

Cover Sheet for

**ENVIRONMENTAL CHEMISTRY METHOD**

***Pesticide Name:*** Triclopyr

***MRID #:*** 444561-09

***Matrix:*** Water

***Analysis:*** GC/MS

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If you have difficulties in downloading the method, or further questions concerning the methods, you may contact Elizabeth Flynt at 228-688-2410 or via e-mail at [flynt.elizabeth@epa.gov](mailto:flynt.elizabeth@epa.gov).

1911

THE UNIVERSITY OF CHICAGO

DEPARTMENT OF CHEMISTRY

RESEARCH REPORT

NO. 100

1911

The following report was prepared by the author under the supervision of the Director of the Department of Chemistry, University of Chicago, during the summer of 1911. The work was supported by the National Science Foundation.

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DowElanco  
Study ID: QMAP97002  
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GRM: 95.18  
EFFECTIVE: April 11, 1996  
SUPERSEDES: ACR 76.08, ACR 84.03

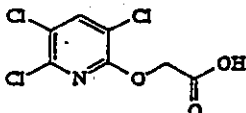


Determination of Residues of Triclopyr, 3,5,6-Trichloro-2-pyridinol,  
and 2-Methoxy-3,5,6-trichloropyridine in Water  
by Capillary Gas Chromatography with Mass Selective Detection

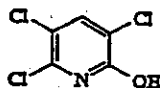
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A. Scope

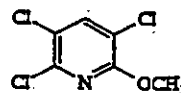
This method is applicable for the quantitative determination of residues of triclopyr ((3,5,6-trichloro-2-pyridinyl)oxy)acetic acid) and its metabolites, 3,5,6-trichloro-2-pyridinol (3,5,6-TCP), and 2-methoxy-3,5,6-trichloropyridine (2-MP) in water over the concentration range 0.10-10.0 ng/mL with a validated limit of quantitation of 0.10 ng/mL.



Triclopyr  
CAS No. 55335-06-3



3,5,6-TCP  
CAS No. 6515-38-4



2-MP  
CAS No. 31557-34-3

B. Principle

Residues of triclopyr and its metabolites are extracted from acidified water using 1-chlorobutane. The 1-chlorobutane is concentrated to less than 1 mL, and an acetone solution containing fluoxypyr analogs as internal standards is added. The sample is then derivatized with *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) to form the *tert*-butyldimethylsilyl (TBDMS) derivatives of triclopyr and 3,5,6-TCP. The sample is then analyzed by capillary gas chromatography with mass selective detection (GC/MSD).

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Initial: C14

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#### C. Safety Precautions

1. Each analyst must be acquainted with the potential hazards of the reagents, products, and solvents used in this method before commencing laboratory work. SOURCES OF INFORMATION INCLUDE: MATERIAL SAFETY DATA SHEETS, LITERATURE, AND OTHER RELATED DATA. Safety information on non-DowElanco products should be obtained from the container label or from the supplier. Disposal of reagents, reactants, and solvents must be in compliance with local, state, and federal laws and regulations.
2. Acetone and 1-chlorobutane are flammable and should be used in well-ventilated areas away from ignition sources.
3. Hydrochloric acid is corrosive and can cause severe burns. It is imperative that proper eye and personal protection equipment be worn when handling these reagents.

#### D. Equipment (Note L.1.)

1. Balance, analytical, Model AE200, Mettler Instrument Corporation, Hightstown, NJ 08520.
2. Centrifuge, with rotor to accommodate 45-mL vials, Model Centra-8, International Equipment Company, Needham Heights, MA 02194.
3. Evaporator, N-Evap, Model 111, Organomation Associates, Inc., South Berlin, MA 01549. (Note L.2.)
4. Gas chromatograph, Model 5890A Series II, Hewlett-Packard, Wilmington, DE 19808.
5. Injector, automatic, Model 7673, Hewlett-Packard.
6. Mass selective detector, Model 5971A, Hewlett-Packard, Palo Alto, CA 94304.
7. Mass selective detector data system, Model G1034C, Hewlett-Packard.
8. Oven, Model OV-490A-2, Blue M Electric Company, Blue Island, IL 60406.
9. Shaker, variable speed reciprocating with box carrier, Model 6000, Eberbach Corporation, Ann Arbor, MI 48106.
10. Ultrasonic cleaner, Model 1200, Branson Cleaning Equipment Company, Shelton, CT 06484.
11. Vortex mixer, Model G-560, Scientific Industries, Inc., Bohemia, NY 11716.
12. Water purification system, Model Milli-Q UV Plus, Millipore Corporation, Milford, MA 01757.

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**E. Glassware and Materials (Note L.1.)**

1. Column, capillary gas chromatography, Durabond-1701 liquid phase, 10 m x 0.18 mm I.d., 0.4- $\mu$ m film thickness, catalog number 121-0713, J & W Scientific, Folsom, CA 95630.
2. Column, capillary guard, deactivated, 5 m x 0.53 mm I.d., catalog number 10045, Restek Corporation, Bellefonte, PA 16823.
3. Column connector, Press-Tight capillary, catalog number 20446, Restek Corporation.
4. Filter, charcoal, catalog number 7972, Chrompack, Inc., Raritan, NJ 08869. (Note L.3.)
5. Filter, moisture, catalog number 7971, Chrompack, Inc. (Note L.3.)
6. Filter, oxygen, catalog number 7970, Chrompack, Inc. (Note L.3.)
7. Flask, volumetric, 100-mL, catalog number F4300-100, National Scientific Company, Lawrenceville, GA 30243.
8. Flask, volumetric, 200-mL, catalog number F4300-200, National Scientific Company.
9. Gas, helium, 99.995% purity, Airco, Murray Hill, NJ 07974.
10. Gas, nitrogen, 99.99% purity, Airco.
11. Inlet sleeve, double gooseneck splitless, catalog number 20784, Restek Corporation.
12. Pipet, volumetric, 1.0-mL, catalog number 261-6011, National Scientific Company.
13. Pipet, volumetric, 2.5-mL, catalog number 261-6084, National Scientific Company.
14. Pipet, volumetric, 5.0-mL, catalog number 261-6015, National Scientific Company.
15. Pipet, volumetric, 20-mL, catalog number 261-6030, National Scientific Company.
16. Pipet, volumetric, 25-mL, catalog number 261-6035, National Scientific Company.
17. Syringe, 25- $\mu$ L, Model 702N, Hamilton Company, Reno, NV 89520.
18. Syringe, 50- $\mu$ L, Model 705N, Hamilton Company.
19. Syringe, 100- $\mu$ L, Model 710N, Hamilton Company.
20. Syringe, 250- $\mu$ L, Model 725N, Hamilton Company.
21. Syringe, 500- $\mu$ L, Model 750N, Hamilton Company.
22. Vial, autosampler, 2-mL, catalog number C4000-1, National Scientific Company.
23. Vial, 12-mL, catalog number 60810-1965, Kimble/Kontes, Vineland, NJ 08360.
24. Vial, 45-mL, catalog number 60258A-11, Kimble/Kontes.

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25. Vial cap, for autosampler vial, catalog number C4000-34B, National Scientific Company.
26. Vial cap, for 12-mL vial, PTFE-lined, catalog number 5201-100, Qorpack, Bridgeville, PA 15017.
27. Vial cap, for 45-mL vial, PTFE-lined, catalog number 5205-100, Qorpack.

**F. Reagents and Chemicals (Note L.1.)**

1. Acetone, OmniSolv grade, catalog number AXD142-1, EM Science, Gibbstown, NJ 08027.
2. 1-Chlorobutane, OmniSolv grade, catalog number CX0914-1, EM Science.
3. Hydrochloric acid, 2.0 N, ACS reagent grade, certified concentration, catalog number SA431-500, Fisher Scientific, Pittsburgh, PA 15219.
4. MTBSTFA (*N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide), catalog number 48920, Pierce Chemical Company, Rockford, IL 61105.
5. Sodium chloride, ACS reagent grade, catalog number S271-1, Fisher Scientific.
6. Standards
  - a. triclopyr (((3,5,6-trichloro-2-pyridinyloxy)oxy)acetic acid)
  - b. 3,5,6-trichloro-2-pyridinol (3,5,6-TCP)
  - c. 2-methoxy-3,5,6-trichloropyridine (2-MP)
  - d. fluroxypyr (((4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy)acetic acid)
  - e. 4-amino-3,5-dichloro-6-fluoro-2-pyridinol (fluroxypyr-DCP)
  - f. 4-amino-3,5-dichloro-6-fluoro-2-methoxypyridine (fluroxypyr-MP)

Obtain from Test Substance Coordinator, DowElanco, 9330 Zionsville Road, Building 306/A1, Indianapolis, IN 46268-1053.

**G. Preparation of Standards**

**1. Preparation of Spiking Solutions/Calibration Standards**

- a. Weigh 0.1000 g of triclopyr analytical standard and quantitatively transfer to a 100-mL volumetric flask. Dilute to volume with acetone to obtain a 1000- $\mu$ g/mL stock solution.
- b. Weigh 0.1000 g of 3,5,6-trichloro-2-pyridinol analytical standard and quantitatively transfer to a 100-mL volumetric flask. Dilute to volume with acetone to obtain a 1000- $\mu$ g/mL stock solution.
- c. Weigh 0.1000 g of 2-methoxy-3,5,6-trichloropyridine analytical standard and quantitatively transfer to a 100-mL volumetric flask. Dilute to volume with acetone to obtain a 1000- $\mu$ g/mL stock solution.

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- d. Pipet 20.0 mL of each of the stock solutions in Sections G.1.a.-c. into a single 200-mL volumetric flask and adjust to volume with acetone to obtain a solution containing 100.0 µg/mL of each compound.
- e. Prepare solutions for spiking water samples by diluting the solution from Section G.1.d with acetone as follows:

Aliquot of Initial Soln. µL	Final Soln. Volume mL	Spiking Soln. Final Conc. ng/mL	Equivalent Sample Conc. <sup>a</sup> ng/mL
12.5	200	6.25	0.050
25.0	200	12.5	0.100
50.0	200	25.0	0.200
100	200	50.0	0.400
250	200	125	1.00
500	200	250	2.00
1000	200	500	4.00
2500	200	1250	10.0

<sup>a</sup> The equivalent sample concentration is based on fortifying a 25.0-mL water sample with 200 µL of spiking solution.

- f. Prepare calibration standards by dispensing 200 µL of the solutions from Section G.1.e. into 12-mL vials containing 0.5 mL of 1-chlorobutane and derivatizing according to the procedure described in Section I.1.k.-a. The concentration range of these calibration standards is from 1.25-250 ng/mL.

