

Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pesticide Name: Propanil

MRID #: 422005-01

Matrix: Soil

Analysis: GC/NPD

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MEMORANDUM FOR THE DIRECTOR, FBI

DATE: 10/10/54

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RE: [Illegible]

[Illegible typed text]

Very truly yours,
[Illegible Signature]

APPENDIX H. EN-CAS ANALYTICAL LABORATORIES METHOD ENC-4/90

WILDLIFE INTERNATIONAL LTD. PROJECT NO.: 271-109

EN-CAS Method No. ENC-4/90

Analytical Method for the Determination of Propanil
and Free 3,4-Dichloroaniline in Soil
Using Capillary Gas Chromatography

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Total Pages = 17

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TITLE: Analytical Method for the Determination of Propanil And Free 3,4-Dichloroaniline in Soil Using Capillary Gas Chromatography	QA APPROVAL <i>William J. Int. Lab.</i> NEXT APPROVAL <i>Best Clayton</i>	

1.0 INTRODUCTION AND SUMMARY

1.1 Scope

This method is used for the determination of propanil and the "free" form of its primary metabolite, 3,4-dichloroaniline (3,4-DCA) in soil. "Free" 3,4-DCA consists of unbound or loosely bound 3,4-DCA which can be extracted from soil by shaking in an appropriate organic solvent (e.g. 1:1 acetone:toulene). It should be noted that a significant portion of the 3,4-DCA produced from propanil in soil becomes strongly or irreversibly bound to the soil. A portion can be freed but this requires hydrolysis in strong base. A procedure to accomplish this is described in EN-CAS Method ENC-9/90.

Method validation results from EN-CAS report 89-0122 PTF, Method Validation for the Determination of Total Dichloroaniline, Propanil and Free Dichloroaniline in Soil, are included in this report (see Tables I to VI). See Figure 1 for a flowchart of the method.

1.2 Principle

Soil samples which may contain propanil and "free" 3,4-DCA are first crushed and homogenized in a Hobart food processor with dry ice. The dry ice is allowed to sublime in a refrigerator or at room temperature before taking a soil subsample. The sample is extracted by first adding acetone to dissolve soil-bound water so that agglomeration of

1.2 Principle (continued)

the soil during extraction is minimized. Toluene is then added in an equal volume of acetone and the sample is shaken on a mechanical shaker. The extracted sample is vacuum filtered and the acetone is removed from the sample by rotary evaporation leaving primarily toluene. The 3,4-DCA is extracted from the toluene by partitioning into 0.5N HCl (saturated with toluene). The resulting organic phase (toluene) contains the propanil, and the aqueous phase contains the 3,4-DCA.

The organic phase is drained through a sodium sulfate pad and evaporated to incipient dryness on a rotary evaporator. Methanol is added to dissolve the propanil residue. The acidic aqueous phase is neutralized and buffered to pH 6.7 - 7.0 and then combined with the methanol from the organic phase. The sample (now containing both propanil and 3,4-DCA) is then loaded onto a pre-conditioned C-18 Mega Bond Elut cartridge. The analytes are eluted from the cartridge with ethyl acetate. The ethyl acetate is dried using anhydrous sodium sulfate. The sample extract is adjusted to a final volume of 10 ml with ethyl acetate and placed into a GC vial. Gas chromatographic analysis is performed using an alkali flame (N/P) detector equipped with a capillary DB-17 or DB-1701 column. A limit of quantitation (LOQ) of 0.01 ppm for either propanil or 3,4-DCA has been achieved for soil.

2.0 APPARATUS

All equipment and apparatus may be replaced by equivalent items from alternate sources.

- 2.1 16 oz. Nalgene plastic bottles and/or 16 oz. French square bottles
- 2.2 Buchner funnels, 11 cm
- 2.3 Side-arm filter flasks, 500 ml
- 2.4 Whatman GF/C filters, 9.0 cm diameter
- 2.5 Erlenmeyer flasks, 250 ml, with 24/40 ground glass fittings
- 2.6 Stoppers, ground glass, 24/40
- 2.7 Separatory funnels, 500 ml

2.0 APPARATUS (continued)

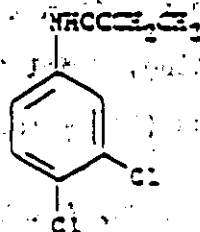
- 2.8 Powder funnels, metal, 4 inch diameter
- ✓ 2.9 Centrifuge tubes, 15 ml graduated
- 2.10 Test tubes, borosilicate glass, 16 x 100 mm, disposable
- 2.11 Pasteur pipettes, 23 cm
- 2.12 Glass wool
- 2.13 C-18 Mega Bond Elut cartridges, 2 gram (Analytichem International)
- 2.14 Filter paper, 9 cm diameter (Whatman GC/C)
- 2.15 Reservoirs, 75 ml capacity, Analytichem International
- 2.16 Luer stopcocks, plastic (Analytichem International)
- ✓ 2.17 Mechanical Shaker (G10 Gyrotory)
- ✓ 2.18 Rotary evaporators (Buchi Rotavapor, model #RE111)
- ✓ 2.19 Air Pump (Neptune Dyna-Pump, Model 4K)
- 2.20 Hobart homogenizer (model 8142 or 84142)
- ✓ 2.21 pH meter (Corning, Model 106)
- ✓ 2.22 Vac-Elut System (Analytichem International #SPS24)
- ✓ 2.23 Top loading balance, (Fisher Scientific, Model XT-3KD)
- ✓ 2.24 Mettler analytical balance capable of ± 0.00002 g accuracy, for weighing analytical standards

3.0 REAGENTS

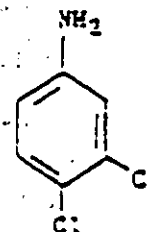
- 3.1 Acetone, pesticide grade
- 3.2 Toluene, pesticide grade
- 3.3 Concentrated HCl, ACS Reagent grade
- 3.4 Sodium Hydroxide (NaOH), ACS reagent or Optima
- 3.5 Methanol, pesticide grade
- 3.6 Ethyl Acetate, pesticide grade
- 3.7 Potassium Dihydrogen Phosphate (KH₂PO₄), ACS reagent grade

Prepare a 1M KH₂PO₄ solution by dissolving 136.09 g of KH₂PO₄ in 750 ml of H₂O, adjusting the pH to 6.5 with 5N NaOH, and bringing the solution up to volume (1000 ml).

- 3.8 Sodium Sulfate (Na₂SO₄), Anhydrous, ACS certified, oven baked at 600°F for 2 hours
- ✓ 3.9 Deionized water (Milli-Q system or equivalent)

4.0 TEST SUBSTANCES

Propanil
C₉H₉Cl₂NO
M.W. 219.09



3,4-Dichloroaniline
C₆H₅Cl₂N
M.W. 162.03

5.0 PREPARATION OF ANALYTICAL STANDARDS

5.1 Fortification Standards

Weigh 10 mg of active ingredient (i.e., propanil, 3,4-dichloroaniline). Transfer the test substances to separate 100 ml volumetric flasks. Dissolve and dilute to volume with methanol to prepare 100 µg/ml stock solutions. Serially dilute the 100 µg/ml standards to prepare 10 µg/ml, 1.0 µg/ml, and 0.25 µg/ml standard solutions for propanil and 3,4-DCA. Use these solutions to fortify soil control samples in order to monitor procedural recovery. The stock standard solution (100 µg/ml) is stable for at least 12 months. [Note: Store all standard solutions in a freezer at a temperature of -23°C to -27°C.]

5.2 Gas Chromatographic Standards

Use the 100 µg/ml propanil and 3,4-dichloroaniline fortification standards (in methanol) that were prepared for the fortifying solutions to make combined 10 µg/ml and 1.0 µg/ml standard solutions in ethyl acetate. Serially dilute these standards in ethyl acetate to prepare a range of standards from 0.025 µg/ml to 0.25 µg/ml to be used as gas chromatographic (GC) calibration standards. The GC calibration standards are stable for 6 months. [Note: Store all standard solutions in a freezer at a temperature of -23°C to -27°C.]

6.0 ANALYTICAL PROCEDURE

6.1 Sample Processing

Homogenize soil samples using a Hobart food processor and dry ice. Mix the samples for 5-10 minutes until a homogeneous mixture is obtained. Allow the dry ice to sublime in a refrigerator or at room temperature. Weigh a 50 gram subsample into either a 500 ml Nalgene bottle or a 16 oz. French square bottle.

