UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Captan Method Evaluation - Report No. ECM0067S1-S2. Methods Validated by BEAD/ACB/ECS.

TO: , PM Team #
Special Review and Reregistration Division (7508W)

FROM: Richard J. Mahler, Hydrologist
Environmental Chemistry Review Section I
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (7507C)

THROUGH: Henry M. Jacoby, Chief
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (7507C)

Paul J. Mastradone, Chief
Environmental Chemistry Review Section I
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (7507C)

The Environmental Chemistry Section (ECS) of BEAD/ACB has completed the Environmental Chemistry Method Evaluation (ECME) of the analytical methods taken from a study entitled "Captan 50-WP field dissipation study on California strawberries" (MRID 40823901). The Ecological Effects Branch/EFED has requested an Environmental Chemistry Methods Validation for soil.

In summary, it was found that the method can be used to monitor soil for the presence of captan and its degradate, Tetrahydrophthalimide (THPI), at the levels claimed by the registrant. No major madifications were necessary for the ECME. From the results, the method provided satisfactory measurement for residues of captan and THPI between 10.0 and 300.0 ppb.

Method performance met recovery (70-120%) and precision (Relative Standard Deviation, RSD, $\leq$20%) objectives at all spiking levels (10.0-300.0 ppb). For example, captan had a RSD of 3.0% at the LOD of 10.0 ppb and 6.6% at 300.0 ppb. The mean recoveries were 105.5% at the LOD and 100.4% at 300.0 ppb. The results obtained for recoveries and precision were comparable to those reported by the registrant.

It was stated by ECS that the registrant, ICI Americas, reported that the validated sensitivity of the method to be 10.0 ppb (Limit of Detection, LOD).

The ECS estimated the LOD to be 10.0 ppb and the estimated Limit of Quantitation (LOQ) to be 30.0 ppb using a 1.5 *ul* injection for captan and a 3.5 *ul* injection for THPI.

Please request that the registrant send a copy of the non-confidential method to the following address for inclusion in the new ECM manual:

Laboratory Chief
U.S. Environmental Protection Agency
Environmental Chemistry Laboratory
Building No. 1105
Stennis Space Center, MS 39529

If you have questions, please call me at (703) 305-7991.

CAPTAN

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ENVIRONMENTAL CHEMISTRY SECTION
BUILDING 1105—JOHN C. STENNIS SPACE CENTER
STENNIS SPACE CENTER, MISSISSIPPI 39529-6000
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MAR 18 1996

MEMORANDUM

SUBJECT: Captan Method Evaluation-Report No. ECM0067S1-S2.

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

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

THRU: Donald A. Marlow, Chief
BEAD/Analytical Chemistry Branch (7503W)

The EFED/Ecological Effects Branch has requested an Environmental Chemistry Method Validation for soil. The method was taken from a study entitled "Captan 50-WP Field Dissipation Study on California Strawberries" (MRID 408239-01) , performed by the registrant, ICI Americas. The method evaluation was performed at three levels on soil and reagent blanks at fortification levels of 0.01, 0.03 and 0.3 parts per million(ppm).

The attached method evaluation reports includes three parts:

Part I: Summary and Conclusions

In this section any problems encountered with the method and how they were handled are discussed. ECS'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 (601) 688-2443 or Aubry Dupuy at (601) 688-3212.

cc: Christian Byrne, QA Officer
BEAD/ACB/ECS

Charles Kennedy
BEAD/ACB/ECS

Captan and THPI

Report Number ECM0067S1-S2

Final Report

Environmental Chemistry Section
Analytical Chemistry Branch
Biological and Economic Analysis Division

Prepared by: Charles Kennedy Charles Kennedy 2/29/96
ECS Chemists Signature Date

Reviewed by: Christian Byrne Christian Byrne 3/13/96
ECS/QA Coordinator Signature Date

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Part I

Summary and Conclusions

We have completed the Environmental Chemistry Method Evaluation (ECME) "Captan and THPI Residues in Soil". The method used to accomplish the analyses was sponsored by ICI Americas Inc. in support of registration (MRID No. 408239-01). The method worked well for Captan and its principal metabolite Tetrahydrophthalimide (THPI) and no major modifications were necessary for this ECME. From the results, the method provided satisfactory measurement for the residues of Captan and THPI between 10.0 ppb and 300.0 ppb.

Residues of Captan and THPI were quantitated by gas chromatography. Captan was analyzed using the Hall detector in the halogen mode. THPI was analyzed using the Hall detector in the nitrogen mode. Captan was extracted from the sample matrix by blending the matrix with acetone. The extracts were then filtered and the solvent removed and then reconstituted in dichloromethane. Acidic methanol was then blended with the same matrix and the THPI extracts centrifuged. The two residue extracts were then transferred to a separatory funnel and partitioned with dichloromethane in the presence of water and a saturated NaCl solution. The residual material was then placed on a nuchar/silica gel column. Column elution with various eluents accomplished cleanup and analyte separation. Results are calculated using linear regression from external standards. The final extract for Captan was made in hexane and that for THPI in toluene for GC analysis. The validated sensitivity of the method, which was determined by ICI Americas performing lab, Morse Laboratories, is 10.0 ppb (LOD) for both Captan and THPI.

ECS's Limit Of Detection (LOD) was 10.0 ppb and the estimated Limit of Quantitation (LOQ) was 30.0 ppb using a 1.5 ul injection for Captan and 3.5 ul injection for THPI. In order to evaluate this method we fortified a soil matrix with Captan and THPI at 10.0, 30.0, and 300.0 ppb. All samples were done in replicates of four at each level. The ICI method limit of detection (LOD) of 10.0 ppb and ECS estimated limit of quantitation (LOQ) of 30.0 ppb were confirmed by our data. We found the precision to be well within our target limits of $\leq$20% relative standard deviation (RSD) at or above the (LOQ) for both Captan and its primary metabolite, THPI. For example Captan had a (RSD)= 3.0% at (LOD) of 10.0ppb and 6.6% at 300.0 ppb. The mean recoveries of 100.4% at 300.0 ppb and 105.5% at the (LOD) are well within the 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. Captan

Recovery Values for Soil Fortified at 10, 30, and 300.00 ppb in four replicates on Hall 700A(HCL Mode).

(3) Fortified (ppb)	(4) Recovery (ppb)	(5) Recovery %	(7) SD	(8) RSD
Matrix Blk (1)	--	--	--	--
Run#1 10.00	10.6	106.7	3.22	3.05
Run#2 10.00	10.9	109.2	--	--
Run#3 10.00	10.1	101.7	--	--
Run#4 10.00	10.4	104.2	--	--
(2) Mean(6) Recovery	10.5	105.5	--	--
Run#1 30.0	27.5	91.8	6.47	6.39
Run#2 30.0	31.9	106.4	--	--
Run#3 30.0	30.6	102.2	--	--
Run#4 30.0	31.3	104.3	--	--
Mean Recovery	30.3	101.2	--	--
Run#1 300.0	279.4	93.1	6.65	6.62
Run#2 300.0	318.1	106.0	--	--
Run#3 300.0	316.9	105.6	--	--
Run#4 300.0	289.4	96.5	--	--
Mean Recovery	300.9	100.4	--	--

Results:

2. THPI

Recovery Values for Soil Fortified at 10, 30 and 300.0 ppb in four replicates on Hall 700A(Nitrogen Mode).

(3) Fortified (ppb)	(4) Recovery (ppb)	(5) Recovery %	(7) SD	(8) RSD
Matrix Blk (1)	--	--	--	--
Run#1 10.0	8.6	85.9	4.52	5.44
Run#2 10.0	8.6	85.9	--	--
Run#3 10.0	7.6	76.4	--	--
Run#4 10.0	8.4	84.0	--	--
(2) Mean(6) Recovery	8.3	83.1	--	--
Run#1 30.0	27.6	92.0	10.83	10.15
Run#2 30.0	34.9	116.3	--	--
Run#3 30.0	31.5	105.0	--	--
Run#4 30.0	33.8	112.7	--	--
Mean Recovery	31.9	106.6	--	--
Run#1 300.0	272.2	90.7	4.10	4.27
Run#2 300.0	300.0	100.0	--	--
Run#3 300.0	285.6	95.2	--	--
Run#4 300.0	295.1	98.4	--	--
Mean Recovery	288.2	96.1	--	--

Notes:

(1) Limit of Detection (LOD), equivalent to 10.0 ppb in soil sample.

Limit of Quantitation (LOQ), equivalent to 30.0 ppb in soil sample.

(2) The four values (Run#1, Run#2, Run#3, Run#4) are replicate soil analyses at each of three concentration levels of 10.0,

30.0 and 300 ppb.

(3) Fortified(ppb) = Captan and THPI Fortification Levels.

(4) Recovery(ppb) = Captan and THPI Recovery Levels in Terms of Concentration.

(5) Recovery % = Percent Recovery of Captan and THPI as referred to in the Calculation Section.

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

(7) SD = Standard Deviation of Four Replicate Runs Of Captan and THPI.

(8) RSD = Relative Standard Deviation of Four Replicate Runs Of Captan and THPI.