Chemical structures of the underivatized and derivatized triolopyr, 3,5,6-TCP, and 2-MP are shown in Figure 1.

## 2. Preparation of Internal Standard Solution

- a. Weigh 0.1000 g of fluroxypr analytical standard and quantitatively transfer to a 100-mL volumetric flask. Dilute to volume with acetone to obtain a 1000-µg/mL stock solution.
- b. Weigh 0.1000 g of 4-amino-3,5-dichloro-6-fluoro-2-pyridinol analytical standard and quantitatively transfer to a 100-mL volumetric flask. Dilute to volume with acetone to obtain a 1000-µg/mL stock solution.
- c. Weigh 0.1000 g of 4-amino-3,5-dichloro-6-fluoro-2-methoxypyridine analytical standard and quantitatively transfer to a 100-mL volumetric flask. Dilute to volume with acetone to obtain a 1000-µg/mL stock solution.
- d. Pipet 20.0 mL of each of the stock solutions in Sections G.2.a.-c. into a single 200-mL volumetric flask and adjust to volume with acetone to obtain a solution containing 100.0 µg/mL of each compound.
- e. Pipet 25.0 mL of the solution in Section G.2.d. into a 200-mL volumetric flask and adjust to volume with acetone to obtain a mixture containing 12.5 µg/mL of each compound.

Chemical structures of the underivatized and derivatized fluroxypr, fluroxypr-DCP, and fluroxypr-MP are shown in Figure 2.

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## E. Gas Chromatography/Mass Spectrometry

### 1. Column

Connect the guard column (Section E.2.) to the capillary column (Section E.1.) using a Press-Tight column connector (Section E.3.) Install the splitless column inlet sleeve (Section E.11.) and capillary column assembly in the split/splitless injection port of the GC/MSD following the manufacturer's recommended procedures.

### 2. Typical Operating Conditions

Instrumentation:	Hewlett-Packard Model 5890A gas chromatograph Hewlett-Packard Model 7673 automatic injector Hewlett-Packard Model 5971A mass selective detector Hewlett-Packard Model G1034C data system software
Columns:	
Guard	Restek fused silica capillary 3 m x 0.53 mm I.D. deactivated
Analytical	J & W Scientific fused silica capillary Durabond-1701 liquid phase 10 m x 0.18 mm I.D. 0.4- $\mu$ m film thickness
Temperatures:	
Column	60 °C for 1.0 min 60 °C to 255 °C at 10 °C/min 255 °C to 290 °C at 20 °C/min 290 °C for 2.75 min
Injector	250 °C
Interface	280 °C
Carrier Gas:	helium
Head Pressure	50 kPa
Linear Velocity	approximately 25 cm/s
Injection Mode:	splitless
Purge Delay	0.9 min
Splitter Flow	50 mL/min
Septum Purge	1.0 mL/min
Injection Volume:	5 $\mu$ L
Detector:	electron impact selected ion monitoring
Calibration Program	maximum sensitivity autome (Note L.4.)
Electron Multiplier	1775 volts (= 280 volts above autome)



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**Ions Monitored:**

Triclopyr-TBDMS	<i>m/z</i> 312 (quantitation) <i>m/z</i> 254, 256, 314 (confirmation) (Section K.2.)
3,5,6-TCP-TBDMS	<i>m/z</i> 254 (quantitation) <i>m/z</i> 256 (confirmation)
2-MP	<i>m/z</i> 211 (quantitation) <i>m/z</i> 182, 210, 212, 213 (confirmation) (Section K.2.)
Fluroxypyr-TBDMS	<i>m/z</i> 311 (internal standard for triclopyr-TBDMS)
Fluroxypyr-DCP-TBDMS	<i>m/z</i> 253 (internal standard for 3,5,6-TCP-TBDMS)
Fluroxypyr-MP	<i>m/z</i> 210 (internal standard for 2-MP)

Dwell Time: 75 ms

Mass spectra of the above triclopyr and fluroxypyr compounds are shown in Figures 3-8, respectively.

**3. Calibration Curves**

Typical calibration curves for the determination of triclopyr, 3,5,6-TCP, and 2-MP are shown in Figures 9-11, respectively.

**4. Typical Chromatograms**

Typical chromatograms of a standard, control sample, and a 0.10- $\mu\text{g/mL}$  recovery sample for the determination of triclopyr, 3,5,6-TCP, and 2-MP in water are illustrated in Figures 12-20, respectively. None of the control samples in the method validation study contained interference peaks at the retention times of the analytes or internal standards.

**I. Determination of Recovery of Triclopyr and Metabolites from Water**

**1. Preparation of Recovery Samples**

- a. Pipet 25.0-mL portions of the control water sample into a series of 45-mL vials.
- b. For preparing fortified samples, use some of the samples as controls and fortify the remaining samples by adding 200- $\mu\text{L}$  aliquots of the appropriate spiking solutions (Section G.1.e.) to obtain concentrations ranging from 0.10 to 10.0  $\mu\text{g/mL}$ . Also analyze a sample consisting of only distilled/deionized water to serve as a reagent blank.
- c. Add 1.0 mL of 2.0 N hydrochloric acid, 10 g of sodium chloride (enough to saturate the solution), and 5.0 mL of 1-chlorobutane to the sample vial.
- d. Cap the vial with a PTFE-lined cap, and shake the sample for 30 minutes on a reciprocating shaker at approximately 180 excursions/minute.
- e. Centrifuge the sample vial for 5 minutes at 2500 rpm.
- f. Transfer the 1-chlorobutane (top) layer into a clean 12-mL vial. (Note I.5.)

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- g. Add an additional 5.0 mL of 1-chlorobutane to the sample vial. Cap the vial, and shake the sample for 30 minutes on a reciprocating shaker at approximately 180 excursions/minute.
- h. Centrifuge the sample vial for 5 minutes at 2500 rpm.
- i. Combine the 1-chlorobutane layer from Step L1.h. with the 1-chlorobutane extract from Step L1.f. and mix thoroughly. (Note L.5.)
- j. Concentrate the solution from Step L1.i. to less than 0.8 mL (but not to dryness) using an N-Evap evaporator. (Note L.2.)
- k. Add 100  $\mu$ L of the internal standard solution (Section G.2.a.) and 100  $\mu$ L of MTBSTFA derivatizing reagent to the sample vial.
- l. Adjust the volume in the sample vial to 1.0 mL with 1-chlorobutane and firmly seal with a PTFE-lined cap. Vortex the sample for 5-10 seconds, and then sonicate the sample for 5-10 seconds.
- m. Place the sample vial in an oven set at 60 °C and allow the mixture to react for 60 minutes.
- n. Remove the sample vial from the oven and allow the reaction mixture to cool to room temperature.
- o. Transfer the sample to a 2-mL autosampler vial and seal the vial with a cap.
- p. Analyze the calibration standards from Section G.1.f. and samples by capillary gas chromatography/mass spectrometry as described in Section H.2. Determine the suitability of the chromatographic system using the following performance criteria:
  - (1) Standard curve linearity: Determine that the correlation coefficient equals or exceeds 0.99 for the least squares equation which describes the detector response as a function of standard curve concentration. If power regression is used, the power exponent should be between 0.90-1.10.
  - (2) Peak resolution: Visually determine that sufficient resolution has been achieved for the analytes and internal standards relative to background interferences.
  - (3) Appearance of chromatograms: Visually determine that the chromatograms resemble those shown in Figures 12-20 with respect to peak response, baseline noise, and background interference. Visually determine that a minimum signal-to-noise ratio of 5:1 has been attained for each analyte in the 2.50- $\mu$ g/mL calibration standard (equivalent to 0.10 ng/mL in water samples).

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## 2. Calculation of Percent Recovery

- a. Inject the series of calibration standards described in Section G.1.f. and determine the peak areas for the analytes and internal standards as indicated below.

Triclopyr-TBDMS	<i>m/z</i> 312 (quantitation), <i>m/z</i> 256 (confirmation)
3,5,6-TCP-TBDMS	<i>m/z</i> 254 (quantitation), <i>m/z</i> 256 (confirmation)
2-MP	<i>m/z</i> 211 (quantitation), <i>m/z</i> 182 (confirmation)
Fluroxypyr-TBDMS	<i>m/z</i> 311 (internal standard for triclopyr-TBDMS)
Fluroxypyr-DCP-TBDMS	<i>m/z</i> 253 (internal standard for 3,5,6-TCP-TBDMS)
Fluroxypyr MP	<i>m/z</i> 210 (internal standard for 2-MP)

- b. For each standard, calculate each analyte's confirmation ratio. Use the average confirmation ratio for each analyte to confirm the presence of the analyte in the water samples.

For example, using the data for triclopyr from Figure 12:

$$\text{Confirmation Ratio} = \frac{\text{peak area of confirmation ion}}{\text{peak area of quantitation ion}}$$

$$\text{Confirmation Ratio} = \frac{\text{peak area at } m/z \text{ 256}}{\text{peak area at } m/z \text{ 312}}$$

$$\text{Confirmation Ratio} = \frac{2259}{1746}$$

$$\text{Confirmation Ratio} = 1.2938$$

Confirmation of the presence of the analyte is indicated when the confirmation ratio for the sample is within the range of  $\pm 15\%$  of the average found for the standards.

- c. For each standard, calculate each analyte's quantitation ratio.

For example, using the data for triclopyr from Figure 12:

$$\text{Quantitation Ratio} = \frac{\text{peak area of quantitation ion}}{\text{peak area of internal standard ion}}$$

$$\text{Quantitation Ratio} = \frac{\text{peak area at } m/z \text{ 312}}{\text{peak area at } m/z \text{ 311}}$$

$$\text{Quantitation Ratio} = \frac{1746}{475879}$$

$$\text{Quantitation Ratio} = 0.00367$$

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- d. Prepare a standard curve for each analyte by plotting the equivalent analyte concentration (as ng/mL) on the abscissa (x-axis) and the respective quantitation ratio on the ordinate (y-axis) as shown in Figures 9-11. Using regression analysis, determine the equation for the curve with respect to the abscissa.

For example, using power regression (1) with the triclopyr data from Figure 9:

$$Y = \text{constant} \times X^{\text{(exponent)}}$$

$$X = \left( \frac{Y}{\text{constant}} \right)^{1/\text{exponent}}$$

$$\text{Triclopyr Conc. (ng/mL)} = \left( \frac{\text{triclopyr quantitation ratio}}{\text{constant}} \right)^{1/\text{exponent}}$$

$$\text{Triclopyr Conc. (ng/mL)} = \left( \frac{\text{triclopyr quantitation ratio}}{0.03458} \right)^{1/0.96175}$$

- e. Determine the gross concentration in each recovery sample by substituting the quantitation ratio obtained into the above equation and solving for the concentration.

