

METHOD OF ANALYSIS

The analytical method used for the analysis of the soil samples in this Independent Lab Validation (ILV) was the BASF (1988) Task Force method from Adpen Labs #TSKF9301 entitled "Analytical Method for the Determination of Dichlorprop-P (2,4-DP-p); 2,4-Dichlorophenol (2,4-DCP); 2,4-Dichloroanisole (2,4-DCA); and 2,4-DP-p 2-EHE (2-EHE) in Soil". (attached copy in Appendix 5).

Briefly, the method involves extracting 2,4-DP-p 2-ethylhexyl ester, 2,4-DP-p acid, 2,4-DCP and 2,4-DCA from 10 g samples of soil using 5% acetic acid in methanol, 5% acetic acid in 1:1 (v/v) methanol/water and 10% acetone in a basic buffer solution.

METHOD OF ANALYSIS cont'd

The combined extracts are diluted with water, acidified and eluted through a C₁₈ SPE cartridge. The column is dried and the analytes are eluted in 2 fractions. One fraction contains 2,4-DP-p 2-EHE, 2,4-DCP and 2,4-DCA and the second fraction contains 2,4-DP-p acid. The fraction containing 2,4-DP-p acid is methylated with BF₃/MeOH prior to combining the 2 fractions. The combined fractions are concentrated to 1 mL and analyzed by GC/MS.

TABLE 2: DATES OF EXTRACTION AND ANALYSIS (analytical dates of the various successful trials)						
Site	Trial 1		Trial 2		Trial 3	
	Extraction	Analysis	Extraction	Analysis	Extraction	Analysis
New York GR9445	Set 1 1/5/96 Set 2 1/8/96	Set 1 1/22/96 Set 2 1/23/96	--	--	--	--
Washington GR9451	--	--	Set 1 5/6/96 Set 2 5/6/96	Set 1 5/12/96 Set 2 5/26/96	--	--
Georgia GR9481	--	--	Set 1 5/1/96 Set 2 5/1/96	Set 1 5/24/96 Set 2 5/24/96	--	--
California GR9442	Set 1 1/3/96 Set 2 1/4/96	Set 1 1/19/96 Set 2 1/21-22/96	--	--	--	--
Indiana GR9452	--	--	--	--	Set 1 5/7/96 Set 2 5/7/96	Set 1 5/13/96 Set 2 5/14/96

MODIFICATIONS TO METHOD TSKF9301

Two minor modifications were made to method TSKF9301. These modifications did not significantly alter the method.

1. The deactivated glass injection port liner did not contain a small wad of silanized glass wool as specified in the method.

MODIFICATIONS TO METHOD TSKF9301 cont'd

2. A pre-column (1 m of deactivated fused silica) was installed using a "glass seal connector" to the front of the analytical capillary column. This was used to keep the analytical column clean.

These changes were made after discussion with Adpen Labs. (See Appendix 3)

ANALYTICAL STANDARDS**Reference substances:**

Common Name: Dichlorprop-P (2,4-DP-p)
Chemical Name: (+)-(R)-2-(2,4-dichlorophenoxy) propionic acid
Lot No.: 39-171-2
Purity: 99.6%
Supplier: BASF Corporation
Date Received at ETL: November 20, 1995
Storage Cond.: Freezer -20°C
Expir./Reanalysis Date: March 1997

Common Name: 2,4-DCP
Chemical Name: 2,4-dichlorophenol
Lot No.: 01313-075
Purity: 99.0%
Supplier: BASF (Aldrich)
Date Received at ETL: November 20, 1995
Storage Cond.: Freezer -20°C
Expir./Reanalysis Date: Not assigned

Common Name: 2,4-DCA
Chemical Name: 2,4-dichloroanisole
Lot No.: 129-149A, 37-46
Purity: 98%, 99.5%
Supplier: Chem Service, DowElanco
Date Received: November 10, 1995, December 5, 1995
Storage Cond.: Freezer -20°C
Expir./Reanalysis Date: July 2000, October 4, 1997

