

1.0 INTRODUCTION

1.1 SCOPE

This method is used to determine the residues of Dichlorprop-P; Dichlorprop-P 2-Ethylhexyl Ester and its metabolites 2,4-Dichlorophenol; and 2,4-Dichloroanisole. The soil is extracted with a combination of acetic acid, methanol and water, as well as a basic buffer solution. The compounds of interest are extracted from the resulting aqueous solution by passing through a C_{18} SPE column. The metabolites of Dichlorprop-P, as well as Dichlorprop-P 2-Ethylhexyl Ester, are extracted from the column with an acetone/hexane mixture. The Dichlorprop-P residue is extracted from the column with a methanol/acetone mixture and is then methylated with BF_3 /methanol. The two C_{18} elutions are combined and quantitated using a Gas Chromatography/Mass Spectrometry.

The basic methodology for determining residues of similar phenoxy acid compounds and their metabolites in soil was supplied by the 2,4-DP (1988) Task Force and modified by ADPEN Laboratories, Inc.

1.2 PRINCIPLE OF THE METHOD

The soil is extracted with 20 mL of 5% acetic acid in methanol followed by 20 mL of 5% acetic acid in 1:1 methanol:water followed by 20 mL of a basic buffer solution, 10% acetone in 0.5 M KCl/0.10 M NaOH [buffer solution prepared by bringing 37.3 g KCl, 4.8 mL NaOH (50/50), and 100 mL of acetone to one liter with deionized water. The pH will be 12-14.]. The extraction solvents are combined, diluted with 430 mL of water and the pH reduced to less than 2 with the addition of 2.5 mL of phosphoric acid. The dilute aqueous solution is then passed through a pre-conditioned C_{18} solid phase extraction column. The column is dried with vacuum and 2,4-DCA; 2,4-DCP; and 2-EHE are eluted with 9 mL of 2% acetone in hexane. The 2,4-DP-P is then eluted with 9 mL of 50% methanol in acetone. The methanol solution is concentrated to 1 mL after the addition of 1 mL of hexane. The 2,4-DP-P is methylated at 70°C for 30 minutes with the addition of 1 mL of a 14% BF_3 in methanol solution. The methylated 2,4-DP-P is diluted with 8 mL of distilled water and then partitioned into 5 mL of hexane. The methylated 2,4-DP-P in hexane is combined with the metabolites in the 2% acetone in hexane elution of the C_{18} column. The combined sample is concentrated to 1 mL prior to injection on the Gas Chromatography/Mass Spectrometry. A flow chart of the procedure is shown in Figure 1.

3.0 EQUIPMENT

Names of equipment manufacturers and brands are suggested. These may be substituted and equivalent equipment may be used.

- 3.1 Bath, Branson Ultrasonic, Model 2200
- 3.2 Bath, Buchi Water, Model B-461
- 3.3 Bottles, 500 mL, Boston round
- 3.4 Centrifuge, (SpeedVac model ESC 2000, Savant, can be used as centrifuge)
- 3.5 Concentration tube, 15-mL, standard tapered joints, Corning or equivalent
- 3.6 General laboratory glassware
- 3.7 Mechanical shaker, Eberbach
- 3.8 N-Evap (Nitrogen Evaporator): Organomation Assoc.
- 3.9 Solid Phase Extraction (SPE) column, 1000 mg, Octadecyl (C₁₈), J.T. Baker
- 3.10 Solid Phase Extraction, vacuum manifold
- 3.11 Syringe, Gastight, 1 mL, Hamilton
- 3.12 Tubing, Teflon, 1/8"
- 3.13 Volumetric flasks, miscellaneous sizes
- 3.14 Volumetric pipettes, type A, various sizes
- 3.15 Vortex Mixer, Lab-Line Instruments

4.0 SAFETY

All analysts must be familiar with the potential hazards of each of the reagents, solvents, and products used in this method before any laboratory work is done. Material Safety Data Sheets (MSDS), Laboratory Safety Manual, product information, and other related materials should be consulted. Exposure to all chemicals should be reduced to the lowest possible level. Analysts should also be aware of OSHA regulations regarding the safe handling of the chemicals specified in this method. Disposal of all chemicals must be in compliance with local, state, and federal laws and regulations.