For example, using the triclopyr data from Figure 14:

$$\text{Triclopyr Conc. (gross ng/mL)} = \left( \frac{\text{triclopyr quantitation ratio}}{0.03458} \right)^{1/0.96175}$$

$$\text{Triclopyr Conc. (gross ng/mL)} = \left( \frac{0.00392}{0.03458} \right)^{1/0.96175}$$

$$\text{Triclopyr Conc.} = 0.104 \text{ ng/mL}$$

- f. Determine the net concentration in each recovery sample by subtracting any apparent triclopyr concentration in the control sample from that of the gross triclopyr concentration in the recovery sample.

For example, using the triclopyr data from Figures 13 and 14:

$$\text{Triclopyr Conc. (net ng/mL)} = \text{Triclopyr Conc. (gross ng/mL)} - \text{Triclopyr Conc. (control ng/mL)}$$

$$\text{Triclopyr Conc. (net ng/mL)} = 0.104 \text{ ng/mL} - 0.000 \text{ ng/mL}$$

$$\text{Triclopyr Conc. (net)} = 0.104 \text{ ng/mL}$$

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- g. Determine the percent recovery by dividing the net concentration of each recovery sample by the theoretical concentration added.

$$\text{Recovery} = \frac{\text{Concentration Found}}{\text{Concentration Added}} \times 100\%$$

$$\text{Recovery} = \frac{0.104 \text{ ng/mL}}{0.100 \text{ ng/mL}} \times 100\%$$

$$\text{Recovery} = 104\%$$

J. Determination of Triclopyr and Metabolites in Water

1. Prepare reagent blank, control, recovery, and treated samples as described in Section I.1.
2. Prepare a standard calibration curve for triclopyr, 3,5,6-TCP, and 2-MP and determine the percent recovery for each analyte as described in Section I.2.
3. Determine the gross concentration of each analyte in each treated sample by substituting the quantitation ratio obtained into the equation for the standard calibration curve, and calculating the uncorrected residue result as described in Section I.2.c.
4. For those analyses that require correction for method recovery, use the average recovery of all the recovery samples to correct for method efficiency. The following procedure is used:
  - a. Determine the gross analyte concentrations in the water sample as described in Section I.2.c.
  - b. Determine the corrected analyte concentrations in the water sample as follows:

$$\text{Triclopyr Conc. (corrected ng/mL)} = \text{Triclopyr Conc. (gross ng/mL)} \times \left( \frac{100}{\text{Average Percent Recovery}} \right)$$

$$\text{Triclopyr Conc. (corrected ng/mL)} = 0.104 \text{ ng/mL} \times \frac{100}{101}$$

$$\text{Triclopyr Conc. (corrected)} = 0.103 \text{ ng/mL}$$

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## K. Results and Discussion

### 1. Method Validation

#### a. Recovery Levels and Precision

A method validation study was conducted to determine the recovery levels and the precision of the method for the determination of triclopyr, 3,5,6-TCP, and 2-MP in water. The results are summarized in Tables I-III.

Recovery values of triclopyr from samples of water fortified over the concentration range of 0.10 to 10.0 ng/mL averaged 101% with one standard deviation equal to 7% (Table I). Recovery values of 3,5,6-TCP from samples of water fortified over the concentration range of 0.10 to 10.0 ng/mL averaged 91% with one standard deviation equal to 7% (Table II). Recovery values of 2-MP from samples of water fortified over the concentration range of 0.10 to 10.0 ng/mL averaged 93% with one standard deviation equal to 6% (Table III).

#### b. Standard Curve Linearity

For the power least squares regression equations describing the detector response as a function of the standard calibration curve concentrations, the correlation coefficients ( $r^2$ ) were greater than 0.995 for all three analytes, while the power exponents were between 0.96 and 1.03.

#### c. Calculated Limits of Quantitation and Detection

Following established guidelines (2), the limits of quantitation (LOQ) and detection (LOD) were calculated using the standard deviation from the 0.10-ng/mL recovery results. The LOQ was calculated as ten times the standard deviation (10s), and the LOD was calculated as three times the standard deviation (3s) of the results of the analysis of ten samples. The results are tabulated in Tables I-III.

The calculated LOQ ranged from 0.046-0.060 ng/mL for the three analytes, which is lower than the targeted method LOQ of 0.10 ng/mL. Results should not be quantified, however, at levels below which no recovery samples have been analyzed.

In a similar fashion, the calculated LOD ranged from 0.014-0.018 ng/mL for the three analytes. However, since the lowest level of fortification for recovery samples was 0.05 ng/mL, the method LOD is considered to be 0.05 ng/mL. In actual residue samples, numerical results should be reported as less than the LOQ (<0.10 ng/mL) for residues that are above the LOD but less than the validated LOQ.

### 2. Confirmation of Residue Identity

Confirmation of the presence of residues is described in Section L2.b. For the three analytes, confirmation is by comparison of the retention time (gas chromatography) as well as the peak area ratios resulting from selected ion monitoring (mass spectrometry). Confirmation of the presence of the analytes is indicated when the retention times match those of the standards and the confirmation ratio is in the range of  $\pm 15\%$  of the average found for the standards. If additional confirmation is required beyond that discussed in this method, the mass spectra of triclopyr-TBDMS and triclopyr-MP contain additional ions (Section H2.) that may be used for confirmation.

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### 3. Assay Time

A typical analytical run consists of a minimum of four standards encompassing the expected range of sample concentrations, distilled/deionized water serving as a reagent blank, a control (a non-fortified sample), a minimum of two fortified controls (one of which must be at the LOQ), and forty samples. This typical analytical run can be prepared in approximately eight hours, followed by the chromatographic analysis.

There are several acceptable "stopping points" in the method, where sample preparation (Section I) may be suspended without deleterious effects on the sample analysis. These are indicated below:

- a. Step L.I.f.
- b. Step L.I.i.
- c. Step L.I.n.

If the samples are to be stored overnight, the vials should be capped with PTFE-lined caps.

### L. Notes

1. Equipment, glassware, materials, reagents, and chemicals considered to be equivalent to those specified may be substituted with the understanding that their performance must be confirmed by appropriate tests. Common laboratory supplies are assumed to be readily available and are, therefore, not listed.
2. The N-Evap evaporator should be set at a water bath temperature of 30 °C and a nitrogen flow rate of approximately 200 mL/min. At elevated water bath temperatures, the 3,5,6-TCP and 2-MP may volatilize, thereby reducing recoveries.
3. The filters are used in the carrier gas supply lines to purify the helium entering the gas chromatograph.
4. Several tuning, or calibration, options are available for the Model 597X series of MSDs. The "Maximum Sensitivity Autotune" feature was found to consistently yield approximately 5-10 times the sensitivity compared to that of the "Standard Autotune".
5. In transferring the 1-chlorobutane layer, it is important not to remove any water from the lower layer. Contaminating the 1-chlorobutane with water will have deleterious effects on the derivatization and subsequent GC/MSD analysis.

### M. References

1. *HP-41C/41CV Standard Applications Handbook*, Hewlett-Packard Publication No. 00041-9040Z, 1982, pp 42-48.
2. Keith, L. H.; Crummett, W.; Deegan, J.; Libby, R. A.; Taylor, J. K.; Wentler, G. *Anal. Chem.*, 1983, 55, 2210-2218.

Effective Date: April 11, 1996

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Table I. Recovery of Triclopyr from Water

Sample Number	Date of Analysis	Triclopyr, ng/mL		Percent Recovery	Statistical Calculations
		Added	Found		
14390104 <sup>a</sup>	24-Jan-1995	0.000	0.0000	--	
14390104	24-Jan-1995	0.000	0.0000	--	
14420701 <sup>b</sup>	24-Jan-1995	0.000	0.1711	--	
14420701	24-Jan-1995	0.000	0.2104	--	
14421501 <sup>c</sup>	24-Jan-1995	0.000	0.0000	--	$\bar{X} = 0.1908$
14421501	24-Jan-1995	0.000	0.0000	--	
15082701 <sup>d</sup>	24-Jan-1995	0.000	0.0000	--	
15082702 <sup>e</sup>	24-Jan-1995	0.000	0.0000	--	
Tap Water <sup>f</sup>	24-Jan-1995	0.000	0.0000	--	
15082703 <sup>g</sup>	24-Jan-1995	0.000	0.2455	--	
15082703	24-Jan-1995	0.000	0.2242	--	$\bar{X} = 0.2349$
14421501	24-Jan-1995	0.050	<0.100	NA <sup>h</sup>	
15082701	24-Jan-1995	0.050	<0.100	NA	
15082702	24-Jan-1995	0.050	<0.100	NA	
Tap Water	24-Jan-1995	0.050	<0.100	NA	
14390104	24-Jan-1995	0.100	0.1082	108	
14390104	24-Jan-1995	0.100	0.1041	104	
14421501	24-Jan-1995	0.100	0.0947	95	
14421501	24-Jan-1995	0.100	0.1087	109	
15082701	24-Jan-1995	0.100	0.0941	94	
15082701	24-Jan-1995	0.100	0.0961	96	$\bar{X} = 0.0992$
15082702	24-Jan-1995	0.100	0.0926	93	$s = 0.0058$
15082702	24-Jan-1995	0.100	0.0959	96	$(3s) = 0.0175$
Tap Water	24-Jan-1995	0.100	0.0998	100	$(10s) = 0.0584$
Tap Water	24-Jan-1995	0.100	0.0980	98	RSD = 6%
14390104	24-Jan-1995	0.200	0.1922	96	
14390104	24-Jan-1995	0.200	0.1942	97	
14420701	24-Jan-1995	0.200	0.2287	114	
14421501	24-Jan-1995	0.200	0.2006	100	
15082701	24-Jan-1995	0.200	0.1927	96	$\bar{X} = 0.1956$
15082702	24-Jan-1995	0.200	0.1695	85	$s = 0.0175$
Tap Water	24-Jan-1995	0.200	0.1914	96	RSD = 9%
14390104	24-Jan-1995	0.400	0.3821	96	
14390104	24-Jan-1995	0.400	0.3971	99	$\bar{X} = 0.3931$
14420701	24-Jan-1995	0.400	0.4088	102	$s = 0.0123$
14421501	24-Jan-1995	0.400	0.3845	96	RSD = 3%
15082701	24-Jan-1995	1.00	1.023	102	
15082702	24-Jan-1995	1.00	1.088	109	$\bar{X} = 1.012$
Tap Water	24-Jan-1995	1.00	0.927	93	$s = 0.066$
15082703	24-Jan-1995	1.00	1.009	101	RSD = 7%

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Table L (Cont.) Recovery of Triclopyr from Water

