

# Pronamide-02

## STUDY TITLE

An Improved Analytical Method for the Determination of  
Kerb® Residues in Crops and Soil

## DATA REQUIREMENT

Guideline 171-4

## AUTHOR

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## STUDY COMPLETED ON

April 13, 1993

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## LABORATORY PROJECT ID

Technical Report No. 34-93-33

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*S. Smith*  
7/2/93

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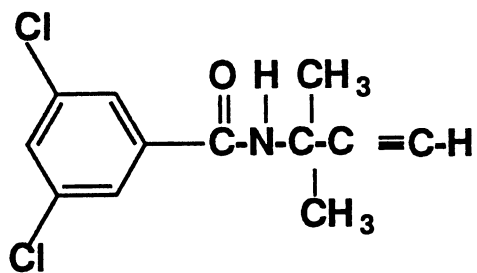
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**SUBJECT:** Analytical Method for the Determination of  
Kerb® Residues in Crops and Soil

## I. INTRODUCTION

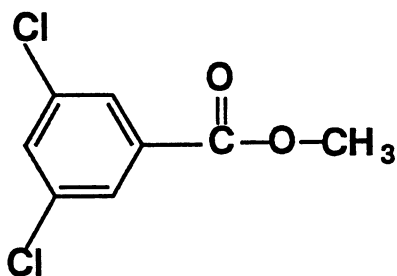
Residues of Kerb® [N-(1,1-dimethylpropynyl)-3,5-dichlorobenzamide] Compound I and corresponding metabolites are determined by digesting the sample with sulfuric acid and methanol to convert residues to methyl 3,5-dichlorobenzoate Compound II. This compound is codistilled from the reaction medium, purified by chromatography on Florisil, and measured by electron capture gas-liquid chromatography. The method is sensitive to 0.01 ppm.

## II. EXPERIMENTAL COMPOUNDS



Kerb®, 3,5-dichloro-N-(1,1-dimethyl-2-propynyl)-benzamide

Compound I



Methyl-3,5-Dichlorobenzoate (MDCB)

Compound II

### III. Chemicals and Equipment

#### Chemicals

1. Methanol (HPLC Grade), J. T. Baker Inc., Phillipsburg, NJ 08865
2. Deionized Ultrapure Water, by Milli-Q Purification System
3. Sulfuric Acid (96%) Mallinkrodt, Inc., Paris, KY 40361
4. Sulfuric Acid (15 N).\*
5. Sodium Sulfate, anhydrous, granular, Reagent Grade Mallinkrodt, Inc.
6. Boiling Stones, Teflon, Fisher Scientific, Inc., Fair Lawn, NJ 07410
7. Toluene, (HPLC Grade), J. T. Baker
8. Hexane (HPLC Grade), J. T. Baker
9. Florisil, 100/200 mesh, (5% deactivated\*\*) US Silica Co., Berkeley Springs, W. Va., 25411
10. Florisil liquid-solid chromatographic column\*\*\*
11. Methyl-3,5-Dichlorobenzoate (MDCB), Analytical Standard, Rohm and Haas Co., Phila. PA 19105
12. Sodium Chloride, granular, Fisher Scientific, Inc.
13. P-10 gas (10% methane in argon), Air Products Inc., Lehigh Valley, PA 18001
14. 10% OV-11 on 80/100 Gas Chrom. Q, Supelco, Inc., Bellefonte, PA 16823

15. Kerb<sup>®</sup>, 3,5-dichloro-N-(1,1-dimethyl-2-propynyl)-benzamide, Analytical Standard, Rohm and Haas Co., Phila., PA 19105
- \* Slowly add 167 ml of Sulfuric Acid (96%) to 233 ml of ultrapure deionized water in a 1000 ml glass Erlenmeyer flask (1 ml acid + 1.4 ml H<sub>2</sub>O = 15N). Since the reaction of water and acid is exothermic, this operation should be performed using an ice bath. Extreme caution should be exercised in acid handling with proper laboratory apparel that includes a face shield, heavy elbow length impervious gloves, lab coat, and spill apron. Use spill pillow in case of an emergency. Neutralize residual acid with lime (CaO) by adding it slowly with copious water for high dilution.
  - \*\* Activate Florisil at 150°C for 24 hours. Transfer to a glass jar equipped with a foil lined cap. Add 10 ml of Ultrapure Water (Milli-Q) to 200g of Florisil. Cap tightly and mix well on a tumbler for 30 minutes. Store in a dessicator. Let stand overnight before use.
  - \*\*\* Add 8.0 cc of deactivated Florisil to a glass-wool plugged liquid chromatographic column (10.5 mm ID, 250 mm long Ace Glass Co. glass column w/200 ml reservoir). After packing Florisil using a vibrator, top the column with 2g of Sodium Sulfate. Columns should be prepared immediately before use. Dispose of used Florisil into a Non-hazardous solid waste container. Each batch of Florisil should be checked after deactivation to confirm elution pattern.

### Equipment

1. Standard taper one-neck round bottom flasks (500 ml)
2. Standard taper condensers, 12" long with 1 cm ID maximum
3. Standard 24/40 Ts stoppers
4. Dean-Stark receivers (grad. 10 ml) with Teflon stopcocks (modified by Custom Scientific Glass, Inc. Bear, DE 19701)
5. Liquid chromatographic column (10.5 mm ID, 250 mm long, glass, with 200 ml reservoir, Teflon stopcocks), Ace Glass Inc., Vineland, NJ 08360
6. Graduated cylinders: 50, 100, 250 ml sizes
7. Separatory funnels, pear shaped, 500 ml with teflon stopcock
8. Volumetric flasks, 10, 100, 500 ml sizes
9. 2 oz. glass screw-capped jar, foil caps
10. Lab-Line/Isopad Labsafe Thermal Mantles, Fisher Scientific, 500 ml
11. Variable Transformers (powerstats), Fisher Scientific
12. I<sup>2</sup>R Water-Guards, Cheltenham, PA 19012
13. TRACOR 560 GC, with a <sup>63</sup>Ni ECD, Tracor Inc., Austin, TX 78721
14. Glass GC column, 8' x 1/4" O.D., Supelco, Inc., Bellefonte, PA 16823
15. Hobart Food Processor - Model 84145 Hobart Corp., Troy, Ohio 45374
16. Thermalyne Oven - Model OV35325, Thermalyne Corp. Dubuque, Iowa USA (for Florisil activation)

Note: Equivalent Chemicals and Equipment may be used.

#### IV. METHOD

##### A. Sample Processing

Crop samples are homogenized in a Hobart food processor with dry ice. The dry ice is removed by sublimation in a freezer at -10°C overnight. Samples are stored frozen at -10°C until analyzed.

Soil samples are screened through a 2 mm screen (ASTM No. 10) to remove stones and plant debris. Representative subsamples are taken for moisture determination.