- 4.1 Acetone, acetonitrile, methanol, and hexane are flammable. Care should be taken to use these solvents in well ventilated areas away from ignition sources.
- 4.2 All open flask evaporations with an N-Evap should be done inside a hood.

5.0 REAGENTS

Names of chemical manufacturers and brands are suggested. These may be substituted and equivalent reagents may be used.

- 5.1 Acetic acid, Glacial, Mallinckrodt, AR Select grade
- 5.2 Acetone, Burdick & Jackson, pesticide residue grade
- 5.3 Acetonitrile, Burdick & Jackson, pesticide residue grade
- 5.4 BF₃/Methanol, 14% w/w, Pierce
- 5.5 Hexane, Burdick & Jackson, pesticide residue grade
- 5.6 Methanol, Burdick & Jackson, pesticide residue grade
- 5.7 pH Indicator strips, Baxter Scientific Products
- 5.8 Phosphoric acid, 85%, Mallinckrodt, AR Grade
- 5.9 Water, deionized, house
- 5.10 NaOH (50/50, w/w)
- 5.11 KCl

6.0 INSTRUMENTATION

Names of instrument manufacturers are suggested, equivalent brands may be substituted.

- 6.1 Gas Chromatograph-Mass Spectrometer, Hewlett Packard 5890 Series II, Hewlett Packard Series II Plus or equivalent equipped with a Hewlett Packard 5971 or 5972 Mass Selective Detector operated according to conditions outlined in Table IIa and IIb.
- 6.2 Gas Chromatography Capillary Column, HP-5 MS, 30-meter column, 0.25 μ m film thickness, 0.25 mm ID, or DB[®]-1, 15-meter column, 0.25 μ m film thickness, 0.25 mm ID. J & W.
- 6.3 Inlet liner, 4mm ID., deactivated, tapered on one end, 5181-3316, Hewlett-Packard.

7.0 PREPARATION OF STANDARD SOLUTIONS

Analytical standards of 2,4-DP-P; 2,4-DCP; 2,4-DCA; 2,4-DP-P 2-EHE; and Methyl 2,4-DP-P shall be kept at room temperature. All solutions of standards shall be kept in amber bottles and stored in a refrigerator. The details given for making dilutions are suggested. Concentrations and method of dilution may be modified if needed. A complete description of the test and reference substances may be found in Table I.

7.1 STOCK SOLUTIONS

Prepare a 1000 ng/ μ L stock solution of each standard by accurately weighing 0.100 g of standard into a 100 mL volumetric flask. Dissolve in acetonitrile and dilute to the mark.

7.2 STANDARD FORTIFICATION SOLUTIONS

Prepare 10.0 ng/ μ L, 1.0 ng/ μ L, and 0.1 ng/ μ L mixed stock solutions of 2,4-DCP; 2,4-DCA; 2,4-DP-P; and 2-EHE from the 1.0 ng/ μ L stock solutions and dilute in acetonitrile. These solutions are used for fortification and shall be prepared fresh every six months.

7.3 STANDARD SOLUTIONS FOR GAS CHROMATOGRAPHY / MASS SPECTROMETRY

Calibration standards containing 2,4-DCP; 2,4-DCA; Methyl 2,4-DP-P; and 2-EHE were prepared by diluting the 1000 ng/ μ L stock solutions with acetone for the intermediate standard. The final calibration standards were then prepared by serial dilutions of the intermediate standard with hexane.