6.2 Extraction

Add 50 ml of acetone, swirl by hand, and wait for 5 minutes. Add 50 ml of toluene to the sample, cap the bottle, and place it on the mechanical shaker for 15 minutes at 200 rpm. [Adding the acetone separately allows the soil moisture to be extracted from the soil and thus prevents the soil from clumping during the shaking step].

Vacuum filter the extract using a Buchner funnel and Whatman #2 (9 cm) filter paper, into a 500 ml side-arm flask. Rinse the Nalgene bottle that contained the sample with 2 x 10 ml aliquots of a 1:1 acetone:toluene solution and add to the side-arm flask. Transfer the solution in the side-arm flask to an Erlenmeyer flask. Rinse the side-arm flask with 10 ml of 1:1 acetone:toluene solution and add to the Erlenmeyer flask. Evaporate the acetone from the sample using a rotary evaporator with a water bath at ambient temperature (the rotary evaporator condenser is cooled by dry ice). [Extreme care must be taken at this point in the procedure due to the volatility of the metabolite (3,4-DCA). The sample should be evaporated just until acetone stops distilling into the collection flask. However, care must also be taken to assure that most of the acetone is removed since an excess of residual acetone will alter the analyte distribution in the partition step which follows. Evaporating to a volume of approximately 70 ml appears to provide a good balance between retention of 3,4-DCA and proper partitioning in the partition step.]

Partition the sample (now mainly toluene) with 3 x 50 ml of 0.5N HCl (saturated with toluene). Retain both the organic layer (top) and the aqueous layer (bottom).

Organic phase (Propanil) - Pass the organic layer through a pad of sodium sulfate approximately one and a half inches thick contained in a funnel. Rinse the pad with 2 x 10 ml toluene. Evaporate the toluene filtrate to dryness using rotary evaporation, keeping the bath temperature at 40°C - 50°C. Reconstitute the sample with 5 ml of methanol. Proceed to step 6.3.

6.2 Extraction (continued)

Aqueous phase (3,4-DCA) - Neutralize the aqueous phase to pH 6.7 - 7.0 with 5N NaOH. Use a pH meter to verify the pH. Add 25 ml of 1M Potassium Monohydrogen Phosphate (K_2HPO_4) as a buffer. Proceed to step 6.3.

6.3 Clean-up Step Using C-18 Mega Bond-Elut Cartridges

Combine the methanol reconstituted organic phase (step 6.2) with the neutralized and buffered aqueous phase using 2 x 5 ml methanol as a rinse for the organic phase container. Using a Vac-Elut system, pre-condition the C-18 Mega Bond Elut cartridge with 2 x 10 ml methanol and 2 x 10 ml d.i. water (column should not go dry). Add the sample to the C-18 Mega Bond Elut cartridge and allow it to pass through the cartridge at a flow rate of approximately 5-10 ml/min. Discard the sample load. Elute the analytes with 2 x 4 ml of ethyl acetate at a flow rate of approximately 5-10 ml/min. Pass the eluate through a manually packed micro-column (pasteur pipette with a glass wool plug filled with -4 cm x 5 mm of sodium sulfate) to dry the samples. Rinse the sodium sulfate with 2 x 1 ml of ethyl acetate. Adjust the sample to a final volume of 10 ml with ethyl acetate. Transfer the extract to a GC vial and analyze by gas chromatography using N/P detection.

6.4 Gas Chromatographic Determinations

Use a 30 m x 0.32 mm, 0.25 μ m film thickness capillary DB-17 or DB-1701 column to achieve gas chromatographic separations. Use a Hewlett-Packard Model 5890-A Gas Chromatograph with an alkali flame, nitrogen/phosphorus (N/P) detector to provide adequate sensitivity and selectivity. Gas chromatographic conditions are listed in Section 7.0 of this method.

6.5 Safety Precautions

Use normal safety precautions, including the wearing of gloves, safety glasses and a fume hood to minimize exposure to the analytes and organic solvents used in this procedure.

6.6 Time Required for Analysis

An experienced technician can process a set of ~10 samples (including controls and recoveries), and prepare for injection on the gas chromatograph in two man-days.

6.7 Measurement Limit

For all of the soil samples validated herein, this method is proven effective to a LOQ of 0.01 ppm for both propanil and 3,4-DCA. Adjust the instrument sensitivity, GC calibration standards and final sample volumes to allow detection of propanil and free 3,4-DCA at 50% of the LOQ.

6.8 Interference and Potential Problems

A loss of 15-20% of 3,4-DCA may occur if more than 50% (70 ml) of the original extraction volume of 1:1 acetone/toluene is removed by rotary evaporation (see step 6.2). Significant loss of 3,4-DCA can also occur by not using the appropriate stopping points in the method. Acceptable stopping points are as follows:

- 1). After the filtration of the extracted samples (if this stopping point is used, the samples should be refrigerated after the filtration).
- 2). After the reduction of sample volume following the filtration step.
- 3). After the sample has been through the C-18 Mega Bond Elut clean-up.

All of these stopping points are designated by footnotes in the flowchart of the method (see Figure 1).

In applying this method to soil from rice fields, it is recommended that the control soils be pre-screened prior to use. Many of these soils have been found to contain bound 3,4-DCA which could, if freed by weathering processes, result in background levels of the analyte. In addition, other crop protection agents applied to rice fields may produce close-lying interferences. The GC conditions have been shown to separate propanil and 3,4-DCA from two commonly applied herbicides, Ordram and Bolero, and a common metabolite, 3,5-DCA, as demonstrated in Figures 15 and 16.

7.0 GAS CHROMATOGRAPHIC ANALYSIS**7.1 Description and Typical Operating Conditions**

Instrument: Hewlett-Packard Model 5890-A Gas Chromatograph with an alkali flame, nitrogen/phosphorus (N/P) detector equipped with a 7673A Automatic Sampler. Collect and process data with a Hewlett-Packard 3396A Integrator.

Column: Capillary DB-17 or DB-1701
30 m x 0.32 mm, 0.25 μ m film thickness (J & W Scientific)

Gases: Carrier: Helium = 3.80 ml/min.
Detector: Hydrogen = 4.20 ml/min.
Air = 110 ml/min.
Aux He = 20.2 ml/min.

Injection: 2 μ l, splitless

Temperatures: Injector: 250°C
Detector: 275°C
Column Temperature Program:
Initial Oven Temp. = 50°C
Initial Time = 1.5 min.
Ramp A = 30°C/min.
Final Oven Temp. = 195°C
Final Time = 2.0 min.
Ramp B = 40°C/min.
Final Oven Temp. = 240°C
Final Time = 2.0 min.
Ramp C = 40°C/min.
Final Oven Temp. = 275°C
Final Time = 10.0 min.
Run Length = 33.6 min.

Retention Times: Free 3,4-DCA = 5.8 min.
Propanil = 8.6 min.

7.1 Description and Typical Operating Conditions (continued)

Integrator

Parameters: Hewlett-Packard 3396A Integrator

Parameter Definitions	Run Parameters	Timetable Events
0. SET BASELINE NOW	ZERO = 20	0.000 INTG / = 2
1. SET BASELINE NEXT VALLEY	ATT 2° = 1	0.000 INTG / = 8
2. SET BASELINE ALL VALLEYS	CHT SP = 0.0	0.000 INTG / = 9
3. SKIN FROM NEXT PEAK	AR REJ = 0	5.000 CHT SP = 2.0
4. DISABLE AUTO-TANGENT SKIPPING	THRESH = 0	5.005 ZERO = 20
5. EXTEND BASELINE HORIZONTALLY	PK WD = 0.02	5.010 INTG / = -9
6. MEASURE AND UPDATE THRESHOLD		6.500 INTG / = 9
7. TURN OFF RETENTION TIME LABELING		6.505 CHT SP = 0.0
8. TURN ON START/STOP MARKS		8.000 CHT SP = 2.0
9. TURN OFF INTEGRATION		8.005 ATT 2° = -1
10. INCREMENT THRESHOLD		8.010 ZERO = 20
11. INVERT NEGATIVE PEAKS		8.015 INTG / = -9
12. CLAMP NEGATIVE PEAKS		9.500 INTG / = 9
13. SHOW IPI1, IPI2		9.505 CHT SP = 0.0
14. START PEAK SEARCH WINDOW		9.510 ATT 2° = 10
		9.515 PK WD = 0.02
		9.520 PK WD = 2.5
		9.600 CHT SP = 0.0

7.2 Calibration

Use the combined propanil and 3,4-DCA GC calibration standards in ethyl acetate in concentrations ranging from 0.025 µg/ml to 0.25 µg/ml to calibrate the instrument. Inject appropriate standards at the beginning of the run, after approximately every two or three samples throughout the run, and at the end of the run. A linear regression function is generated using the resulting peak height (obtained from the integrator) vs. nanograms injected (see Figure 12). The correlation coefficient for the line should generally be equal to or greater than 0.990. The sample nanograms found are determined by inserting the sample peak height values into the standard curve linear regression equation.

