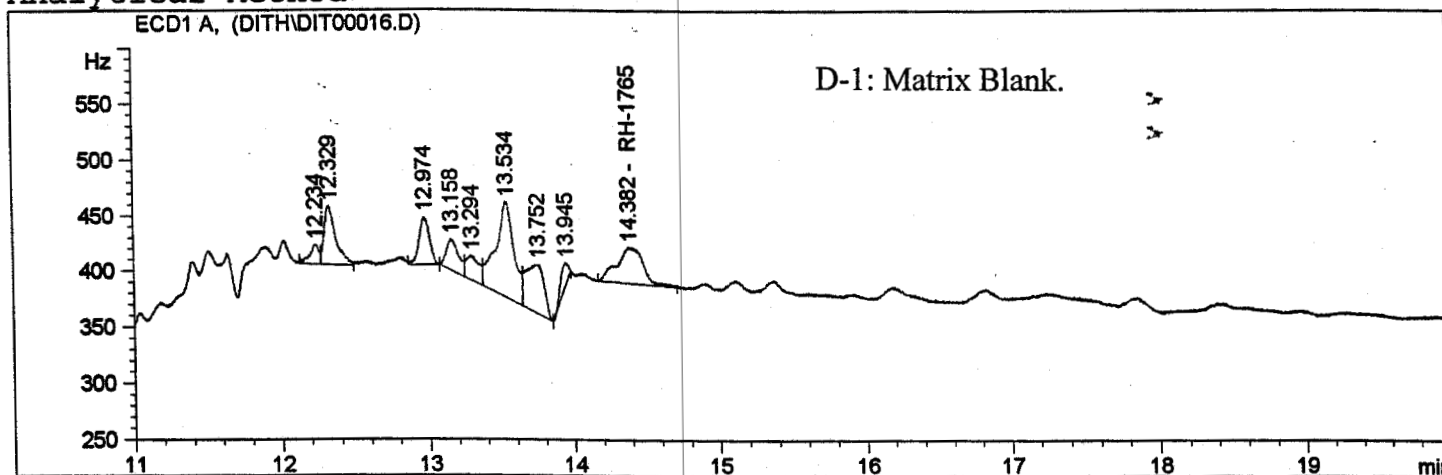
RetTime [min]	Type	Height [Hz]	Amt/Height	Amount [ng/ml]	Grp	Name
12.445	MM	18.65087	1.30331e-1	2.43079		RH-3972
14.379	PV	102.40196	6.28920e-2	6.44026		RH-1765
14.701	VV	69.89948	5.45503e-2	3.81304		RH-1766
17.569	MM	87.81566	4.75892e-2	4.17908		Dithiopyr

Totals : 16.86317

Results obtained with enhanced integrator!

D. Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 Fortification at 0.01 ppm Analyzed by Electron Capture GC.

ECM0167S1-S4: Study Title-" Dithiopyr and Its Metabolites Soil Residue Analytical Method"



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

Sorted By : Signal  
 Calib. Data Modified : 09/11/2000 2:32:17 PM  
 Multiplier : 1.0000  
 Dilution : 1.0000

Signal 1: ECD1 A,

RetTime [min]	Type	Height [Hz]	Amt/Height	Amount [ng/ml]	Grp	Name
12.444		-	-	-		RH-3972
14.382	VB	32.31815	4.16327e-2	1.34549		RH-1765
14.704		-	-	-		RH-1766
17.572		-	-	-		Dithiopyr

Totals : 1.34549

Results obtained with enhanced integrator!  
 1 Warnings or Errors :