##### B. Sample Esterification

1. Weigh 10g of a homogeneous sample and transfer to a 500 ml round bottom flask that has been placed in an ice bath. Slowly, add 100 ml of 15N sulfuric acid to the flask. Swirl the flask to assist cooling the sample mixture. Caution is advised since this step is very exothermic. See safety precautions in the reagent list for Sulfuric Acid.
2. Slowly add 50 ml of methanol to the round bottom flask. Caution is advised to prevent the methanol from "boiling out." Swirl and mix well.
3. Add 5-6 boiling chips to each flask. Immediately connect the flask to the Dean-Stark apparatus and condenser. Check glassware for cracks. Slowly apply adequate heat for reflux (setting approximately 70/140 max. on each Powerstat). Turn water to the condensers on. Check water hose integrity and operational status of the Water-Flow Guards.

After reflux has started, adjust distillation rate to approximate 60 drops per minute. No more than three condensers should be connected in series with each Waterguard®. Effluent water from last condenser in series should not exceed 60-65°F (cooling water bath may be necessary). Wrap the tops of the reflux pots with aluminum foil to help maintain a more even temperature within the pots and prevent bumping.

4. Reflux a total of five hours. Distill five cuts of methanol (approximately 22 ml each) from the third hour to the end of the reflux period. When each distillate is removed from the Dean-Stark apparatus, carefully add back an identical amount of fresh methanol through the top of the condenser. Combine the five distillates in a stoppered 100 ml graduate.

See schedule below.

<u>Cut #</u>	<u>Vol.</u>	<u>Time of reflux /Collection (Hours)</u>
1	22	3
2	22	3.5
3	22	4
4	22	4.5
5	22	5

**Note:** For disposal of remaining pot contents, dilute with water, neutralize with lime and divert to waste stream. eg. 25 g. lime/diluted pot contents in 8 liters of water.

### C. Partitioning

Immediately after reflux/distillation, the distillate is transferred into a 500 ml separatory funnel. Add 75 ml of 10% aq. NaCl solution to the distillate.

Rinse the 100 ml graduate with 40 ml of hexane and add to the separatory funnel. Vigorously shake the separatory funnel for two minutes with frequent venting to avoid excess pressure buildup in the funnel.

Allow the phases to separate completely. After distillation, the MDCB should not be in contact with water any longer than necessary. Therefore after partitioning, the aqueous phases should be separated from the hexane as soon as phase separation is complete.

Drain off and discard the lower aqueous layer and pour the upper organic layer into a 2 oz. jar containing 5 g. of sodium sulfate. Seal with a foil lined screw cap. The sample may be stored overnight at room temperature. Do not store the solutions beyond 24 hours.

**D. Florisil Column Chromatography**

1. Prepare a <sup>1.05 cm</sup> 1.5 cm I.D. glass chromatography column containing 8 cm of 5% deactivated Florisil and top with 2 grams of anhydrous granular sodium sulfate.
2. Pour the upper organic layer from the jar directly onto the column. After the hexane has reached the sodium sulfate layer, rinse the jar twice with 5 ml portions of hexane and add to the column. When this hexane reaches the sodium sulfate layer, elute the methyl ester of 3,5-dichlorobenzoic acid from the column with 35 ml of 30% toluene in hexane (v/v). Save this solution for GLC analysis (note volume, do not concentrate sample).

**E. Preparation of Standard Solutions**

1. Weigh 0.05 g of Kerb<sup>®</sup> analytical standard into a 25 ml beaker on an analytical balance. Quantitatively transfer to a 500 ml volumetric flask using methanol. Fill to the 500 ml mark with methanol. The resulting solution is a 100 µg/ml stock solution of Kerb<sup>®</sup>. This stock solution is serially diluted with acetone in 100 ml volumetric flask and will be used for method fortification purposes. Prepare 10, 5 and 1 µg/ml solutions.
2. Weigh a 0.04 g of MDCB analytical standard into a 25 ml beaker on an analytical balance. Quantitatively transfer to a 500 ml volumetric flask using toluene. Fill to the 500 ml mark with toluene. The resulting solution is an 80 µg/ml stock solution of MDCB which is equivalent to 100 µg/ml of Kerb<sup>®</sup>. The ratio of the molecular weight of MDCB (205.9 g/m) to Kerb<sup>®</sup> (256.13 g/m) is 0.8. This stock solution is serially diluted with 30% toluene in hexane to 0.8 µg/ml MDCB in a 100 ml volumetric flask and will be used for the preparation of GC standards.
3. By serial dilution of the 0.8 µg/ml MDCB stock solution make standard solutions of 0.001, 0.005, 0.010, 0.025 and 0.05 µg/ml (Kerb<sup>®</sup> equivalent). (The conversion factor from MDCB to Kerb<sup>®</sup> is 1.25.) These will be used as standards for gas chromatographic analysis. Make up these solutions in 100 ml volumetric flask using 30% toluene in hexane for dilution.

**F. GLC Quantitation****1. Instruments and Conditions**

Instrument : Hewlett Packard 5890 II equipped with a 7673 A autoinjector  
Column: RTX-5, 30 m x 0.53 mm, 1.5  $\mu$  film thickness  
Carrier Gas: He, 10 ml/min.  
Detector: ECD, 300°C  
Detector Purge: N<sub>2</sub>, 50ml/min.  
Oven Temperature: Initial temp. = 100°C, hold for 2 min.  
20°C/min. to 150°C, hold for 3 min.  
20°C/min. to 270°C, hold for 4 min.  
Run Time: 17.5 min.  
Injector: Isothermal, 250°C  
Volume Injected: 2  $\mu$ l

**2. Preparation of Standard Curves**

Inject 2.0  $\mu$ l of each standard into the GC column, allowing the MDCB Standard peak to elute before injecting the next standard. Measure the peak height for each injected standard in mm. Plot peak height in mm versus  $\mu$ g/ml Kerb<sup>®</sup> to obtain standard curve. A new standard curve is generated for each set of samples. Sample standard chromatograms and standard curves are given in Appendix I.

**3. Quantitation**

Two microliters of the sample, section E are injected into the GLC. If necessary, the sample is diluted to an appropriate volume to give a response within the standard curve range. The peak height is measured and the concentration is determined from the standard curve. Standards should be injected during and after sample analysis to demonstrate detector linearity.