Sample Number	Date of Analysis	Triclopyr, ng/mL		Percent Recovery	Statistical Calculations
		Added	Found		
14390104	24-Jan-1995	2.00	2.018	101	$\bar{X} = 1.966$ $s = 0.137$ RSD = 7%
14390104	24-Jan-1995	2.00	1.908	95	
14420701	24-Jan-1995	2.00	2.126	106	
14421501	24-Jan-1995	2.00	1.810	91	
15082701	24-Jan-1995	4.00	4.285	107	$\bar{X} = 4.287$ $s = 0.049$ RSD = 1%
15082702	24-Jan-1995	4.00	4.261	107	
Tap Water	24-Jan-1995	4.00	4.357	109	
15082703	24-Jan-1995	4.00	4.246	106	
14390104	24-Jan-1995	10.0	11.747	117	$\bar{X} = 11.189$ $s = 0.628$ RSD = 6%
14390104	24-Jan-1995	10.0	11.713	117	
14420701	24-Jan-1995	10.0	10.572	106	
14421501	24-Jan-1995	10.0	10.725	107	

$\bar{X} = 101$   
 $s = 7$   
 $n = 37$

- a SN14390104 — Domestic well in Little Rock, AR.
- b SN14420701 — Rice paddy in Opelousas, LA. Recovery results from samples prepared using this sample were corrected for the amount of triclopyr found in the control.
- c SN14421501 — Rice paddy in Little Rock, AR.
- d SN15082701 — Municipal supply from Zionsville, IN.
- e SN15082702 — Oak Ridge pond in Zionsville, IN.
- f Tap Water — Municipal supply from Indianapolis, IN.
- g SN15082703 — DowElanco pond in Indianapolis, IN. Recovery results from samples prepared using this sample were corrected for the amount of triclopyr found in the control.
- h NA = not applicable. The residue was below the 0.10-ng/mL limit of quantitation.
- i Calculated limit of detection.
- j Calculated limit of quantitation.

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Table II. Recovery of 3,5,6-Trichloro-2-pyridinol from Water

Sample Number	Date of Analysis	3,5,6-TCP, ng/mL		Percent Recovery	Statistical Calculations
		Added	Found		
14390104 <sup>a</sup>	24-Jan-1995	0.000	0.0000	--	
14390104	24-Jan-1995	0.000	0.0000	--	
14420701 <sup>b</sup>	24-Jan-1995	0.000	0.0000	--	
14420701	24-Jan-1995	0.000	0.0000	--	
14421501 <sup>c</sup>	24-Jan-1995	0.000	0.0000	--	
14421501	24-Jan-1995	0.000	0.0000	--	
15082701 <sup>d</sup>	24-Jan-1995	0.000	0.0000	--	
15082702 <sup>e</sup>	24-Jan-1995	0.000	0.0000	--	
Tap Water <sup>f</sup>	24-Jan-1995	0.000	0.0000	--	
15082703 <sup>g</sup>	24-Jan-1995	0.000	0.0000	--	
15082703	24-Jan-1995	0.000	0.0000	--	
14421501	24-Jan-1995	0.050	<0.100	NA <sup>h</sup>	
15082701	24-Jan-1995	0.050	<0.100	NA	
15082702	24-Jan-1995	0.050	<0.100	NA	
Tap Water	24-Jan-1995	0.050	<0.100	NA	
14390104	24-Jan-1995	0.100	0.1045	105	
14390104	24-Jan-1995	0.100	0.1022	102	
14421501	24-Jan-1995	0.100	0.0942	94	
14421501	24-Jan-1995	0.100	0.0956	96	
15082701	24-Jan-1995	0.100	0.0980	98	
15082701	24-Jan-1995	0.100	0.0989	99	$\bar{X} = 0.0964$
15082702	24-Jan-1995	0.100	0.0895	90	$s = 0.0046$
15082702	24-Jan-1995	0.100	0.0944	94	$(3s) = 0.0137$
Tap Water	24-Jan-1995	0.100	0.0924	92	$(10s) = 0.0456$
Tap Water	24-Jan-1995	0.100	0.0939	94	RSD = 5%
14390104	24-Jan-1995	0.200	0.1853	93	
14390104	24-Jan-1995	0.200	0.1821	91	
14420701	24-Jan-1995	0.200	0.1831	92	
14421501	24-Jan-1995	0.200	0.1788	89	
15082701	24-Jan-1995	0.200	0.1846	92	$\bar{X} = 0.1815$
15082702	24-Jan-1995	0.200	0.1773	89	$s = 0.0031$
Tap Water	24-Jan-1995	0.200	0.1791	90	RSD = 2%
14390104	24-Jan-1995	0.400	0.3689	92	
14390104	24-Jan-1995	0.400	0.3591	90	$\bar{X} = 0.3526$
14420701	24-Jan-1995	0.400	0.3452	86	$s = 0.0141$
14421501	24-Jan-1995	0.400	0.3373	84	RSD = 4%
15082701	24-Jan-1995	1.00	0.873	87	
15082702	24-Jan-1995	1.00	0.854	85	$\bar{X} = 0.862$
Tap Water	24-Jan-1995	1.00	0.847	85	$s = 0.014$
15082703	24-Jan-1995	1.00	0.874	87	RSD = 2%

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Table II. (Cont.) Recovery of 3,5,6-Trichloro-2-pyridinol from Water

Sample Number	Date of Analysis	3,5,6-TCP, ng/mL		Percent Recovery	Statistical Calculations
		Added	Found		
14390104	24-Jan-1995	2.00	1.822	91	
14390104	24-Jan-1995	2.00	1.808	90	X = 1.780
14420701	24-Jan-1995	2.00	1.760	88	s = 0.042
14421501	24-Jan-1995	2.00	1.732	87	RSD = 2%
15082701	24-Jan-1995	4.00	3.549	89	
15082702	24-Jan-1995	4.00	3.586	90	X = 3.586
Tap Water	24-Jan-1995	4.00	3.557	89	s = 0.047
15082703	24-Jan-1995	4.00	3.653	91	RSD = 1%
14390104	24-Jan-1995	10.0	9.554	96	
14390104	24-Jan-1995	10.0	9.884	99	X = 8.453
14420701	24-Jan-1995	10.0	7.231	72 <sup>b</sup>	s = 1.466
14421501	24-Jan-1995	10.0	7.152	72 <sup>b</sup>	RSD = 17%

X = 91  
 s = 7  
 n = 37

- <sup>a</sup> SN14390104 — Domestic well in Little Rock, AR.
- <sup>b</sup> SN14420701 — Rice paddy in Opelousas, LA.
- <sup>c</sup> SN14421501 — Rice paddy in Little Rock, AR.
- <sup>d</sup> SN15082701 — Municipal supply from Zionsville, IN.
- <sup>e</sup> SN15082702 — Oak Ridge pond in Zionsville, IN.
- <sup>f</sup> Tap Water — Municipal supply from Indianapolis, IN.
- <sup>g</sup> SN15082703 — DowElanco pond in Indianapolis, IN.
- <sup>h</sup> NA = not applicable. The residue was below the 0.10-ng/mL limit of quantitation.
- <sup>i</sup> Calculated limit of detection.
- <sup>j</sup> Calculated limit of quantitation.
- <sup>k</sup> These samples were inadvertently dried during sample preparation. Although some loss of 3,5,6-TCP occurred, the results were used in the statistical calculations.

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Table III. Recovery of 2-Methoxy-3,5,6-trichloropyridine from Water

Sample Number	Date of Analysis	2-MP, ng/mL		Percent Recovery	Statistical Calculations
		Added	Found		
14390104 <sup>a</sup>	24-Jan-1995	0.000	0.0000	--	
14390104	24-Jan-1995	0.000	0.0000	--	
14420701 <sup>b</sup>	24-Jan-1995	0.000	0.0000	--	
14420701	24-Jan-1995	0.000	0.0000	--	
14421501 <sup>c</sup>	24-Jan-1995	0.000	0.0000	--	
14421501	24-Jan-1995	0.000	0.0000	--	
15082701 <sup>d</sup>	24-Jan-1995	0.000	0.0000	--	
15082702 <sup>e</sup>	24-Jan-1995	0.000	0.0000	--	
Tap Water <sup>f</sup>	24-Jan-1995	0.000	0.0000	--	
15082703 <sup>g</sup>	24-Jan-1995	0.000	0.0000	--	
15082703	24-Jan-1995	0.000	0.0000	--	
<hr/>					
14421501	24-Jan-1995	0.050	<0.100	NA <sup>h</sup>	
15082701	24-Jan-1995	0.050	<0.100	NA	
15082702	24-Jan-1995	0.050	<0.100	NA	
Tap Water	24-Jan-1995	0.050	<0.100	NA	
<hr/>					
14390104	24-Jan-1995	0.100	0.0943	94	
14390104	24-Jan-1995	0.100	0.0941	94	
14421501	24-Jan-1995	0.100	0.0932	93	
14421501	24-Jan-1995	0.100	0.0915	92	
15082701	24-Jan-1995	0.100	0.1010	101	
15082701	24-Jan-1995	0.100	0.1053	105	
15082702	24-Jan-1995	0.100	0.0948	95	X = 0.0977
15082702	24-Jan-1995	0.100	0.0913	91	s = 0.0060
Tap Water	24-Jan-1995	0.100	0.1056	106	(3s) <sup>i</sup> = 0.0181
Tap Water	24-Jan-1995	0.100	0.1056	106	(10s) <sup>j</sup> = 0.0502
					RSD = 6%
<hr/>					
14390104	24-Jan-1995	0.200	0.1775	89	
14390104	24-Jan-1995	0.200	0.1892	95	
14420701	24-Jan-1995	0.200	0.1823	91	
14421501	24-Jan-1995	0.200	0.2035	102	
15082701	24-Jan-1995	0.200	0.1953	98	
15082702	24-Jan-1995	0.200	0.1791	90	X = 0.1888
Tap Water	24-Jan-1995	0.200	0.1949	97	s = 0.0097
					RSD = 5%
<hr/>					
14390104	24-Jan-1995	0.400	0.3566	89	
14390104	24-Jan-1995	0.400	0.3253	81	
14420701	24-Jan-1995	0.400	0.3547	89	X = 0.3502
14421501	24-Jan-1995	0.400	0.3638	91	s = 0.0169
					RSD = 5%
<hr/>					
15082701	24-Jan-1995	1.00	0.979	98	
15082702	24-Jan-1995	1.00	0.870	87	
Tap Water	24-Jan-1995	1.00	0.914	91	X = 0.905
15082703	24-Jan-1995	1.00	0.858	86	s = 0.055
					RSD = 6%