8.0 SAMPLE WORK-UP

8.1. RECOVERY TEST

The validity of the procedure should be demonstrated by recovery tests before analysis of unknown samples is attempted. Untreated (control) and fortified samples shall also be processed with each set of samples analyzed. Typically, one of the fortification samples is run at the limit of quantitation. For each fortified sample, an appropriate quantity of 2,4-DCP; 2,4-DCA; 2,4-DP-P; and 2-EHE mixed standard solution is added to a control sample. Fortifications are made onto the sample prior to the start of the analytical procedure.

8.2 PREPARATION FOR EXTRACTION

8.2.1 Each lot of SPE columns should be profiled to determine if the lot being used will provide adequate recovery of each compound of interest. Elution parameters may be modified if needed.

8.2.2 Keep all samples frozen until ready for analysis.

8.2.3 Weigh 10.0g of soil into a 50 mL screw cap polypropylene centrifuge tube.

8.3 EXTRACTION OF RESIDUE

- 8.3.1 Add 20 mL of 5% acetic acid in methanol to each sample.
- 8.3.2 Cap the tube and vortex to mix at the highest speed for approximately 30 seconds.
- 8.3.3 Suspend the tube in an ultrasonic water bath. The water in the bath should be at room temperature and level with the slurry in the sample tube. Use a mild soap solution with tap water to improve sonication. Keep soil in active area of sonication.
- 8.3.4 Sonicate the sample for 20 minutes. Cavitation of the sample should be evident.
- 8.3.5 After sonication centrifuge at approximately 2000 rpm for approximately 10 minutes.
- 8.3.6 Decant the supernatant into a 500 mL glass screw-cap bottle.
- 8.3.7 Repeat steps 8.3.2 - 8.3.6 using 20 mL 5% acetic acid in 1:1 methanol:water as the extraction solvent. Combine the supernatant with the supernatant from step 8.3.6.
- 8.3.8 Repeat steps 8.3.2 - 8.3.6 using 20 mL 10% acetone in 0.5 M KCl/0.1 M NaOH. Combine the supernatant with previous two supernatants.
- 8.3.9 Add ~430 mL of de-ionized water to the combined extracts.
- 8.3.10 Acidify the sample by adding 2.5 mL of phosphoric acid (~85%).
- 8.3.11 Cap the bottle with a Teflon lined screw cap and shake the bottle by hand for approximately 30 seconds. Ensure that the pH of the sample is less than 2 with pH indicator strips..

8.4 SPE COLUMN CLEAN-UP

- 8.4.1 Condition a 1 g, 6 mL, C₁₈ Solid Phase Extraction cartridge attached to a SPE manifold with 10 mL of methanol followed by 10 mL of 1.5% phosphoric acid in water. The flow rate should be maintained at approximately 1-2 mL/minute. Do not allow the cartridge to dry prior to loading the sample.
- 8.4.2 Using a Pasteur pipet, transfer a portion of each sample to the cartridge and then connect the SPE cartridge to the sample bottle using a SPE adapter.

- 8.4.3 Charge the diluted solutions onto the SPE cartridges at a flow rate of approximately 5 mL/min. using a vacuum manifold. The vacuum should be set at <10" Hg. All of the SPE eluate may be discarded at this point.
- 8.4.4 After the diluted extraction solution has completely passed through the SPE cartridge dry the excess water from the cartridge walls with a cotton swab and allow the cartridge to dry under a vacuum of >20" Hg for a minimum of 30 minutes.
- 8.4.5 Remove the cartridges from the SPE manifold and rinse the manifold port with acetone to remove water. Replace the SPE cartridges.
- 8.4.6 Elute the SPE cartridges with a flow rate of <2 ml/min Into 15 mL conical centrifuge tubes as follows:
- Fraction A: Elute the cartridge with 9 mL of 2% acetone in hexane.
- Fraction B: Elute the cartridge with 9 mL of 50% methanol in acetone.
- 8.4.7 Add 1.0 mL of hexane to Fraction B and concentrate to a final volume of 0.5 - 1.0 mL using a N-Evap with a room temperature water bath. The needle should be maintained at a height of 2 - 3 cm above the sample and the nitrogen flow set so that the surface of the sample is dimpled but bubbles are not formed.