The Kerb<sup>®</sup> residue concentration is determined as follows:

$$\frac{\text{Total Volume (mL)} \times \text{concentration } (\mu\text{g/ml}) \times 100}{\text{Average Recovery (\%)} \times \text{Sample Weight (g)}} = \text{ppm}$$

#### 4. Fortification Recovery

For samples fortified with known amounts of Kerb<sup>®</sup> prior to extraction, measure the peak height, determine  $\mu\text{g/ml}$  from the standard curve, correct for any background in the control sample, and calculate % recovery from the following equation.

$$\frac{(\mu\text{g/ml Found}) \times \text{Final Sample Volume ml} \times 100}{\text{Fortification } (\mu\text{g})} = \% \text{ recovery}$$

#### 5. Confirmatory Column Analysis

##### Instruments and Conditions

Instrument : Hewlett Packard 5890 II equipped with a 7673 A autoinjector  
 Column: RTX-200 30 m x 0.53 mm, 1.0  $\mu$  film thickness  
 Carrier Gas: He, 10 ml/min.  
 Detector: ECD, 300°C  
 Detector Purge: N<sub>2</sub>, 40ml/min.  
 Oven Temperature: Initial temp. = 100°C, hold for 2 min.  
 20°C/min. to 200°C, hold for 2 min.  
 20°C/min. to 270°C, hold for 2 min.  
 Run Time: 14.5 min.  
 Injector: 250°C  
 Volume Injected: 2  $\mu\text{l}$

Confirmatory chromatograms of control and fortified samples are given in Appendix II with a typical standard curve.

**G. Recoveries**

Average recoveries for fortifications are expected to be greater than 75%.

Chromatograms of control and fortified samples are given in Appendix I.

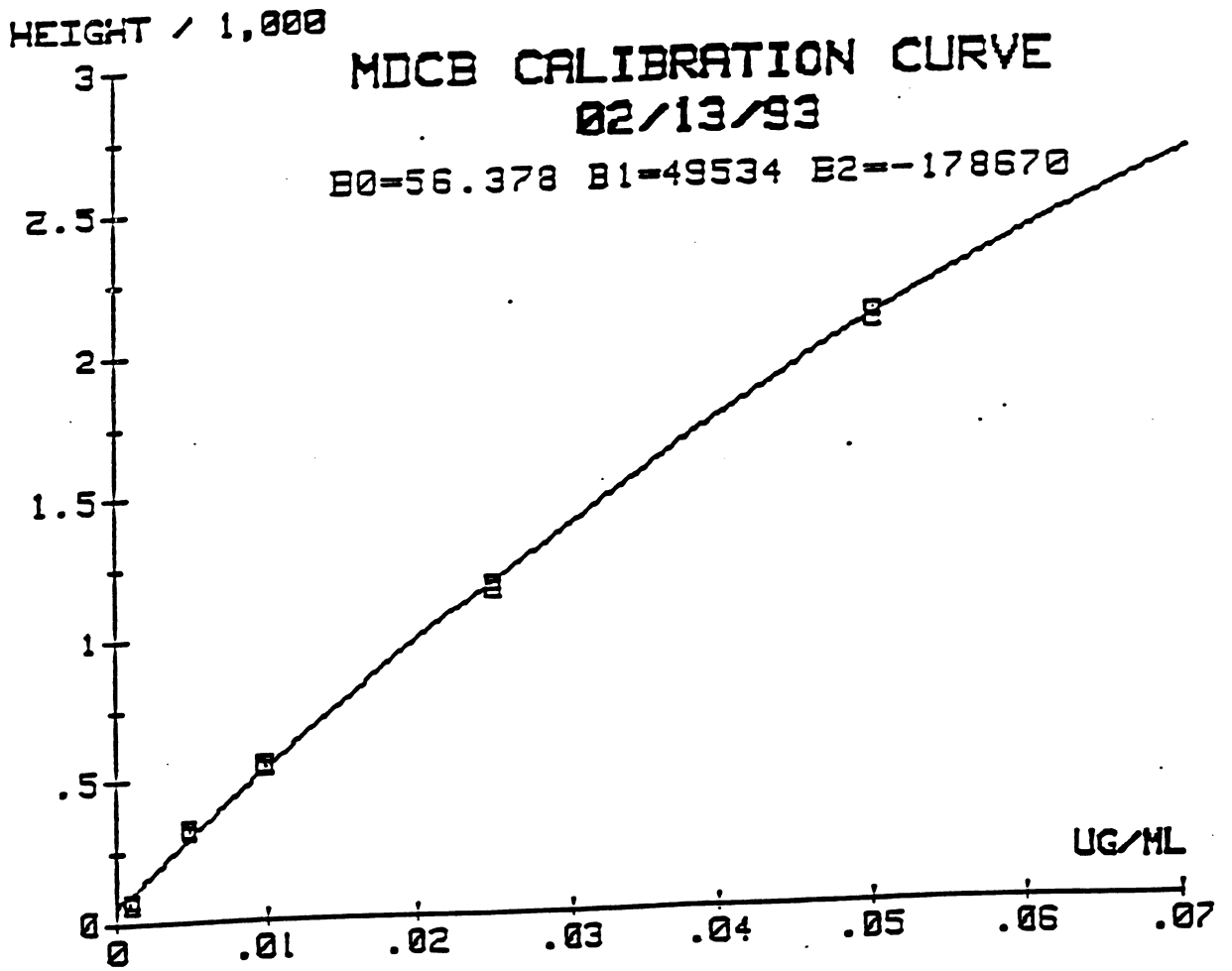
**H. Sensitivity**

The limit of quantitation (LOQ) has been shown to be 0.01 ppm determined by actual fortification at this level.

The limit of detection (LOD) is estimated at 0.003 ppm based on background levels present in control samples.

## **APPENDIX I**

### **Standard Curve and Sample Chromatograms**



Concentrations in report are calculated from equation:  
 $HEIGHT = B0 + B1(UG/ML) + B2(UG/ML)^2$   
 obtained by least-squares fit of standard injection data.