Part III

Experimental Details

General description of method:

Briefly, this method involves soil extractions with acetone and acid-methanol, and partitioning Captan and THPI into dichloromethane. Cleanup and separation of Captan and THPI are accomplished using a nuchar:silica gel column.

A 20 gram sample of soil was transferred to a pint jar with 150ml acetone and blended for 5 minutes on a Omni-mixer. After the extract was filtered, the extraction and filtration step was done two more times using 100ml acetone. After the third acetone extraction, the soil was extracted with 75ml acidic methanol by blending for 5 minutes. The acidic methanol extract was then centrifuged at 2000 rpm and then decanted into an Erlenmeyer flask. The soil was then transferred back to the extraction jar and re-extracted for the second time. The acetone extraction was evaporated to dryness and the residue dissolved in 75ml of dichlormethane and transferred to a 500 ml separatory funnel. The acidic methanol extract was also added to the separatory funnel with 100ml of deionized water and 10ml saturated NaCl. This mixture was shaken for 1 minute and then the dichlormethane extract filtered through sodium sulfate. The aqueous mixture was then partitioned two more times using 75ml dichloromethane. These extracts were combined and evaporated to 10ml in preparation for cleanup and separation. A glass wool plug was placed in the bottom of a chromatographic column followed by 15 grams of nuchar:silica

gel(5:95 w/w) mixture. The column was sequentially washed with 100ml of 5% ethyl acetate in dichloromethane and two 25ml portions of dichloromethane. The 10ml dichloromethane extract was added to the column, and two 10ml portions of dichloromethane were used to complete a quantitative transfer. The dichloromethane was allowed to drain until the liquid level dropped to the top of the glass wool plug. The column was then eluted with 20ml of dichloromethane which was discarded. The Captan was then eluted with 150ml of 5% ethyl acetate in dichloromethane and collected for rotary evaporation. THPI was eluted with 150ml of 20% acetone in dichloromethane and evaporated to near dryness. The Captan residue was then dissolved in hexane and the THPI residue dissolved in toluene both to a volume of 1ml before proceeding with gas chromatographic analyses.

Table 1 (page 8) summarizes the retention times observed for the Tracor 540 gas chromatograph with a Hall 700A Detector in the HCL and Nitrogen mode.

The structural formula of Captan and of THPI is shown in Appendix A.

Modification to method:

1. No modification necessary.

Sources of analytical reference standards:

Captan analytical NEAT standard was received from US Environmental Protection Agency Pesticides Repository, Research Triangle Park, NC 27709. Fax Number: (919)541-2971.

THPI analytical NEAT standard was received from Zeneca Repository of Arkansas. Fax Number: (501)231-5019

1. Captan, Code#P-051020-001-01, Lot#N302, CAS#133-06-2, 99.0% purity.

2. THPI, Code#F-003821-001-01, Lot#WRC 14617-44-1, CAS#ASW1685A, 99.7% purity.

Source of sample matrix:

The soil was part obtained from the Univ. of California received at ECS on 05/05/95. See Appendix B for a characterization of this soil.

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

Tracor 540(GC): Equipped with Hall 700A Detector(HCL & Nitrogen Mode)

Injection(GC): Manual 1.5ul(Captan), 3.5ul(THPI)

Instrumentation for confirmation: Not applicable.

Relative retention parameters for the present evaluation:

Table 1

Analyte	Chemical Abstracts Registry No.	Retention Time minutes
Captan	P-051020-001-01	3.1 (GC-HCL)
THPI	F-003821-001-01	14.4 (GC-N2)

Notes on analytical procedures:

ECS/EPA found the method to work well for both Captan and THPI. No additional cleanup was required in our method evaluation. The method does suggest additional work may be needed.

Comments:

At least 3 working days (assuming 9-hr working day) would be needed to complete processing and to start GC Hall 700A analysis for a set of six soil samples.

Calibration:

The Tracor 540 gas chromatograph equipped with a Hall 700A was calibrated with Captan and THPI standards with concentrations of 10, 30, 100, and 300ppb. The correlation coefficient was 0.9995 for Captan and 0.9995 for THPI linear curves. A calibration standard was analyzed before each set of four fortified runs at a particular concentration level and peak height counts in millimeters was determined.

Calculation Formula

A standard curve was constructed by linear regression analysis of concentrations of external standards (ppb) versus peak height counts (mm) for each analyte. The recovery concentration of the analyte (ppb) in fortified soil was determined from the linear regression equation for the analyte:

$$\text{Recovery(ppb)} = \frac{\text{(Peak Height of Sample)} - \text{(y intercept)}}{\text{Slope}}$$

The percent recovery of each analyte from fortified soil samples was calculated by the following equation:

$$\text{Recovery (\%)} = \frac{\text{ppb recovered in Fortified Sample} \times 100\%}{\text{ppb Added}}$$

Actual Sample Calculation:

Sample: Run #3 @ 30.0 ppb for Captan

Peak Height Count(Sample) = 21.0mm
y-intercept(Captan) = -3.541
Slope(Captan) =.800

$$\text{Recovery(Sample @ 30.0 ppb)} = \frac{21.0 + 3.541}{.800} = \frac{24.541}{.800} = 30.67\text{ppb}$$

$$\text{Recovery (\%)} = \frac{30.67 \text{ ppb}}{30.0 \text{ ppb}} \times 100\% = 102.2\%$$

Chromatograms and Linear Regression Curves

A. Captan Calibration Standards Analyzed by GC-Hall (HCl Mode) 700A Detector at 10.0, 30.0, and 300.0 ppb.

A-1: 10.0 ppb.

A-2: 30.0 ppb.

A-3: 300.0 ppb.

B. THPI Calibration Standards Analyzed by GC-Hall 700A (N2 Mode) Detector at 10.0, 30.0 and 300 ppb.

B-1: 10.0 ppb.

B-2: 30.0 ppb.

B-3: 300 ppb.

C. Linear Regression Curves for Captan and THPI

C-1: Linear Regression Curve for Captan

C-2: Linear Regression Curve for THPI

D. Captan Fortification Analyzed by GC-Hall 700A (HCl Mode) at 10.0 ppb.

D-1: Matrix Blank

D-2: Soil Fortified at 10.0 ppb.

E. Captan Fortification Analyzed by GC-Hall 700A (HCl Mode) at 30.0 ppb.

E-1: Matrix Blank

E-2: Soil Fortified at 30.0 ppb.

F. Captan Fortification Analyzed by GC-Hall 700A (HCl Mode) at 300.0 ppb.

F-1: Matrix Blank

F-2: Soil Fortified at 300.0 ppb.

G. THPI Fortification Analyzed by GC-Hall 700A (N2 Mode) at 10.0 ppb.

G-1: Matrix Blank

G-2: Soil Fortified at 10.0 ppb.

H. THPI Fortification Analyzed by GC-Hall 700A (N2 Mode) at 30.0 ppb.

H-1: Matrix Blank

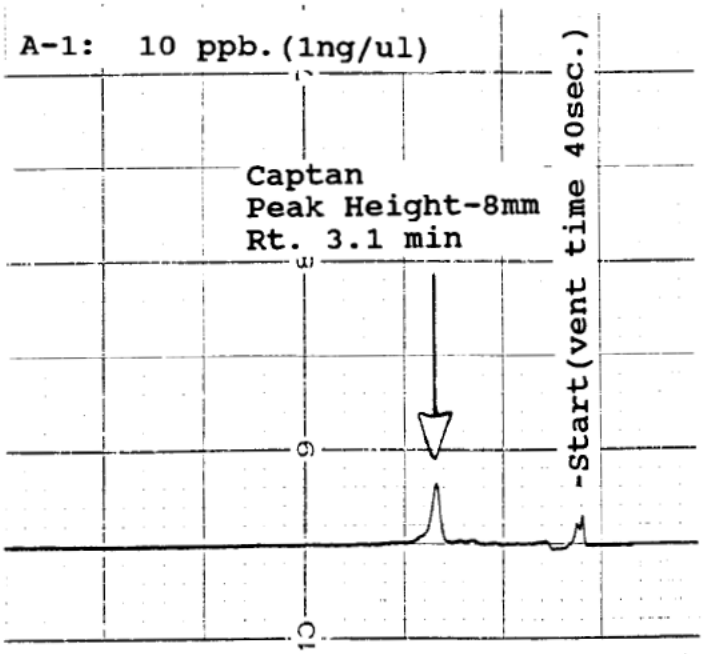
H-2: Soil Fortified at 30.0 ppb.

