Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Pendimethalin

MRID #: 445276-01

Matrix: Soil/Water

Analysis: GC/NPD

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AMERICAN CYANAMID COMPANY
AGRICULTURAL PRODUCTS RESEARCH DIVISION
HUMAN AND ENVIRONMENTAL SAFETY
P.O. BOX 400
PRINCETON, NEW JERSEY 08543-0400

Recommended Method of Analysis - M 2514

PROWL® Herbicide, pendimethalin (CL 92,553): GC Method for the Determination of CL 92,553 Residues in Soil

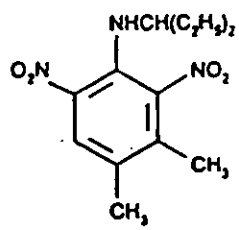
A. PRINCIPLE

Residues of CL 92,553 are acidified and then extracted from soil with 2% hydrochloric acid in methanol. CL 92,553 is subjected to suitable cleanup involving solid phase extraction techniques. Measurement of the CL 92,553 is accomplished by gas chromatography using an instrument equipped with a nitrogen-phosphorus detector. Results are calculated by the direct comparison of peak heights to those of external standards. The validated sensitivity (LOQ, limit of quantitation) of the method is 10 ppb.

B. REAGENTS (Items from manufacturers other than those listed may be used provided they are proven to be functionally equivalent.)

1. Analytical Standard: Analytical grade of known purity, obtained from American Cyanamid Company, Agricultural Products Research Division, P.O. Box 400, Princeton, New Jersey, 08543-0400.

CL 92,553: N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine



M.W. = 281.3

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2. Water: High purity, deionized (Milli-Q water system)

3. Solvents: High purity, (Burdick and Jackson, Inc.)

   a. Methanol
   b. Hexane

4. Chemicals: "Baker Analyzed" Reagents, J.T. Baker Company

   Hydrochloric Acid, concentrated

5. Solutions:

   a. 0.1N Hydrochloric Acid: Add 8.3 mL of concentrated hydrochloric acid to 500 mL of deionized water in a 1-liter volumetric flask. Dilute to 1 liter with deionized water and mix well.

   b. Acidic Methanol (2%): Add 20 mL of concentrated hydrochloric acid to approximately 500 mL of methanol in a 1-liter volumetric flask. Dilute to 1 liter with methanol and mix well.

   c. 1% Methanol in Hexane: Add 1 mL of methanol to 50 mL of hexane in a 100-mL volumetric flask. Dilute to 100 mL with hexane and mix well.

C. APPARATUS (Items from manufacturers other than those listed may be used provided they are proven to be functionally equivalent.)

1. Gas Chromatograph: Hewlett Packard Model 5890 equipped with a nitrogen-phosphorus detector and a Hewlett Packard autosampler Model 7673A.

2. Integrator: Hewlett Packard Model 3396A.

3. Balance: Analytical, Sartorius, precision ± 0.05 mg.

4. Balance: Pan, Sartorius, Model L610, precision ± 5 mg.

5. General Laboratory Glassware: Assorted beakers, graduated cylinders, volumetric and filter flasks, and volumetric pipets.

6. Flasks: 50-mL pear-shaped.

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7. Rotary Evaporator: Buchler Instruments, equipped with a heated water bath maintained at approximately 35°C in which the evaporation flasks can be partially submerged.

8. Capillary Column: Fused silica capillary column, 15 m x 0.53 mm nominal I.D, Rtx-20 bonded phase with a film thickness of 1.0 micron, Catalog Number 10352, Restek, Inc.

9. Solid Phase Extraction Cartridge: Isolute C18 (200 mg/3 mL) endcapped, International Sorbent Technology, Catalog Number 221-0020-B, distributed by Jones Chromatography.