ANALYTICAL STANDARDS cont'd

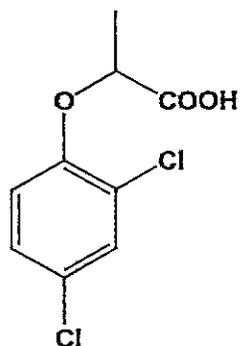
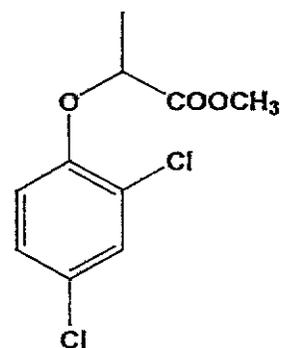
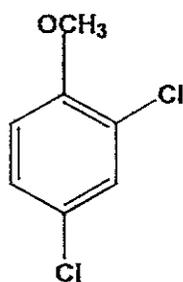
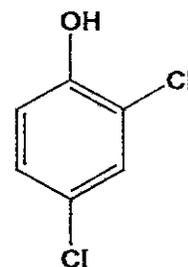
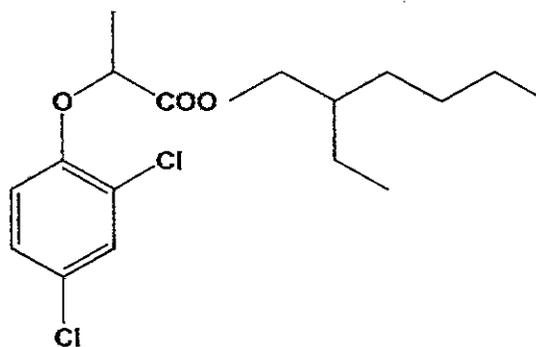
Reference substances: cont'd

Common Name: 2,4-DP-p 2-EHE (2-EHE)
Chemical Name: (+)-(R)-2-(2,4-dichlorophenoxy) propionic acid 2-ethylhexyl ester
Lot No.: 00937-18
Purity: 98.3%
Supplier: BASF Corporation
Date Received: November 20, 1995
Storage Cond.: Freezer -20°C
Expir./Reanalysis Date: March 1999

Common Name: 2,4-DP-p, methyl ester
Chemical Name: (+)-(R)-2-(2,4-dichlorophenoxy) propionic acid methyl ester
Lot No.: B212-38B
Purity: >99%
Supplier: ---
Date Received: November 10, 1995
Storage Cond.: Freezer -20°C
Expir./Reanalysis Date: December 5, 1995

Common Name: 2,4-DP-p methyl ester
Chemical Name: (+)-(R)-2-(2,4-dichlorophenoxy) propionic acid methyl ester
ETL I.D.: A3979
Purity: Compared by GC/MS to above standard.
(within 5% of above standard)
Date Received: 2,4-DP-p acid received November 20, 1995.
(ME esters prepared throughout study; prepared Nov.30,
1995)
Storage Cond.: Freezer -20°C
Expir./Reanalysis Date: November, 1996

STRUCTURES OF THE TEST SUBSTANCES

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)

CONTROL SOIL SAMPLES

Control soil samples (0-12" depth) were processed at Grayson Research, Creedmoor, NC, using a Homolaid Fitz Mill and shipped to Enviro-Test Labs with dry ice on October 12, 1995. The fortification was done by spiking soil with 0.5-1.0 mL of acetonitrile standard solutions directly onto the soil. The soil was mixed and extracted with 15 minutes.

The soils came from the 5 soil sites [Georgia (GR9481), Indiana (GR9452), New York (GR9445), California (GR9442) and Washington (GR9451)] where the 2,4-DP-p Terrestrial Field Dissipation studies were conducted.

The soil types were as follows:

NY (GR9445); 0-12" classified as loam.

WA (GR9451); 0-12" classified as sand.

GA (GR9481); 0-12" classified as loamy sand.

CA (GR9442); 0-12" classified as sandy loam/loamy sand.

IN (GR9452); 0-12" classified as loam/clay loam.

REAGENTS

The following reagents were used in this ILV and are the same or equivalent to those listed in the method TSKF9301.

Acetic acid - BDH, Analar®
Acetone - EM Science, OmniSolv®
Acetonitrile - EM Science, OmniSolv®
BF₃/methanol, 14% w/w - Sigma
Hexane - EM Science, OmniSolv®
Methanol - EM Science, OmniSolv®
pH indicator strips - Macherey-Nagel
Phosphoric acid, 85% - BDH, Assured®
Water, deionized, in-house
NaOH (50/50, w/w) - Fisher Scientific, Certified A.C.S.
Potassium chloride - BDH, Assured®

EQUIPMENT

The following equipment was used in this ILV and are equivalent to those listed in the method TSKF9301.

Ultrasonic water bath - Fisher Scientific, Model FS-28
Erlenmeyer flasks - Kimax
Centrifuge - Sorvall®, model RC2-B
Culture tubes, 15 mL - Kimble
General laboratory glassware
Mechanical shaker - New Brunswick Scientific
N-Evap (nitrogen evaporator) - Organomation Assoc.