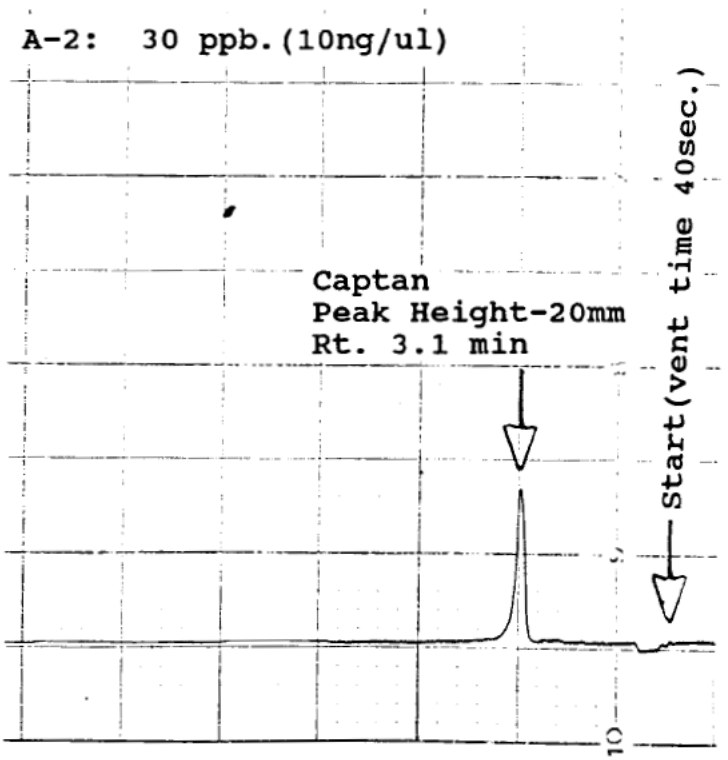
I. THPI Fortification Analyzed by GC-Hall 700A (N2 Mode) at 300.0 ppb.

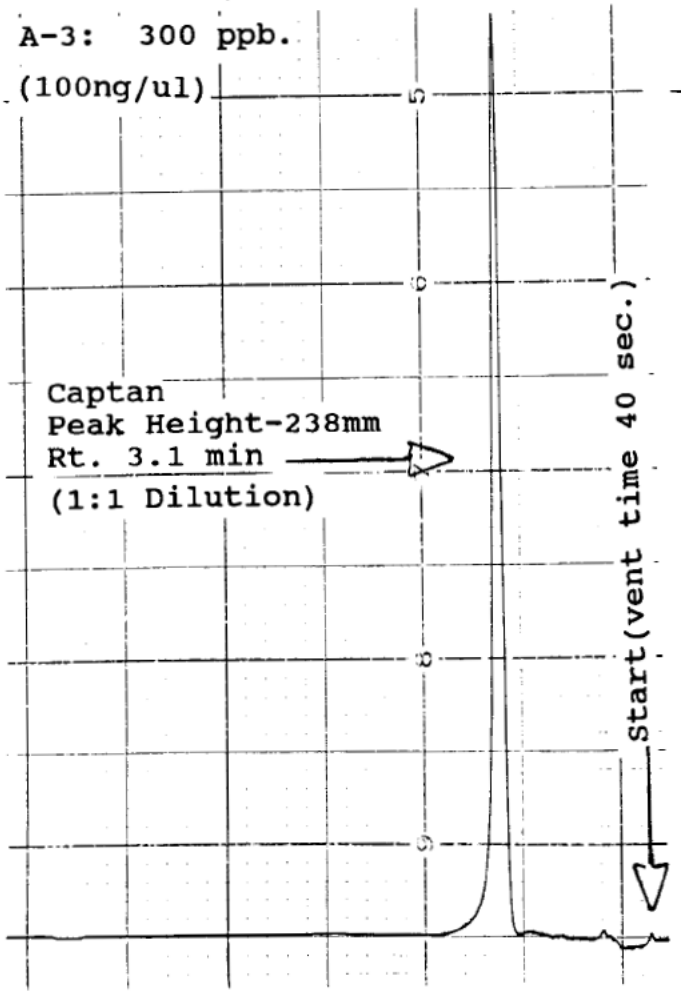
I-1: Matrix Blank

I-2: Soil Fortified at 300.0 ppb.

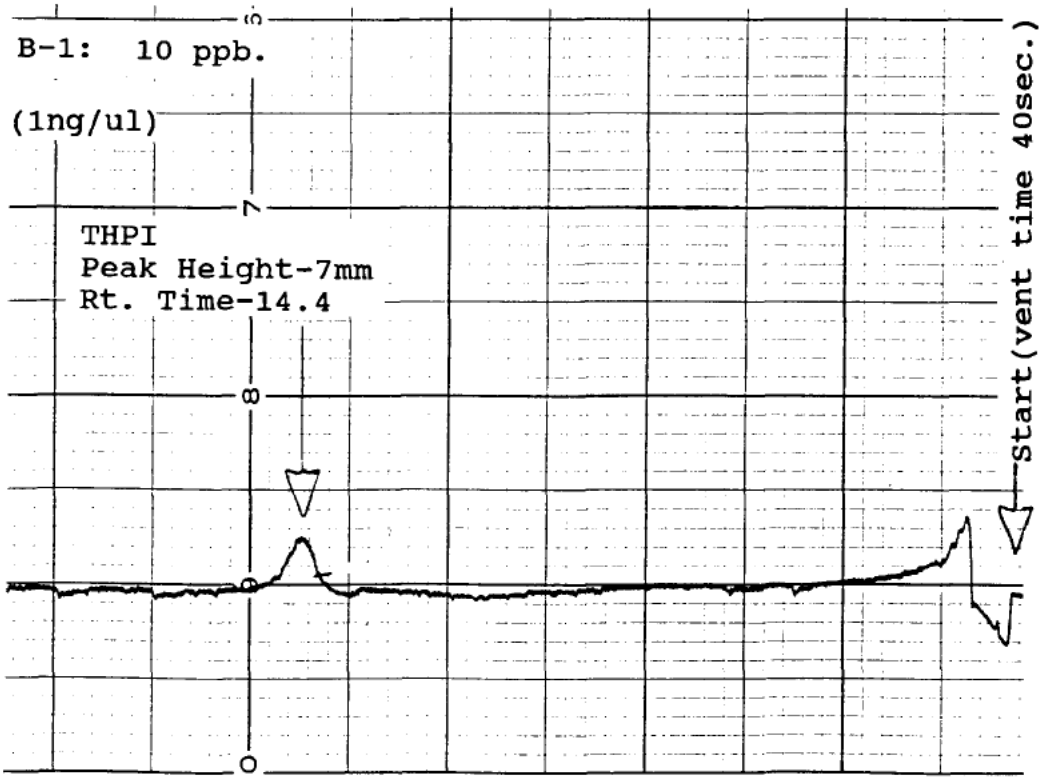
A. Captan Calibration Standard Analyzed by GC-Hall (HCL Mode) 700A Detector at 10.0, 30.0 and 300 ppb.