7.3 Representative Chromatograms

Typical chromatograms illustrating GC calibration standards as well as soil controls, and soil recoveries, from both Louisiana and Arkansas rice field soils are shown in Figures 2 to 11. Typical calibration curves for propanil and free 3,4-DCA are shown in Figure 12 and Figure 13.

8.0 CALCULATIONS

Note: Residue samples may be corrected for procedural recovery and/or procedural recovery may be corrected for control sample background as per client request.

8.1 Calculations for Propanil and Free 3,4-Dichloroaniline in Soil.

The ng of analyte found is determined from a standard curve prepared as discussed in section 7.2. The calculation is performed as follows:

$$\text{ng found in injected sample} = \frac{\text{sample peak height} - \text{standard curve y intercept}}{\text{standard curve slope}}$$

$$\text{ng-equiv. injected} = \frac{\text{ng sample extracted} \times \mu\text{l injected}}{\mu\text{l final volume} \times \text{dilution factor}}$$

$$\text{ppm found} = \frac{\text{ng found}}{\text{ng-equiv. injected}}$$

8.1 Calculations for Propanil and Free 3,4-Dichloroaniline in Soil (continued)

Obtain the nanograms (ng) of analyte found by constructing a standard curve using linear regression analysis of GC calibration standards.

For example:

$$\text{ng found} = \frac{(5188 \text{ counts} - (-429.39 \text{ counts}))}{17243.84 \text{ counts/ng}} = 0.326 \text{ ng}$$

$$\text{ng equiv injected} = \frac{50,000 \text{ ng} \times 2 \text{ } \mu\text{l}}{5,000 \text{ } \mu\text{l} \times 10} = 2.0 \text{ ng}$$

$$\text{ppm found} = \frac{0.326 \text{ ng}}{2.0 \text{ ng}} = 0.163 \text{ ppm 3,4-Dichloroaniline}$$

8.2 Soil Moisture Calculations

Determine the percent of moisture in the soil by weighing 10 grams of soil in duplicate, drying overnight at an oven temperature of 110°C, and reweighing the soil. The average of the duplicate soil moistures is to be used in the residue calculation.

Percent moisture in a sample:

$$\frac{\text{wet wt.} - \text{dry wt.}}{\text{wet wt.}} \times 100 = \% \text{ moisture}$$

8.2 Soil Moisture Calculations (continued)

<p>For example:</p> $\frac{10.03 \text{ g} - 7.02 \text{ g}}{10.03 \text{ g}} = 0.300 \times 100 = 30\%$
--

8.3 Calculation of Soil Residues on a Dry Weight Basis

Dry sample ppm is determined by:

$\text{ppm dry} = \frac{\text{ppm wet}}{(1 - \text{decimal } \% \text{ moisture})}$

<p>For example:</p> $\text{ppm dry} = \frac{0.163 \text{ ppm}}{(1 - 0.31\%)} = 0.236 \text{ ppm 3,4-Dichloroaniline}$ <p>* This value is different than the value obtained from the % moisture calculation shown above, because it is an average of the duplicate soil moisture results.</p>
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9.0 VALIDATION RESULTS

See Tables I to VI in this report.

9.1 Statistical Method

The mean recoveries and standard deviations are calculated from the validation data and appear in Tables I to VI.

9.2 Discussion of Validation Results

Approximately 90% of the analyzed recovery samples for propanil and 3,4-DCA in soil fall within the optimal 70% to 120% recovery range. Recovery data are presented in Tables I to VI. Recovery means and standard deviations calculated for the method validations indicate a reliable method for the determination of propanil and 3,4-DCA in soil by gas chromatography.

10.0 REFERENCES

1. Evaluation of the Bleidner Techniques for Analysis of Soil-Bound 3,4 Dichloroaniline Residues, J. Agric. Food Chem (1982), 30:1145-1147.
2. Analytical Methods for Pesticides and Plant Growth Regulators. Vol. VI, 1972, p. 694, Zweig.
3. The Determination of Substituted Aromatic Amines in Water and Sediment Samples, Anal. Chem., (1988), 331:282-289, Fresenius, Z.
4. Pesticide Analytical Manual, Vol II, Pesticide Regulations Section, 180.274, Method I and II.
5. U.S. Environmental Protection Agency, August 17, 1989, Pesticide Programs; Good Laboratory Practice Standards: Final Rule (40 CFR, Part 160).

Table I
 Method Validation
 Propanil and Free 3,4 Dichloroaniline
 in Louisiana Soil
 Fortifications at 0.01 ppm with Propanil
 and 3,4 Dichloroaniline

EN-CIS ID #	Set #	Date Extracted	Date Analyzed	% Recovered		
				Propanil	3,4-DCI	
NV4-C	NV-4	7/02/90	7/16/90	<0.01	<0.01	
NV4-Sol7.81k.	NV-4	7/02/90	7/16/90	<0.01	<0.01	
NV4-S1	NV-4	7/02/90	7/16/90	90%	70%	
NV4-S2	NV-4	7/02/90	7/16/90	90%	72%	
NV4-S3	NV-4	7/02/90	7/16/90	88%	68%	
NV4-S4	NV-4	7/02/90	7/16/90	100%	78%	
NV4-S5	NV-4	7/02/90	7/16/90	100%	80%	
NV4-S6	NV-4	7/02/90	7/16/90	92%	73%	
NV4-S7	NV-4	7/02/90	7/16/90	89%	72%	
				Mean =	92.7%	73.2%
				Standard Deviation =	5.1	4.3
				(n=10)		

NOTE: Any contribution from the control sample was used to correct the recovery value.

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Table II

Method Validation

Propanil and Free 3,4 Dichloroaniline
in Louisiana SoilFortifications at 0.10 ppm with Propanil
and 3,4 Dichloroaniline

EH-CIS ID #	Set #	Date Extracted	Date Analyzed	% Recovered	
				Propanil	3,4-DCI
NV2-C	NV-2	6/18/90	6/20/90	<0.01	<0.01
NV2-2-solv.3lk.	NV-2	6/18/90	6/22/90	<0.01	<0.01
NV2-51	NV-2	6/18/90	6/20/90	81%	67%
NV2-52	NV-2	6/18/90	6/20/90	86%	86%
NV2-53	NV-2	6/18/90	6/20/90	96%	85%
NV2-54	NV-2	6/18/90	6/20/90	74%	78%
NV2-55	NV-2	6/18/90	6/20/90	65%	80%
NV2-56	NV-2	6/18/90	6/20/90	86%	86%
NV2-57	NV-2	6/18/90	6/20/90	70%	76%
			Mean =	79.7%	79.7%
			Standard Deviation =	10.7%	6.3%
			(n-1=6)		

NOTE: Any contribution from the control sample was used to correct the recovery value.

Table III

Method Validation

Propanil and Free 3,4 Dichloroaniline
in Louisiana Soil

Fortification at 1.0 ppm with Propanil
and 3,4 Dichloroaniline

EP-GLS ID #	Set #	Date Extracted	Date Analyzed	% Recovered	
				Propanil	3,4-DCI
NV1-0	NV-1	5/14/90	6/18/90	<0.01	<0.01
NV-1-Solv. 3lk.	NV-1	6/14/90	6/18/90	<0.01	<0.01
NV1-01	NV-1	5/14/90	6/18/90	67%	90%
NV1-02	NV-1	5/14/90	6/18/90	73%	96%
NV1-03	NV-1	5/14/90	6/18/90	83%	90%
NV1-04	NV-1	5/14/90	6/18/90	69%	84%
NV1-05	NV-1	5/14/90	6/18/90	74%	89%
NV1-06	NV-1	5/14/90	6/18/90	87%	89%
NV1-07	NV-1	5/14/90	6/18/90	78%	84%
			Mean =	76.5%	88.3%
			Standard Deviation =	7.2%	4.1%
			(n=10)		

NOTE: Any contribution from the control sample was used to correct the recovery value.

