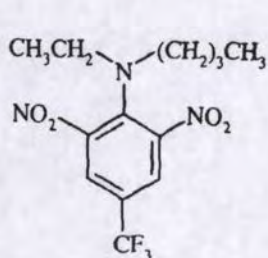


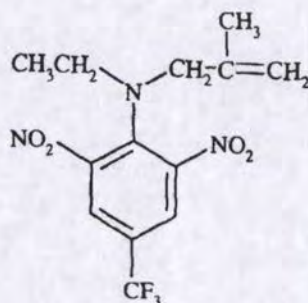
## INTRODUCTION

Benfluralin, ethalfluralin, and trifluralin are members of the cell division inhibitor class of herbicides. The mode of action is that of a selective soil herbicide, which acts as an inhibitor of various physiological growth processes (1).



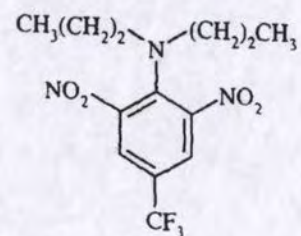
Benfluralin

CAS Number 1861-40-1



Ethalfluralin

CAS Number 55283-68-6



Trifluralin

CAS Number 1582-09-8

Common and chemical names, the molecular formulas, and the nominal masses for the above structures are given in Table 1 of method GRM 07.07 (Appendix A).

This study was conducted to fulfill the data requirements outlined in the U.S. EPA Residue Chemistry Test Guidelines, OPPTS 850.7100 (2), the European Commission Guidance Document on Residue Analytical Methods, SANCO/3029/99 rev.4 (3) and SANCO/825/00 rev.7 (4), and the PMRA Residue Chemistry Guidelines Dir98-02 (5).

Method GRM 07.07 is suitable for post-registration monitoring of residues of benfluralin, ethalfluralin, and trifluralin in soil by gas chromatography with electron impact mass spectrometry detection (6). The purpose of this study was to provide validation data to define the accuracy, precision, specificity, and ruggedness of the method.

## EXPERIMENTAL

### Sample Origin, Numbering, Preparation and Storage

Untreated control soil samples were obtained from the Dow AgroSciences LLC Control Soil Database. Soil characterization data for the soil samples used in the validation study are given in the table below.

Sample Number	(USDA textural classification)	pH	% Organic Carbon
M641	Soil (Silt Loam)	6.2	1.0
M649	Soil (Clay Loam)	7.6	2.9

Upon receipt at Dow AgroSciences LLC, unique sample numbers were assigned to the soil samples to track them during receipt, storage, and analysis. The samples were stored under ambient conditions on arrival from the field sites and sieved through a 2-mm sieve. Soil samples were stored in polyethylene bags under refrigerated conditions (<10 °C). Aliquots of the above soil samples were then acquired for the validation study. Soil samples were stored in airtight metal cans in temperature-monitored freezers (<-10 °C), except when removed for analysis.

### Test Substance/Analytical Standard

The test substances and analytical standards used for this validation study were:

Test Substance/ Analytical Standard	TSN Number	Percent Purity	Certification Date	Reference
Benfluralin	TSN 100015	99.9	03-Mar-2004	04-425-L
Ethalfuralin	TSN 101281	99.8	20-Jan-05	FA&PC 043413
Trifluralin	TSN100244	99.4	17-Aug-2006	FAPC 063340

### Preparation of Spiking Solutions and Calibration Standards

The benfluralin, ethalfluralin, and trifluralin spiking solutions and calibration standards were originally prepared as described in Dow AgroSciences LLC Laboratory Notebook E2357, p 61. The preparation of the applicable solutions for the validation study are cross-referenced to Section 7 of Method GRM 07.07.

### Fortification of Recovery Samples

The soil samples were fortified as described in Dow AgroSciences LLC Laboratory Notebook C2197, p3, which is cross-referenced to Section 9 of method GRM 07.07.

On the day of analysis, untreated soil samples were freshly fortified with benfluralin, ethalfluralin, and trifluralin over the concentration range of 0.010-2.00  $\mu\text{g/g}$  for the generation of method validation recovery data. Reagent blank and untreated control samples—those that received no fortification—were also prepared for analysis along with the recovery samples to check for the presence of any background interferences. Additional untreated soil samples were also fortified at 0.003  $\mu\text{g/g}$  to demonstrate the method limit of detection.