Data file: F15C4                      Type: STANDARD

---

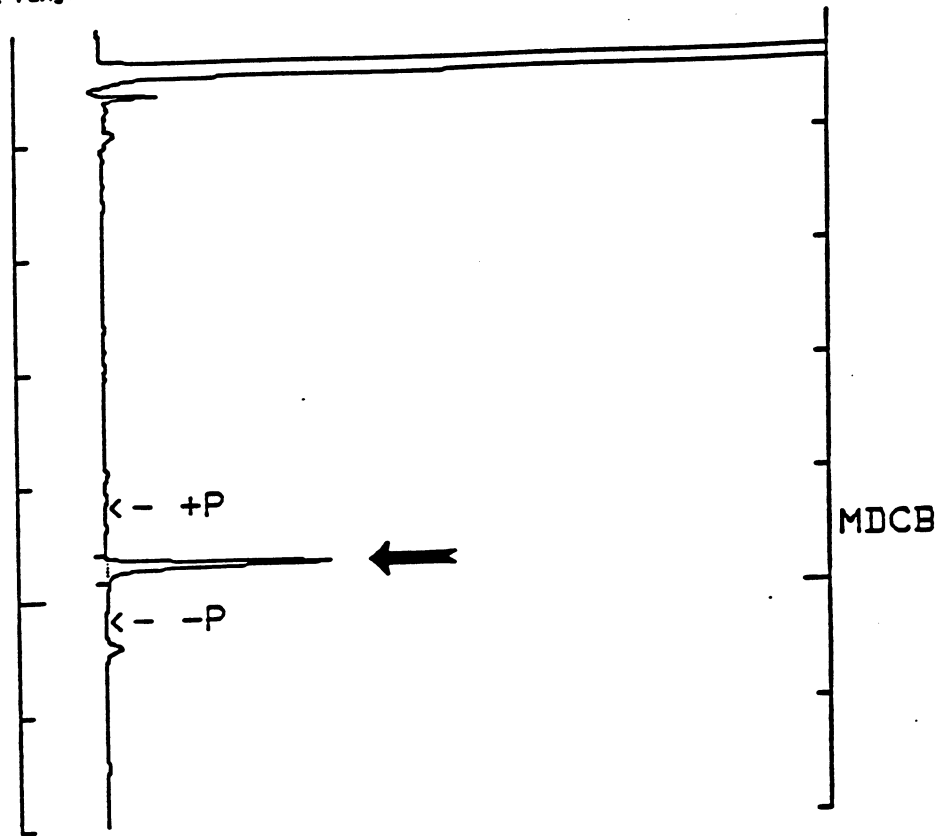
Sample Name: N/A    Cal. Curve: 02/15/93  
 Date: 15 Feb 1993 21:51    Method: KERBa                      Analyst: CL    ZLL  
 Interface: 711                      Cycle#: 4                      Channel#: A

---

Instrument: HP-5890 II  
 Column: RTX-5 , 1.50um df, 30m, 0.53mm    Column Length: 30    Meters  
 Start Temp-Time (deg-min): 100-2                      Ramp Hold (deg-min): 150-3  
 Program Rate (deg/min): 20                      End Time-Temp (deg-min): 270-4  
 Prog Slope (# or Linear): NA                      Inj Port Temp: 250  
 Flowrate/Gas: 10/He                      Split Ratio: NA  
 Det 1-Type & Temp: ECD/300                      ~~Det 2-Type & Temp: FPD/200~~ *sd.*

---

Plot times: 0 to 7 minutes  
 Plot range: 40 millivolts (-5.3 mv offset)



Retention Time	Compound Name	PPM Injected	Area	Height
4.71	MDCB	0.025	7.600E+00	1.120E+03

Example chromatogram of a 0.025 µg/ml standard

Data file: F1807  
 Method file: KERBm  
 Type: SAMPLE

RAR number: 92-0016  
 Sample No: 001  
 Component: SOIL

Sample Name: N/A

Cal. Curve: 02/18/93

Date: 18 Feb 1993 20:26 Method: KERBm  
 Interface: 711 Cycle#: 7

Analyst: ZCL *ZCL*  
 Channel#: A

Instrument: HP-5890 II

Column: RTX-5, 1.50um df, 30m, 0.53mm Column Length: 30 Meters

Start Temp-Time (deg-min): 100-2 Ramp Hold (deg-min): 150-3

Program Rate (deg/min): 20 End Time-Temp (deg-min): 270-4

Prog Slope (# or Linear): NA Inj Port Temp: 250

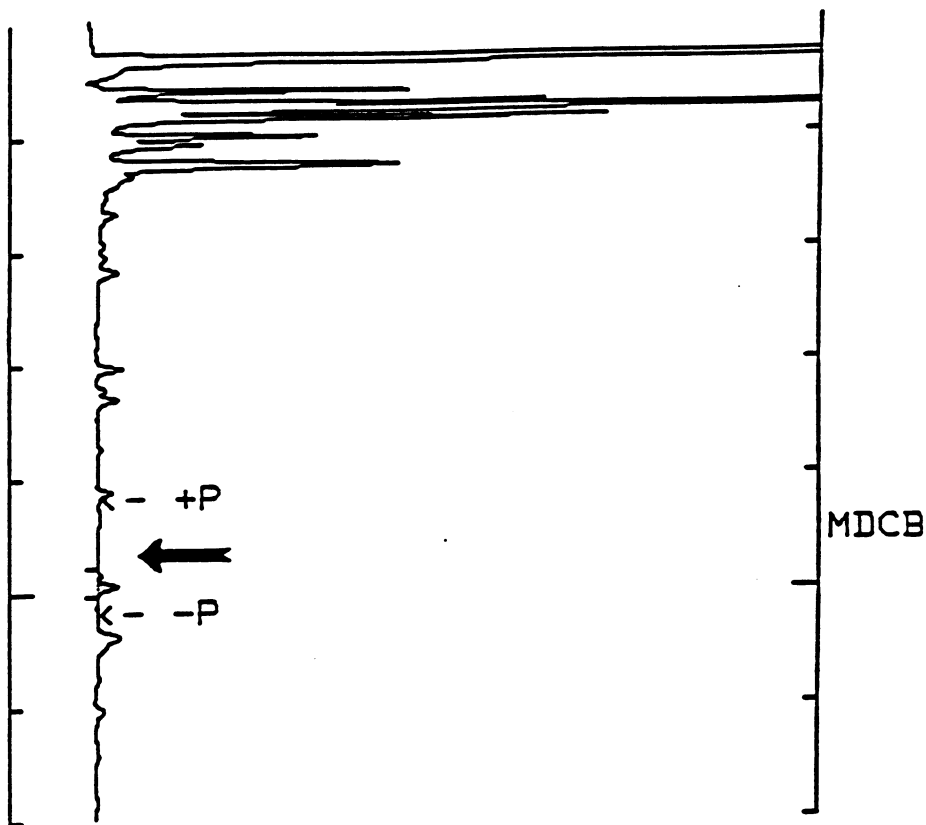
Flowrate/Gas: 10/He Split Ratio: NA

Det 1-Type & Temp: ECD/300

~~Det 2-Type & Temp: FPD/200~~ *ES*

Plot times: 0 to 7 minutes

Plot range: 40 millivolts (-5.4 mv offset)



Ret. Time	Compound Name	Peak Area	Peak Height	Volume (ml)	Samp Wt.
4.69	MDCB	0.000E+00	.000E+00	35.0	10.0