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Table XII

Method Validation

Propanil and Free 3,4 Dichloroaniline
in Arkansas SoilFortifications at 0.01 ppm with Propanil
and 3,4 Dichloroaniline

EH-CAS ID #	Set #	Date Extracted	Date Analyzed	% Recovered		
				Propanil	3,4-DCI	
NV13-C	NV-13	7/26/90, 8/16/90	8/06/90, 8/21/90	<0.01, <0.01	<0.01, <0.01	
NV13-Solv. Blk.	NV-13	7/26/90	8/06/90	<0.01	<0.01	
NV13-S1 a	NV-13	8/16/90	8/21/90	81%	66%	
NV13-S2 a	NV-13	8/16/90	8/21/90	92%	67%	
NV13-S3	NV-13	7/26/90	8/06/90	83%	69%	
NV13-S4	NV-13	7/26/90	8/06/90	67%	71%	
NV13-S5	NV-13	7/26/90	8/06/90	93%	69%	
NV13-S6	NV-13	7/26/90	8/06/90	70%	75%	
NV13-S7	NV-13	7/26/90	8/06/90	89%	81%	
				Mean =	82.1%	71.1%
				Standard Deviation =	± 10.3	± 5.2
				(n=6)		

a Samples NV13-S1 and NV13-S2 were reanalyzed due to analytical error. Another control (NV13-C) was analyzed with these two samples.

NOTE: Any contribution from the control sample was used to correct the recovery value.

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Table 7

Method Validation

Propanil and Free 3,4 Dichloroaniline
in Arkansas SoilFortifications at 0.10 ppm with Propanil
and 3,4 Dichloroaniline

ES-CIS ID #	Set #	Data Extracted	Data Analyzed	% Recovered	
				Propanil	3,4-DCI
NV10-C	NV-10	7/23/90	8/03/90	<0.01	<0.01
NV10-Solv.3lk.	NV-10	7/23/90	8/03/90	<0.01	<0.01
NV10-51	NV-10	7/23/90	8/03/90	74%	78%
NV10-52	NV-10	7/23/90	8/03/90	98%	92%
NV10-53	NV-10	7/23/90	8/03/90	86%	87%
NV10-54	NV-10	7/23/90	8/03/90	90%	96%
NV10-55	NV-10	7/23/90	8/03/90	86%	90%
NV10-56	NV-10	7/23/90	8/03/90	87%	78%
NV10-57	NV-10	7/23/90	8/03/90	85%	82%
Mean =				86.7%	86.1%
Standard Deviation =				± 7.1%	± 7.0%
(n-1=6)					

NOTE: Any contribution from the control sample was used to correct
the recovery value.

EN-CIS Method No. ZNC 4/90

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Table 71

Method Validation

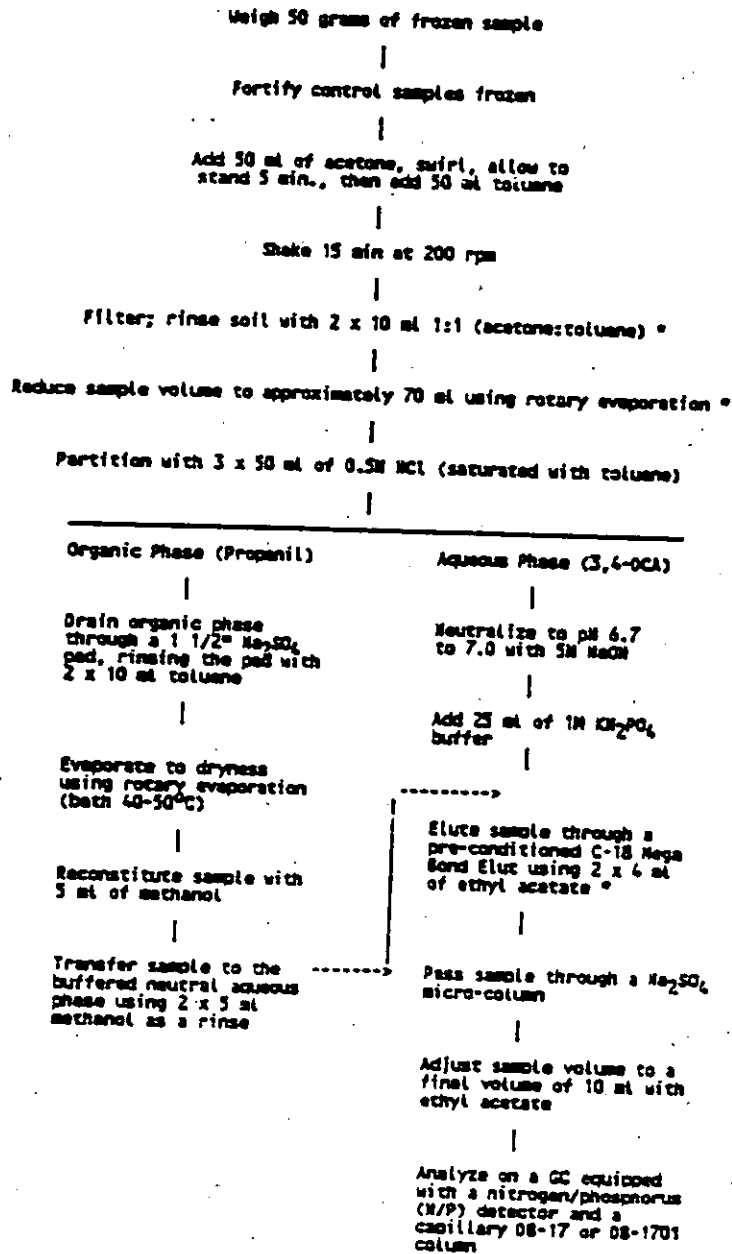
Propanil and Free 1,4-Dichloroaniline
in Arkansas SoilFortifications at 1.0 ppm with Propanil
and 1,4-Dichloroaniline

EN-CIS ID #	Sat #	Date Extracted	Date Analyzed	% Recovered	
				Propanil	1,4-DCI
NV8-C	NV-3	7/19/90	8/02/90	<0.01	<0.01
NV8-Sol7.31%	NV-3	7/19/90	8/02/90	<0.01	<0.01
NV8-S1	NV-3	7/19/90	8/02/90	84%	94%
NV8-S2	NV-3	7/19/90	8/02/90	82%	94%
NV8-S3	NV-3	7/19/90	8/02/90	81%	96%
NV8-S4	NV-3	7/19/90	8/02/90	85%	82%
NV8-S5	NV-3	7/19/90	8/02/90	83%	93%
NV8-S6	NV-3	7/19/90	8/02/90	80%	79%
NV8-S7	NV-3	7/19/90	8/02/90	92%	99%
Mean =				83.9%	91.3%
Standard Deviation = (n-1=6)				± 4.0%	± 7.5%

NOTE: Any contribution from the control sample was used to correct the recovery value.

