DowElanco
9330 Zionsville Road
Indianapolis, IN 46268-1054

GRM: 95.18
EFFECTIVE: April 11, 1996
SUPERSEDES: ACR 76.08, ACR 84.03

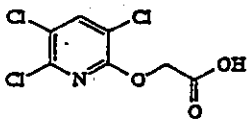
DowElanco

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

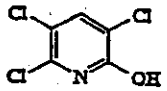
E. L. Olberding
North American Environmental Chemistry Laboratory
DowElanco
Indianapolis, Indiana 46268-1053

A. Scope

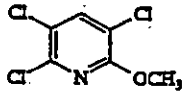
This method is applicable for the quantitative determination of residues of triclopyr ((3,5,6-trichloro-2-pyridinyl)oxy)acetic acid) and its metabolites, 3,5,6-trichloro-2-pyridinol (3,5,6-TCP), and 2-methoxy-3,5,6-trichloropyridine (2-MP) in water over the concentration range 0.10-10.0 ng/mL with a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

Copy of Original
Date: 10-17-97
Initial: CLH

21

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.

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-µm 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-µL, Model 702N, Hamilton Company, Reno, NV 89520.
18. Syringe, 50-µL, Model 705N, Hamilton Company.
19. Syringe, 100-µL, Model 710N, Hamilton Company.
20. Syringe, 250-µL, Model 725N, Hamilton Company.
21. Syringe, 500-µL, 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 60958A-11, Kimble/Kontes.

25. Vial cap, for autosampler vial, catalog number C4000-54B, 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 AX0142-1, 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-pyridinyl)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-µg/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-µg/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-µg/mL stock solution.

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.	Final Soln. Volume	Spiking Soln. Final Conc.	Equivalent Sample Conc.[a]
µL	mL	ng/mL	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

[a] 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.-o. The concentration range of these calibration standards is from 1.25-250 ng/mL.

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

2. Preparation of Internal Standard Solution

a. Weigh 0.1000 g of fluroxypyr 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 fluroxypyr, fluroxypyr-DCP, and fluroxypyr-MP are shown in Figure 2.

23

H. 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 5 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-µm 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	260 °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 µL
Detector:	electron impact selected ion monitoring
Calibration Program	maximum sensitivity autotune (Note L.4.)
Electron Multiplier	1775 volts (= 280 volts above autotune)

Ions Monitored:

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

L. 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-µL aliquots of the appropriate spiking solutions (Section G.1.a.) to obtain concentrations ranging from 0.10 to 10.0 ng/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 L.5.)

24

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 I.1.h. with the 1-chlorobutane extract from Step I.1.f. and mix thoroughly. (Note I.5.)

j. Concentrate the solution from Step I.1.i. to less than 0.8 mL (but not to dryness) using an N-Evap evaporator. (Note I.2.)

k. Add 100 µL of the internal standard solution (Section G.2.a.) and 100 µL 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-ng/mL calibration standard (equivalent to 0.10 ng/mL in water samples).

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

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

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

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

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

Confirmation of the presence of the analyte is indicated when the confirmation ratio for the sample is within the range of ±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:

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

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

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

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

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:

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

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

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

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.e.

4. For those analytes 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.e.

   b. Determine the corrected analyte concentrations in the water sample as follows:

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

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

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

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 I.1.f.

b. Step I.1.i.

c. Step I.1.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".

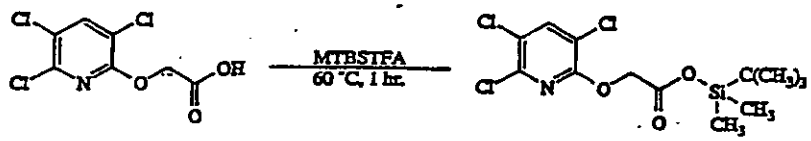
5. In transferring the 1-chlorobutane layer, it is important not to remove any water from the lower layer. Contaminating the 1-chlorobutane with water will have deleterious effects on the derivatization and subsequent GC/MSD analysis.

M. References

1. *HP-41C/41CV Standard Applications Handbook*, Hewlett-Packard Publication No. 00041-90402, 1982, pp 42-48.

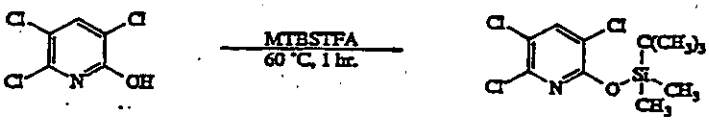
2. Keith, L. H.; Crummett, W.; Deegan, J.; Libby, R. A.; Taylor, J. K.; Wentler, G. *Anal. Chem.*, 1983, *55*, 2210-2218.

27



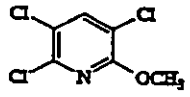
Triclopyr
Formula: $C_7H_4Cl_3NO_3$
Molecular Weight: 255

Triclopyr-TBDMS
Formula: $C_{13}H_{18}Cl_3NO_3Si$
Molecular Weight: 369



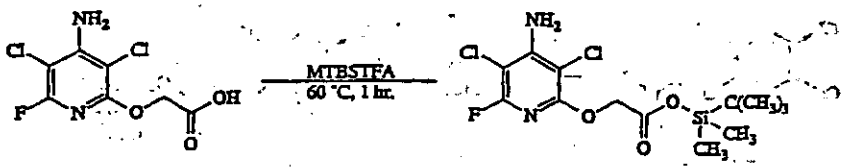
3,5,6-TCP
Formula: $C_5H_2Cl_3NO$
Molecular Weight: 197

3,5,6-TCP-TBDMS
Formula: $C_{11}H_{16}Cl_3NOSi$
Molecular Weight: 311



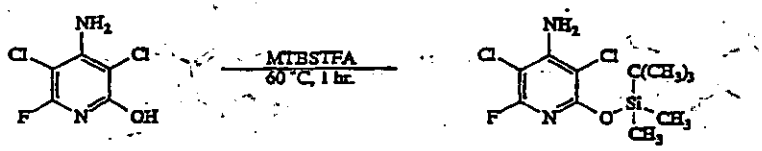
2-MP
Formula: $C_6H_4Cl_3NO$
Molecular Weight: 211

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



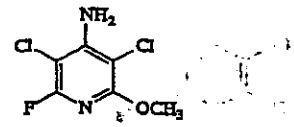
Fluroxypyr
Formula: $C_7H_5Cl_2FN_2O_3$
Molecular Weight: 254

Fluroxypyr-TBDMS
Formula: $C_{13}H_{19}Cl_2FN_2O_3Si$
Molecular Weight: 368



Fluroxypyr-DCP
Formula: $C_5H_3Cl_2FN_2O$
Molecular Weight: 196

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



Fluroxypyr-MP
Formula: $C_6H_5Cl_2FN_2O$
Molecular Weight: 210

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