Example chromatogram of a control sample for Soil

Data file: F1809  
 Method file: KERBm  
 Type: FORTIFICATION

RAR number: 92-0016  
 Sample No: 001  
 Component: SOIL

---

Sample Name: N/A  
 Date: 18 Feb 1993 21:10  
 Interface: 711

Method: KERBm  
 Cycle#: 9

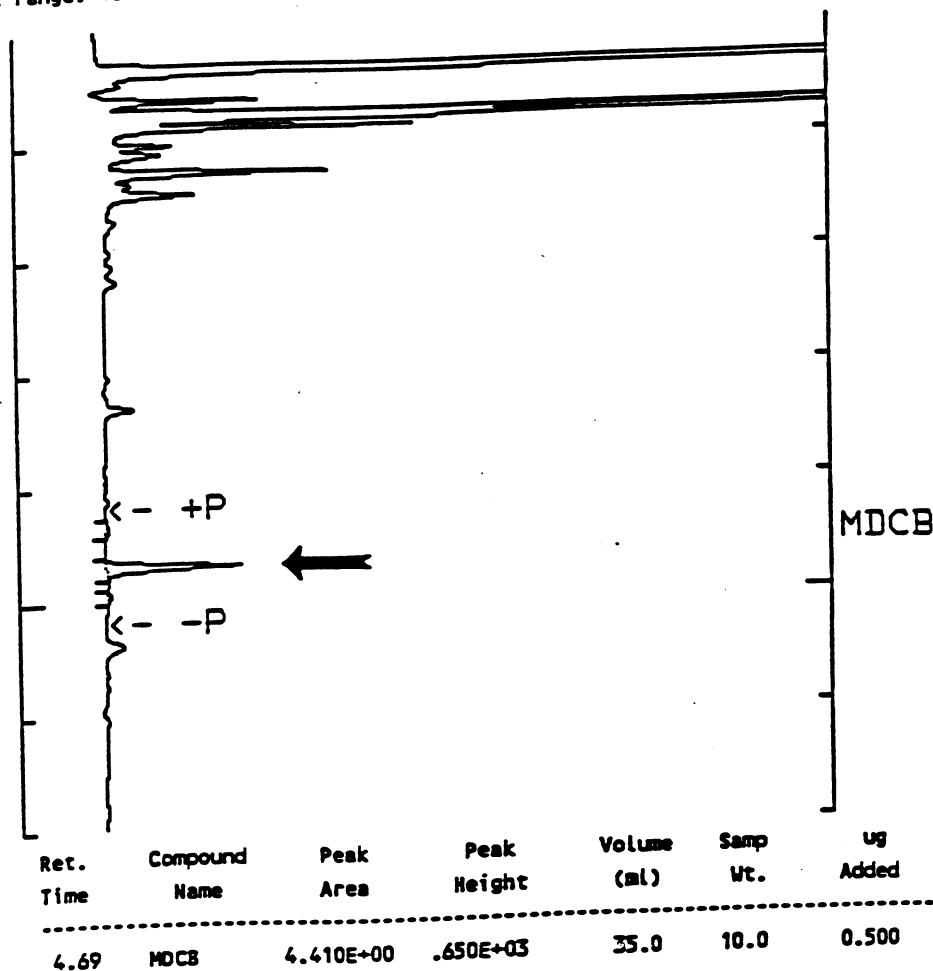
Analyst: ZCL *ZCL*  
 Channel#: A

Cal. Curve: 02/18/93

---

Instrument: HP-5890 II  
 Column: RTX-5 , 1.50um df, 30m, 0.53mm Column Length: 30 Meters  
 Start Temp-Time (deg-min): 100-2 Ramp Hold (deg-min): 150-3  
 Program Rate (deg/min): 20 End Time-Temp (deg-min): 270-4  
 Prog Slope (# or Linear): NA Inj Port Temp: 250  
 Flowrate/Gas: 10/He Split Ratio: NA  
 Det 1-Type & Temp: ECD/300 ~~Det 2-Type & Temp: FPD/200-1d~~

Plot times: 0 to 7 minutes  
 Plot range: 40 millivolts (-5.5 mv offset)



Example chromatogram of a Soil sample fortified at 0.05 ppm

Data file: F15C7  
 Method file: KERBm  
 Type: SAMPLE

RAR number: CAL  
 Sample No: 418  
 Component: LETTUCE

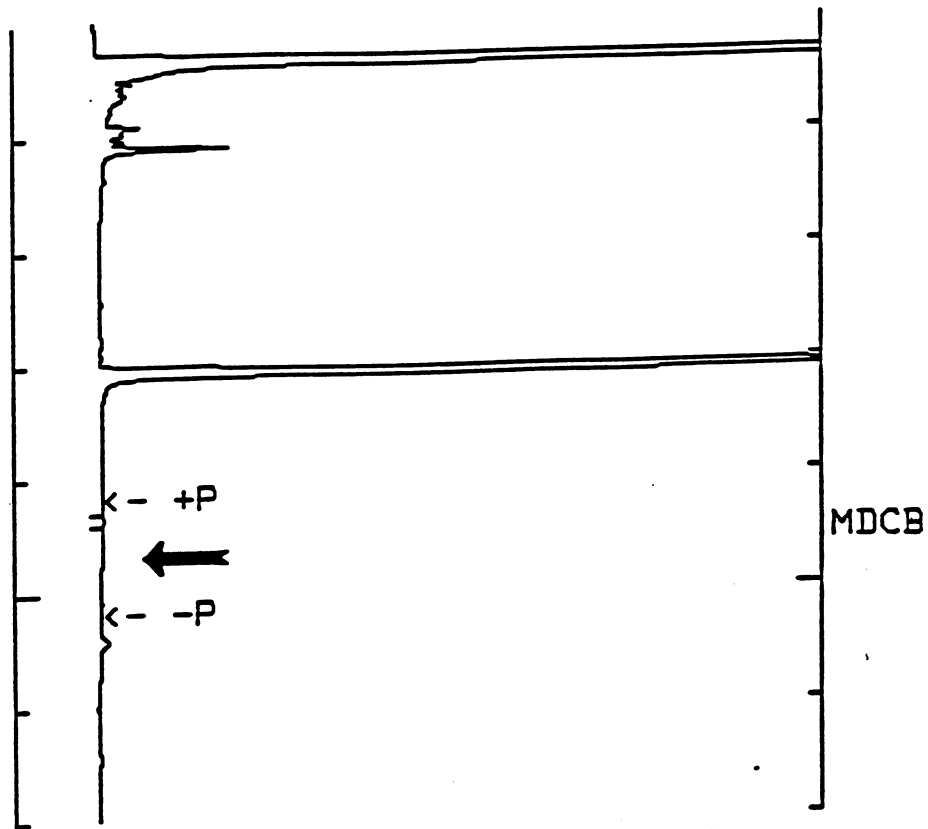
Sample Name: N/A  
 Date: 15 Feb 1993 22:56  
 Interface: 711