8.5 DERIVATIZATION

- 8.5.1 Add 1.0 mL of 14% BF_3 /methanol solution to each sample (Fraction B only). Cap tightly with a Teflon lined screw cap and shake to mix.
- 8.5.2 Immerse the samples in a 70° C ± 2° C water bath for 30 minutes.
- 8.5.3 Allow the reaction mixture to cool to room temperature and add 8 mL of distilled water and 5 mL of hexane to the sample.
- 8.5.4 Shake the samples for 10 minutes at high speed using a mechanical shaker.
- 8.5.5 Allow the layers to separate and remove and discard the aqueous layer.
- 8.5.6 With a Pasteur pipet transfer the hexane layer of fraction B to the centrifuge tube containing fraction A. Then rinse fraction B centrifuge tube with 1 mL of hexane which is also combined with centrifuge tube containing fraction A.
- 8.5.7 Using a N-Evap with a room temperature water bath. The needle should be maintained at a height of 2 - 3 cm above the sample and the nitrogen flow set so that the surface of the sample is dimpled but bubbles are not formed. Concentrate the samples to a final volume of 1 mL.

8.5.8 Vortex the samples and dilute as necessary for analysis.

9.0 CHROMATOGRAPHY

- 9.1 The suggested chromatographic conditions are given in Tables IIa and IIb. The chromatography should be checked for response whenever a new injection port liner, column, or instrument is used. Approximately 5 cm. of the inlet end of the GC column should be cut off if the peak shape or sensitivity deteriorates. The GC column should be conditioned with several injections of sample extracts and standards prior to injecting samples to be quantitated. See Figures 4 and 5 for typical chromatograms.
- 9.2 Change the deactivated glass injection port liner if deterioration of peak shape or sensitivity occurs. The liner should contain a very small wad of silanized glass wool. Replace the septum daily or after approximately 100 injections have been made if Hewlett-Packard 5181-1263 low-bleed red septa or equivalent is used.
- 9.3 Inject 2- μ l aliquots of the standards and samples. A small injection size is suggested to protect the capillary column, a 1- μ l injection size may be used if necessary. Calibrate the detector response and retention times by injections of the standard solutions throughout a set of analyses. Standards shall also be injected at the beginning and at the end of a set of analyses.
- 9.4 Sample residues are determined as described in Section 13.1 through 13.4. Fortification recoveries are determined as described in Section 13.5.

10.0 TIME REQUIRED FOR ANALYSIS

Analysis of a set of 12 soil samples requires about 12 man hours. GC analysis may be done overnight by autosampler. Data entry, integration and reporting may take up to an additional 3 man hours.

11.0 INTERFERENCES

11.1 SAMPLE MATRICES

Baseline resolution was attained for each compound of interest when using the an HP-5 MS column. If interfering peaks from the matrix occur in the chromatogram, change the GC/MS operating conditions or use an alternate GC column such as a DB-1 15-meter, or a DB-1701 30-meter. Additional cleanup steps such as florisil chromatography were not evaluated but may be useful.

11.2 OTHER SOURCES

No interfering peaks from pesticides, solvents, or labware are known to occur.

12.0 CONFIRMATORY TECHNIQUES

No problems with interferences or questionable peak identity have been encountered to date. A GC column with different polarity, such as a HP-1701, 30-meter column, may be used for confirmation, if necessary.

13.0 METHODS OF CALCULATION

13.1 STANDARD CALIBRATION CURVE

At least four standard concentration levels shall be used for quantitation. Each standard should be injected at least twice in the analysis set. Standards are injected at the beginning, after every 1 to 3 samples and at the conclusion of the analysis. Peak height or peak area of each injected standard is determined by manual measurement or computer integration. Regression analysis of peak height or peak area versus nanograms injected may be performed by a scientific calculator or a computer chromatography data system. This regression analysis gives an equation for a standard curve for calculation of sample concentration. Nanograms injected can be calculated from the slope and intercept of the standard curve and the chromatographic peak height or area of each sample injection.