FIGURE 1

Flowchart of Analytical Method ENC-4/90
Soils - Propanil and Para 3,4-DCA

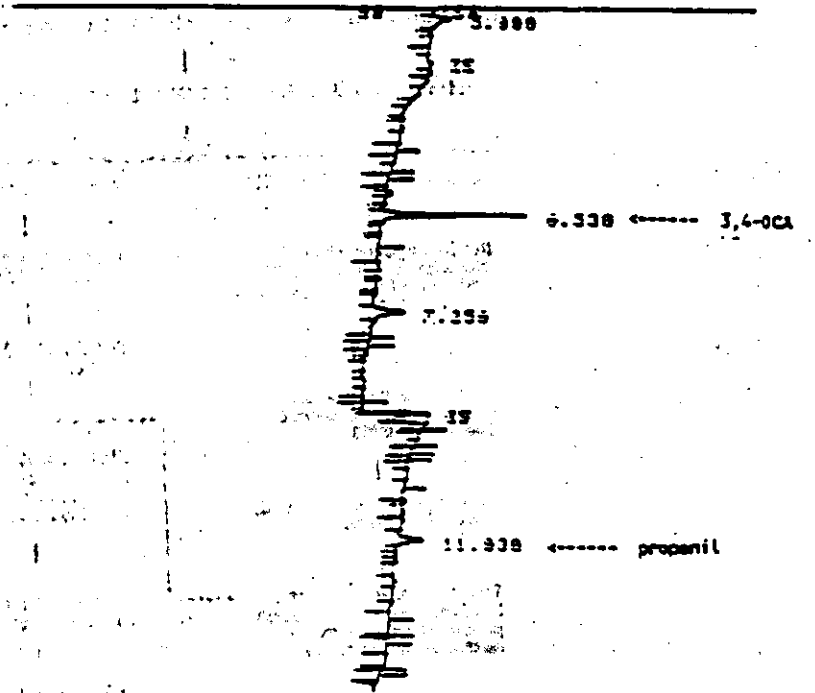


* The procedure may be stopped at this point if necessary. Refrigerate samples at all stopping points.

FIGURE 2
Typical Chromatogram
Free 3,4-Dichloroaniline and Propanil Analysis
in Louisiana Soil

GC Standard
0.025 ug/ml Propanil and DCA

RUN # 17 JUL 16, 1990 17:29:42
START



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0.05 ng injected
GC run # 30310, dated 7/16/90

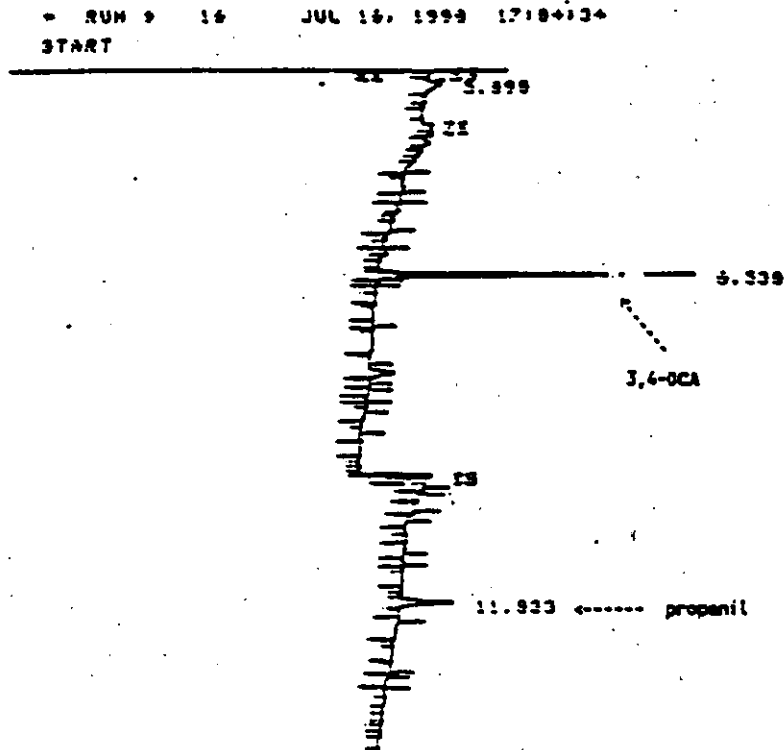
FIGURE 3

Typical Chromatogram

Free 3,4-Dichloroaniline and Propanil Analysis
in Louisiana Soil

GC Standard

0.05 ug/ml Propanil and DCA



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0.10 ng injected
GC run # 30310, dated 7/16/90

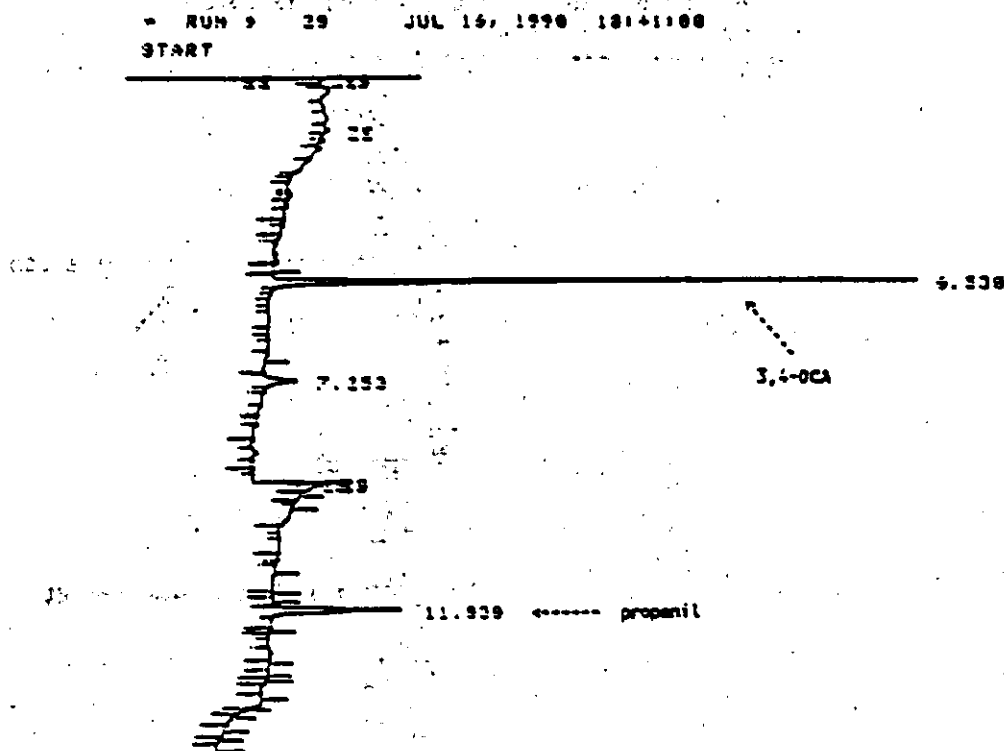
FIGURE 4

Typical Chromatogram

Free 3,4-Dichloroaniline and Propanil Analysis
in Louisiana Soil

GC Standard

0.10 ug/ml Propanil and DCA



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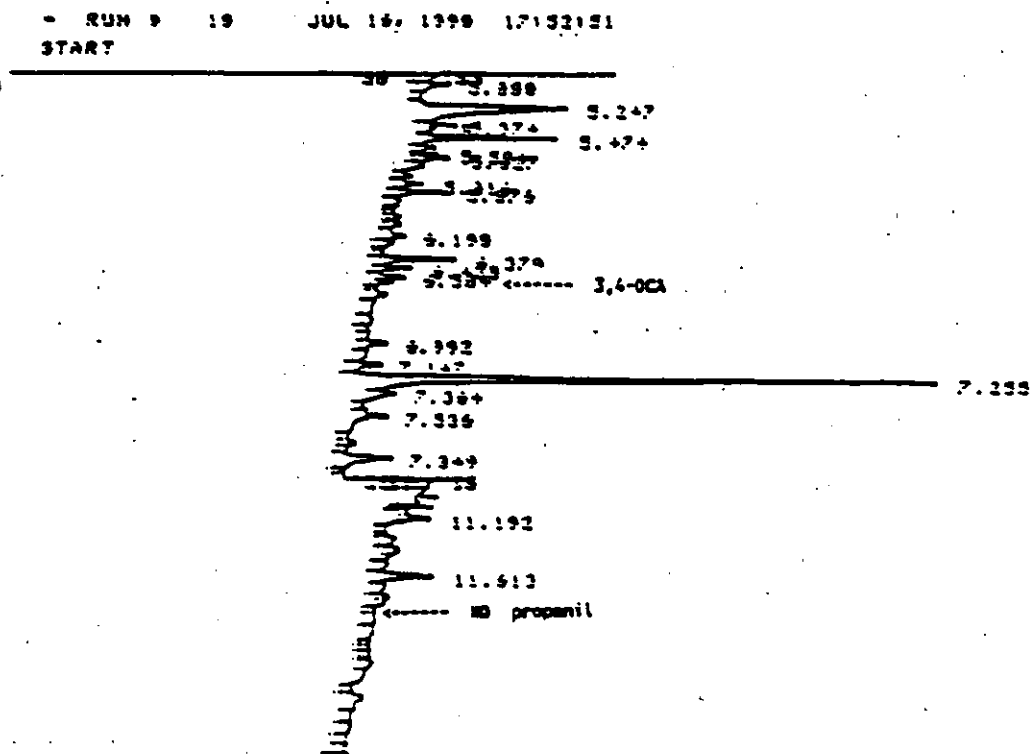
0.20 ng injected
GC run # 30310, dated 7/16/90