10. Visiprep Solid Phase Extraction Vacuum Manifold or Equivalent: Supelco, Inc. Catalog Number 5-7030.

11. Microliter Syringes: Hamilton, Model 701 (10-mcL capacity).

12. Empty Reservoirs, Disposable: 70-mL capacity, International Sorbent Technology, Catalog Number 120-1008-F. Distributed by Jones Chromatography.

13. PTFE SPE Column Adapters: International Sorbent Technology, Catalog Number 120-1100. Distributed by Jones Chromatography.

14. Filtering Funnel: Buchner, porcelain, 9-cm diameter.

15. Filter Paper: 9-cm diameter, Whatman Glass Microfibre Filters, Whatman, Inc., Catalog Number 1827-070.

16. Bottles: Narrow-mouth with polyethylene-lined caps, (Ace Scientific Supply Company), 16 ounces.

17. Reciprocating Shaker: Eberbach Corporation, Catalog No. 6010.

D. PREPARATION OF STOCK SOLUTIONS

1. Stock Solution (Prepare every five months, store in amber bottles in refrigerator.)

   CL 92,553: Weigh accurately a known amount (approximately 10 mg) of CL 92,553 into a 100-mL volumetric flask. Dilute to the mark with hexane and mix well. Calculate and record the exact concentration of CL 92,553, correcting for the standard purity. Designate this as standard solution A.

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2. Fortification Solutions and Gas Chromatographic Solutions

a. Pipet into a 100-mL volumetric flask an appropriate amount of standard solution A to deliver 500 mcg of CL 92,553. Dilute to the mark with hexane and mix well. Designate this solution which contains 5.0 mcg/mL of CL 92,553 as standard solution B.

b. Pipet into a 100-mL volumetric flask 20 mL of standard solution B. Dilute to the mark with hexane and mix well. Designate this solution which contains 1.0 mcg/mL of CL 92,553 as standard solution C.

c. Pipet into a 100-mL volumetric flask 10 mL of standard solution B. Dilute to the mark with hexane and mix well. Designate this solution which contains 0.5 mcg/mL of CL 92,553 as standard solution D.

d. Pipet into a 100-mL volumetric flask 10 mL of standard solution C. Dilute to the mark with hexane and mix well. Designate this solution which contains 0.1 mcg/mL of CL 92,553 as standard solution E.

e. Pipet into a 200-mL volumetric flask 10 mL of standard solution C. Dilute to the mark with hexane and mix well. Designate this solution which contains 0.05 mcg/mL of CL 92,553 as standard solution F.

f. Pipet into a 200-mL volumetric flask 5 mL of standard solution C. Dilute to the mark with hexane and mix well. Designate this solution which contains 0.025 mcg/mL of CL 92,553 as standard solution G.

g. Pipet into a 100-mL volumetric flask 25 mL of standard solution F. Dilute to the mark with hexane and mix well. Designate this solution which contains 0.0125 mcg/mL of CL 92,553 as standard solution H.

E. GAS CHROMATOGRAPHIC CONDITIONS

1. Instrument: Hewlett Packard Series II Model 5890 gas chromatograph.

2. Detector: Hewlett Packard N-P detector. Bead setting of 600 to 800 to give a peak height of approximately 30% - 50% full-scale deflection (FSD) for a 0.15-ng injection of CL 92,553 standard.

3. Column: Fused Silica Capillary, 15 m x 0.53 mm I.D, Rtx-20 with a film thickness of 1.0 micron.

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4. Instrument Conditions:

a.	Column Temperature	Initial Temp: 180°C Rate: 5.0°C/minute Final Temp: 230°C Hold: 2 minutes
b.	Inlet Temperature	250°C
c.	Detector Temperature	250°C
d.	Carrier Gas (Helium) Flow Rate	5-10 mL/min.
e.	Auxiliary Gas (Helium)	22 mL/min.
f.	Hydrogen Flow Rate	approx. 3.5 mL/min.
g.	Air Flow Rate	100-110 mL/min.
h.	Input Attenuation	0
i.	Chart Speed	0.5 cm/min.

