128994

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ENVIRONMENTAL CHEMISTRY SECTION
BUILDING 1105—JOHN C. STENNIS SPACE CENTER
STENNIS SPACE CENTER, MISSISSIPPI 39529-6000
TELEPHONE (601) 688-3216

AUG 29 1996

MEMORANDUM

SUBJECT: ECM Evaluation Report for Dithiopyr in Soil (ECM 0101S1)

FROM: Aubry E. Dupuy, Jr., Section Chief
BEAD/ACB/Environmental Chemistry Section

THRU: Donald A. Marlow, Branch Chief
BEAD/Analytical Chemistry Branch

TO: Henry M. Jacoby, Branch Chief (7507C)
EFED/Environmental Fate and Groundwater Branch

A laboratory evaluation of the environmental chemistry method for dithiopyr has been completed using the method in MRID 424566-01. The results of this method testing are included in the attached six page report, "Method Evaluation for the Determination of Dithiopyr in Soil (ECM 0101S1)".

No major difficulties were encountered, and the results met performance DQOs at all spiking levels.

If you have questions about this report, please contact Bob Maxey at 601-688-1225, or myself at 601-688-3212.

Attachment

cc: Bob Maxey, BEAD/ACB/ECS

0

Table of Contents

1.0 SUMMARY AND CONCLUSIONS

This report describes testing of a Registrant's method (MRID# 424566-01) for the determination of dithiopyr in soil matrix. The current Registrant is Rohm and Haas Company; however, Monsanto Company is the original Registrant who submitted the MRID. The laboratory evaluation, major difficulties, experimental conclusions and comments are presented in this section.

1.1 Laboratory Evaluation

Dithiopyr recoveries ranged from 99.9% to 107.8% with a mean recovery of 103.7% and a relative standard deviation (RSD) of 4.0% for samples fortified at 0.01 µg/g (LOQ). For samples fortified at 0.10 µg/g (10XLOQ), the recoveries ranged from 82.5% to 85.3% with a mean recovery of 84.0% and an RSD of 1.4%.

The instrument response to dithiopyr in samples fortified at the method detection limit (MDL) exceeded noise by a factor greater than three (S/N = 36). The MDL fortification level was 0.004 µg/g. No peaks were found within the retention time window of dithiopyr in either the reagent blank or the matrix blank. The calibration data for dithiopyr were linear over the range 1 to 10 ng/mL (mean calibration factor RSDs was 18.0%). All calibration check standards gave calibration factors differing by less than 20% from the initial mean calibration factor. The dithiopyr retention times for the initial calibration standards, calibration check standards, and for all fortified samples ranged from 5.66 to 5.69 minutes.

1.2 Major Difficulties

No major difficulties were encountered during the evaluation of this method.

1.3 Conclusions

The method performance met project DQOs for dithiopyr at all spiking levels. The method performance values obtained by SAIC for dithiopyr in an ECS program soil fortified at the 0.01 µg/g were better than those reported by the Registrant. The Registrant report a mean recovery of 76% with an RSD of 26.1% for soil samples fortified at 0.01 µg/g.

1.4 Comments

The time required for completing one set of 12 soil samples (4 replicates each of MDL, LOQ, and 10XLOQ), 4 calibration standards, and associated QC samples (matrix blank, reagent blank, instrument blanks, and calibration check) was approximately 2 working days. Sample preparation: 8 hours. GC/ECD analysis (including column preparation and conditioning): 8 hours. Samples can be analyzed overnight and data reduced the following day.

2.0 ANALYTICAL RESULTS

This section presents method testing results. Summary tables are presented along with individual results from each sample at each spiking level. The mean, standard deviation, and relative standard deviation are calculated in terms of percent recovery and in terms of measured concentration.

2.1 Data Summary

Spike Level (µg/g)	Percent Recovery Data			Concentration Data	
	Mean	SD[1]	RSD[2]	Mean	SD[1]
LOQ (0.010) Dithiopyr	103.7	4.2	4.0	0.0104	0.0004
10xLOQ (0.10) Dithiopyr	84.0	1.2	1.4	0.084	0.0012

[1] SD = Standard Deviation
[2] RSD = Relative Standard Deviation

2.2 Analytical Spike Information

Spike Level	Concentration of Spiking Solution (µg/mL)	Amount Spiked (mL)	Concentration in Sample (µg/g)	Sample W_i [1] (g)	Sample V_f [2] (mL)
MDL	0.2	0.20	0.004	10	50
LOQ	0.2	0.50	0.010	10	50
10xLOQ	2.0	0.50	0.10	10	200

[1] W_i = Initial Sample Weight
[2] V_f = Final Sample Volume

2.3 Individual Results in Soils Fortified at 0.010 µg/g (LOQ)

Sample Number	Retention Time (min)	Concentration Found (µg/g)	Conc. Fortified Sample (µg/g)	Percent Recovery
1 Dithiopyr	5.68	0.011	0.010	106.9
2 Dithiopyr	5.67	0.010	0.010	99.9
3 Dithiopyr	5.67	0.010	0.010	100.4
4 Dithiopyr	5.67	0.011	0.010	107.8

2.4 Individual Results in Soils Fortified at 0.10 µg/g (10xLOQ)

Sample Number	Retention Time (min)	Concentration Found (µg/g)	Conc. Fortified Sample (µg/g)	Percent Recovery
1 Dithiopyr	5.67	0.084	0.10	84.4
2 Dithiopyr	5.67	0.082	0.10	82.5
3 Dithiopyr	5.67	0.084	0.10	83.8
4 Dithiopyr	5.66	0.085	0.10	85.3

3.0 EXPERIMENTAL DETAILS

A brief summary of the analytical method as performed by SAIC, notes on the analytical procedure/accommodations to variables, and example calculations are presented in this section.