FIGURE 5

Typical Chromatogram

Free 3,4-Dichloroaniline and Propanil Analysis
in Louisiana Soil

Soil Control



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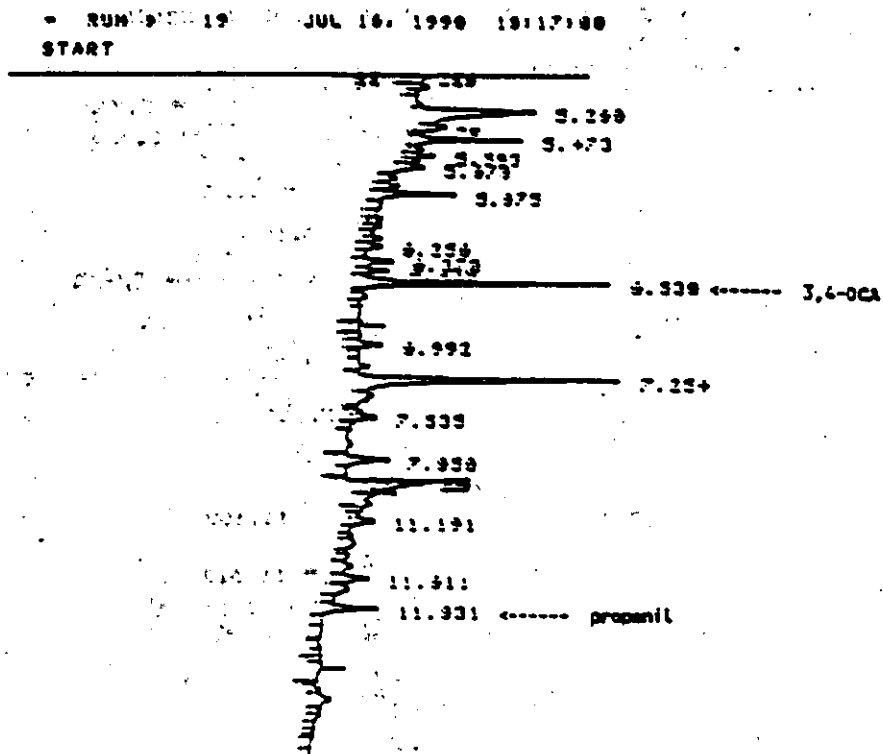
EN-CAS Sample ID #: MV4-C
Free 3,4-Dichloroaniline Found: <0.01 ppm
Free Propanil Found: <0.01 ppm
GC run # 30310, dated 7/16/90

FIGURE 6

Typical Chromatogram

Free 3,4-Dichloroaniline and Propanil Analysis
in Louisiana Soil

Soil Control + 0.01 ppm Propanil and DCA



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EN-CAS Sample ID #: MV4-S1
% Free, 3,4-Dichloroaniline Found: 70% Recovery
% Free Propanil Found: 90% Recovery
GC run # 30310, dated 7/16/90

FIGURE 7

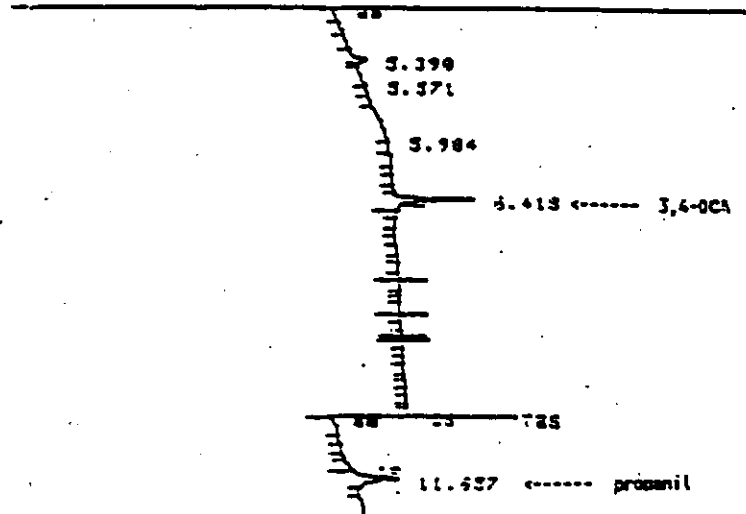
Typical Chromatogram

Free 3,4-Dichloroaniline and Propanil Analysis
in Arkansas Soil

GC Standard

0.025 ug/ml Propanil and DCA

RUN # 19 AUG 6, 1998 22:44:45
START



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0.05 ng injected
GC run # 30444, dated 8/06/90