13.2 CALCULATION OF EQUIVALENT SAMPLE WEIGHT

The milligrams of sample injected must be determined to calculate ppm (Section 13.4). The equivalent sample weight in the final solution is calculated as follows:

$$\text{mg Inj.} = \frac{(W)(V_r) \times 1000}{(V_i)}$$

W = weight of sample extracted (g)
1000 = conversion factor (mg/g)
V_r = total volume of final injection soln. (μl)
V_i = injection volume (μl)

13.3 DETERMINATION OF SAMPLE RESIDUES (NANOGRAMS)

The peak height or area from a sample injection (Section 13.1) and the slope and intercept of the standard curve (Section 13.1) are used to determine the nanograms of residue in each sample injection. This can be done by a chromatography data system, calculator or by graphing a standard curve of nanograms injected versus detector response. The next section shows how to calculate sample residues in parts-per-million.

13.4 DETERMINATION OF SAMPLE RESIDUES (PPM)

Calculate the sample residue for each sample expressed in terms of parts-per-million (ppm) using the following equation:

$$\text{ppm of compound found} = \frac{(\text{ng of compound found})}{(\text{mg of sample injected})}$$

The procedure described in this report requires the methylation of both the unknown sample and the calibration standard. A conversion factor taking into account the molecular weight ratio between 2,4-DP-P and methylated 2,4-DP-P should be used if analytical grade methylated standard is used.

13.5 FORTIFICATION RECOVERIES

The ppm of compound found in the final solution (Section 13.4) is divided by the amount of compound added to the control sample. This ratio times 100 is the percent recovery of the method at that level of fortification.

$$\% \text{ Recovery} = \frac{\text{ppm analyte found in injected solution}}{\text{ppm analyte added to control sample}} \times (100)$$

If the control sample shows a chromatographic response corresponding to the analyte(s) of interest, the ppm value corresponding to this control sample response should be subtracted from the ppm residues found in the fortified samples before the percent recovery calculation is made, i.e.:

$$\text{ppm found in recovery} = \text{ppm in fortified sample} - \text{ppm in control sample}$$

An average recovery value between 70 and 120% for each set of analysis should be acceptable for the 2,4-DCP; 2,4-DCA; and 2-EHE metabolites. An average recovery value between 60 and 120% should be acceptable for the 2,4-DP-P compound.

TABLE I. Description of Test and Reference Substances ^{a/}Test and Reference Substances:

1.	Common Name:	Dichlorprop-P (2,4-DP-P)
2.	Chemical Name:	(+)-(R)-2-(2,4-dichlorophenoxy)propionic acid
3.	Experimental Name:	BAS 044 H
4.	CAS Number:	15165-67-0
5.	Lot number:	CH39/171-1; 39-171-2
6.	Purity:	99.7%; 99.6%
7.	Date Received at ADPEN:	7/17/93; 6/2/94
8.	Storage Conditions at ADPEN:	Room temperature, in the dark
9.	ADPEN Code Number:	P-309, P-355
10.	Expiration or Reassay Date: a/	7/95, 3/97
11.	Empirical formula:	C ₉ H ₈ Cl ₂ O ₃
12.	Molecular weight:	235.07
1.	Common Name:	2,4- DCA
2.	Chemical Name:	2,4-dichloroanisole
3.	Experimental Name:	—
4.	CAS Number:	—
5.	Lot number:	37-46; 37-46
6.	Purity:	99.0%; 99.0%
7.	Date Received at ADPEN:	6/17/93, 5/10/94
8.	Storage Conditions at ADPEN:	Room temperature, in the dark
9.	ADPEN Code Number:	P-305; P-346
10.	Expiration or Reassay Date: a/	3/95, 9/30/94
11.	Empirical formula:	C ₇ H ₆ Cl ₂ O ₁
12.	Molecular weight:	177.03
1.	Common Name:	Dichlorprop-P Methyl Ester
2.	Chemical Name:	(+)-(R)-2-(2,4-dichlorophenoxy)propionic acid methyl ester
3.	Experimental Name:	—
4.	CAS Number:	—
5.	Lot number:	B212-38B
6.	Purity:	>99%
7.	Date Received at ADPEN:	12/21/93; 5/10/94
8.	Storage Conditions at ADPEN:	Room temperature, in the dark
9.	ADPEN Code Number:	P-323; P-347
10.	Expiration or Reassay Date: a/	12/95; 12/95
11.	Empirical formula:	C ₁₀ H ₁₀ Cl ₂ O ₃
12.	Molecular weight:	249.10