3.1 Method Summary

An ECS program soil matrix was fortified with dithiopyr at three different concentrations corresponding to the MDL, the LOQ, and ten times the LOQ. The fortification levels were: 0.004-µg/g, 0.01-µg/g, and 0.10-µg/g. Four replicates at each concentration were prepared and analyzed according to the specified procedure. Sample concentrations were calculated using a mean calibration factor determined from a four-point external standardization. The concentration of the four calibration standards were: 0.001-µg/mL, 0.002-µg/mL, 0.005-µg/mL and 0.010-µg/mL. The low point calibration standard corresponds to the one-half the LOQ. The method protocol is described briefly below.

3.1.1 Sample Preparation

A 10 g soil sample was weighed into a 250-mL Erlenmeyer flask. Ten mL of 20% acetonitrile/water was added to the sample followed with 50 mL of iso-octane. The sample was shaken on a shaker table at 400 rpm for 5 minutes, and the sample allowed to settle for at least 5 minutes. A 1 mL aliquot of the iso-octane (upper layer) was taken for GC-ECD analysis.

3.1.2 Analysis Method

The samples were analyzed by gas chromatography using a Hewlett Packard 5890 Series II GC with an electron-capture detector. Chromatographic conditions are listed below. Deviations from the Registrant's conditions are indicated by noting the Registrant's conditions in parenthesis.

Column:	30 m x 0.53 mm x 1.5 µm DB-5
Injection Volume:	4 µL
Injector Temperature:	250°C
Detector Temperature:	300°C
Detector:	electron-capture detector
Oven Temperature:	190°C for 8 min. then 20°C/min. to 280°C, hold for 4.5 min. (160°C for 1 min. then 10°C/min. to 250°C, hold 4 min.)
Carrier Gas (Helium):	11 mL/min. (Nitrogen @ 8 mL/min.)
Makeup Gas (P5 = 5% methane in argon):	30 mL/min. (Nitrogen @ 22 mL/min.)
Retention Time:	Dithiopyr ca. 5.62 min. (8.0 min.)

Standard Information: Dithiopyr
Rohm & Haas Company
Lot No. PIT-9001-1444A
Neat, 99.9% pure
Received 5/2/96
Prepared 5/10/96

Matrix Information: Provided by OPP
Iowa Batch #1 (10/26/95)
Received 2/6/96

3.2 Procedural Notes and Accommodations to Variables

Although the Registrant's method provides for moisture determinations, these measurements were not made. Recovery and precision values were determined from spiked matrices based on an as-is weight.

The filtration step described in the Registrant's method was omitted since the extract did not contain suspended soil particles.

The extracts resulting from samples fortified at 10xLOQ were diluted by a factor of four to bring the expected analyte concentration within the calibration range.

The GC temperature program was modified slightly from the Registrant's temperature program.

The method was evaluated using a Hewlett-Packard 5890 series II GC rather than the Varian 3700 specified in the the Registrant's method. A four-point calibration was used instead of a five-point calibration.

A mean calibration factor was used for quantitation rather than the least squares linear regression described by the Registrant.

3.3 Calculations

Example calculations are presented for calibration factor, mean calibration factor, extract concentration, sample concentration, and relative standard deviation.

3.3.1 Calibration Factor (chromatogram# 036B4101.D)

$$Calibration\ Factor\ (CF) = \frac{area\ counts}{concentration}$$

for the 5-ng/mL calibration standard, area counts = 2342 and concentration = 5:

$$Calibration\ Factor\ (CF) = \frac{2342}{5} = 468.4$$

3.3.2 Mean Calibration Factor (chromatograms# 034B3901.D - 037B4201.D)

$$CF_{mean} = \frac{(CF_1 + CF_2 + CF_3 + CF_4 + \ldots + CF_n)}{n}$$

where n = number of calibration points

the four-point calibration data for dithiopyr is:

n	concentration (ng/mL)	area counts	CF
1	1	614	614.0
2	2	1113	556.5
3	5	2342	468.4
4	10	4060	406.0

therefore:

$$CF_{mean} = \frac{(614.0 + 556.5 + 468.4 + 406.0)}{4} = 511.2$$

RSD = 18.0% (< 20%), therefore linear response

3.3.3 Extract Concentration (chromatogram# 019B5401.D)

$$Concentration_{extract} = \frac{area\ counts}{CF_{mean}}$$

for replicate 1 LOQ, area counts = 1093 and CF_{mean} = 511.2:

$$Concentration_{extract} = \frac{1093}{511.2} = 2.14\ ng/mL = 0.00214\ ug/mL$$

3.3.4 Sample Concentration (chromatogram# 019B5401.D)

$$Concentration_{sample} = \frac{Conc_{extract} \times Final\ Vol_{extract} \times Dilution\ Factor}{Inital\ Weight_{sample}}$$

for replicate 1 LOQ, $concentration_{extract}$ = 0.00214 ug/mL, final $volume_{extract}$ = 50.0 mL, dilution factor = 1 and initial $weight_{sample}$ = 10 g:

$$Concentration_{sample} = \frac{0.00214\ \mu g/mL \times 50mL \times 1}{10g} = 0.011\ \mu g/g$$