Method: KERBm  
 Cycle#: 7

Cal. Curve: 02/15/93  
 Analyst: CL ZCL  
 Channel#: A

Instrument: HP-5890 II  
 Column: RTX-5, 1.50um df, 30m, 0.53mm Column Length: 30 Meters  
 Start Temp-Time (deg-min): 100-2 Ramp Hold (deg-min): 150-3  
 Program Rate (deg/min): 20 End Time-Temp (deg-min): 270-4  
 Prog Slope (# or Linear): NA Inj Port Temp: 250  
 Flowrate/Gas: 10/He Split Ratio: NA  
 Det 1-Type & Temp: ECD/300 ~~Det 2-Type & Temp: FPD/200~~

Plot times: 0 to 7 minutes  
 Plot range: 40 millivolts (-5.3 mv offset)



Ret. Time	Compound Name	Peak Area	Peak Height	Volume (ml)	Samp Wt.
4.71	MDCB	0.000E+00	.000E+00	35.0	10.0

Example chromatogram of a control sample for Lettuce

Data file: F15C10  
 Method file: KERBm  
 Type: FORTIFICATION

RAR number: CAL  
 Sample No: 418  
 Component: LETTUCE

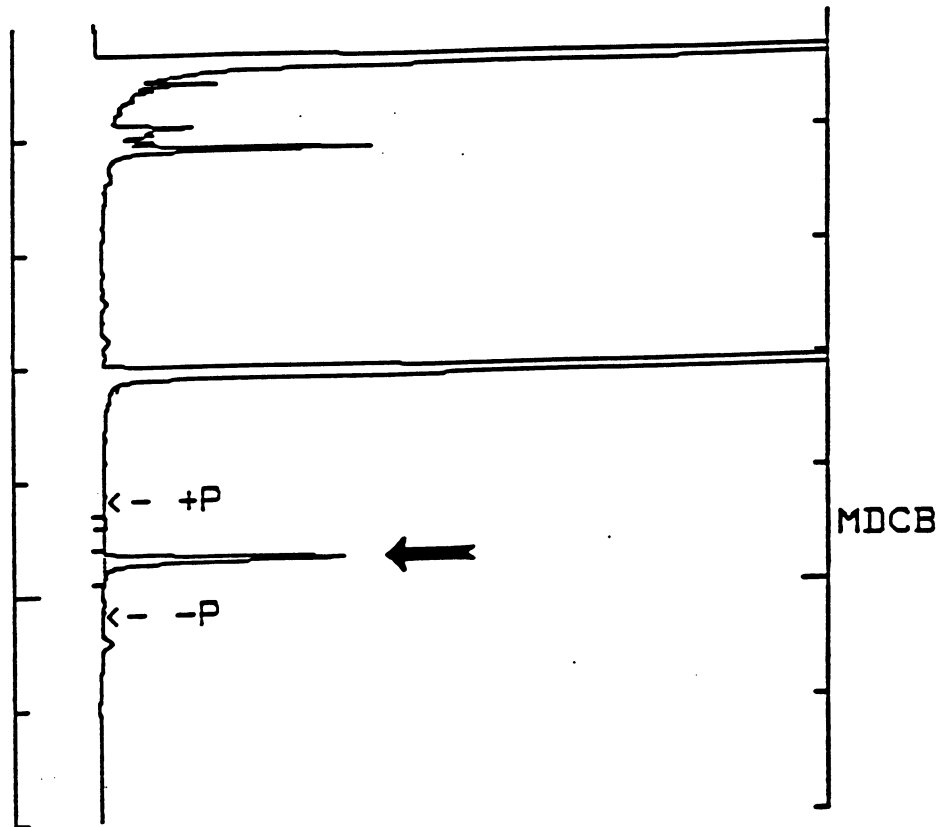
Sample Name: N/A  
 Date: 16 Feb 1993 00:02  
 Interface: 711

Cal. Curve: 02/15/93

Analyst: CL *ZCL*  
 Channel#: A

Instrument: HP-5890 II  
 Column: RTX-5, 1.50um df, 30m, 0.53mm Column Length: 30 Meters  
 Start Temp-Time (deg-min): 100-2 Ramp Hold (deg-min): 150-3  
 Program Rate (deg/min): 20 End Time-Temp (deg-min): 270-4  
 Prog Slope (# or Linear): NA Inj Port Temp: 250  
 Flowrate/Gas: 10/He Split Ratio: NA  
 Det 1-Type & Temp: ECD/300 ~~Det 2-Type & Temp: FPD/200~~

Plot times: 0 to 7 minutes  
 Plot range: 40 millivolts (-5.4 mv offset)