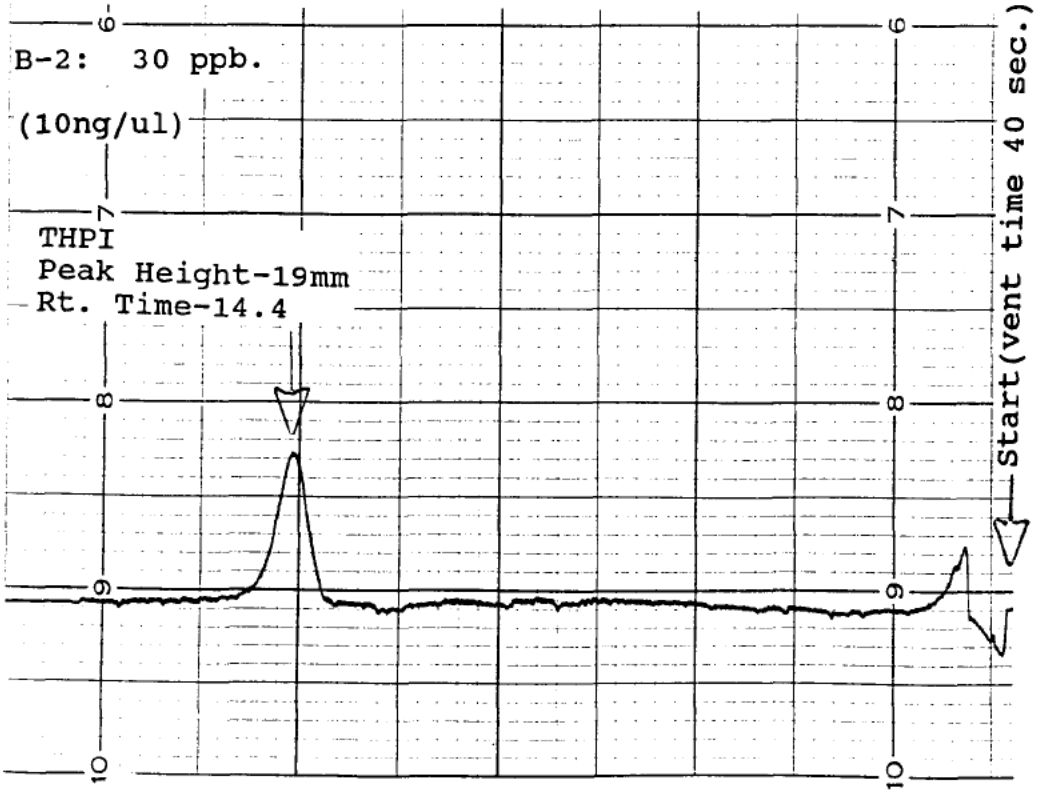


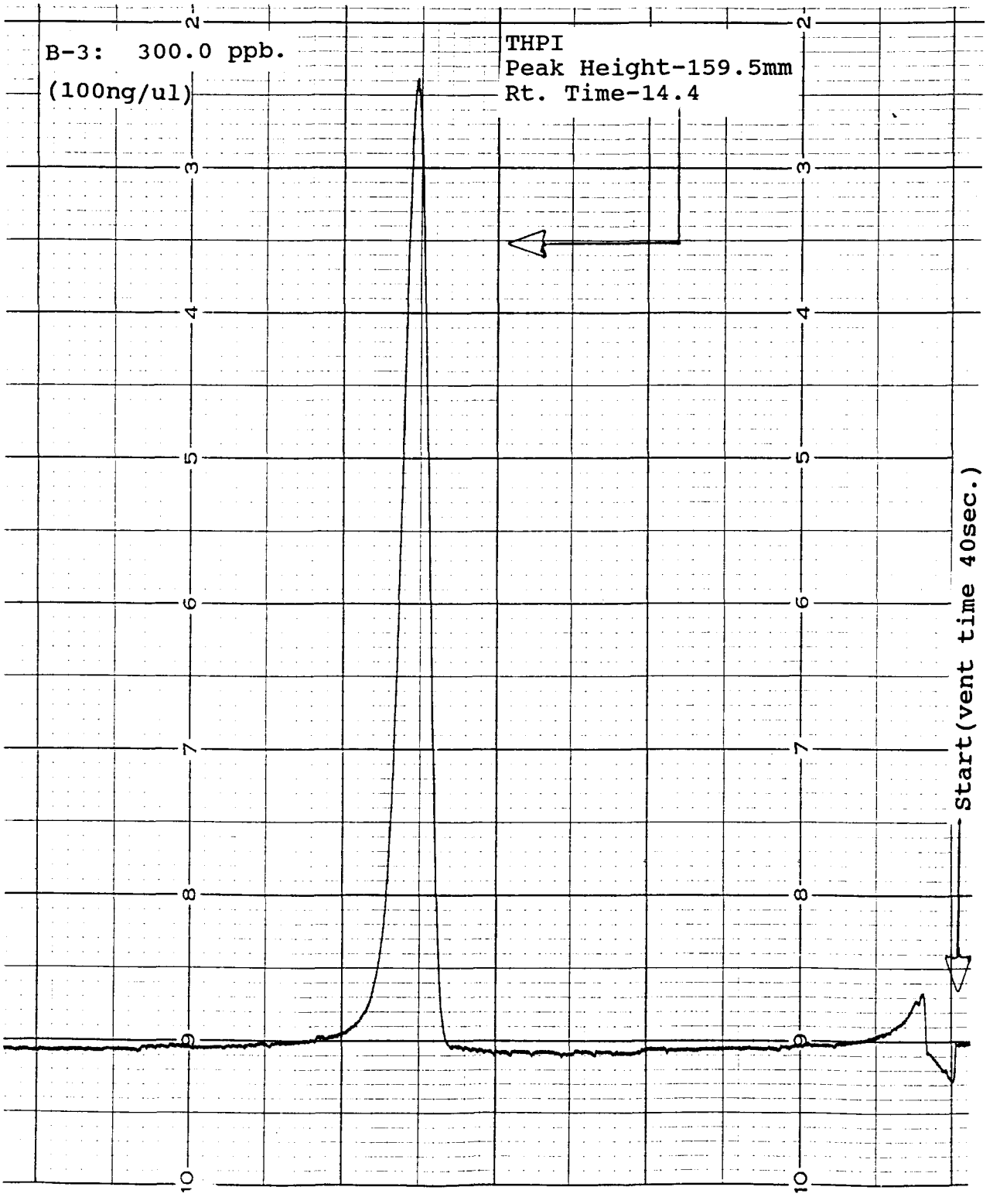




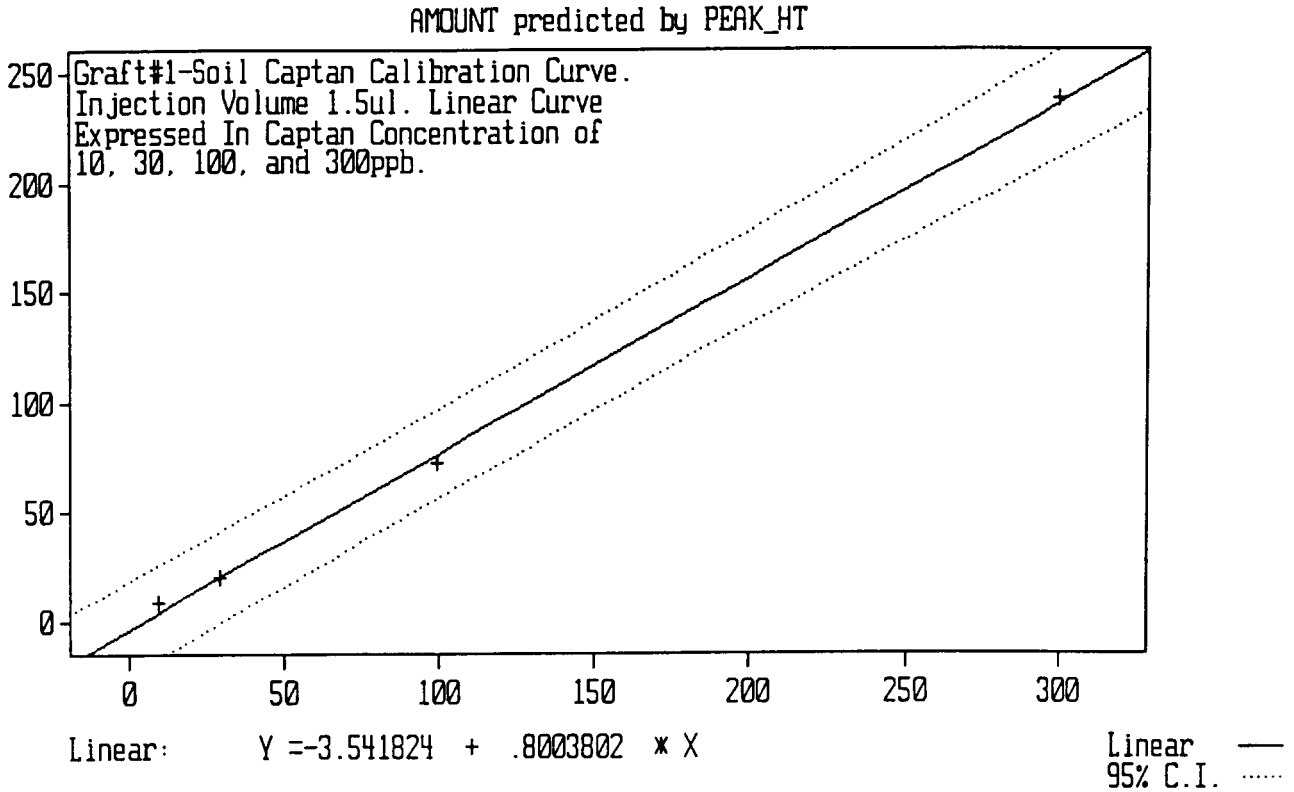
B. THPI Calibration Standards Analyzed by GC-Hall (N2 Mode) 700A Detector at 10.0, 30.0 and 300.0 ppb.