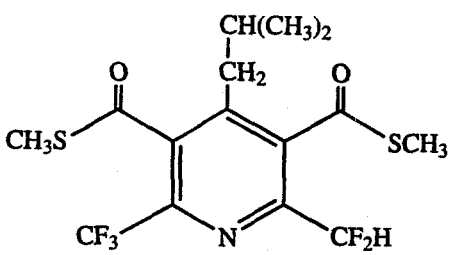
3.3.5 RSD is calculated by dividing the standard deviation of the values by the mean value and multiplying by 100%.

$$Mean = \bar{x} = \frac{\sum x_i}{n}$$

$$std.dev. = s = \sqrt{\frac{\sum(\bar{x} - x_i)^2}{n - 1}}$$

$$Precision\ as\ RSD = \frac{s}{\bar{x}} \times 100\ \%$$

3.4 Chemical Structure Diagram of Dithiopyr



Dithiopyr

Appendix A - Calibration Data

Initial calibration curves and continuing standards data are presented below:

Initial Calibration Data

Analyte	Retention Time (min)	Area Counts	Concentration (ng/mL)	Calibration Factor
Dithiopyr	5.67	614	1	614.0
Dithiopyr	5.67	1113	2	556.5
Dithiopyr	5.67	2342	5	468.4
Dithiopyr	5.67	4060	10	406.0

Mean Calibration Factor = 511.2
Standard Deviation = 92.2
Relative Standard Deviation = 18.0%

Calibration Check Data

Analyte	Calibration Check	Retention Time (min)	Area Count	Concentration (ng/mL)	Response Factor	Percent Difference[1]
Dithiopyr	1	5.67	1089	2	544.5	6.5
Dithiopyr	2	5.66	2468	5	493.6	-3.4

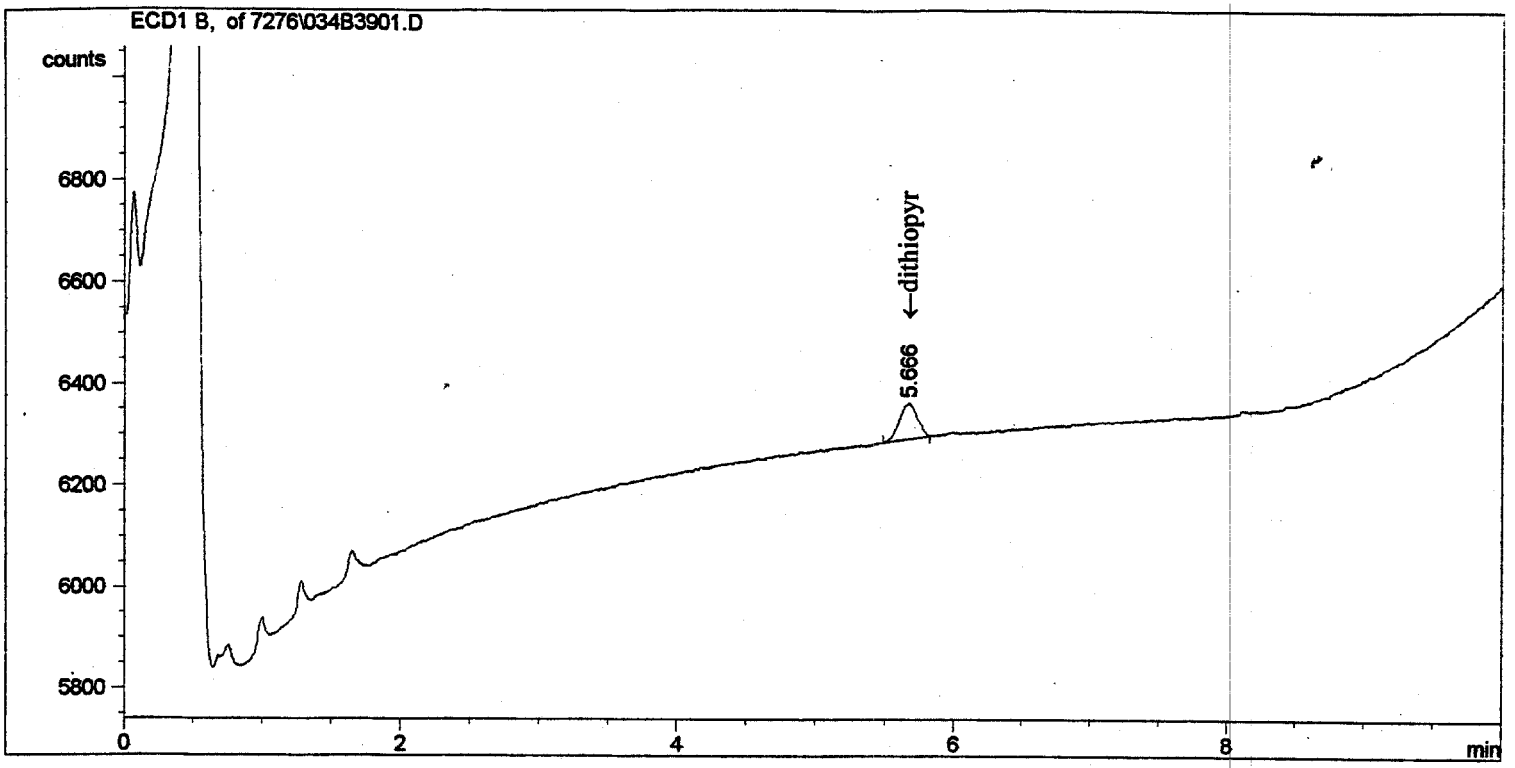
[1] Compared to the mean calibration factor.