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Table III. (Cont.) Recovery of 2-Methoxy-3,5,6-trichloropyridine from Water

Sample Number	Date of Analysis	2-MP, ng/mL		Percent Recovery	Statistical Calculations
		Added	Found		
14390104	24-Jan-1995	2.00	1.834	92	
14390104	24-Jan-1995	2.00	1.712	86	$\bar{x} = 1.775$
14420701	24-Jan-1995	2.00	1.795	90	$s = 0.052$
14421501	24-Jan-1995	2.00	1.759	88	RSD = 3%
15082701	24-Jan-1995	4.00	3.618	90	
15082702	24-Jan-1995	4.00	3.618	90	$\bar{x} = 3.619$
Tap Water	24-Jan-1995	4.00	3.597	90	$s = 0.018$
15082703	24-Jan-1995	4.00	3.642	91	RSD = 1%
14390104	24-Jan-1995	10.0	9.304	93	
14390104	24-Jan-1995	10.0	9.318	93	$\bar{x} = 9.311$
14420701	24-Jan-1995	10.0	0.000	0 <sup>k</sup>	$s = 0.010$
14421501	24-Jan-1995	10.0	0.000	0 <sup>k</sup>	RSD = 0%

$\bar{x} = 93$   
 $s = 6$   
 $n = 35$

- <sup>a</sup> SN14390104 — Domestic well in Little Rock, AR.
- <sup>b</sup> SN14420701 — Rice paddy in Opelousas, LA.
- <sup>c</sup> SN14421501 — Rice paddy in Little Rock, AR.
- <sup>d</sup> SN15082701 — Municipal supply from Zionsville, IN.
- <sup>e</sup> SN15082702 — Oak Ridge pond in Zionsville, IN.
- <sup>f</sup> Tap Water — Municipal supply from Indianapolis, IN.
- <sup>g</sup> SN15082703 — DowElanco pond in Indianapolis, IN.
- <sup>h</sup> NA = not applicable. The residue was below the 0.10-ng/mL limit of quantitation.
- <sup>i</sup> Calculated limit of detection.
- <sup>j</sup> Calculated limit of quantitation.
- <sup>k</sup> These samples were inadvertently dried during sample preparation. The results were not used in the statistical calculations.

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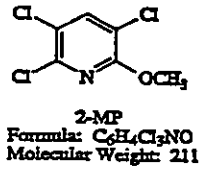
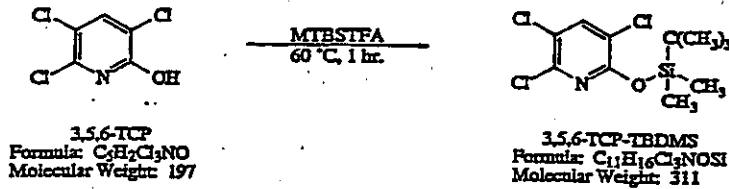
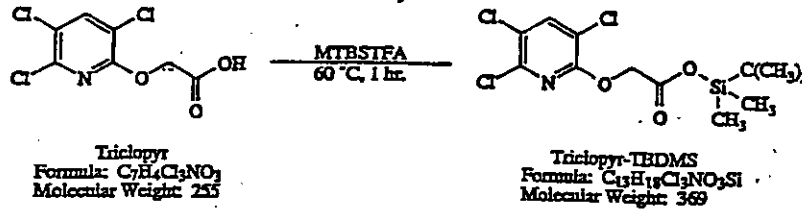


Figure 1. Chemical Structures of Triclopyr, 3,5,6-Trichloro-2-pyridinol and their TBDMS Derivatives, and 2-Methoxy-3,5,6-trichloropyridine

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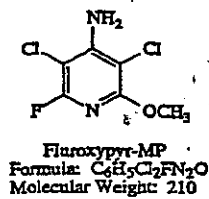
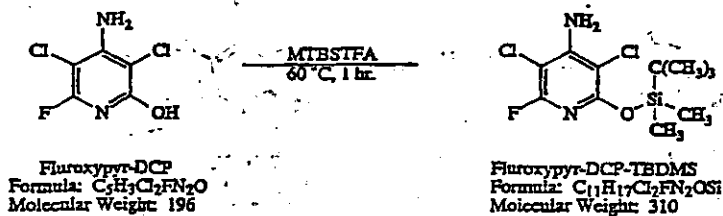
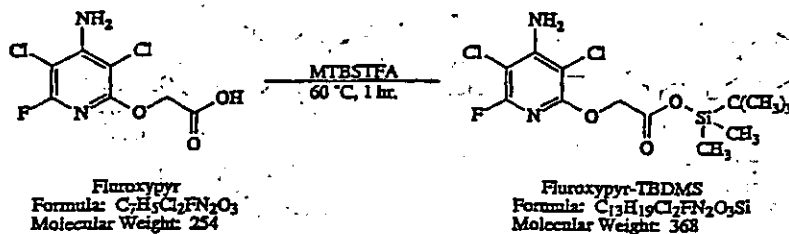
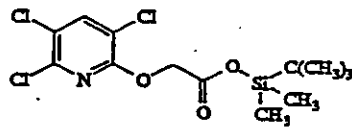
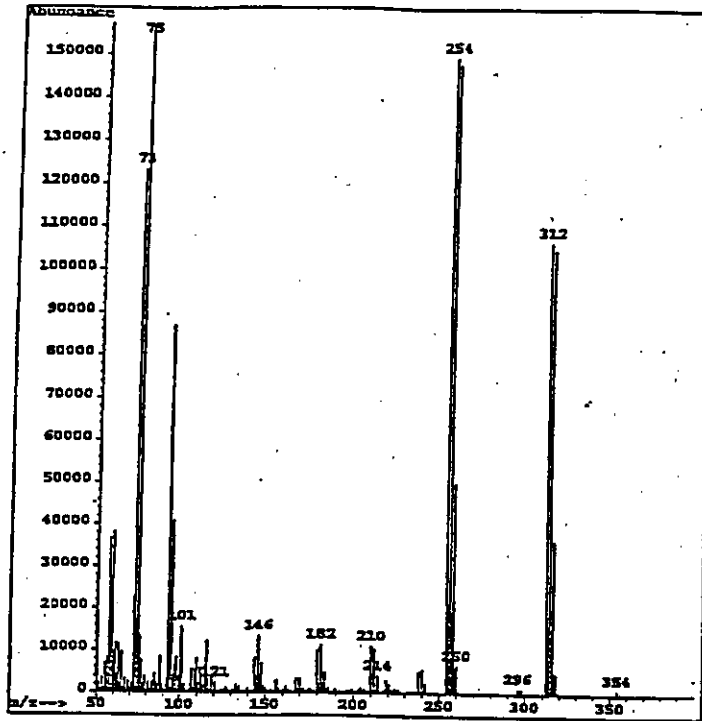


Figure 2. Chemical Structures of Furoxypyr, 4-Amino-3,5-dichloro-6-fluoro-2-pyridinol and their TBDMS Derivatives, and 4-Amino-3,5-dichloro-6-fluoro-2-methoxy-pyridine



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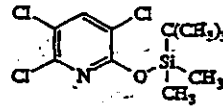
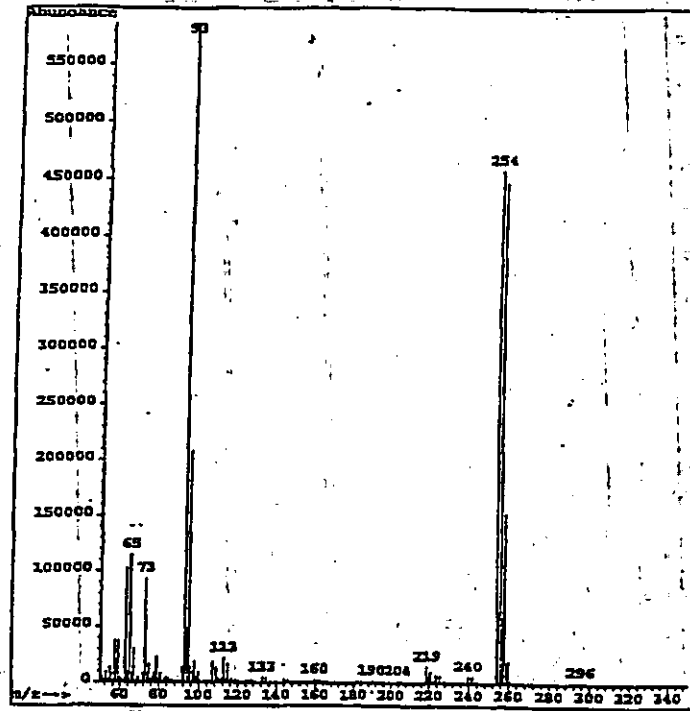
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Triclopyr-TBDMS  
Formula: C<sub>13</sub>H<sub>18</sub>Cl<sub>3</sub>NO<sub>3</sub>Si  
Molecular Weight: 369

Figure 3. Mass Spectrum of the TBDMS Derivative of Triclopyr.

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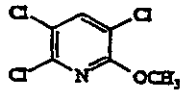
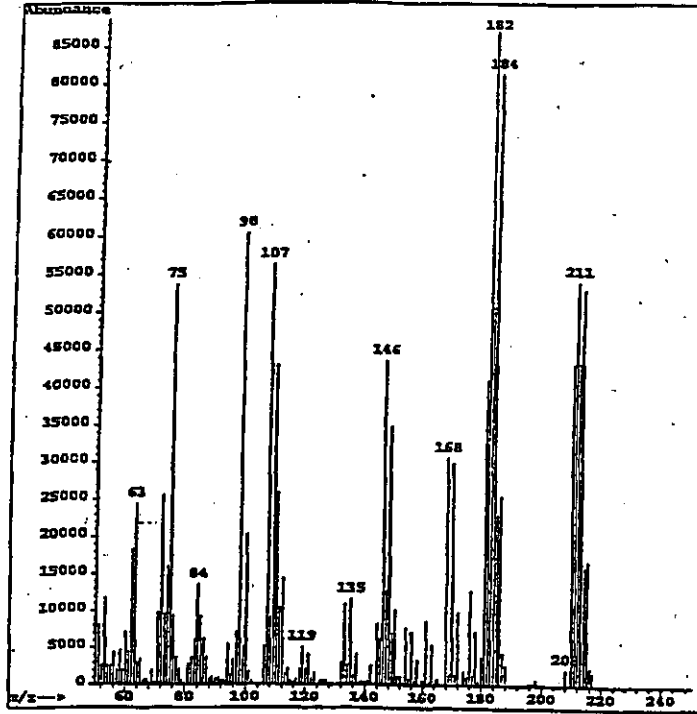