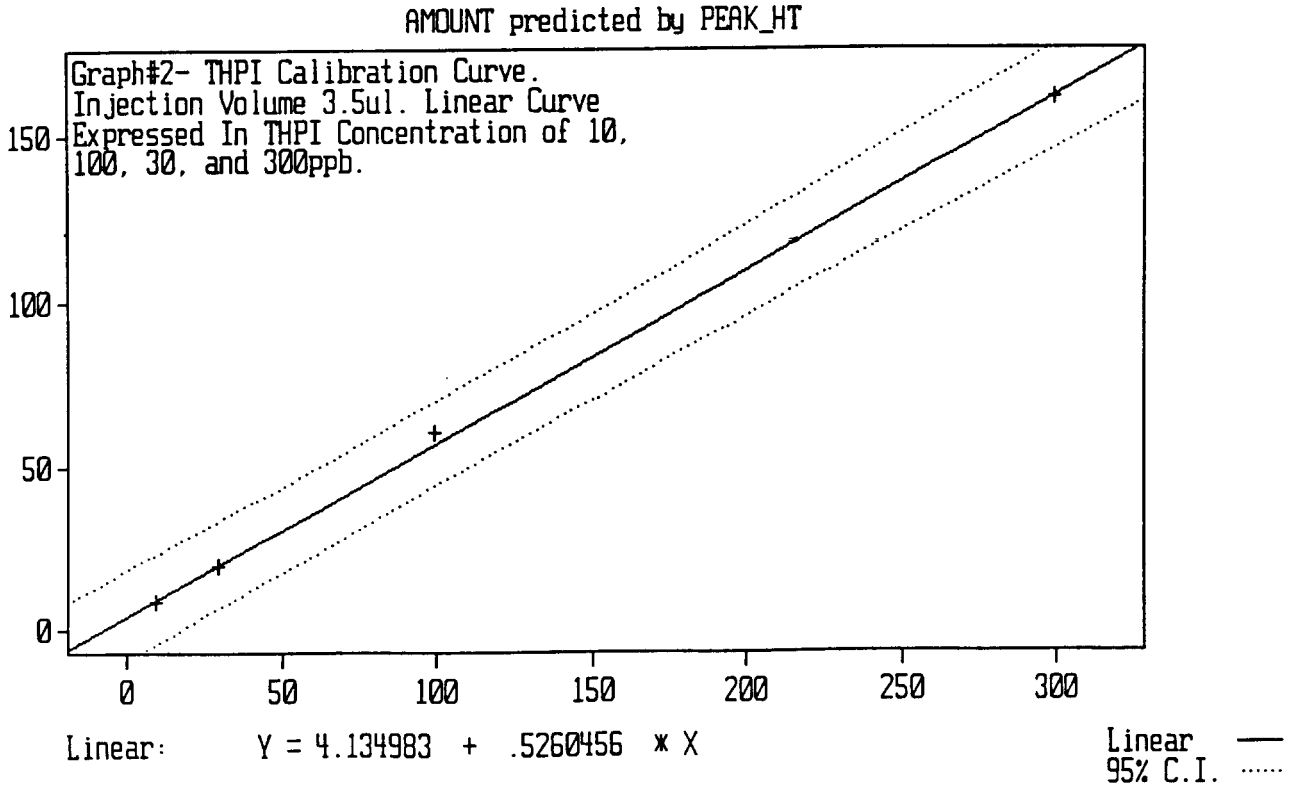



B-3: 300.0 ppb.
(100ng/ul)
THPI
Peak Height-159.5mm
Rt. Time-14.4
Start(vent time 40sec.)

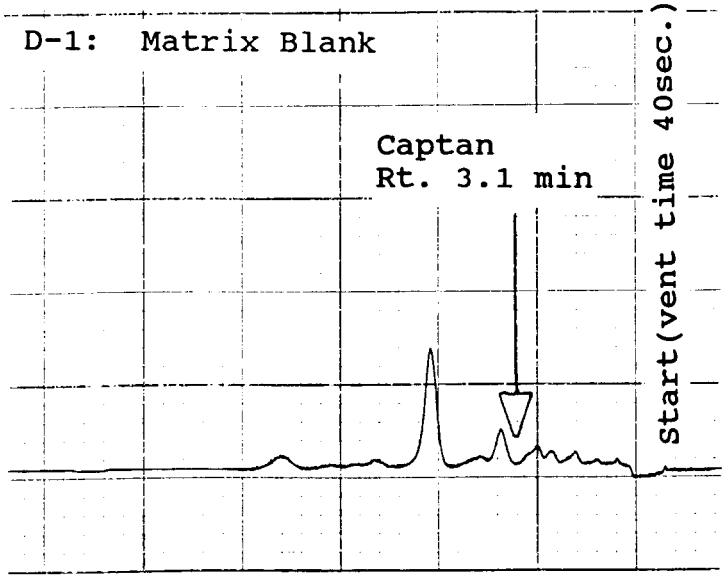
C-1: Linear Regression Curve for Captan

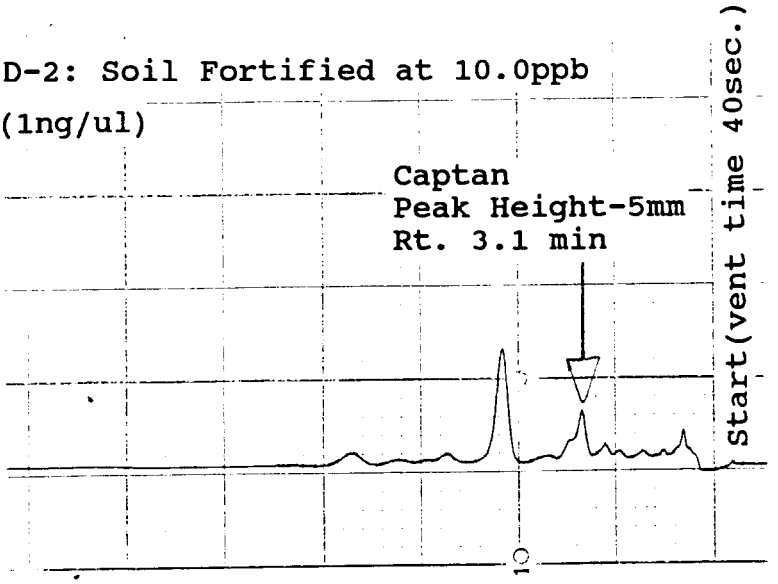


C-2: Linear Regression Curve for THPI

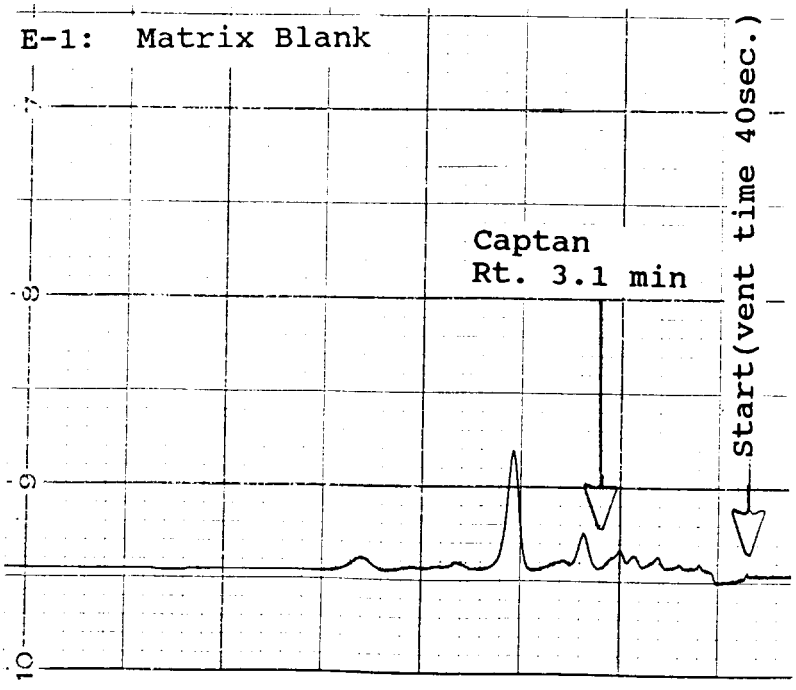


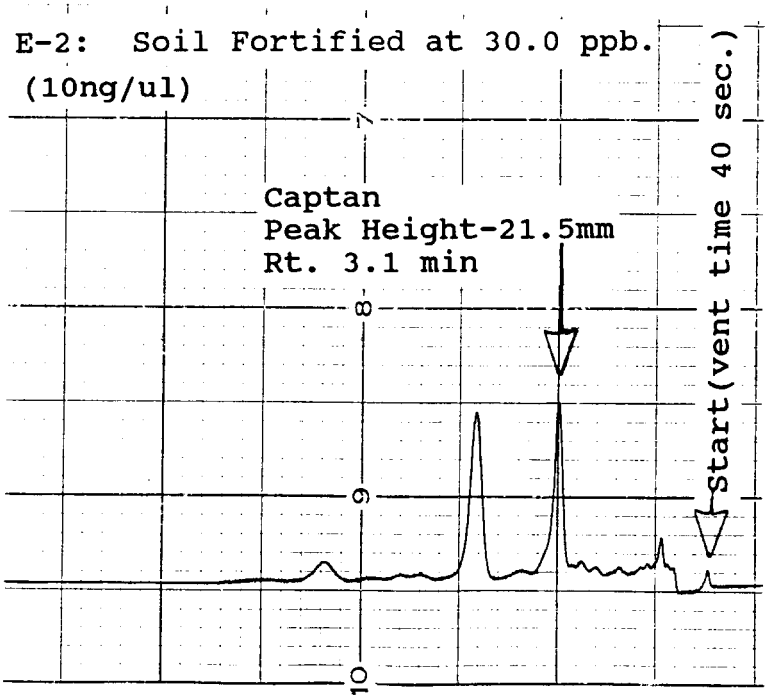
D. Captan Fortification Analyzed by GC-Hall 700A (HCl Mode) at 10.0 ppb.