Appendix B - Representative Chromatograms

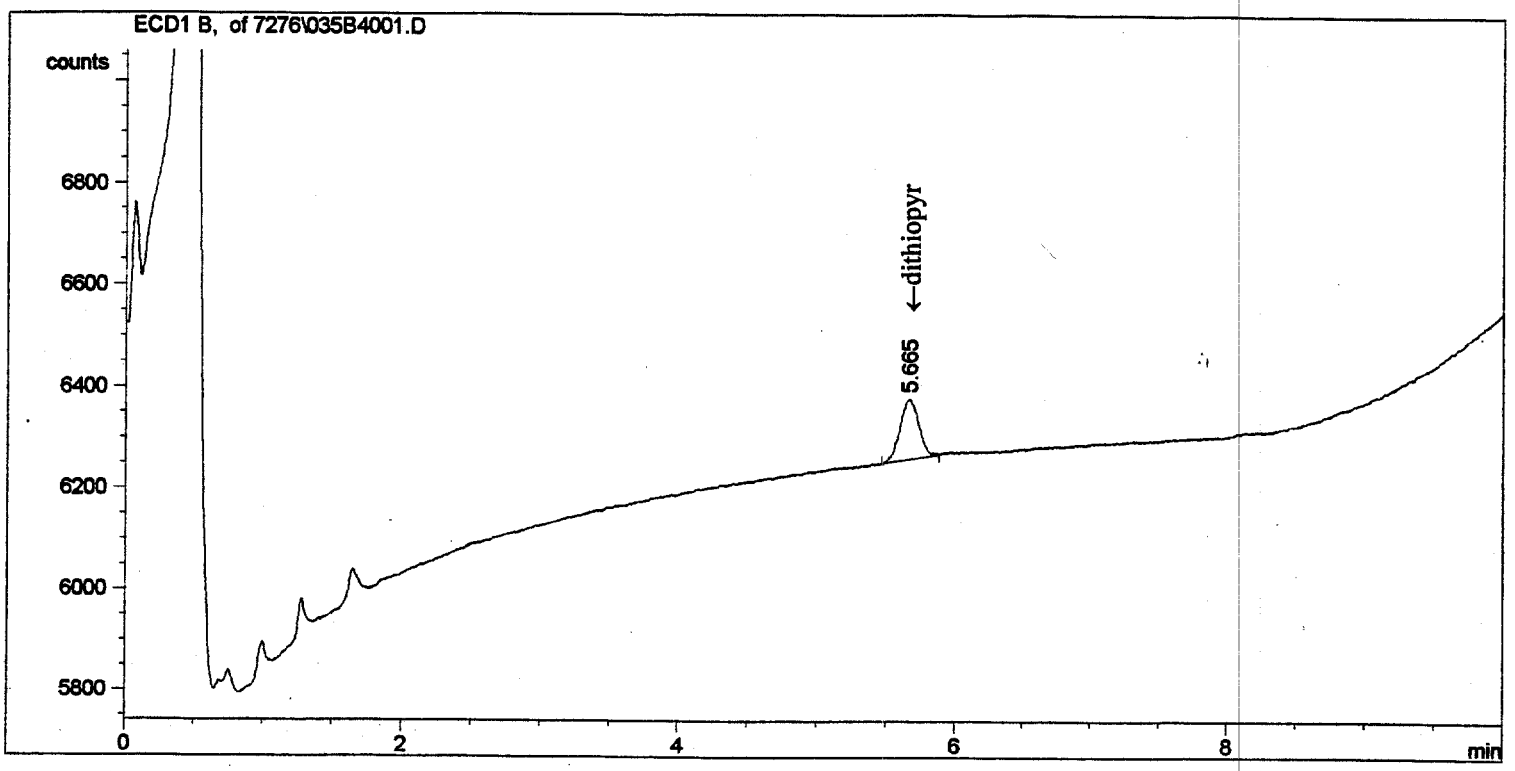
This section contains representative chromatograms of the calibration standards, reagent blank, matrix blank, and spiked samples at each fortification level in the following order:

- Calibration Standards (1, 2, 5 and 10 ng/mL)
- Reagent Blank
- Matrix Blank
- Soil at the MDL (0.0040 µg/g)
- Soil at the LOQ (0.010 µg/g)
- Soil at 10xLOQ (0.10 µg/g)