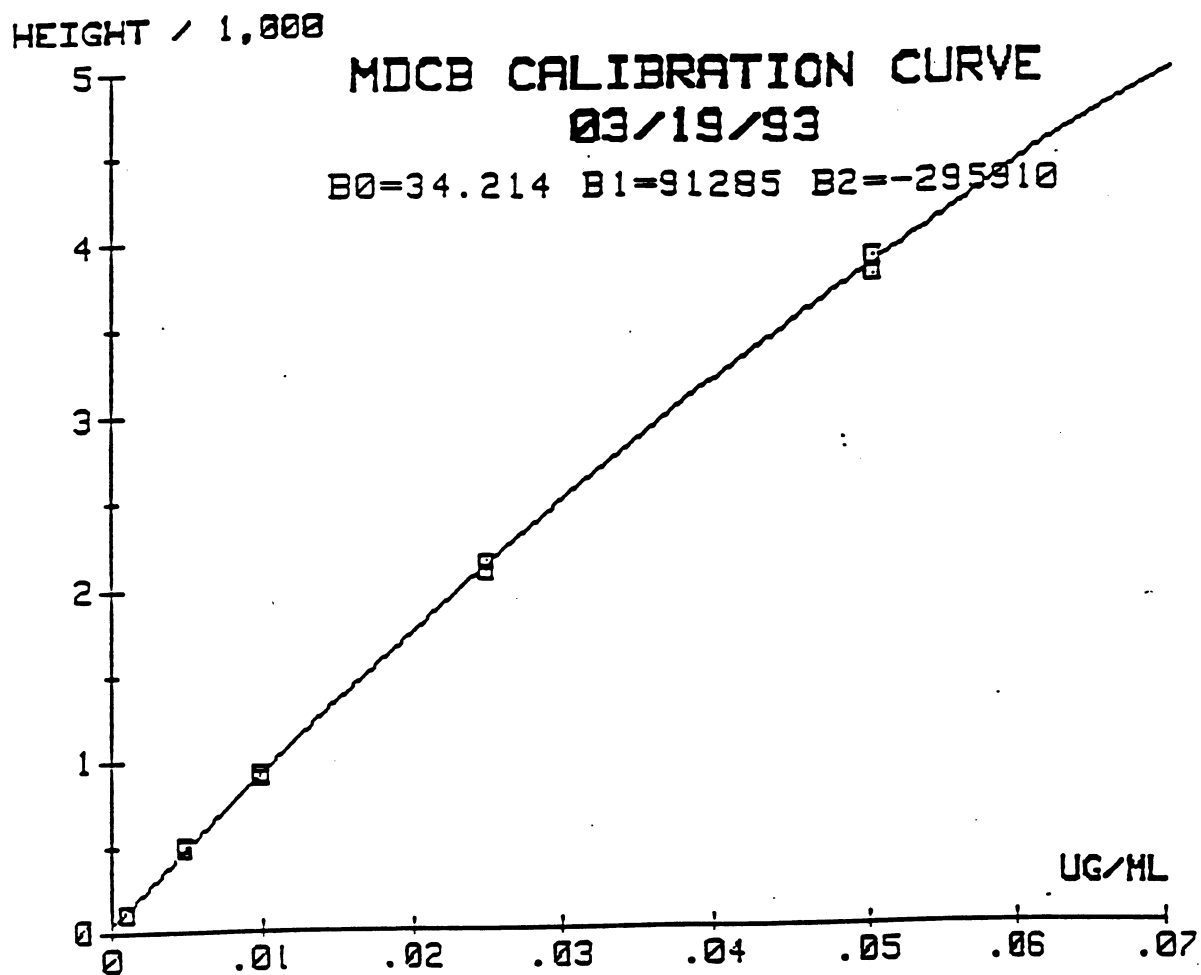


Ret. Time	Compound Name	Peak Area	Peak Height	Volume (ml)	Samp Wt.	ug Added
4.71	MDCB	8.040E+00	.117E+04	35.0	10.0	1.00

Example chromatogram of a Lettuce sample fortified at 0.1 ppm

## **APPENDIX II**

### **Confirmatory Column: Standard Curve and Sample Chromatograms**



Concentrations in report are calculated from equation:  
 $HEIGHT = B0 + B1(UG/ML) + B2(UG/ML)^2$   
obtained by least-squares fit of standard injection data.

Figure 1. Example of a standard Calibration Curve

Data file: M18C14  
 Method file: Km  
 Type: SAMPLE

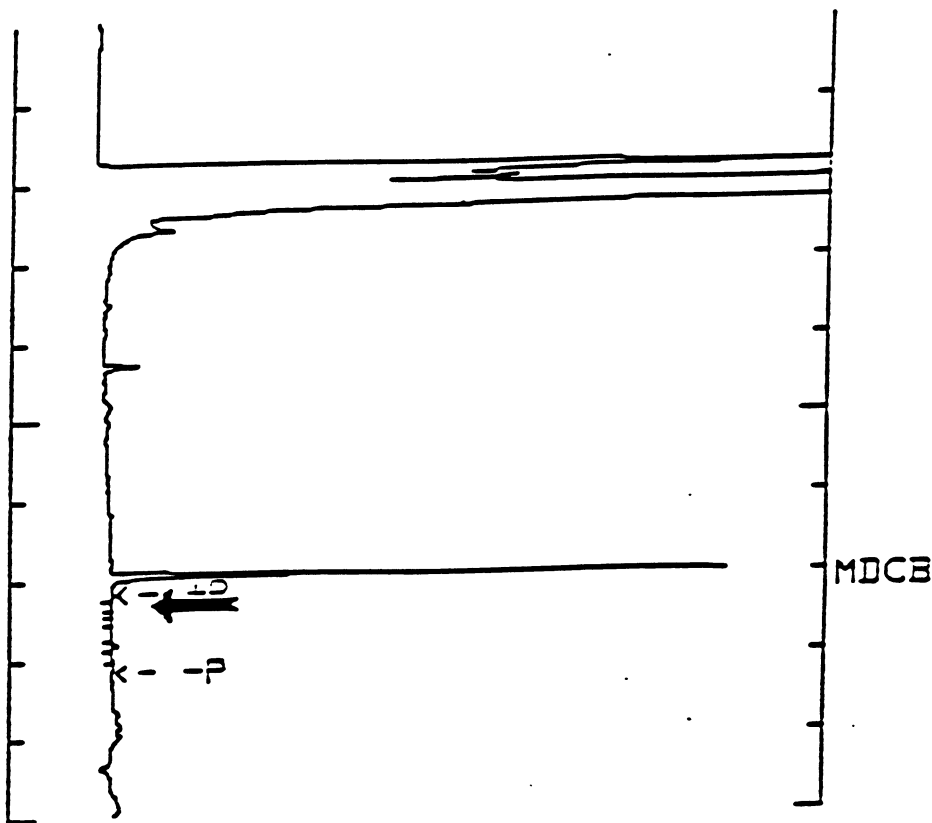
RAR number: CAL  
 Sample No: 418  
 Component: LETTUCE

Sample Name: NA  
 Date: 18 Mar 1993 21:26 Method: Km  
 Interface: 711 Cycles: 14

Cal. Curve: 03/18/93  
 Analyst: ZC  
 Channel#: A

Instrument: HP-5890 II  
 Column: RTX-200, 0.53mm, 30m, 1.0um Column Length: 30 Meters  
 Start Temp-Time (deg-min): 100-2 Ramp Hold (deg-min): 200-2  
 Program Rate (deg/min): 20 End Time-Temp (deg-min): 270-2  
 Prog Slope (# or Linear): NA Inj Port Temp: 250  
 Flowrate/Gas: 10/He Split Ratio: NA  
 Det 1-Type & Temp: ECD/300 ~~Det 2-Type & Temp: FPD/290~~

Plot times: 0 to 10 minutes  
 Plot range: 100 millivolts (-4.1 mv offset)



Ret. Time	Compound Name	Peak Area	Peak Height	Volume (ml)	Sample Wt.
7.35	MDCB	1.180E-01	.134E-02	35.0	10.0

Figure 2. Example chromatogram of a control sample for Lettuce



Data file: M18C18  
 Method file: Km  
 Type: FORTIFICATION

RAR number: CAL  
 Sample No: 418  
 Component: LETTUCE

---

Sample Name: NA  
 Date: 18 Mar 1993 22:39 Method: Km  
 Interface: 711 Cycle#: 18