3,5,6-TCP-TBDMS  
Formula: C<sub>11</sub>H<sub>16</sub>Cl<sub>3</sub>NO<sub>2</sub>  
Molecular Weight: 311

Figure 4. Mass Spectrum of the TBDMS Derivative of 3,5,6-Trichloro-2-pyridinol

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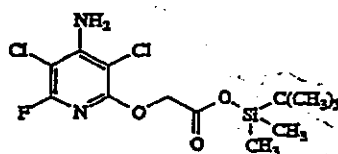
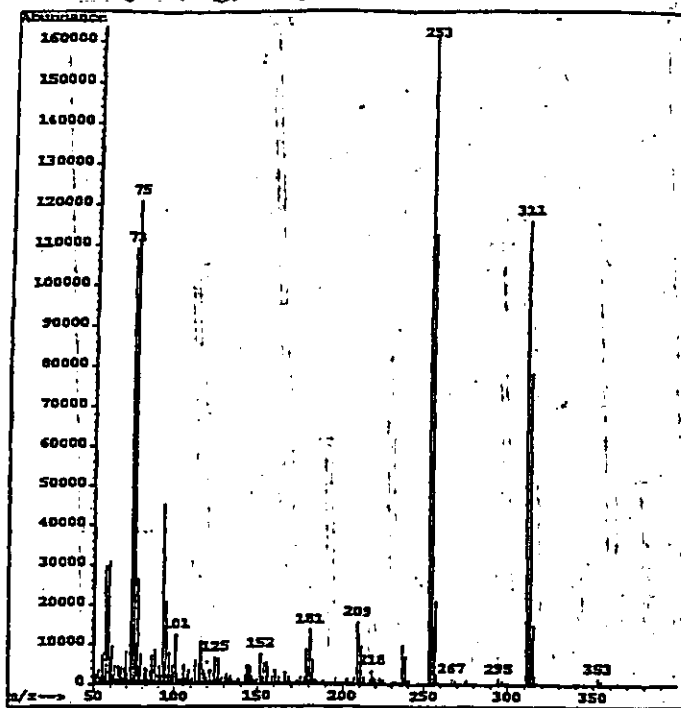


2-MP  
Formula:  $C_6H_4Cl_3NO$   
Molecular Weight: 211

Figure 5. Mass Spectrum of 2-Methoxy-3,5,6-trichloropyridine

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CRM 93.18

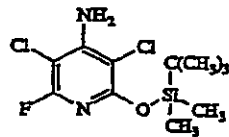
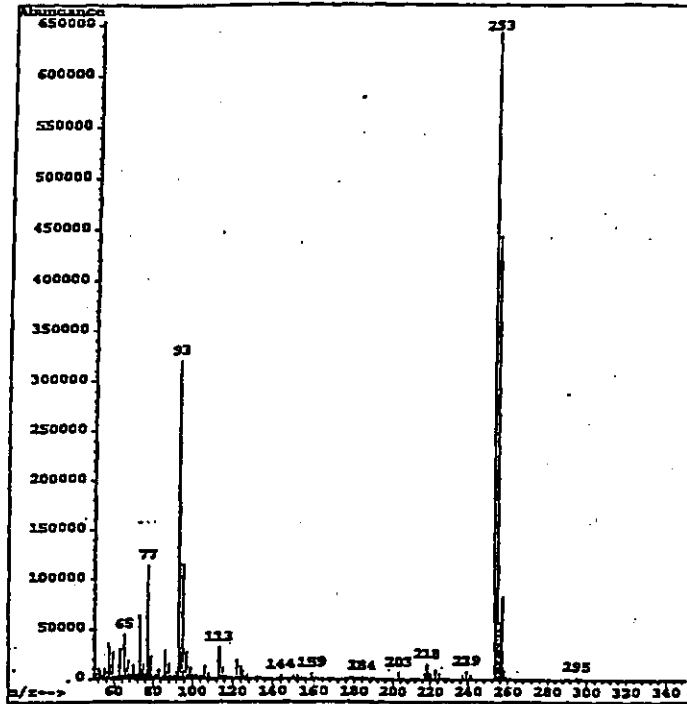


Fluroxypyr-TBDMS  
Formula: C<sub>15</sub>H<sub>19</sub>Cl<sub>2</sub>FN<sub>2</sub>O<sub>3</sub>Si  
Molecular Weight: 368

Figure 6. Mass Spectrum of the TBDMS Derivative of Fluroxypyr

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GRM95.1E

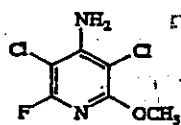
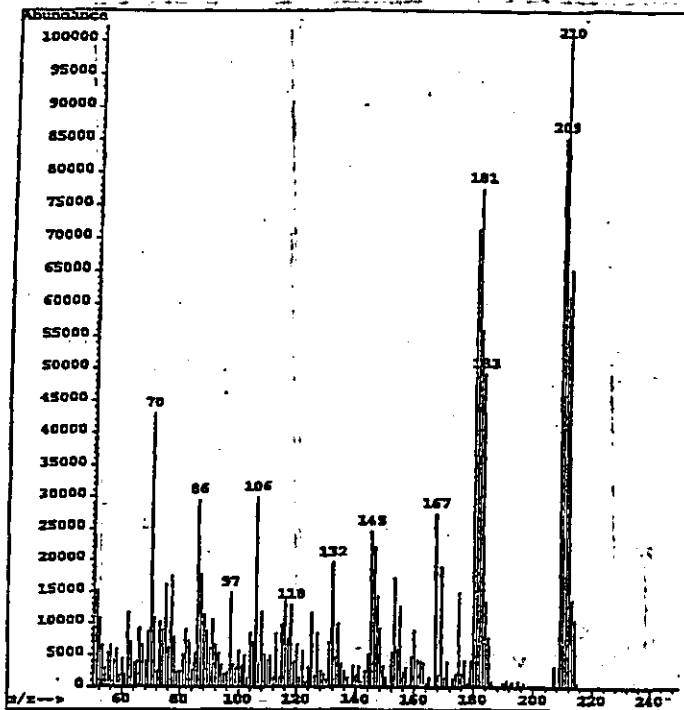


Fluroxypyr-DCP-TBDMS  
Formula:  $C_{11}H_{17}Cl_2FN_2OSi$   
Molecular Weight: 310

Figure 7. Mass Spectrum of the TBDMS Derivative of 4-Amino-3,5-dichloro-6-fluoro-2-pyridinol

Effective Date: April 11, 1996

GRM95.11

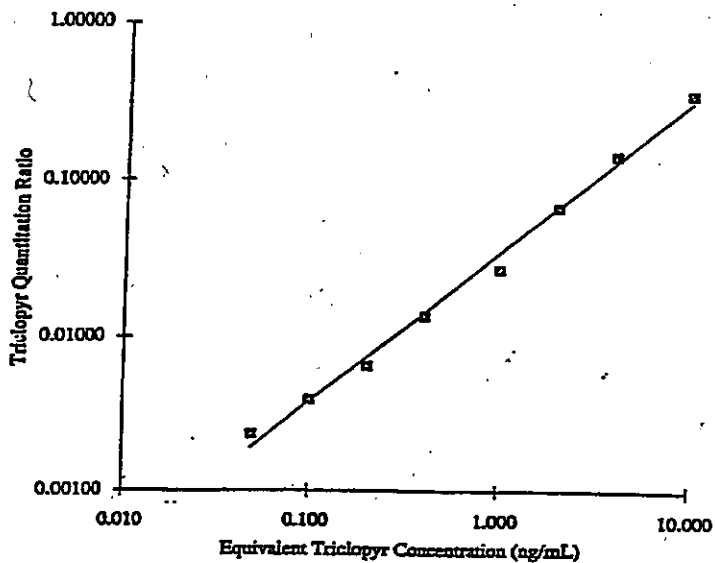


Floxyppy-MP  
Formula:  $C_8H_5Cl_2FN_2O$   
Molecular Weight: 210

Figure 8. Mass Spectrum of 4-Amino-3,5-dichloro-6-fluoro-2-methoxypyridine

Effective Date: April 11, 1996

GRM 95.18

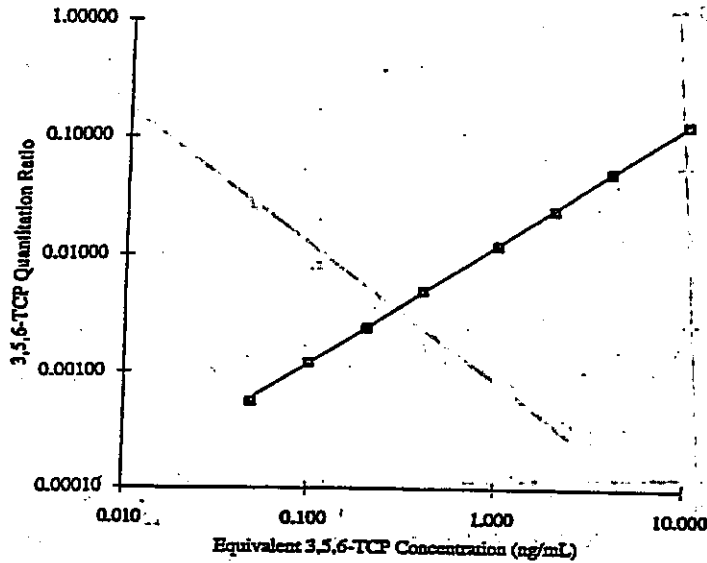


Triclopyr Concentration ng/mL	Equivalent Sample Conc. ug/mL	Average Triclopyr Quantitation Ratio m/z 312 / m/z 311
1.25	0.050	0.00234
2.50	0.100	0.00391
5.00	0.200	0.00645
10.00	0.400	0.01358
25.0	1.00	0.02709
50.0	2.00	0.06704
100.0	4.00	0.14451
250.0	10.0	0.35402

Power Regression Equation:  $X = (Y/0.03458)^{(1/0.96175)}$   
 Coefficient of Determination (r<sup>2</sup>): 0.9938