5. Sensitivity: Attenuation on the recording integrator should be set so that 0.15 ng of CL 92,553 injected gives a peak height of approximately 30% - 50% FSD.

6. Retention Time: Approximately 6.8 minutes for CL 92,553.

F. LINEARITY CHECK

The gas chromatograph should be checked for linearity of response whenever a new column or instrument is used.

1. Adjust the GC conditions to obtain a peak height of approximately 30% - 50% FSD for a 0.15-ng injection of the working standard.

2. Inject 3 mcL aliquots of the analytical standard solutions E, F, G and H prepared in section D.2.

3. Determine the response factor (ratio) for all injections by dividing the peak response by the amount (nanograms) injected. Calculate the average response ratio. A deviation of any standard response factor by more than 15% from the average indicates instrumental or standard difficulties which must be corrected before proceeding with the analyses.

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4. Linearity checks should be performed at least weekly during the analysis of samples from every field residue study and when the chromatographic system has been adjusted or serviced.

G. SAMPLE PREPARATION

1. Keep all samples frozen until ready for analysis.

2. Allow the frozen samples to thaw completely in an air-tight container just prior to extraction.

3. Thoroughly mix the thawed samples to obtain a homogenous sample.

H. RECOVERY TEST

The validity of the procedure should always be demonstrated by recovery tests before analysis of unknown samples is attempted. A fortified sample should also be processed each time a batch of samples is analyzed.

1. Weigh a 10-g sample of finely ground soil into a 16-ounce narrow-mouth bottle.

2. Add by pipet a volume of standard fortification solution appropriate to the fortification level to be tested.

3. Mix the sample well and allow to stand for approximately five minutes.

4. Continue with the extraction and cleanup steps.

I. EXTRACTION AND PRELIMINARY CLEANUP

1. Weigh out 10-g of finely ground soil into a 16-ounce narrow-mouth bottle.

2. Add 25 mL of deionized water to the bottle, stopper and swirl for approximately 15 seconds. Add 75 mL of acidic methanol (2%). Stopper the bottle tightly and shake for one hour on a reciprocating shaker.

3. Filter by gentle suction through glass-fiber filter paper (in a 9-cm Buchner funnel) into a 250-mL filtration flask. Transfer a 25-mL aliquot of the filtrate to a 150-mL beaker and add 25 mL of 0.1N hydrochloric acid.

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J. SOLID PHASE EXTRACTION CLEANUP

1. Prepare a C18 cartridge (200 mg/3 mL endcapped) using a Visiprep SPE Vacuum Manifold by washing the cartridge with 2 mL of methanol followed by 2 mL of deionized water.

2. Assemble an empty 70-mL disposable reservoir onto the top of the prepared C18 cartridge using an adapter.

3. Pass the sample from Step I.3. through the C18 cartridge, using the Visiprep SPE vacuum manifold, at the rate of approximately 1 drop per second.

4. Remove the reservoir and adapter and wash the C18 cartridge with two column lengths of deionized water. Allow the liquid to drain from the cartridge completely.

5. Continue to apply vacuum for approximately 10 minutes to dry the cartridge.

6. Using only slight vacuum, elute the C18 cartridge on the vacuum manifold with 2 mL of 1% methanol in hexane. Collect the eluate in a 50-mL pear-shaped flask.

7. Evaporate the 1% methanol in hexane to dryness using a rotary evaporator equipped with a heated water bath maintained at approximately 35°C.

8. Dissolve the residue in 1 mL of hexane in preparation for gas chromatographic analysis.

K. GAS CHROMATOGRAPHIC ANALYSIS (See Note to Method M 2514)

1. After obtaining a stable GC response as described in Section F, inject a 3-mcL aliquot of sample into a GC equipped with a nitrogen-phosphorus detector.