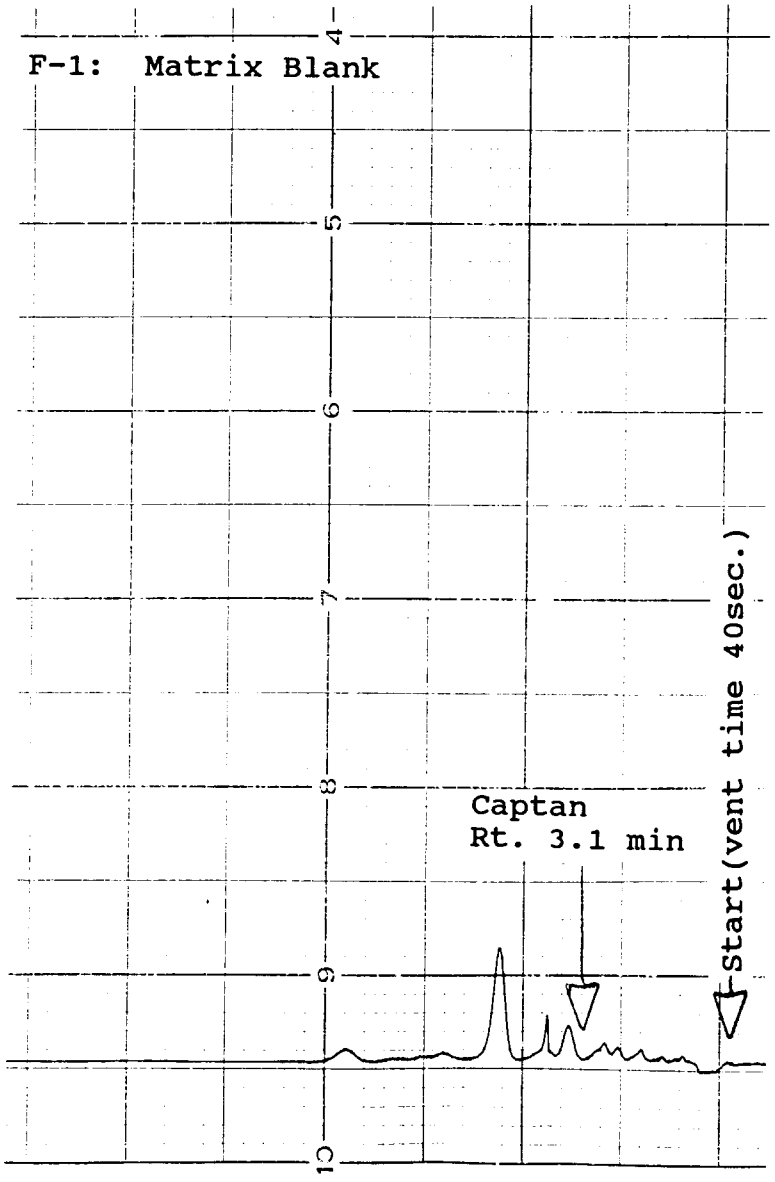


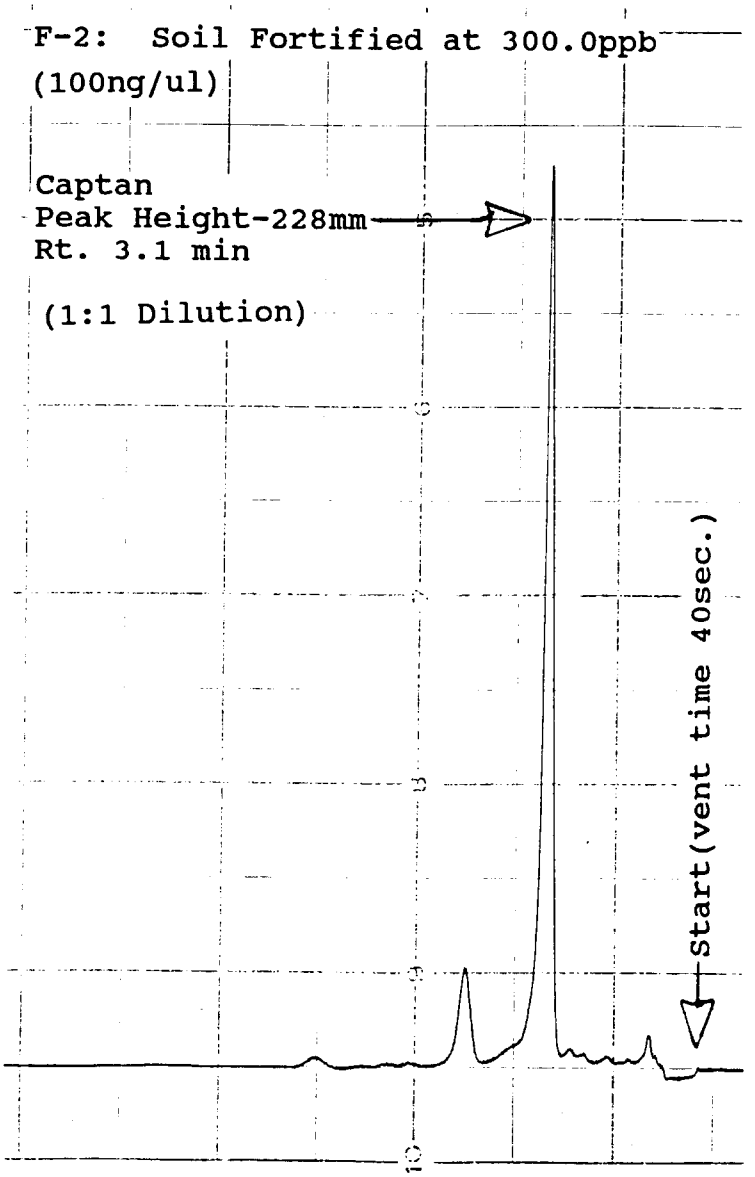
E. Captan Fortification Analyzed by GC-Hall 700A (HCl Mode) at 30.0 ppb.