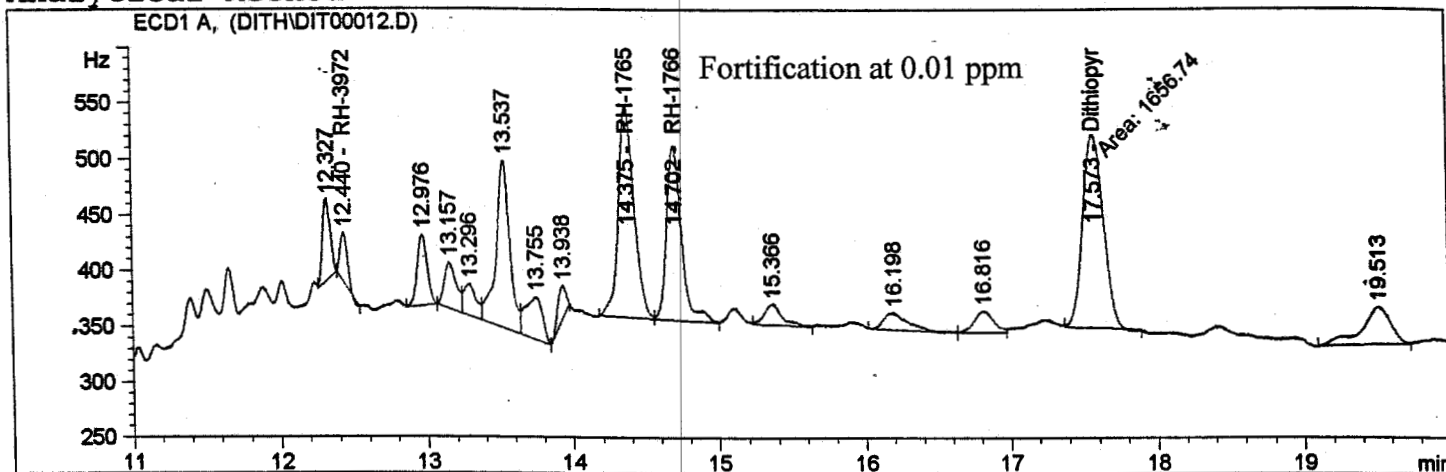
Warning : Calibrated compound(s) not found

=====



D-2: Dithiopyr (RH-16640 and Three Metabolites Sample #2 Fortified Soil.

ECM0167S1-S4: Study Title-" Dithiopyr and Its Metabolites Soil Residue Analytical Method"



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

Sorted By : Signal  
 Calib. Data Modified : 09/11/2000 2:32:17 PM  
 Multiplier : 1.0000  
 Dilution : 1.0000

Signal 1: ECD1 A,

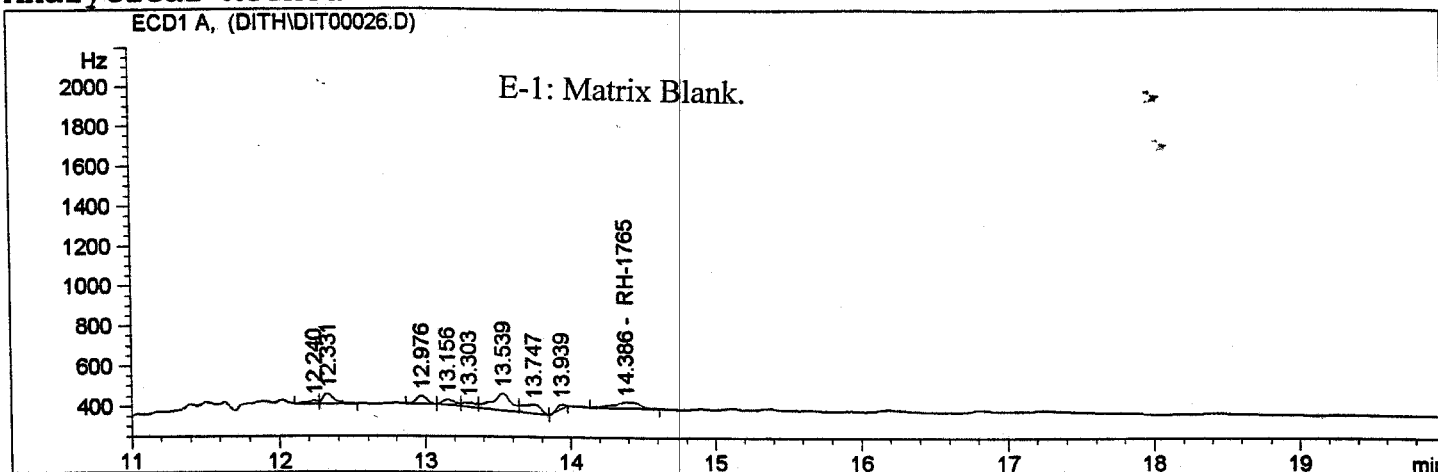
RetTime [min]	Type	Height [Hz]	Amt/Height	Amount [ng/ml]	Grp	Name
12.440	VP	44.15852	1.69911e-1	7.50300		RH-3972
14.375	PV	189.78157	6.74057e-2	12.79236		RH-1765
14.702	VP	155.50970	6.17123e-2	9.59686		RH-1766
17.573	MM	171.81013	5.16556e-2	8.87496		Dithiopyr