2. Compare the peak height with that obtained from a 0.15-ng injection of the 0.05 mcg/mL GC standard solution.

3. If the sample peak exceeds that of the linearity standards, dilute to an appropriate volume and reinject.

4. Make a standard injection after every sample or every other sample and use the average peak height of the standard injection before and after the sample injections for quantitation.

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L. CALCULATIONS

For each sample calculation, use the sample peak height and the average peak height measurement of the external standard obtained before and after the sample injections as follows:

$$PPB = \frac{R(SAMP) \times (V1) \times (V3) \times C(STD) \times (V5) \times D.F.}{R(STD) \times W \times (V2) \times (V4)} \times 1{,}000$$

$$\% \text{ RECOVERY} = \frac{PPB\ FOUND \times 100}{FV \times FC \times 1000/W} = \frac{PPB\ FOUND}{PPB\ ADDED} \times 100$$

Where:

R(SAMP) = Peak height of sample in millimeters

R(STD) = Average peak height of working standard in millimeters

W = Weight of sample taken for analysis in grams (10)

V1 = Volume to which extraction solvent is diluted in milliliters (100)

V2 = Aliquot of extract taken for analysis in milliliters (25)

V3 = Volume of hexane added to dissolve final residues for chromatographic analysis in milliliters (1)

V4 = Volume of sample solution injected in microliters (3)

V5 = Volume of working standard solution injected in microliters (3)

C(STD) = Concentration of working standard solution injected in micrograms per milliliter (0.05)

D.F. = Dilution factor

FV = Fortification volume in mL

FC = Fortification concentration (of standard solution added) in mcg/mL

Typical chromatograms for soil are shown in Figures 1 and 2.

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NOTE TO METHOD M 2514

If the chromatography deteriorates, first try to clean the column by baking-out for 2-3 hours at 280°C. If the chromatography still has not improved, a section of the column may be removed from the inlet end and/or the liner may be replaced. If these changes do not improve the chromatography, a new column may be installed.

If samples are excessively dirty, a guard column of bare-fused silica can be connected between the inlet and the column using a press-tight connector.

APPROVALS:

Author:

S. Singh 01/31/96

S. Singh Date

Group Leader:

M. Safarpour 01/31/96

M. Safarpour Date

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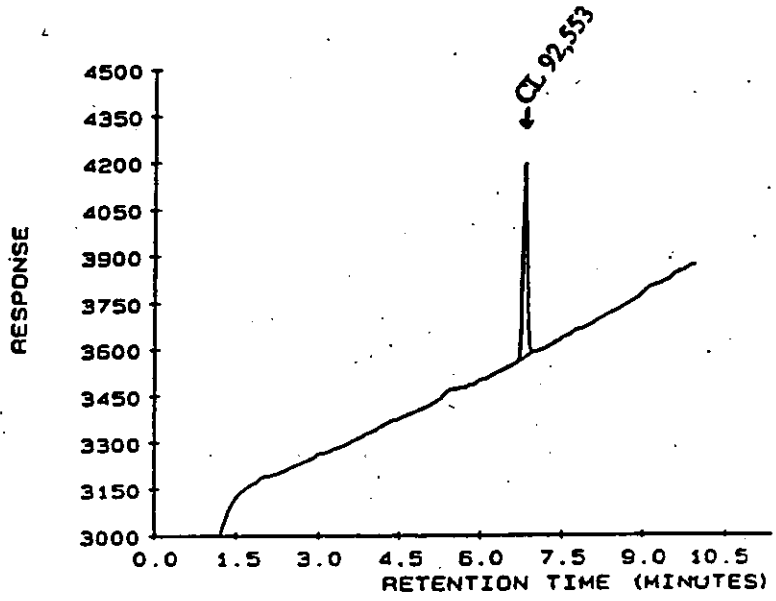
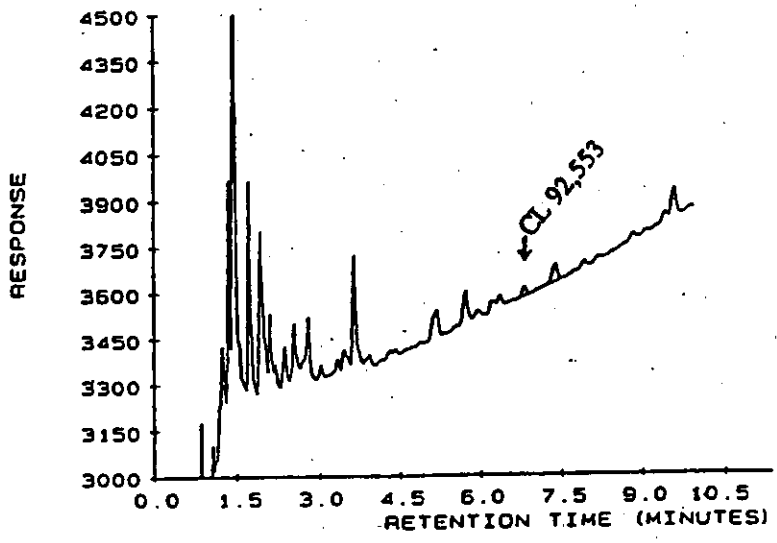
Figure 1: Typical Chromatograms for the Determination of CL 92,553 Residues in Soil