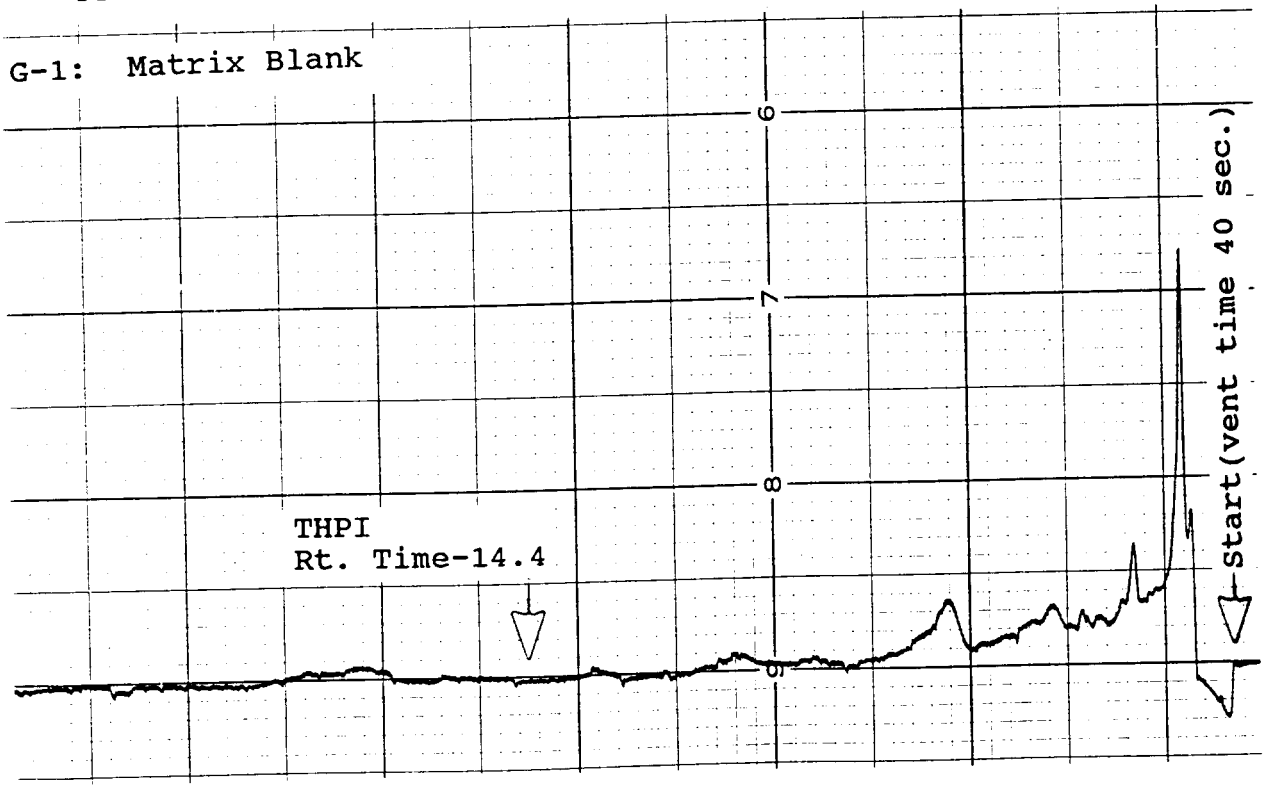


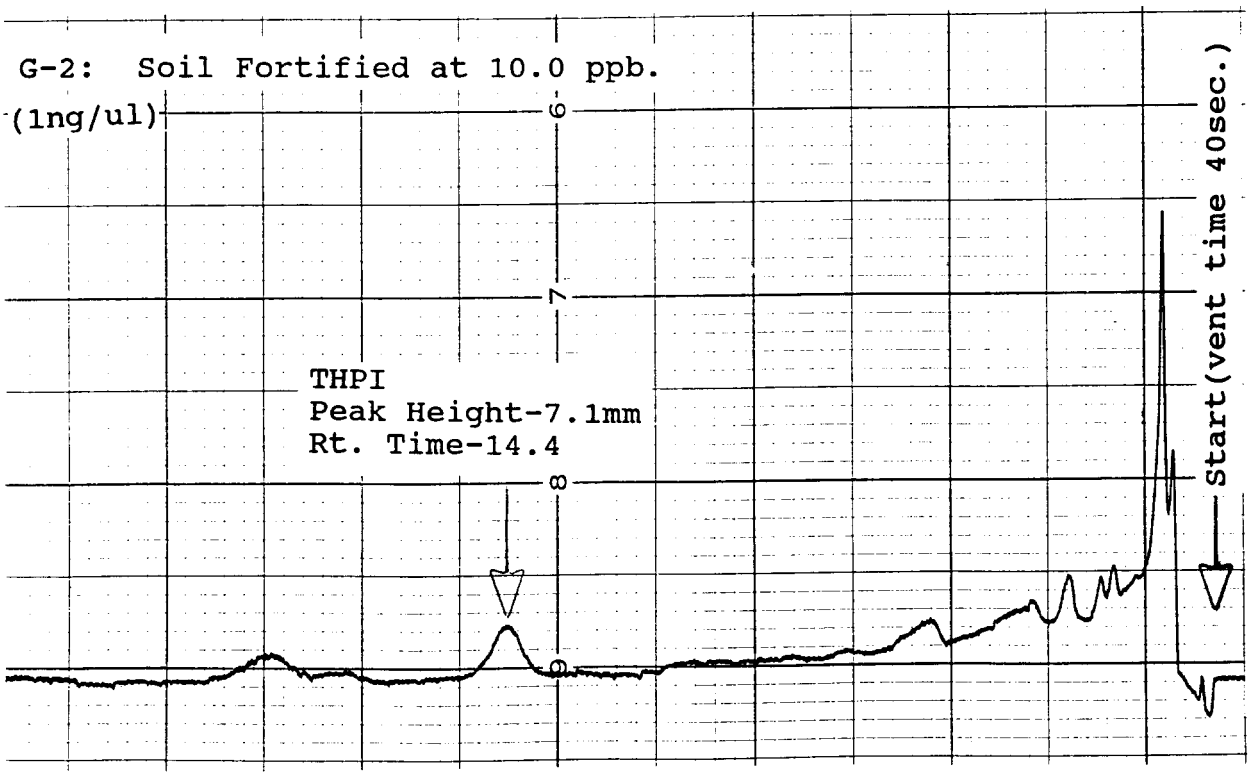
F. Captan Fortification Analyzed by GC-Hall 700A (HCl Mode) at 300.0 ppb.



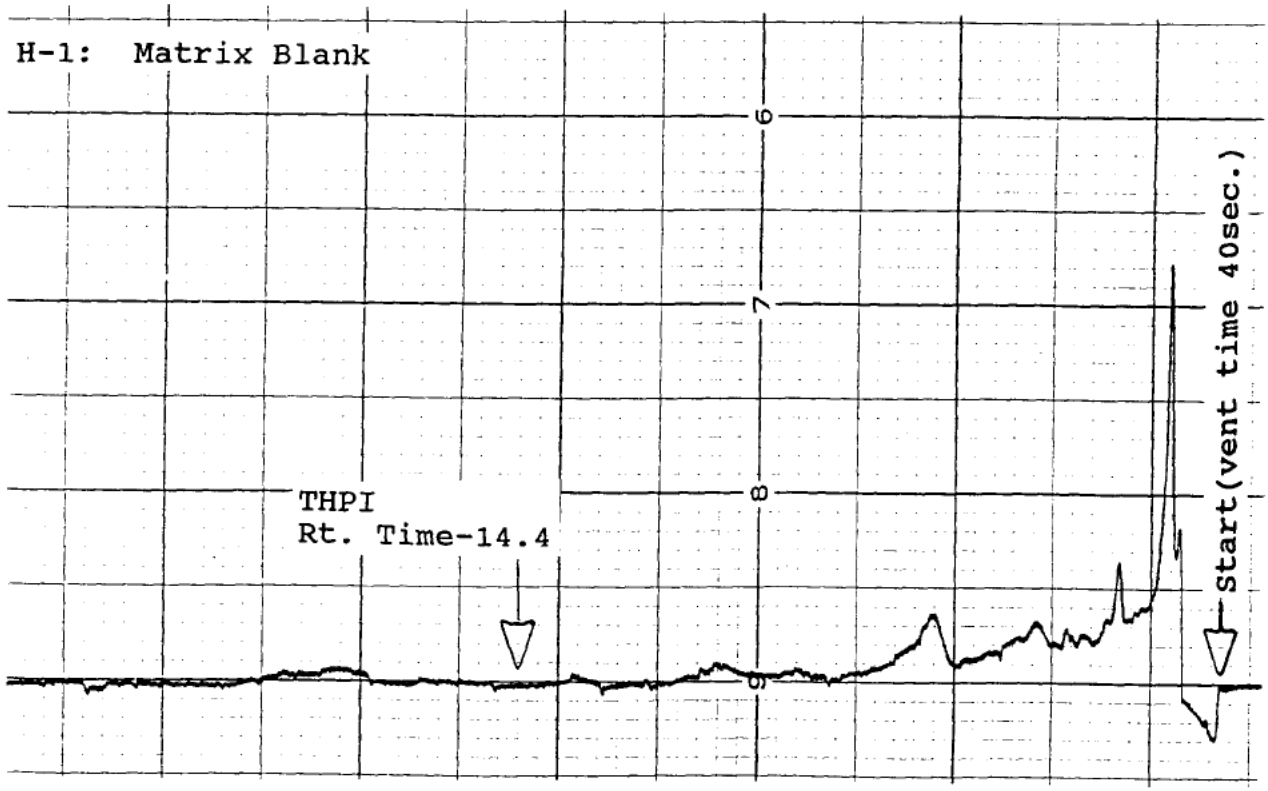


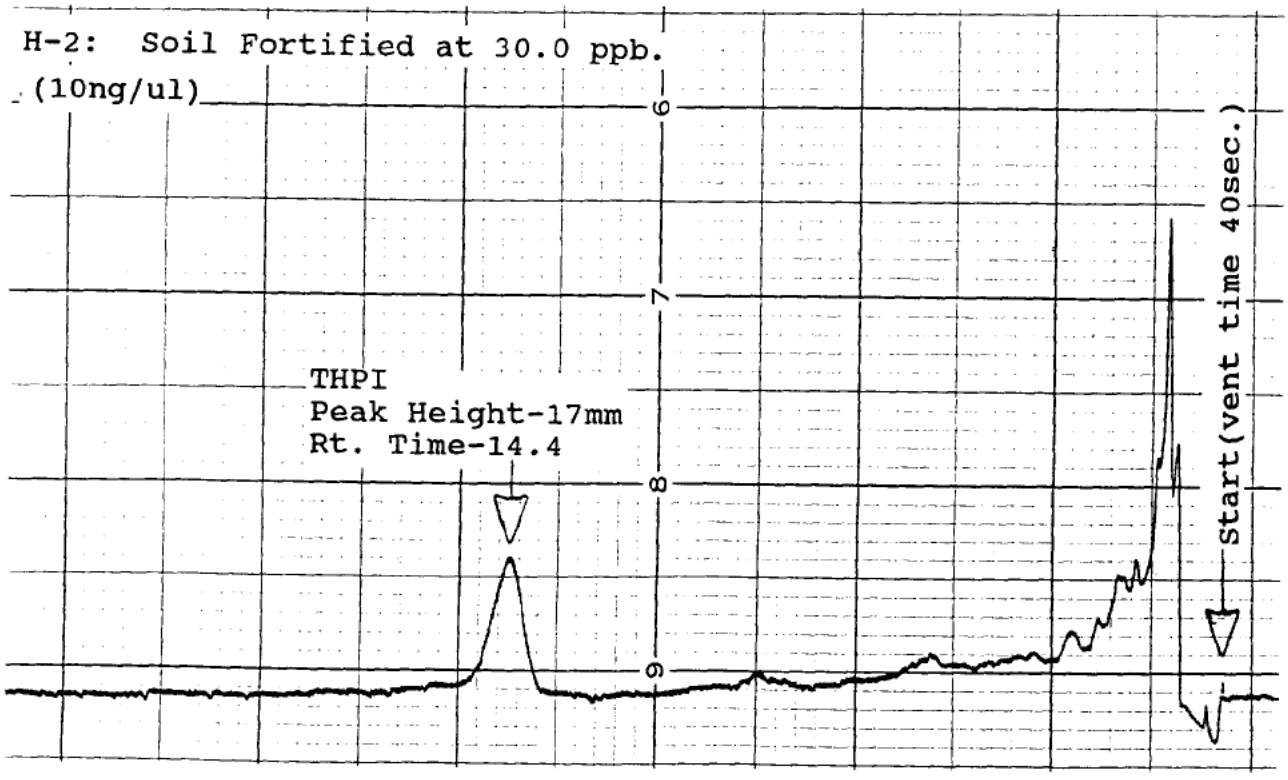
G. THPI Fortification Analyzed by GC-Hall 700A (N2 Mode) at 10.0 ppb.