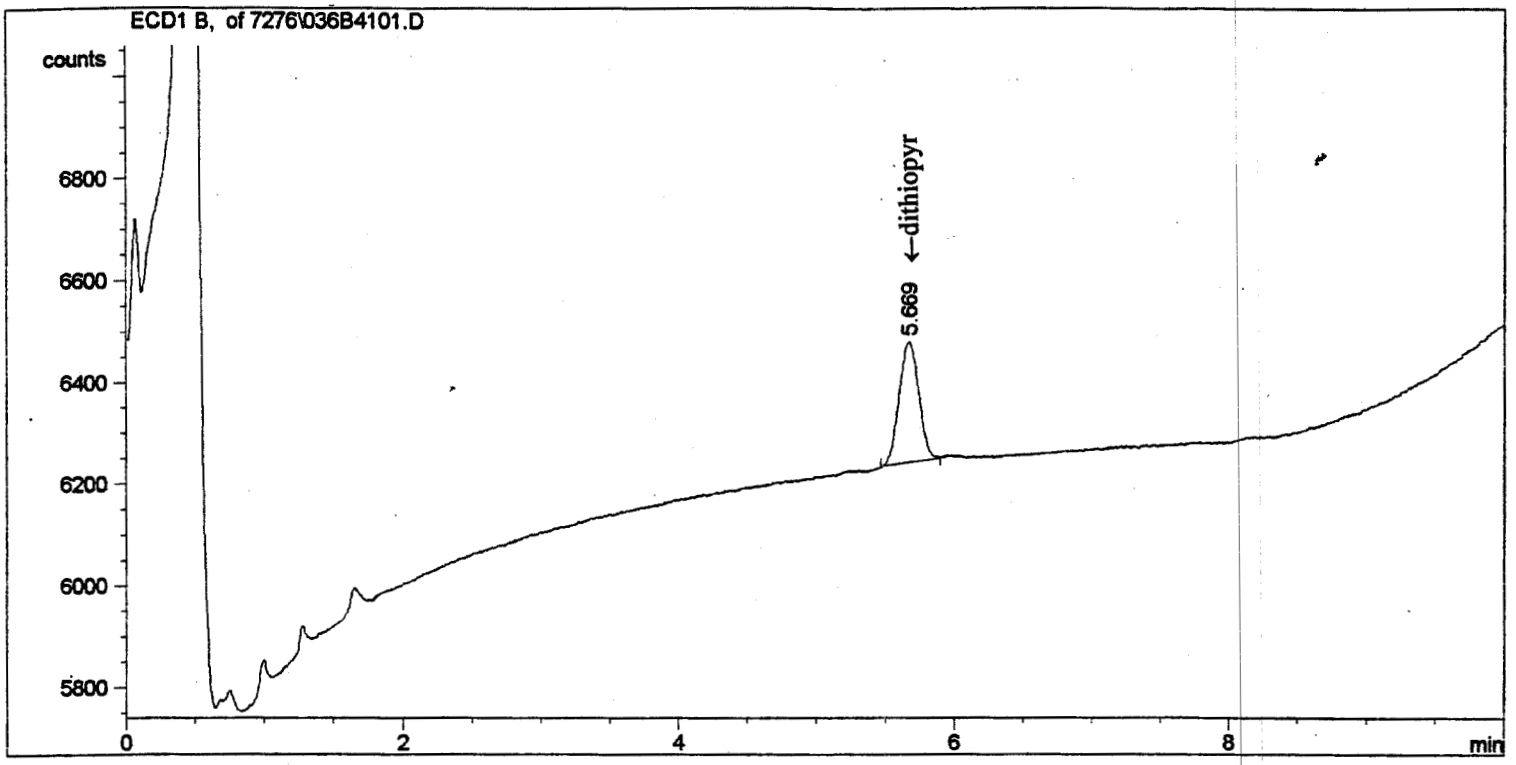
Calibration Standard - 1 ng/mL, 4 μL injection volume



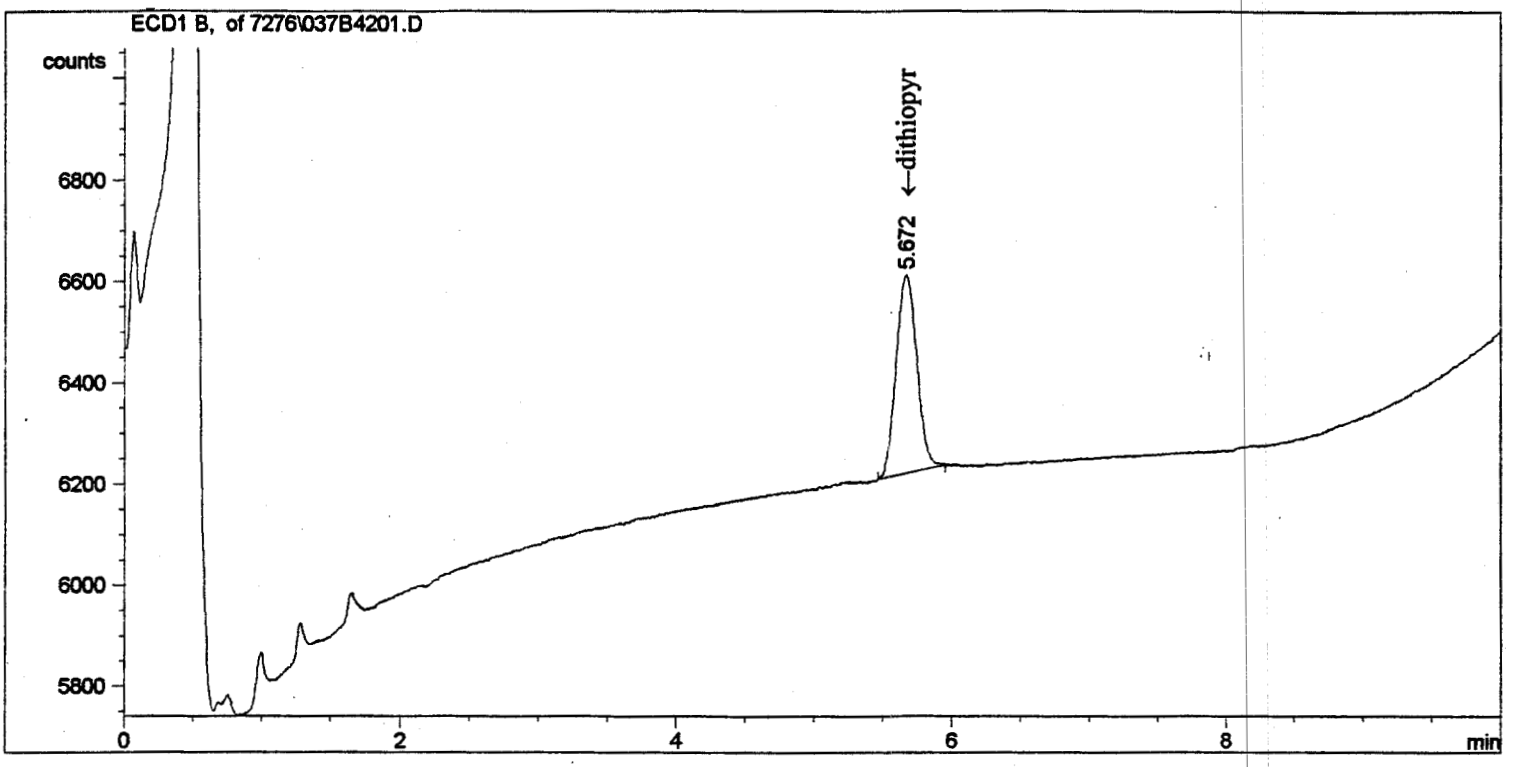
Calibration Standard - 2 ng/mL, 4 μL injection volume