CL 92,553 Standard, 0.15 ng Injected



Control Soil, Tippecanoe Silt Loam (AC 6105.37A), 7.5 mg Injected, 1.05 ppb Apparent CL 92,553 Found

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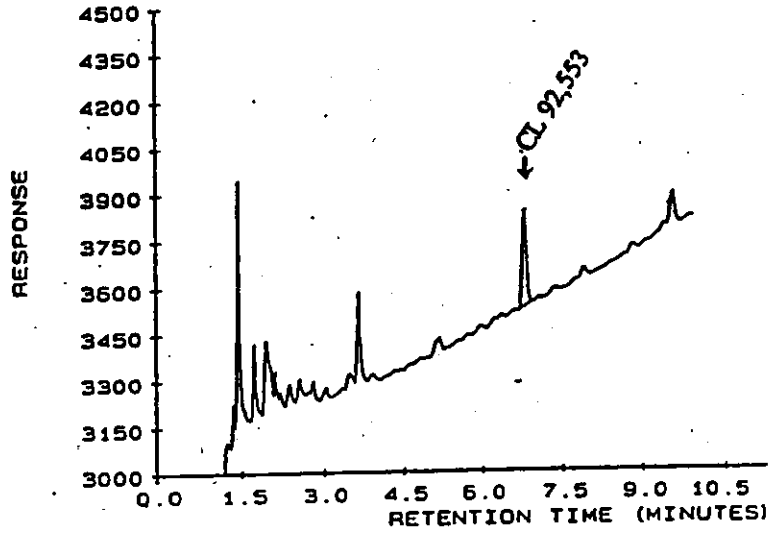
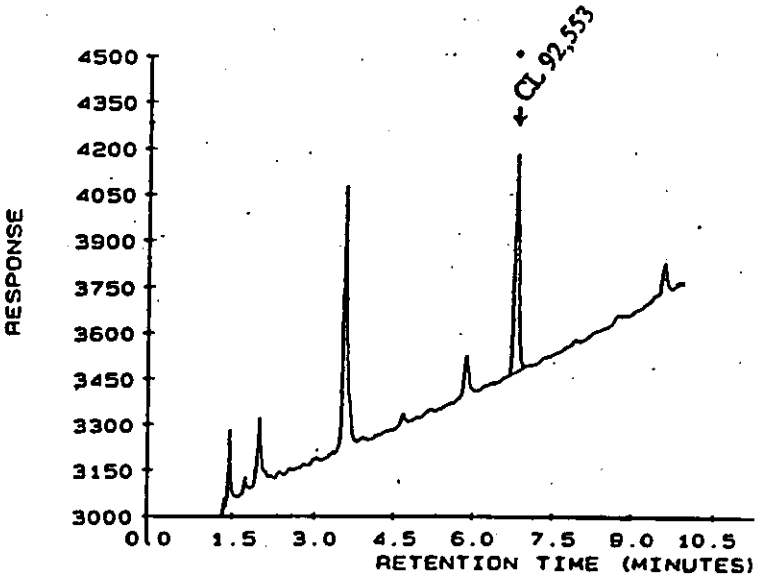
Figure 1: Typical Chromatograms for the Determination of CL 92,553 Residues in Soil (continued)