Figure 9. Typical Calibration Curve for the Determination of Triclopyr in Water

Effective Date: April 11, 1996



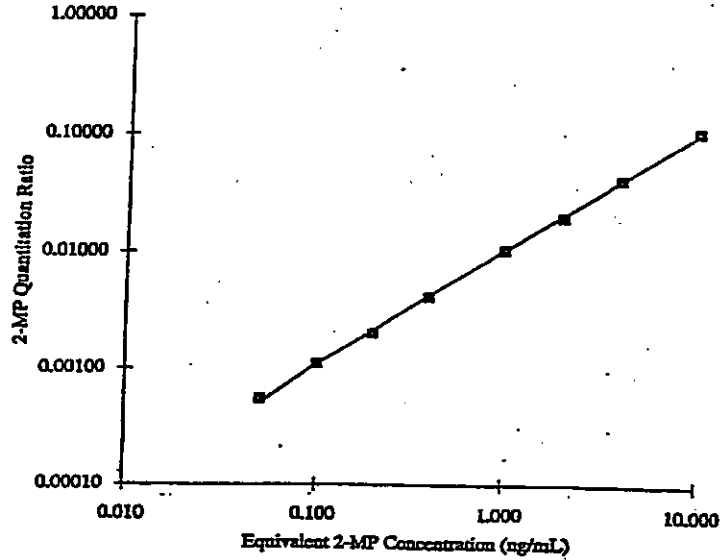
3,5,6-TCP Concentration ng/mL	Equivalent Sample Conc. ng/mL	Average 3,5,6-TCP Quantitation Ratio m/z 254 / m/z 253
1.25	0.050	0.00056
2.50	0.100	0.00122
5.00	0.200	0.00242
10.00	0.400	0.00497
25.0	1.00	0.01224
50.0	2.00	0.02486
100.0	4.00	0.05209
250.0	10.0	0.13475

Power Regression Equation:  $X = (Y/0.01251)^{1/1.02639}$   
 Coefficient of Determination ( $r^2$ ): 0.9998

Figure 10. Typical Calibration Curve for the Determination of 3,5,6-Trichloro-2-pyridinol in Water



Effective Date: April 11, 1996



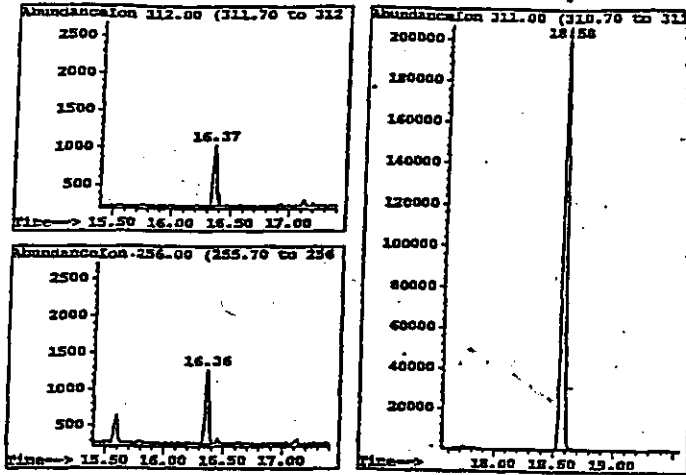
2-MP Concentration ng/mL	Equivalent Serum Conc. ng/mL	Average 2-MP Quantitation Ratio m/z 211 / m/z 210
1.25	0.050	0.00055
2.50	0.100	0.00110
5.00	0.200	0.00201
10.00	0.400	0.00416
25.0	1.00	0.01068
50.0	2.00	0.02057
100.0	4.00	0.04329
250.0	10.0	0.11176

Power Regression Equation:  $X = (Y/0.01069)^{(1/1.00214)}$   
 Coefficient of Determination (r<sup>2</sup>): 0.9996

Figure 11. Typical Calibration Curve for the Determination of 2-Methoxy-3,5,6-trichloropyridine in Water

Effective Date: April 11, 1996

GRM 95.18



Data File : 0601006.D  
ALS Bottle : 6  
Data : 24 Jan 95 10:26 PM  
Data Path : D:\SPC\MSDC\1\DATA\0012493A.MXD  
Instrument : GC/MSD S/N 3040AG1403  
Sample Name: Triclopyr Standard - 0.00250 ng/ul - A  
Sample Info: Equivalent to 00.10 ng/ml in water  
Operator : Edward L. Gilberding

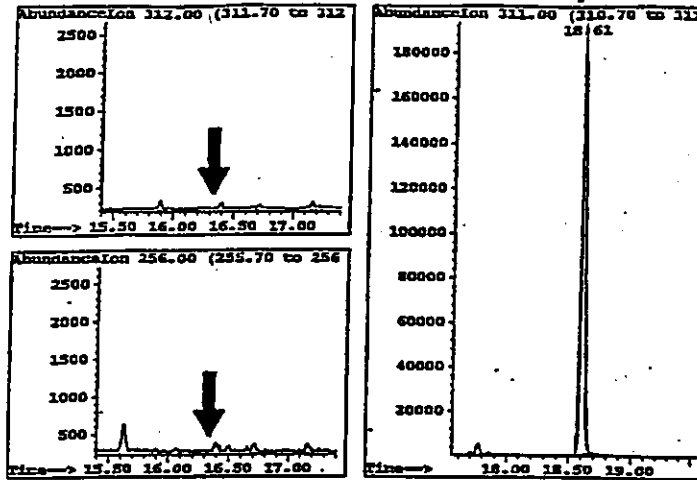
INTERNAL STANDARD RETENTION TIME:	18.57
PEAK AREA (M/Z 311)	475879
TRICLOPYR RETENTION TIME :	16.37
PEAK AREA (M/Z 312)	1746
PEAK AREA (M/Z 256)	2289
TRICLOPYR CONFIRMATION	
RATIO OF M/Z 256/312	1.2938
TRICLOPYR QUANTITATION	
RATIO OF M/Z 312/311	0.0037

Equivalent Triclopyr Concentration: 0.100 ng/mL

Average Confirmation Ratio: 1.3679

Figure 12. Typical Chromatogram of a 2.50-ng/mL Standard Equivalent to 0.100 ng/mL of Triclopyr in Water

Effective Date: April 11, 1996



Data File : 1901019.D  
ALS Bottle : 15  
Data : 25 Jan 95 8:16 am  
Data Path : D:\EPCHEMPC\1\DATA\AQ12495A.ELO\  
Instrument : GC/MSD S/E 3040A01403  
Sample Name: SW14390104 - Control - B  
Sample Info: Sample 044 - Domestic Well - Arkansas  
Operator : Edward L. Olberding

INTERNAL STANDARD RETENTION TIME: 18.61  
PEAK AREA (M/Z 311) : 453395

NO TRICLOPYR FOUND

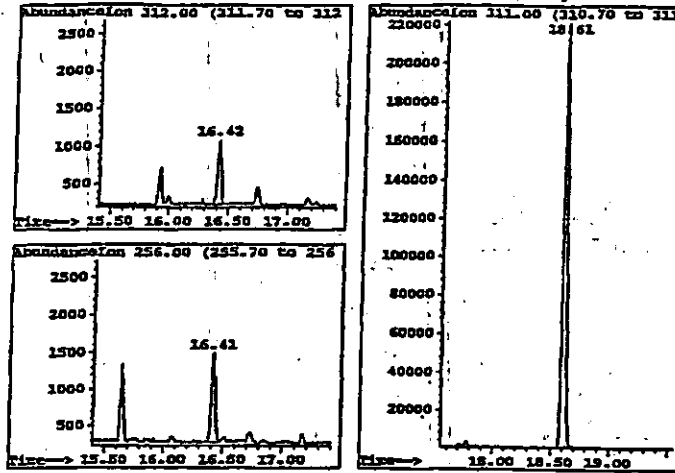
Triclopyr Concentration: 0.000 ng/mL

Average Confirmation Ratio: 1.3579

Figure 13. Typical Chromatogram of a Control Water Sample Containing No Detectable Residue of Triclopyr

3

Effective Date: April 11, 1996



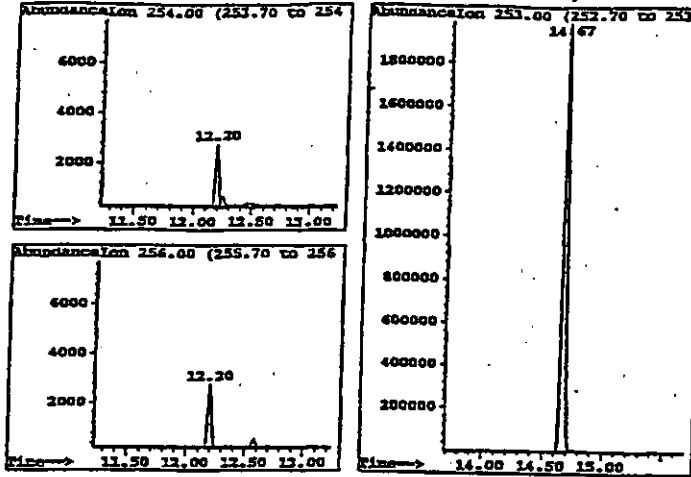
Data File : 3601036.D  
 ALS Bottle : 16  
 Data : 25 Jan 95 3:29 pm  
 Data Path : D:\HPCHEMPC\1\DATA\80124951.ELO\  
 Instrument : GC/HSD S/N 3040A01A05  
 Sample Name: S814390104 - Spiked w/ 08.10 ug/mL - B  
 Sample Info: Sample 059 - Domestic Well - Arkansas  
 Operator : Edward L. Gilberding

INTERNAL STANDARD DETECTION TIME:	18.61
PEAK AREA (M/Z 311)	497048
TRICLOPYR DETECTION TIME:	16.42
PEAK AREA (M/Z 312)	1980
PEAK AREA (M/Z 256)	2713
TRICLOPYR CONFIRMATION	
RATIO OF M/Z 256/312	1.3944
TRICLOPYR QUANTIFICATION	
RATIO OF M/Z 312/311	0.0039

Triclopyr Concentration: 0.104 ng/mL  
 Recovery: 104%  
 Average Confirmation Ratio: 1.3679

Figure 14. Typical Chromatogram of a Control Water Sample Fortified with 0.100 ng/mL of Triclopyr

Effective Date: April 11, 1996



Data File : 0601006.D  
 ALS Bottle : 6--  
 Date : 24 Jan 95 10:26 pm  
 Data Path : G:\BIOCHEM\1\DATA\A012492A.E20\  
 Instrument : GC/MSD S/N 3040A01405

Sample Name: Triclopyr Standard - 0.00250 ng/ul - A  
 Sample Info: Equivalent to 00.10 ng/mL in water  
 Operator : Edward L. Glibarding

INTERNAL STANDARD RETENTION TIME:	14.67
PEAK AREA (M/Z 253)	: 4409589
3,5,6-TCP RETENTION TIME	: 12.30
PEAK AREA (M/Z 254)	: 5194
PEAK AREA (M/Z 256)	: 5191
3,5,6-TCP CONFIRMATION	
RATIO OF M/Z 256/254	: 0.9994
3,5,6-TCP QUANTIFICATION	
RATIO OF M/Z 254/253	: 0.0012