TABLE I. Description of Test and Reference Substances^{a/}
(continued)

1. Common Name:	2,4-DCP
2. Chemical Name:	2,4-dichlorophenol
3. CAS Number:	—
4. Lot number:	OCR-696-132-1; OCR-696-132-1
5. Purity:	99.9% ; 99.6%
6. Date Received at ADPEN:	6/17/93 ; 5/10/94
7. Storage Conditions at ADPEN:	Room temperature, in the dark
8. ADPEN Code Number:	P-306; P-348
9. Expiration or Reassay Date: a/	6/95; 8/95
10. Empirical formula:	C ₆ H ₄ Cl ₂ O
11. Molecular weight	163.00
1. Common Name:	Dichlorprop-P Methyl Ester (Methylated 2,4-DP-P)
2. Chemical Name:	(+)-(R)-2-(2,4-dichlorophenoxy) propionic acid methyl ester
3. CAS Number:	—
4. Lot number:	Not assigned, made daily
5. Purity:	Not assigned, made daily
6. Date Received at ADPEN:	Made from the Dichlorprop-P standard
7. Storage Conditions at ADPEN:	Stored with sample set
8. ADPEN Code Number:	Not assigned, made daily
9. Expiration or Reassay Date:	Not assigned, made daily
10. Empirical formula:	C ₁₀ H ₁₀ Cl ₂ O ₃
11. Molecular weight	249.10
1. Common Name:	2,4-DP-P, 2-EHE
2. Chemical Name:	(+)-(R)-2-(2,4-dichlorophenoxy) propionic acid 2-ethylhexyl ester
3. CAS Number:	—
4. Lot number:	DG/16/13
5. Purity:	96.8
6. Date Received at ADPEN:	9/13/93; 8/30/93
7. Storage Conditions at ADPEN:	Room temperature, in the dark
8. ADPEN Code Number:	P-315; P-314
9. Expiration or Reassay Date:	9/95, 8/95
10. Empirical formula:	C ₁₇ H ₂₄ Cl ₂ O ₃
11. Molecular weight	347.28

a/ The purity of these materials has been determined under GLP's by members of the 2,4-DP Task Force. The 2,4-DP Task Force has archived an aliquot of these standards and has access to documentation relating to the synthesis and characterization of these compounds, including expiration dates / reassay dates.

Table IIa. Suggested Gas Chromatography / Mass Spectrometry Conditions

Gas Chromatograph/Mass Spectrometer: HP 5890 Series II with 5971 Mass Selective Detector

Initial Oven Temperature: 45° C
 Initial Hold Time: 0.5 min.
 Linear Velocity: 31.9 cm/sec.

Temperature Program:

	<u>Rate:</u>	<u>Final Temp.:</u>	<u>Final Time:</u>
Ramp 1	45° C/min.	212° C	1:0 min.
Ramp 2	15° C/min.	250° C	2.0 min.
Ramp 3	45° C/min.	280° C	0.75 min.

Injector Temperature: 245° C
 Injection Type: Splitless
 Injection Volume: 2 µl
 Purge Valve: On Time: 0.5 min.
 Off Time: 9.0 min.