EQUIPMENT cont'd

Solid phase extraction (SPE) column, 1000mg, octadecyl (C₁₈) - J.T. Baker
Solid phase extraction, vacuum manifold
Socorex, 0.5-5 mL
Syringe, gastight, 1 mL - Hamilton
Tubing, teflon, 1/8"
Volumetric flasks, various sizes
Vortex mixer - Fisher Scientific

GAS CHROMATOGRAPH AND CONDITIONS**Instrument:**

Gas Chromatograph: HP 5890A (Serial No. 2643A11313)
Injector: HP 7673A (Serial No. 2449A00421)
Column: HP-5MS; 0.25mm I.D.; 30m; 0.25 μ m film
Injection Port: Split/splitless in splitless mode
Detector: Mass Selective (MS) HP 5970B (Serial No. 96370A1566)

Conditions:

Injection Port: 245°C; single tapered deactivated liner, 4mm I.D.
Oven Temp: 45°C for 0.50 min.
45-212°C @ 45°C/min. hold for 1.0 min.
212-250°C @ 15°C/min. hold for 2.0 min.
250-280°C @ 45°C/min. hold for 0.75 min.
Run Time: 11.16 min.
Detector Temp: 280°C
Carrier Gas: Helium
Injection Volume: 2 μ L

A chromatographic stamp is included for each set run on the instrument outlining the conditions used.

ANALYSIS TIME

Sample Preparation, Fortification, Extraction and Clean-up:

A set of prepared soil (12) can be fortified, extracted and cleaned-up on a C₁₈ SPE cartridge in 5-7 hours.

Derivatization and Concentration:

The BF₃/MeOH derivatization and concentration step requires another 2-3 hours for 12 samples.

Instrumental Analysis:

A set of 12 samples and standards can be run on an overnight sequence using an autosampler. Actual running times varies from 7-9 hours.

EXAMPLES OF CALCULATIONS

A standard curve was generated for each set of samples by plotting analyte concentration versus peak areas. A quadratic regression formula using the equation $Y = aX^2 + bX + c$ was determined where $Y =$ peak area and $X =$ concentration in $\mu\text{g/mL}$. The results of this regression were used for the calculation of sample concentrations. A conversion factor was used to take into account the molecular weight ratio between 2,4-DP-p (235.07) and 2,4-DP-p methyl ester (249.10).

EXAMPLES OF CALCULATIONS cont'd

The following equation was used to determine the concentration of 2,4-DCP, 2,4-DCA and 2-EHE:

$$\text{Conc. (ppm)} = \frac{[-b + \text{SQRT}(b^2 - 4a \{c - \text{Peak Area}\})] \times \text{Final Volume (mL)}}{2a \times \text{Final Dilution} \times \text{Sample Mass (g)}}$$

where: b= Quadratic variable from the regression curve
 a= Quadratic variable from the regression curve
 c= y intercept

The following equation was used to determine the concentration of 2,4-DP-p:

$$\text{Conc. (ppm)} = \frac{[-b + \text{SQRT}(b^2 - 4a \{c - \text{Peak Area}\})] \times \text{Final Volume (mL)}}{2a \times \text{Final Dilution} \times \text{Sample Mass (g)}} \times \text{Conversion Factor}$$

where: Conversion Factor = $\frac{\text{Molar Weight of 2,4-DP-p (235.07)}}{\text{Molar Weight of 2,4-DP-p ME (249.10)}} = 0.944$

$$\% \text{ Recovery} = \frac{\text{ppm Found}}{\text{ppm Spiked}} \times 100$$

Example of Calculation:

E5-10-304-03AC-R1+1, JH523B09.D
Georgia Site - GR9481, Injection May 24, 1996

where from the regression curve: a= -49.7
 b= 189
 c= -0.764
 peak area = 25.3
 sample mass = 10 g
 final volume = 1.0 mL
 final dilution = 0.020 mL/mL

$$\begin{aligned} 2,4\text{-DP-p (ppm)} &= \frac{[-189 + \text{SQRT}(189^2 - \{4 \times -49.7 (-0.764 - 25.3)\})] \times 1.0(\text{mL}) \times 0.944}{2 (-49.7) \times 10 \text{ g} \times 0.020} \\ &= 0.68 \text{ ppm} \end{aligned}$$

$$\% \text{ Recovery} = \frac{0.68 \text{ ppm}}{0.93 \text{ ppm}} \times 100 = 73\%$$