Totals : 38.76718

Results obtained with enhanced integrator!  
 =====

E. Dithiopyr (RH-1664), RH-1765, RH-1766, and RH-3972 Fortification at 0.10 ppm Analyzed by Electron Capture GC.

ECM0167S1-S4: Study Title-" Dithiopyr and Its Metabolites Soil Residue Analytical Method"



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

Sorted By : Signal  
 Calib. Data Modified : 09/11/2000 2:32:17 PM  
 Multiplier : 1.0000  
 Dilution : 1.0000

Signal 1: ECD1 A,

RetTime [min]	Type	Height [Hz]	Amt/Height	Amount [ng/ml]	Grp	Name
12.444	-	-	-	-	-	RH-3972
14.386	PV	30.76229	4.00616e-2	1.23239	-	RH-1765
14.704	-	-	-	-	-	RH-1766
17.572	-	-	-	-	-	Dithiopyr

Totals : 1.23239

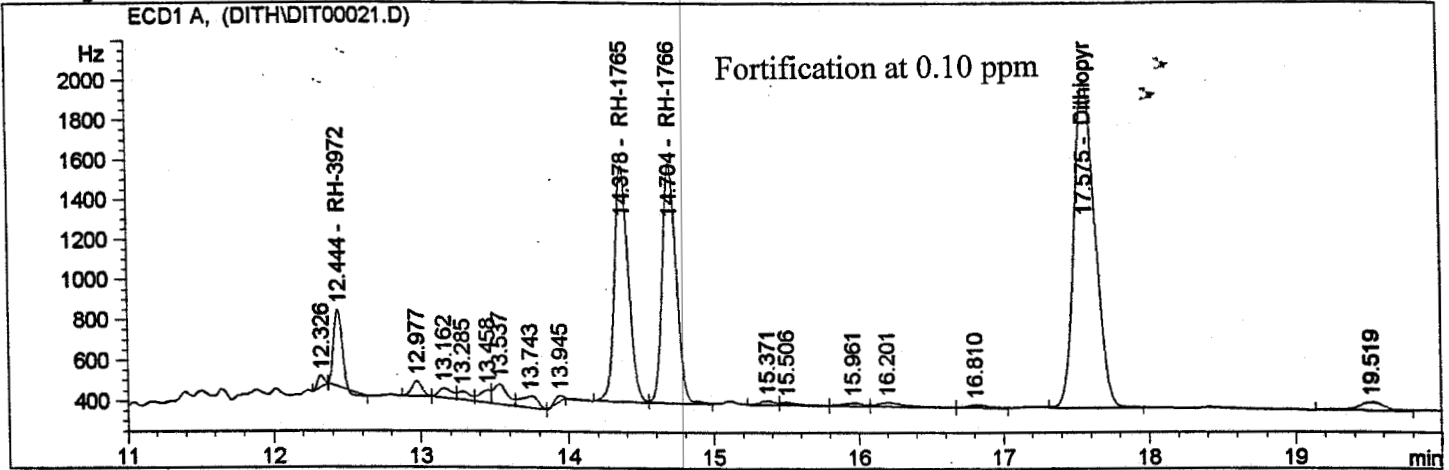
Results obtained with enhanced integrator!  
 1 Warnings or Errors :