Control Soil, Tippecanoe Silt Loam (AC 6105.37A), Fortified with CL 92,553 at 10 ppb, 7.5 mg Injected, 10.4 ppb Found, 104% CL 92,553 Recovered



Control Soil, Tippecanoe Silt Loam (AC 6105.37A), Fortified with CL 92,553 at 50 ppb, 3.75 mg Injected, 48.0 ppb Found, 96% CL 92,553 Recovered

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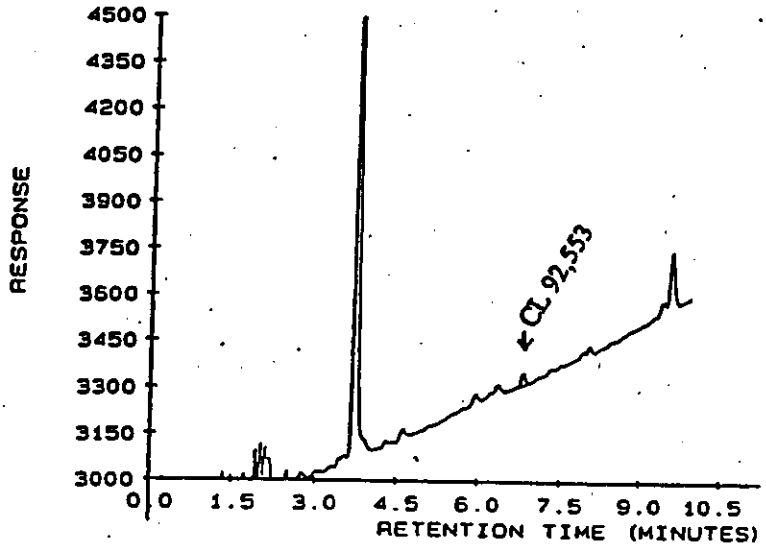
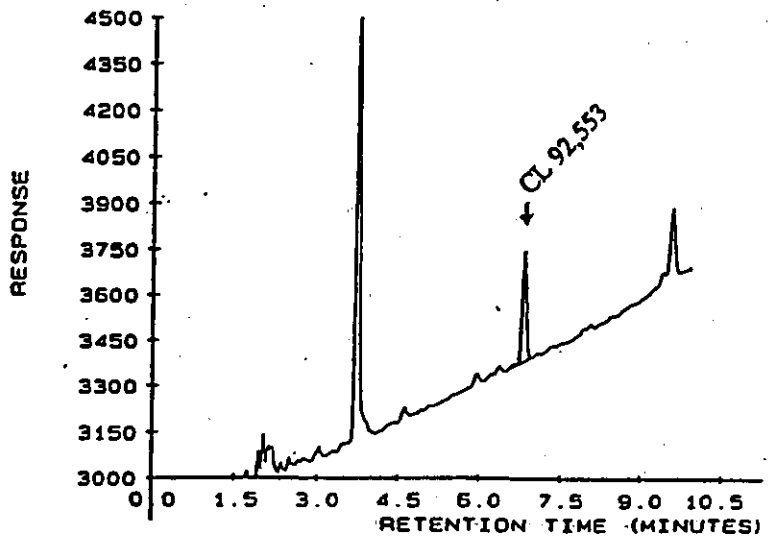
Figure 2: Typical Chromatograms for the Determination of CL 92,553 Residues in Soil