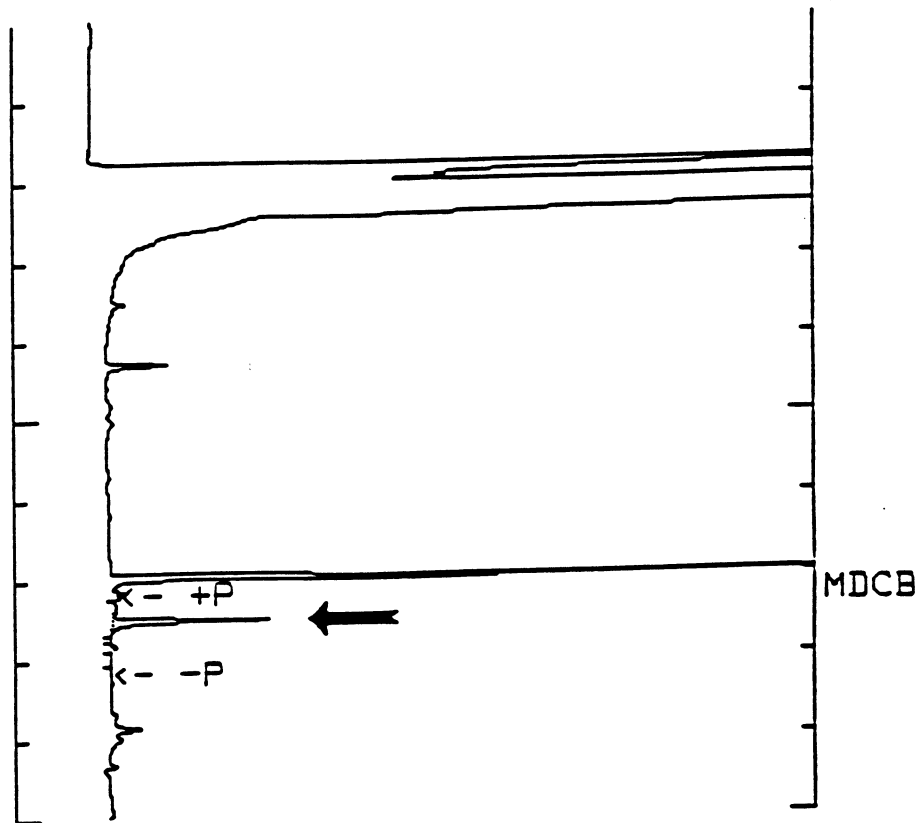
Cal. Curve: 03/18/93  
 Analyst: ZCL  
 Channel#: A

---

Instrument: HP-5890 II  
 Column: RTX-200, 0.53mm, 30m, 1.0um Column Length: 30 Meters  
 Start Temp-Time (deg-min): 100-2 Ramp Hold (deg-min): 200-2  
 Program Rate (deg/min): 20 End Time-Temp (deg-min): 270-2  
 Prog Slope (# or Linear): NA Inj Port Temp: 250  
 Flowrate/Gas: 10/He Split Ratio: NA  
 Det 1-Type & Temp: ECD/300 ~~Det 2 Type & Temp: FPD/200~~

---

Plot times: 0 to 10 minutes  
 Plot range: 100 millivolts (-4.1 mv offset)



Ret. Time	Compound Name	Peak Area	Peak Height	Volume (ml)	Samp Wt.	ug Added
7.50	MDCB	+ 1.210E+01	.197E+04	35.0	10.0	1.00

Figure 4 Example chromatogram of a Lettuce sample fortified at 0.1 ppm

```

Data file: M18011
Method file: Km
Type: FORTIFICATION
RAR number: 920016
Sample No: 001
Component: SOIL
-----
Sample Name: NA
Date: 19 Mar 1993 03:24
Interface: 711
Method: Km
Cycle#: 11
Cal. Curve: 03/19/93
Analyst: ZCL ZCL
Channel#: A
-----
Instrument: HP-5890 II
Column: RTX-200, 0.53mm, 30m, 1.0um
Start Temp-Time (deg-min): 100-2
Program Rate (deg/min): 20
Prog Slope (# or Linear): NA
Flowrate/Gas: 10/He
Det 1-Type & Temp: ECD/300
Column Length: 30 Meters
Ramp Hold (deg-min): 200-2
End Time-Temp (deg-min): 270-2
Inj Port Temp: 250
Split Ratio: NA
Det 2-Type & Temp: FPD/200 AD
-----

```

Plot times: 0 to 10 minutes  
 Plot range: 100 millivolts (-4.5 mv offset)

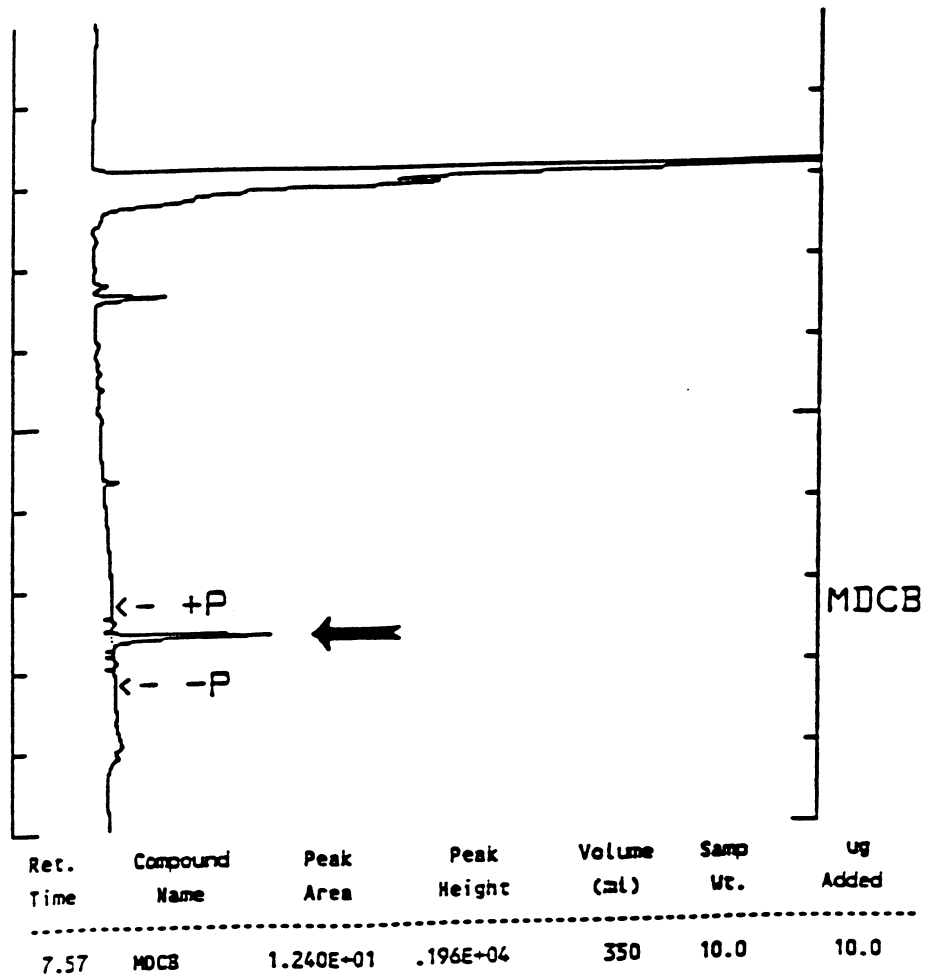


Figure 5. Example chromatogram of a Soil sample fortified at 1.0 ppm