FIGURE 8

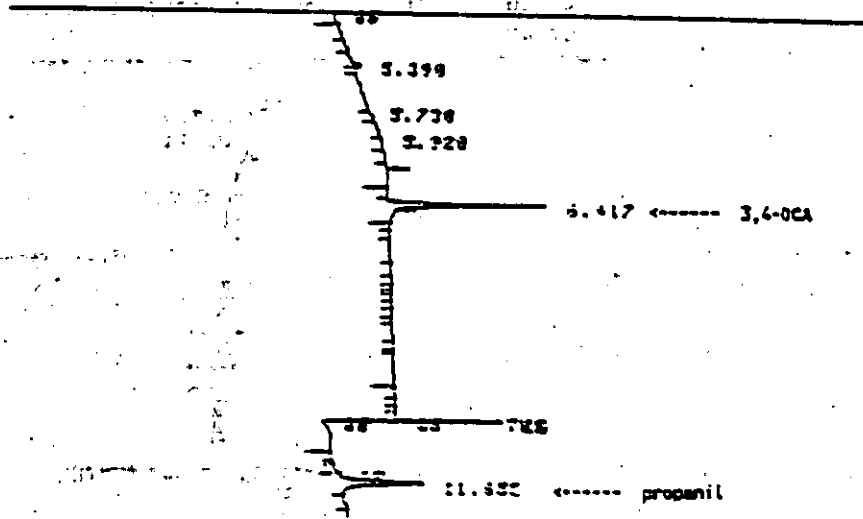
Typical Chromatogram

Free 3,4-Dichloroaniline and Propanil Analysis
in Arkansas Soil

GC Standard

0.05 ug/ml Propanil and DCA

RUN # 18 AUG 6. 1990 22:19:40
START



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0.10 ng injected

GC run # 30444; dated 8/06/90

FIGURE 9

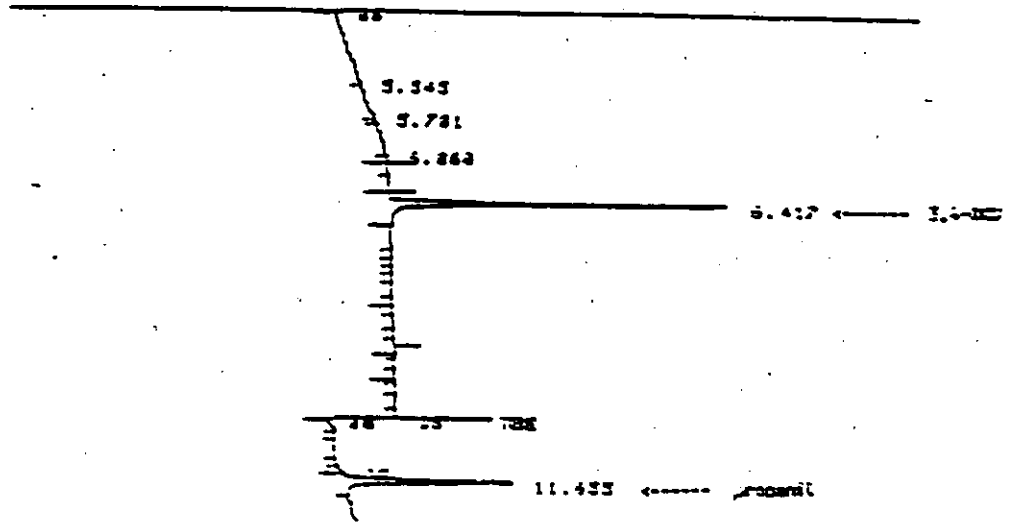
Typical Chromatogram

Free 3,4-Dichloroaniline and Propanil Analysis
in Arkansas Soil

GC Standard

0.10 ug/ml Propanil and DCA

RUN # 22 AUG 7, 1990 08:00:07
START



0.10

0.20 ng injected
GC run # 30444, dated 8/07/90

EN-CAS Method No. ENC 4/90

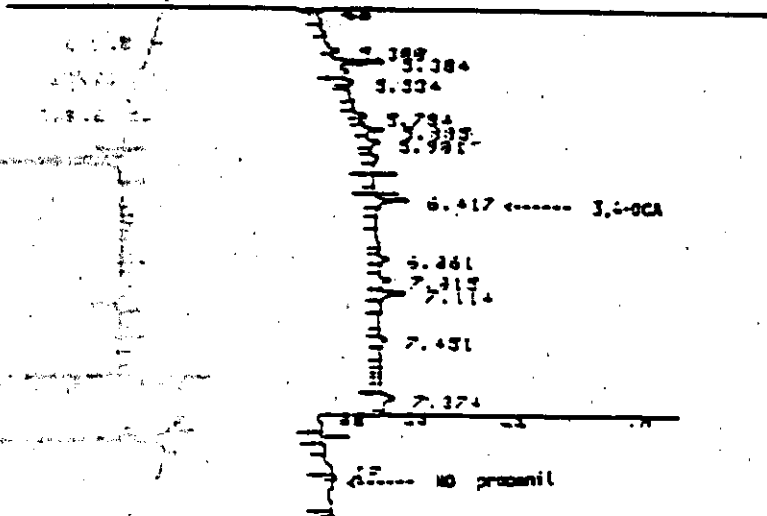
FIGURE 10

Typical Chromatogram

Free 3,4-Dichloroaniline and Propanil Analysis
(in Arkansas Soil)

Soil Control

RUN # 29 AUG 6, 1990 23:09:32
START



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EN-CAS Sample ID #: MV13-C
Free 3,4-Dichloroaniline Found: <0.01 ppm
Free Propanil Found: <0.01 ppm
GC run # 10444, dated 8/06/90

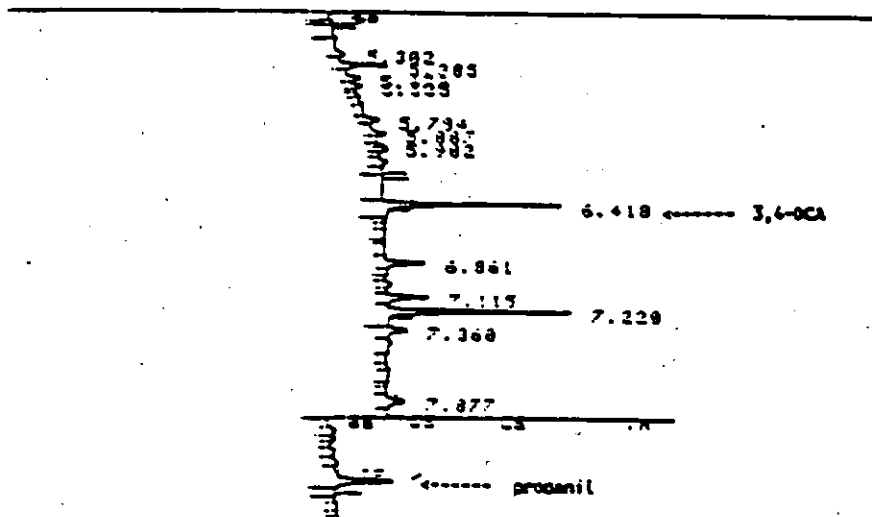
FIGURE 11

Typical Chromatogram

Free 3,4-Dichloroaniline and Propanil Analysis
in Arkansas Soil

Soil Control + 0.01 ppm Propanil and DCA

RUN # 29 AUG 7. 1990 02:55:57
START



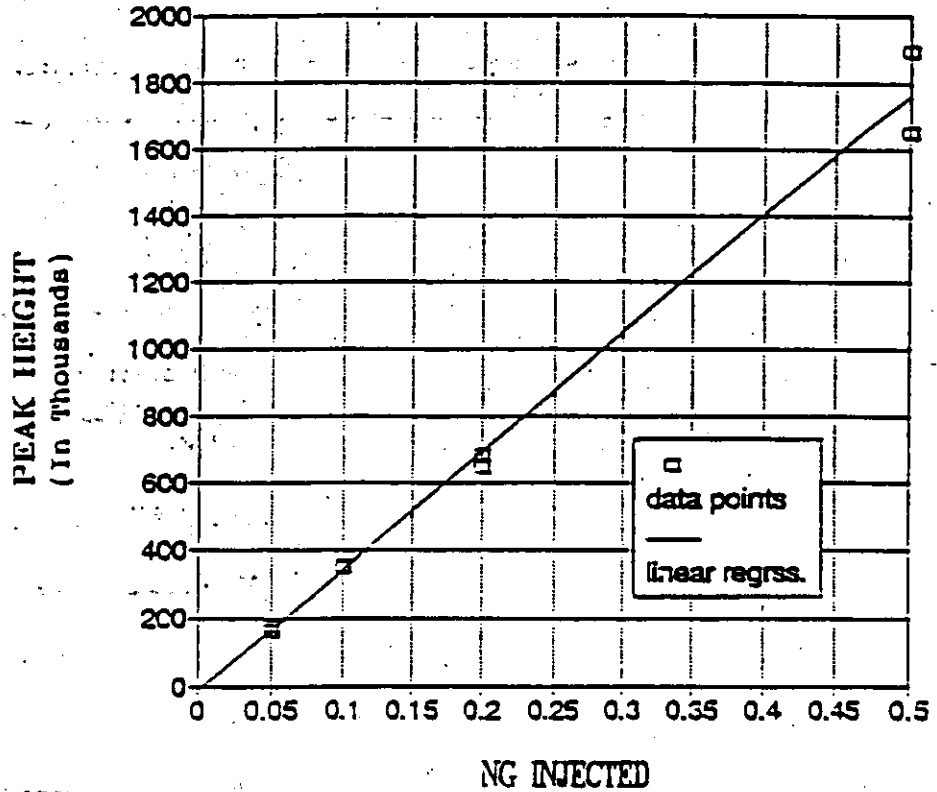
BEST AVAILABLE COPY

EN-CAS Sample ID #: MV13-S6
% Free 3,4-Dichloroaniline Found: 75% Recovery
% Free Propanil Found: 70% Recovery
GC run # 3044, dated 8/07/90