Acquisition Parameters

Solvent Delay: 2.5 min.
 EM Voltage: 2305.9

SIM Parameters:

Compound	Retention Time min.	Dwell Time msec.	Target Ion m/z	Qualifier Ion m/z	Ion Ratio %
2,4-DCP	4.13	40	162	164	67
2,4- DCA	4.61	40	161	176	60
Methyl 2,4-DP-P	6.00	40	162	164, 191, 248	69
2-EHE	9.13	40	162	189, 234, 346	71

GC Column: HP-5 MS, 30 meters, 0.25 µm film thickness, 0.25 mm ID.

Carrier Gas: Helium, at 5 psi column back pressure

Septum Purge: Helium, at 1.9 mL/min

Total Flow at Split Vent: Helium, at 24 mL/min

No needle residence time is specified. A fast injection type autosampler was used for the method validation. These are suggested conditions and may be modified to produce better chromatographic quantitation.

Table IIb. Suggested Gas Chromatography / Mass Spectrometry Conditions

Gas Chromatograph/Mass Spectrometer: HP 5890 Series II Plus with 5972 Mass Selective Detector

Initial Oven Temperature: 50° C
 Initial Hold Time: 0.5 min.
 Linear Velocity: 36.4 cm/sec.

Temperature Program:

Ramp 1	<u>Rate:</u> 45° C/min.	<u>Final Temp.:</u> 240° C 250	<u>Final Time:</u> 5.28 min.
Injector Temperature:	245° C		
Injection Type:	Splitless		
Injection Volume:	2 µL		
Purge Valve:		<u>On Time</u>	<u>Off Time</u>
	A	1.00 min	0.00 min
	B	1.25 min	10.50 min

Acquisition Parameters:

Solvent Delay: 2.5 min.
 EM Voltage: 2247

SIM Parameters:

Compound	Retention Time min.	Dwell Time msec.	Target Ion m/z	Qualifier Ion m/z	Ion Ratio%
2,4-DCP	3.96	40	162	164	65
2,4-DCA	4.41	40	161	176	104
Methyl 2,4-DP-P	5.74	40	162	164	65
2-EHE	8.27	40	162	189	67

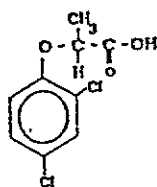
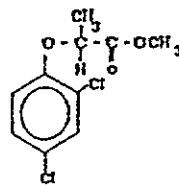
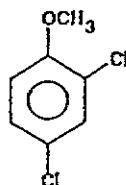
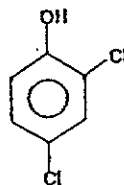
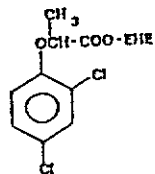
GC Column: HP-5 MS, 30 meters, 0.25 µm film thickness, 0.25 mm ID.

Carrier Gas: Helium, pressure programmed:
 Initial: 5.0 psi
 4.00 Min.: 12.0 psi
 5.00 Min.: 15.0 psi
 Rate: 99 psi/min.

Septum Purge: Helium, at 3.17 mL/min
 Total Flow at Split Vent: Helium, at 44.8 mL/min

No needle residence time is specified. A fast injection type autosampler was used for the method validation. It has been observed that large amounts of glass wool in the insert produces poor detection for 2,4-DCP. These are suggested conditions and may be modified to produce better chromatographic quantitation. Carrier gas programmed pressure is recommended if available, otherwise use 5.0 psi.

Figure 2. Structures of the Test Substance and the Final Analytes

2,4-DP-P
(Dichloroprop-P)Methylated 2,4-DP-P
(2,4-DP-P Methyl Ester)2,4-DCA
(2,4-Dichloroanisole)2,4-DCP
(2,4-Dichlorophenol)2,4-DP-P 2-EHE
(2,4-DP-P 2-Ethylhexyl Ester)