Control Soil, Beardon Clay Loam (AC 6105.37B), 7.5 mg Injected, 1.6 ppb Apparent CL 92,553 Found



Control Soil, Beardon Clay Loam (AC 6105.37B), Fortified with CL 92,553 at 10 ppb, 7.5 mg Injected, 11.2 ppb Found, 112% CL 92,553 Recovered

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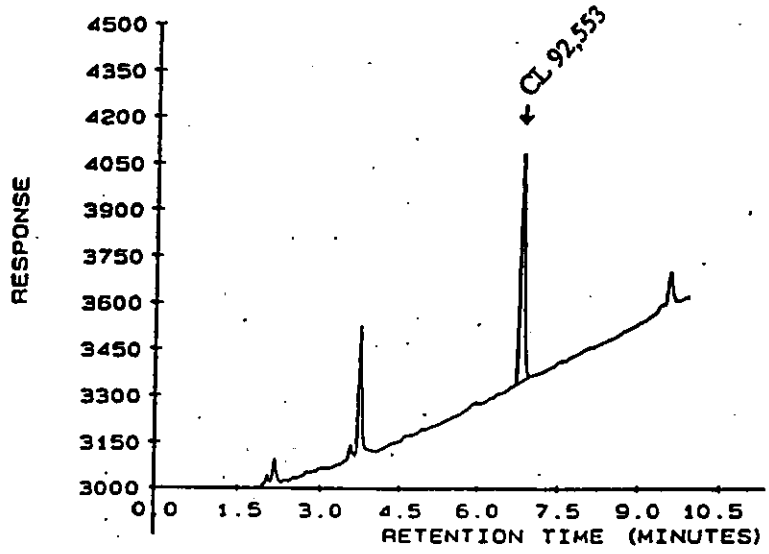
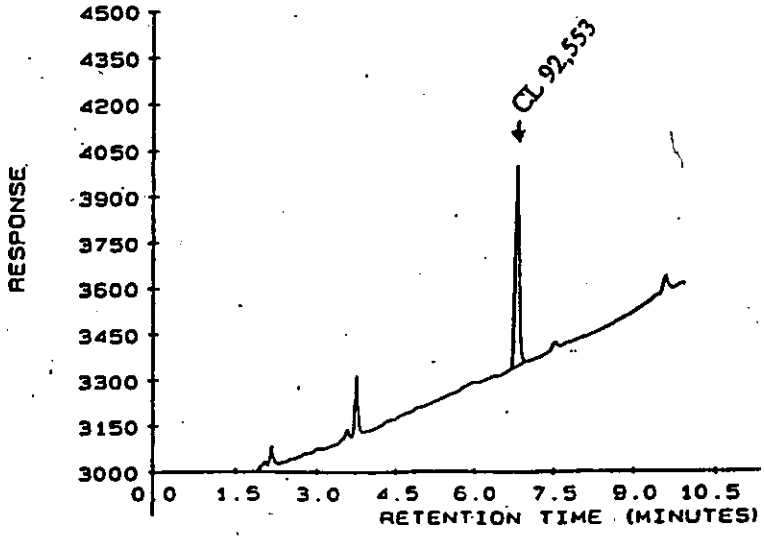
Figure 2: Typical Chromatograms for the Determination of CL 92,553 Residues in Soil (continued)



Control Soil, Beardon Clay Loam (AC 6105.37B),.Fortified with CL 92,553 at 100 ppb, 1.5 mg Injected, 98.4 ppb Found, 98% CL 92,553 Recovered



Control Soil, Beardon Clay Loam (AC 6105.37B), Fortified with CL 92,553 at 200 ppb, 0.75 mg Injected, 174 ppb Found, 87% CL 92,553 Recovered

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