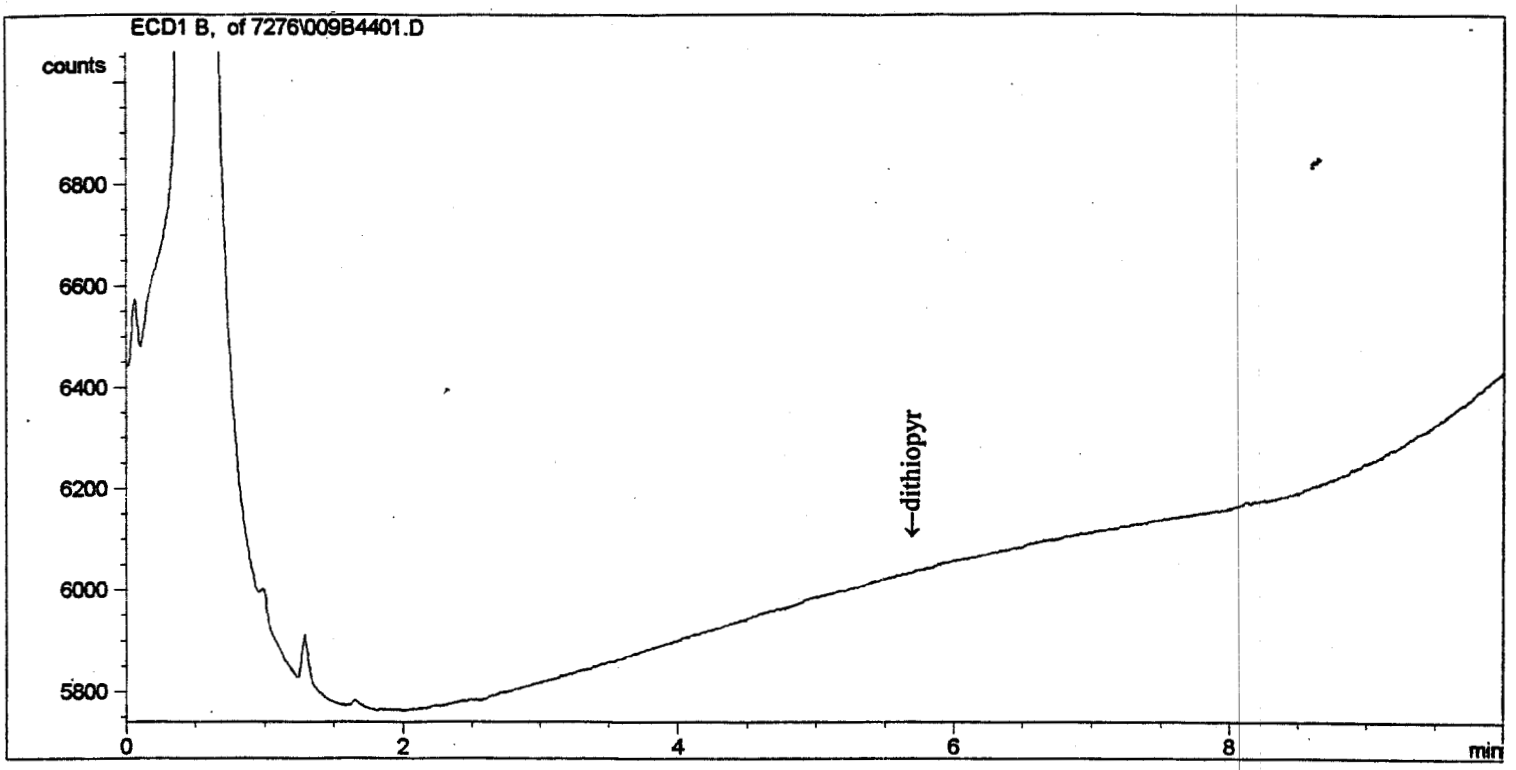
Calibration Standard - 5 ng/mL, 4 μL injection volume