Figure 12

Typical Standard Curve

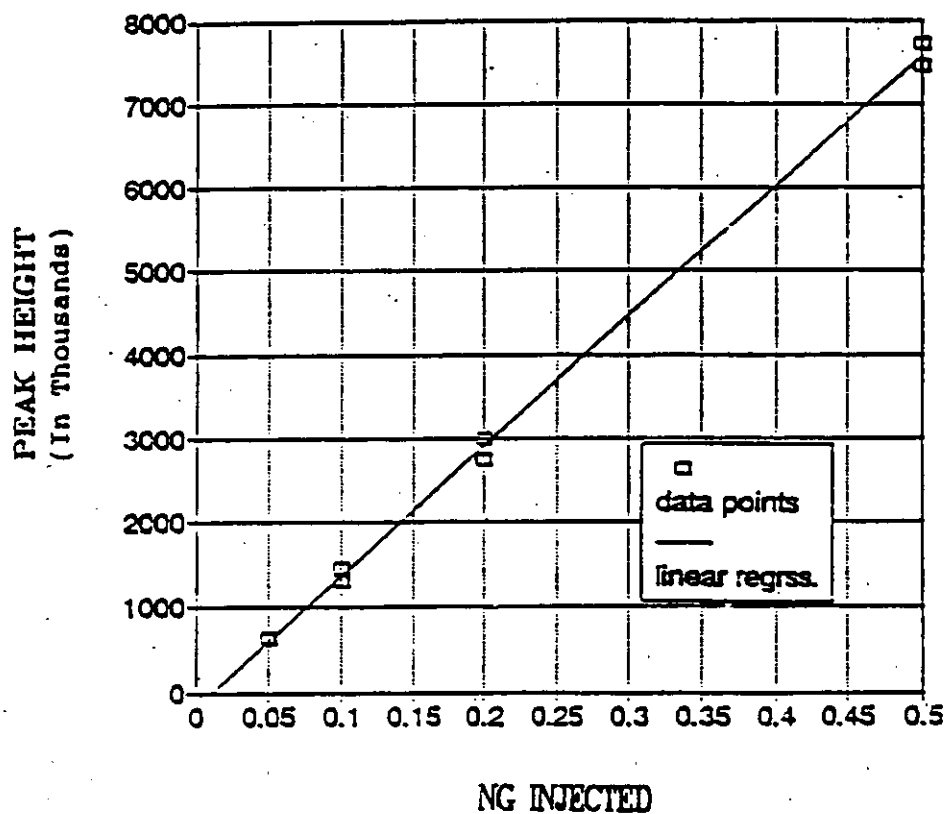
Propanil in Soil



GC Run # 30444
dated 8/07/90

Figure 13

Typical Standard Curve
3,4-Dichloroaniline in Soil



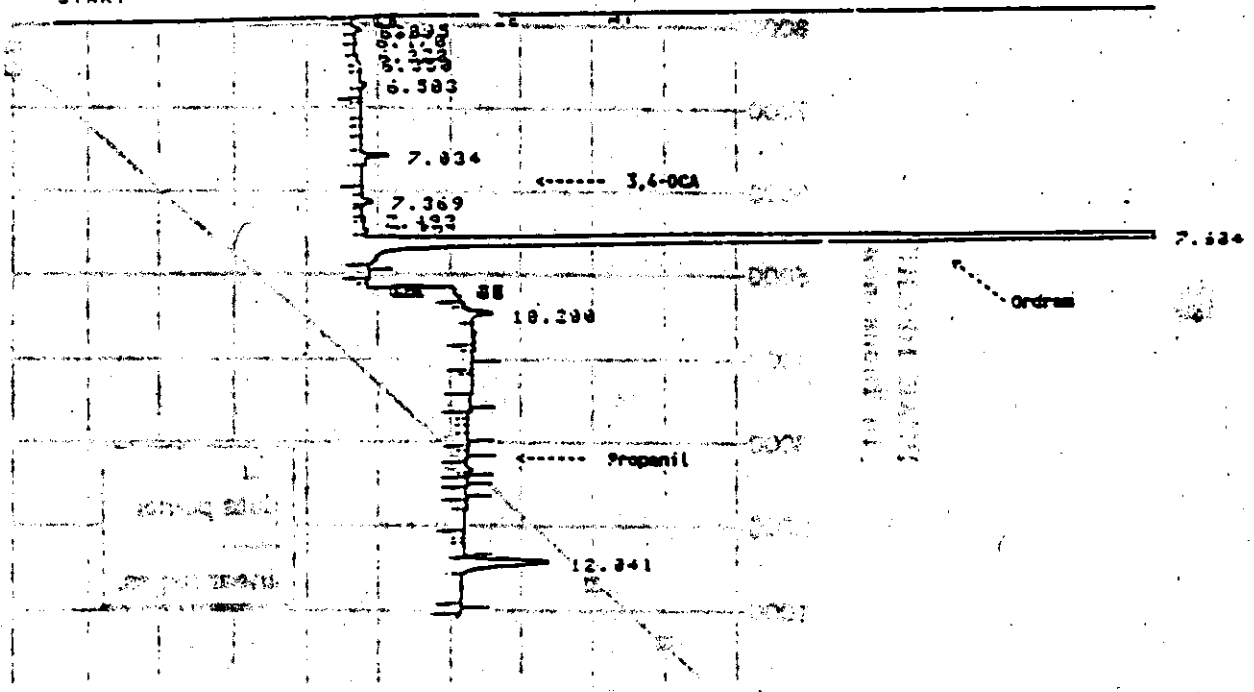
GC Run # 30444
dated 8/07/90

FIGURE 14

Typical Chromatogram

0.25 ug/ml Ordram Standard

RUN # 26 OCT 17, 1990 11:56:12
START



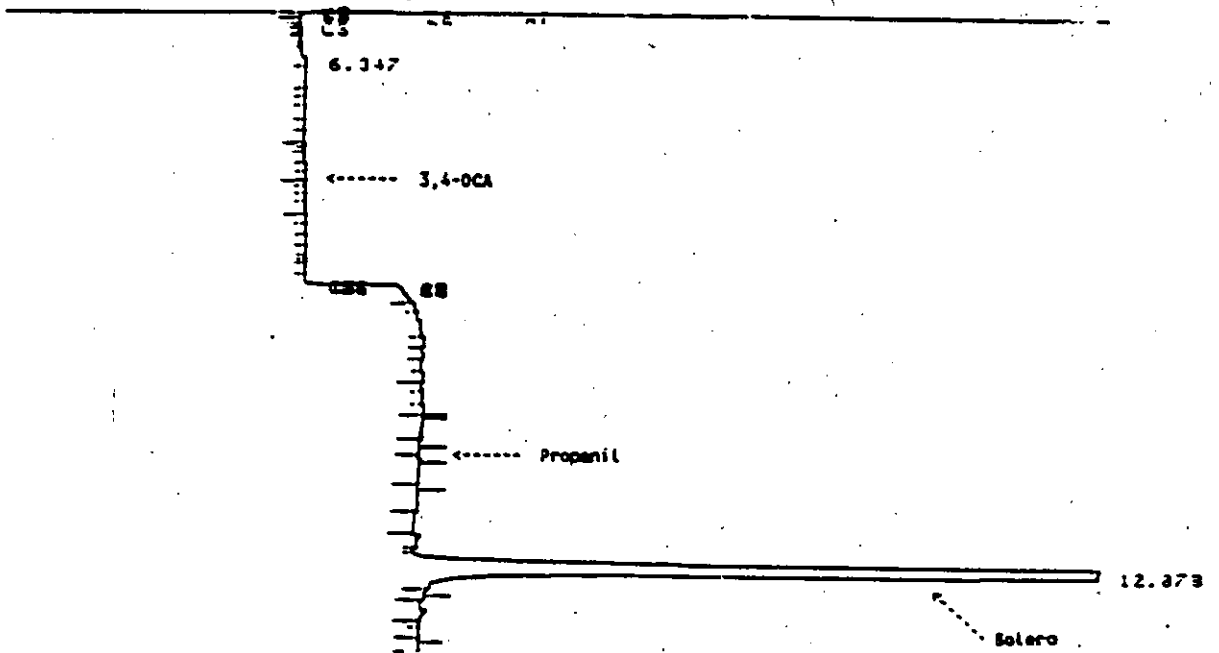
SECRET

0.50 ng injected
dated 10/17/90

FIGURE 15

Typical Chromatogram
0.25 ug/ml Bolero Standard

RUN # 23 OCT 17. 1998 11:28:31
START



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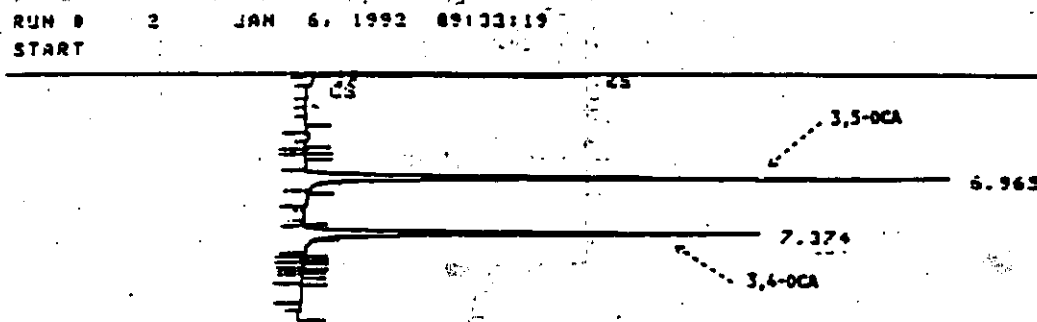
0.50 ng injected
dated 10/17/90

65

FIGURE 16

Typical Chromatogram

0.125 ug/ml 3,4-DCA and 3,5-DCA Combined Standard



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0.25 ng injected
dated 12/31/91