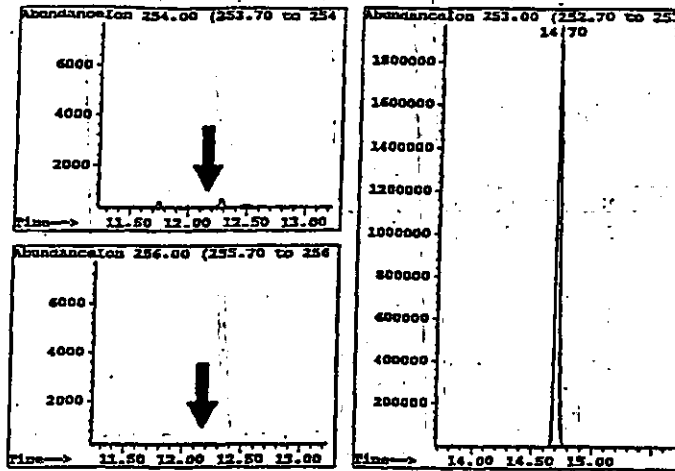
Equivalent 3,5,6-TCP Concentration: 0.100 ng/mL

Average Confirmation Ratio: 1.0093

Figure 15. Typical Chromatogram of a 2.50-ng/mL Standard Equivalent to 0.100 ng/mL of 3,5,6-TCP in Water

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Data File : 1901019.D  
ALS Bottle : 19--  
Data : 25 Jan 95 8:16 am  
Data Path : D:\BPCHEMPC\1\DATA\AQ12492A.FLO\  
Instrument : GC/MSD S/N 3040A01405

Sample Name: SW14390104 - Control - B  
Sample Info: Sample 044 - Domestic Well - Arkansas  
Operator : Edward L. Gilberting

INTERNAL STANDARD RETENTION TIME: 14.70  
PEAK AREA (M/Z 253) : 4560871

NO 3,5,6-TCP FOUND

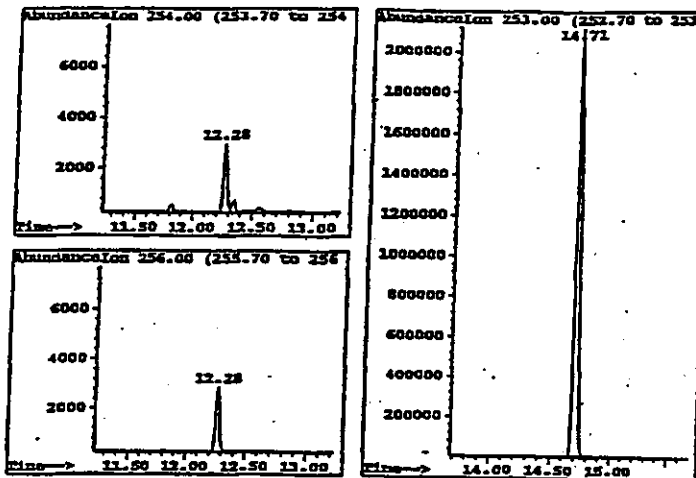
3,5,6-TCP Concentration: 0.000 ng/mL

Average Confirmation Ratio: 1.0093

Figure 16. Typical Chromatogram of a Control Water Sample Containing No Detectable Residue of 3,5,6-TCP

Effective Date: April 11, 1996

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Data File : 3601036.D  
 ALS Bottle : 36...  
 Date : 25 Jan 95 3:29 pm  
 Data Path : D:\HPCHEMPC\1\DATA\00124951.X20\  
 Instrument : GC/MSD S/N 304001405  
 Sample Name: S14390104 - Spiked at 00.10 ng/mL - B  
 Sample Info: Sample 029 - Domestic Well - Arkansas  
 Operator : Edward L. Gilberding

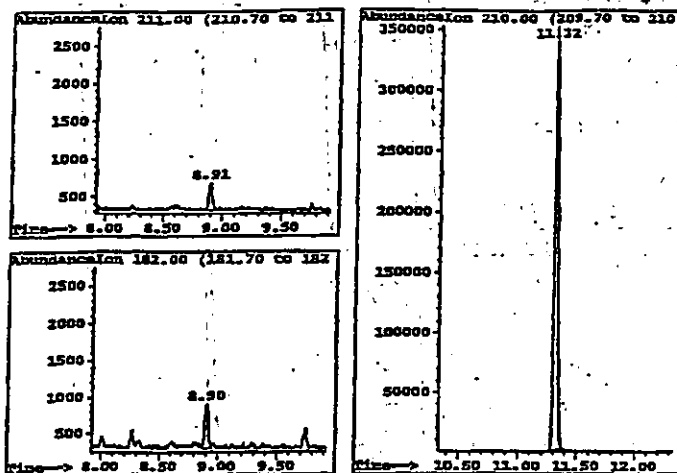
INTERNAL STANDARD RETENTION TIME:	14.72
PEAK AREA (M/Z 253)	: 4914885
3,5,6-TCP RETENTION TIME	: 12.28
PEAK AREA (M/Z 254)	: 3915
PEAK AREA (M/Z 256)	: 3923
3,5,6-TCP CONFIRMATION	
RATIO OF M/Z 256/254	: 1.0014
3,5,6-TCP QUANTIFICATION	
RATIO OF M/Z 254/253	: 0.0012

3,5,6-TCP Concentration: 0.102 ng/mL  
 Recovery: 102%  
 Average Confirmation Ratio: 1.0093

Figure 17. Typical Chromatogram of a Control Water Sample Fortified with 0.100 ng/mL of 3,5,6-TCP

Effective Date: April 11, 1996

GRM9518



Data File : 0601006.D  
 ALS Bottle : 6  
 Data : 24 Jan 95 10:26 PM  
 Data Path : D:\HPCHEMPC\1\DATA\A012498A.MZD\  
 Instrument : GC/MSD S/N 1040A01403

Sample Name: Triclopyr Standard - 0.00250 ng/mL - A  
 Sample Info: Equivalent to 00.10 ng/mL in water  
 Operator : Edward L. Gilberding

INTERNAL STANDARD RETENTION TIME:	11.12	
PEAK AREA (M/Z 210)	746377	
3,5,6-MP RETENTION TIME	8.91	
PEAK AREA (M/Z 211)	809	
PEAK AREA (M/Z 182)	1271	
3,5,6-MP CONFIRMATION RATIO OF M/Z 182/211	1.5711	
3,5,6-MP QUANTIFICATION RATIO OF M/Z 211/210	0.0011	

Equivalent 2-MP Concentration: 0.100 ng/mL

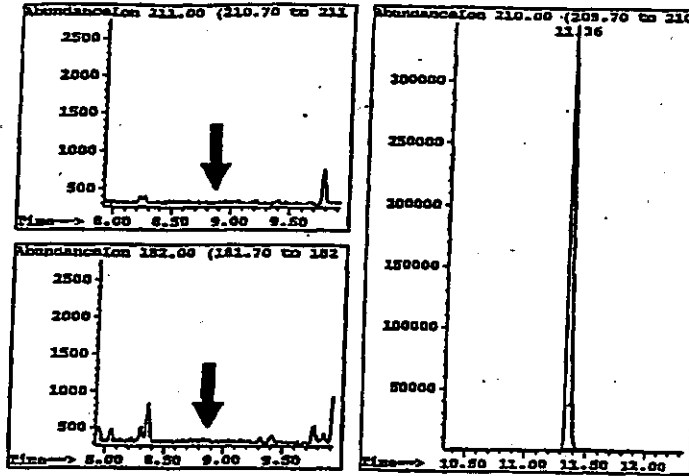
Average Confirmation Ratio: 1.5911

Figure 18. Typical Chromatogram of a 2.50-ng/mL Standard Equivalent to 0.100 ng/mL of 2-MP in Water



Effective Date: April 11, 1996

GRM 95.12



Data File : 1901019.D  
ALS Bottle : 19  
Date : 25 Jan 95 5:16 am  
Data Path : D:\NFCHEMPC\1\DATA\A012495A.Z\O\  
Instrument : GC/MSD S/N 3040AG1403  
Sample Name: 2814390104 - Control - R  
Sample Info: Sample 044 - Domestic Well - Arkansas  
Operator : Edward L. Gilberding

INTERNAL STANDARD RETENTION TIME: 11.36  
PEAK AREA (R/Z 210) : 738071

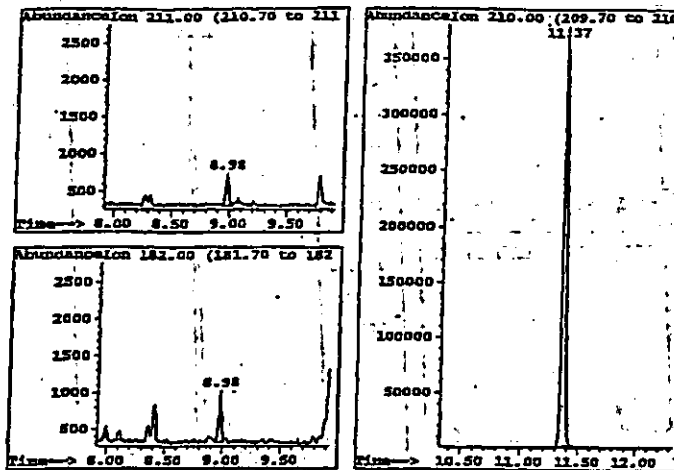
NO 1,5,6-MP FOUND

2-MP Concentration: 0.000 ng/mL

Average Confirmation Ratio: 1.5911

Figure 19. Typical Chromatogram of a Control Water Sample Containing No Detectable Residue of 2-MP

Effective Date: April 11, 1996



Data File : 360206.D  
 ALS Bottle : 36  
 Data : 25 Jan 95 3:29 PM  
 Data Path : D:\HPCHEMPC\11\DATA\A012495A.ELO\  
 Instrument : GC/MSD S/W 3040A01405

Sample Name: SML4390104 - Spiked at 00.10 ug/mL - B  
 Sample Infor: Sample 039 - Domestic Well - Arkansas  
 Operator : Edward L. Gilberding

INTERNAL STANDARD RETENTION TIME:	11.37
PEAK AREA (M/Z 210)	616613
3,5,6-MP RETENTION TIME	8.98
PEAK AREA (M/Z 211)	817
PEAK AREA (M/Z 182)	1238
3,5,6-MP CONFIRMATION	
RATIO OF M/Z 182/211	1.5153
3,5,6-MP QUANTITATION	
RATIO OF M/Z 211/210	0.0010

2-MP Concentration: 0.094 ug/mL  
 Recovery: 94%  
 Average Confirmation Ratio: 1.5911

Figure 20. Typical Chromatogram of a Control Water Sample Fortified with 0.100 ug/mL of 2-MP