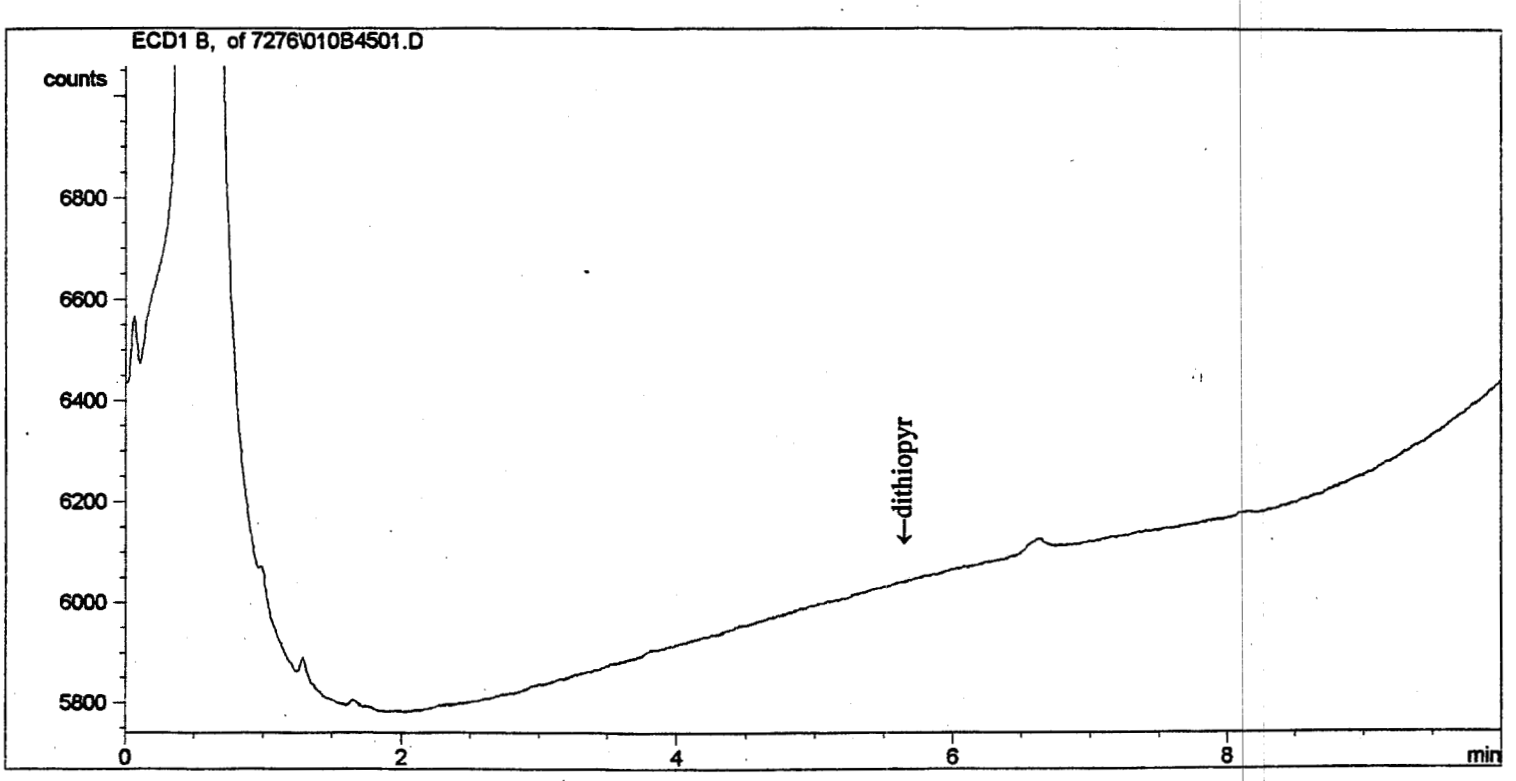
Calibration Standard - 10 ng/mL, 4 μL injection volume



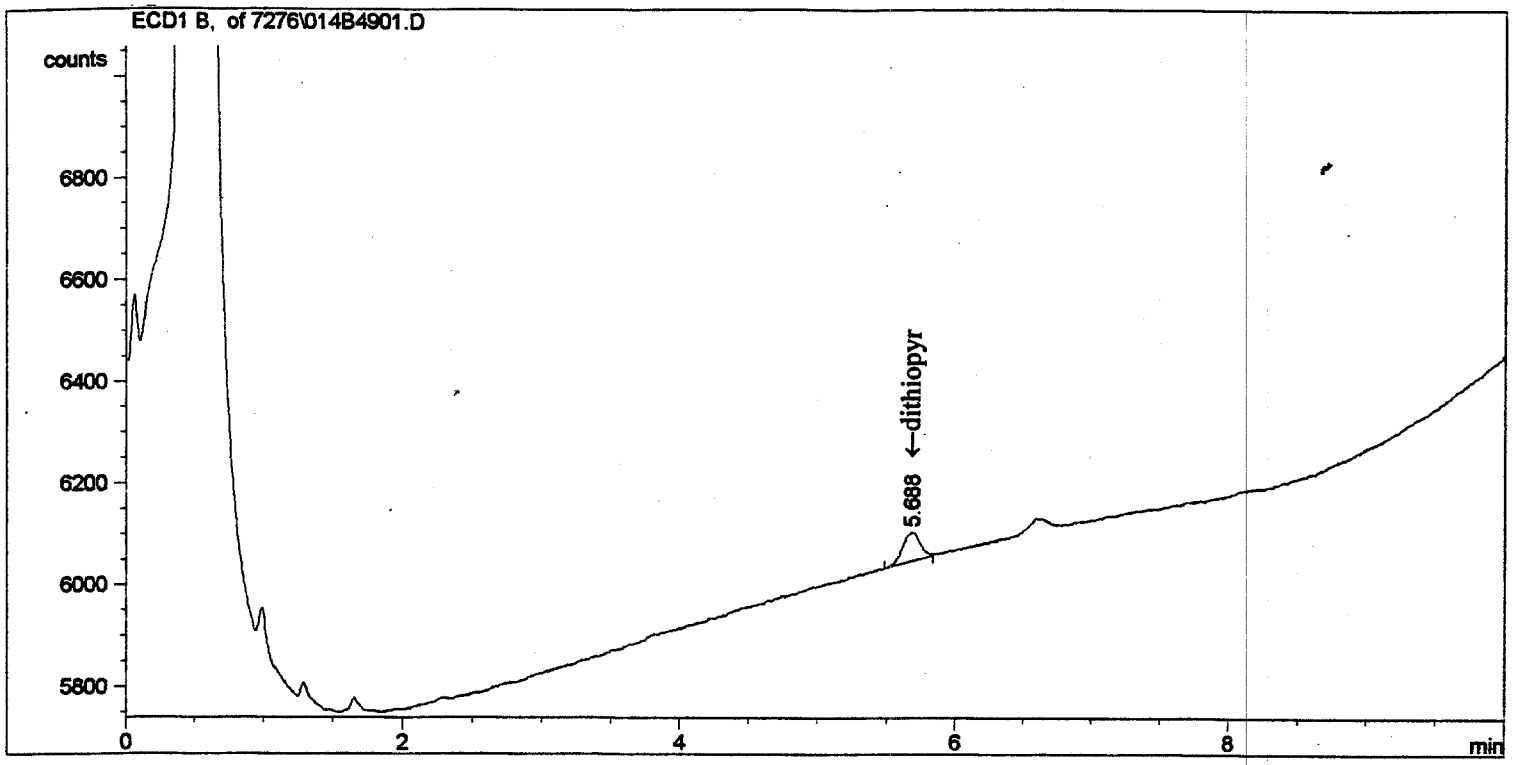
Reagent Blank - 50 mL final extract volume, 4 μL injection volume