Warning : Calibrated compound(s) not found

=====

E-2: Dithiopyr (RH-1664) and Three Metabolites Sample #1 Fortified Soil.

ECM0167S1-S4: Study Title-" Dithiopyr and Its Metabolites Soil Residue Analytical Method"



External Standard Report

Sorted By : Signal  
 Calib. Data Modified : 09/11/2000 2:32:17 PM  
 Multiplier : 1.0000  
 Dilution : 1.0000

Signal 1: ECD1 A,

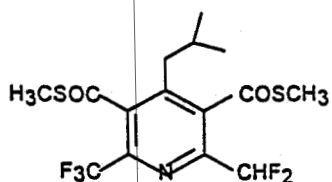
RetTime [min]	Type	Height [Hz]	Amt/Height	Amount [ng/ml]	Grp	Name
12.444	VP	378.19418	1.95471e-1	73.92614		RH-3972
14.378	PV	1174.15112	7.18404e-2	84.35154		RH-1765
14.704	VV	1190.29785	6.67959e-2	79.50706		RH-1766
17.575	VB	1625.87805	5.54578e-2	90.16764		Dithiopyr

Totals : 327.95238

Results obtained with enhanced integrator!

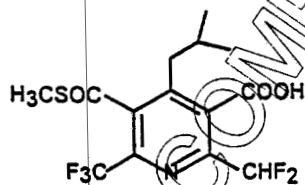
APPENDIX A:

STRUCTURE OF DITHIOPYR (RH-1664) AND ITS THREE DEGRADATE METABOLITES



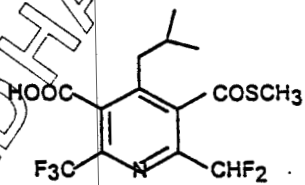
RH-1664

3,5-Pyridinedicarbothioic acid, 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-S,S-dimethylester



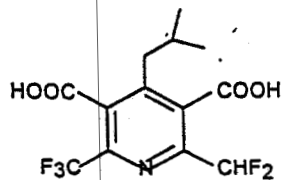
RH-1765

3-Pyridinecarboxylic acid, 2-(difluoromethyl)-4-(2-methylpropyl)-5-[(methylthio)carbonyl]-6-(trifluoromethyl)



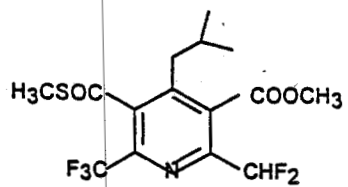
RH-1766

5-Pyridinecarboxylic acid, (difluoromethyl)-4-(2-methylpropyl)-3-[(methylthio)carbonyl]-2-(trifluoromethyl)

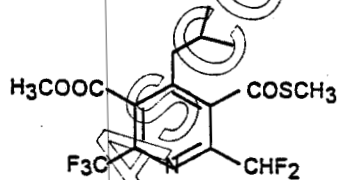


RH-3972

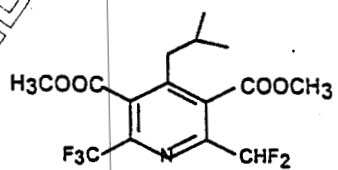
[3,5-pyridinedicarboxylic acid, 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)]



N-Methyl RH-1765



N-Methyl RH-1766



N-Methyl, Methyl RH-3972