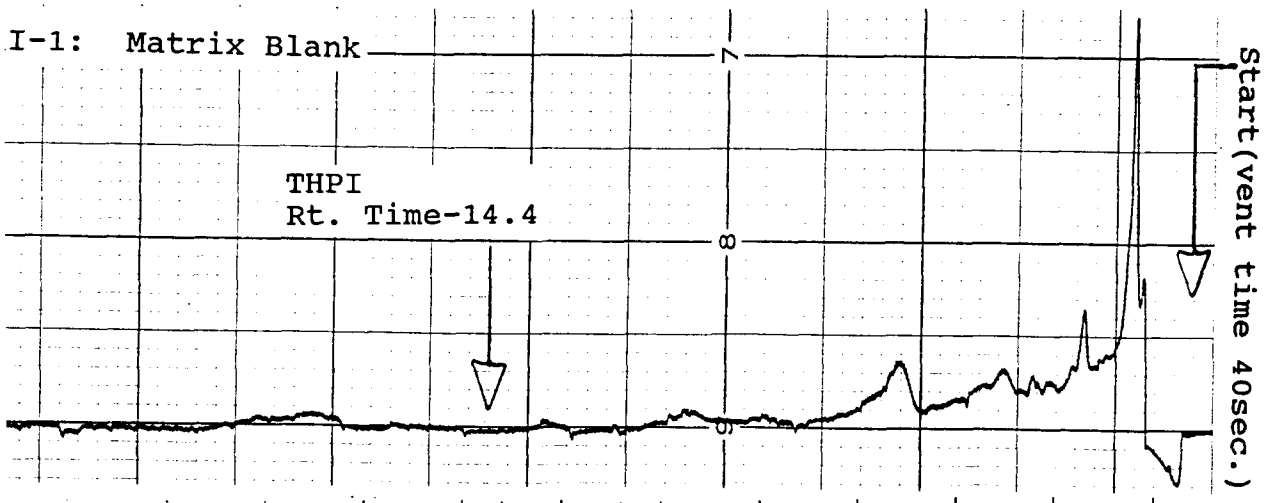
H. THPI Fortification Analyzed by GC-Hall 700A (N2 Mode) at 30.0 ppb.



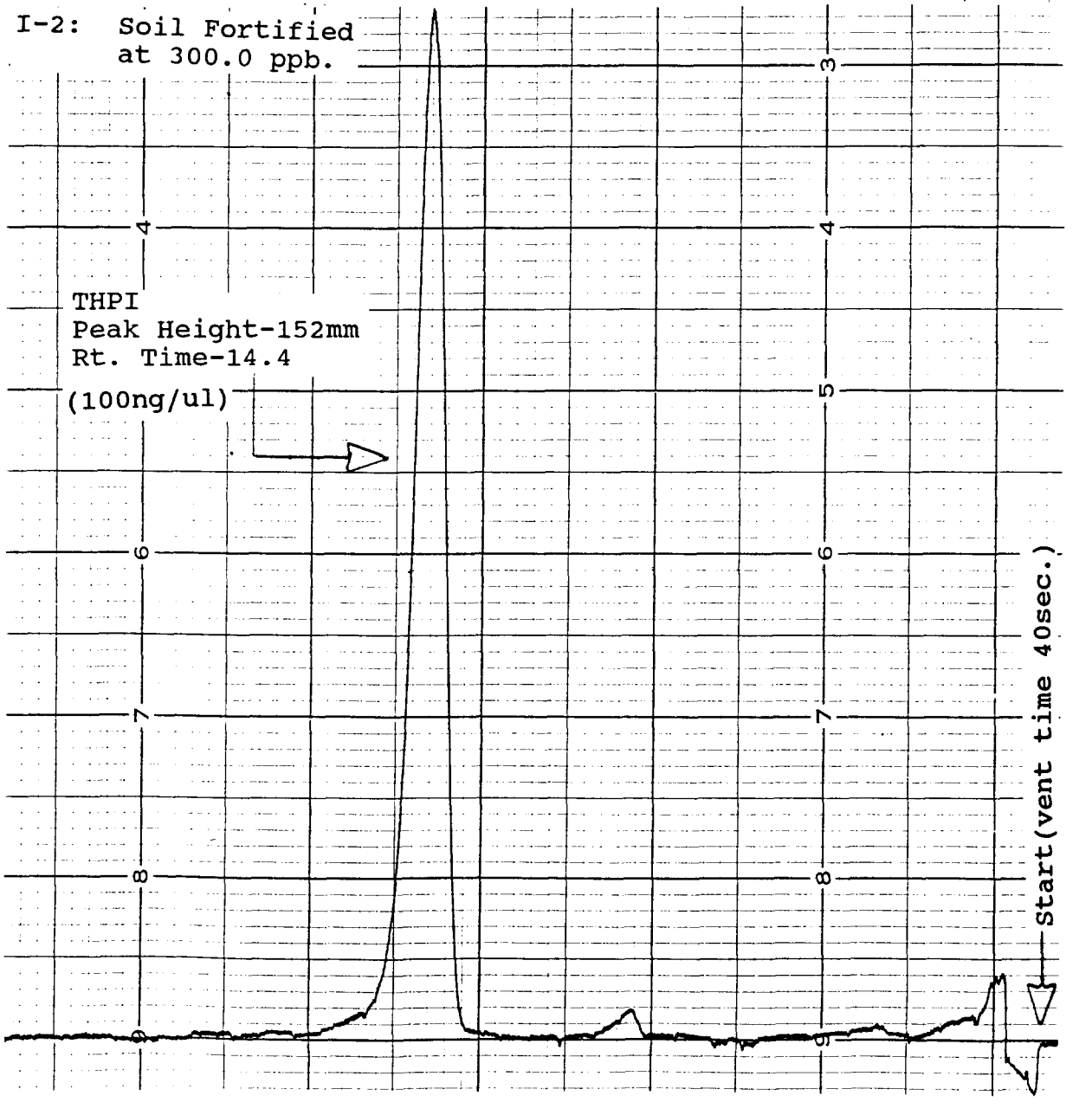


I. THPI Fortification Analyzed by GC-Hall 700A (N2 Mode) at 300.0 ppb.

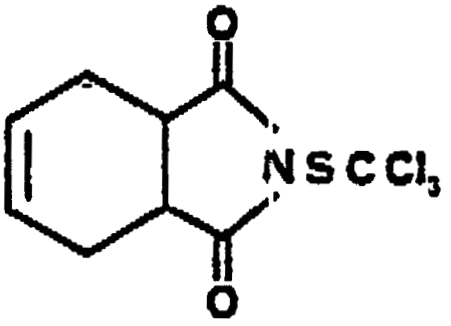
I-1: Matrix Blank



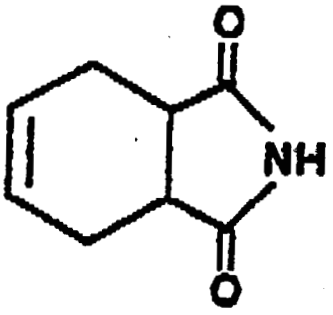
I-2: Soil Fortified at 300.0 ppb.



APPENDIX A: CHEMICAL STUCTURES OF CAPTAN AND THPI



Captan



Tetrahydrophthalimide
(THPI)

APPENDIX B: SOIL CHARACTERIZATION

A&L Analytical Laboratories, Inc.
411 North Third Street • Memphis, TN 38105 • (901) 527-2780 • FAX (901) 526-1031

SOIL ANALYSIS

CLIENT
U.S. EPA/ECS
BLDG. 1105
STENNIS SPACE CNTR, MS 3952

GROWER
GERALD G. GARDNER
U.S. EPA/ECS

DATE RECEIVED: 06/01/95

REPORT 153-050
DATE 06/06/95
ACCOUNT 1502
PAGE 1
A&L AGRONOMIST
Richard Large

LAB NUMBER 08780 **SAMPLE ID** CA1-B1 **SIGNATURE** Richard Large

TEST	RESULTS	SOIL TEST RATINGS					CATION EXCHANGE CAPACITY
		Very Low	Low	Medium	High	Very High	
Soil pH	7.4						6.2 meq/100g
Buffer pH							
Phosphorus (P)	20 ppm						
Potassium (K)	138 ppm						CATION SATURATION
Calcium (Ca)	880 ppm						%K 5.7
Magnesium (Mg)	128 ppm						%Ca 71.0
Sulphur (S)							%Mg 17.2
Boron (B)							%H .0
Copper (Cu)							%Na 5.3
Iron (Fe)							
Manganese (Mn)							
Zinc (Zn)							
Sodium (Na)	76 ppm						SOIL TEST METHOD
Soluble Salts	0.4 mmho/cm						AMMONIUM ACETATE EXTRACTION
Organic Matter	1.4 % ENR 72						
NO_3-N							

SOIL FERTILITY GUIDELINES

CROP: **YIELD GOAL:**

LIME	N	P_2O_5	K_2O	Mg	S	B	Cu	Mn	Zn

LAB NO	SAMPLE IDENTIFICATION	PERCENT SAND	PERCENT SILT	PERCENT CLAY	TEXTURAL CLASSIFICATION
08780	CA1-B1	78	12	10	SANDY LOAM