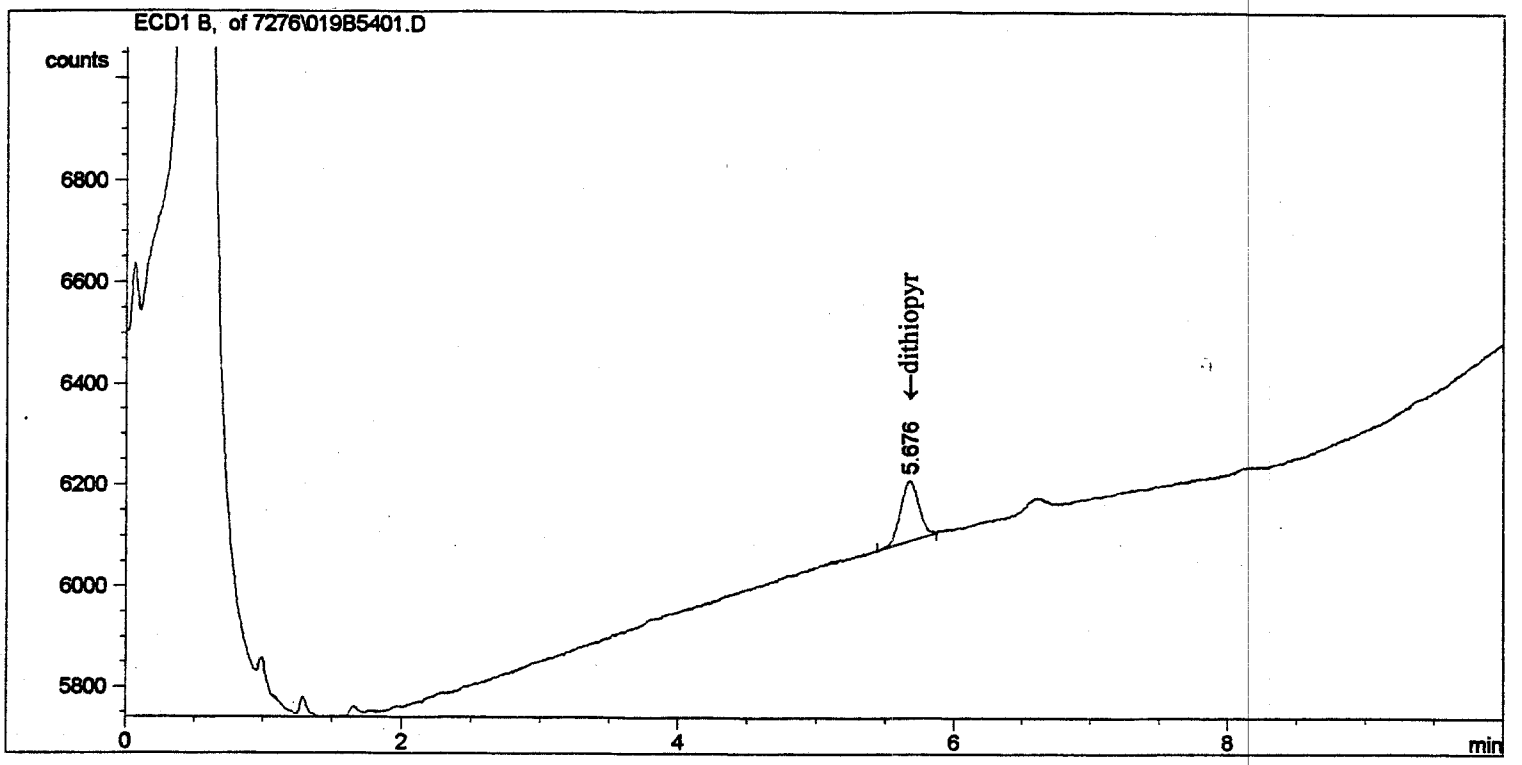
Matrix Blank - 50 mL final extract volume, 4 μL injection volume



Soil Fortified at 0.004 µg/g (MDL): 50 mL final extract volume, 4 µL injection volume



Soil Fortified at 0.010 µg/g (LOQ): 50 mL final extract volume, 4 µL injection volume



Soil Fortified at 0.10 µg/g (10xLOQ): 200 mL final extract volume, 4 µL injection volume