### Sample Extraction and Analysis

The soil samples were extracted and analyzed as described in Dow AgroSciences LLC Laboratory Notebook C2197, p3, which are cross-referenced to Section 9 of method GRM 07.07.

Residues of benfluralin, ethalfluralin, and trifluralin were extracted from a 10-gram soil sample by shaking for 30 minutes with 20 mL of an acetonitrile/water (99:1) solution. The sample was centrifuged and 5 mL of the extraction solution was transferred to a clean 30 mL vial. The sample was diluted by adding 10 mL of water and then thoroughly mixed. The sample was then

purified using a 300-mg multi mode solid (C18, SAX, SCX) phase extraction cartridge. The analytes were eluted with hexane and diluted to 5 mL with hexane containing 0.5 g/L peanut oil.

The sample was then analyzed by gas chromatography with electron impact tandem mass spectrometry. Chromatographic analysis was performed using a J&W Scientific DB-5, 30 m x 0.25 mm, 0.25- $\mu$ m column coupled to an HP 5973N mass spectrometer system as described in Section 8 of method GRM 07.07.

All analyses were performed at the Dow AgroSciences LLC Regulatory Laboratories in Indianapolis, Indiana.

#### Calculation of Percent Recovery

The calculation of percent recovery for fortified samples was performed as described in Section 10.2 of method GRM 07.07.

#### Statistical Treatment of Data

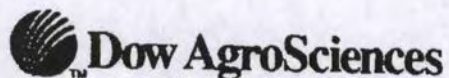
Statistical treatment of data for method GRM 07.07 included the calculation of the power regression equations, the coefficients of determination ( $r^2$ ) describing the linearity of the calibration curves, the calculation of the means, standard deviations, and the relative standard deviations of the results from the fortified recovery samples.

#### Study Personnel

The following personnel were involved with various aspects of validation of Study Number 071040: E. L. Olberding, M. J. Hastings and G. E. Dial, Jr..

APPENDIX A—Dow AgroSciences LLC Method GRM 07.07

GRM: 07.07  
EFFECTIVE: 11-May-2007  
SUPERSEDES: New

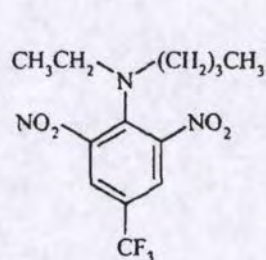


Determination of Residues of Benfluralin, Ethalfluralin, and Trifluralin in Soil  
by Gas Chromatography with Electron-Impact Mass Spectrometry Detection

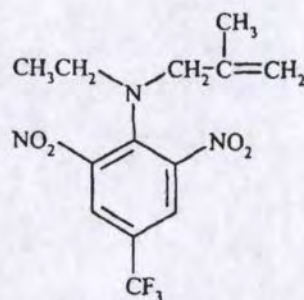
G. E. Dial, Jr.

1. SCOPE

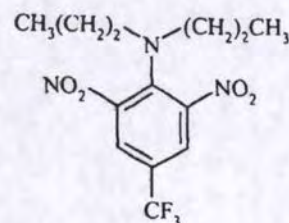
This method is applicable for the quantitative determination of residues of benfluralin, ethalfluralin, and trifluralin in soil. The method was validated over the concentration range of 0.010-2.0  $\mu\text{g/g}$  with a validated limit of quantitation of 0.010  $\mu\text{g/g}$ .



Benfluralin  
CAS Number 1861-40-1



Ethalfluralin  
CAS Number 55283-68-6



Trifluralin  
CAS Number 1582-09-8

Common and chemical names, the molecular formula, and the nominal mass for the above structure are given in Table 1.

2. PRINCIPLE

Residues of benfluralin, ethalfluralin, and trifluralin are extracted from a 10-gram soil sample by shaking for 30 minutes with 20 mL of an acetonitrile/water (99:1) solution. The sample is centrifuged and an aliquot of the extraction solution is diluted with water. The diluted extraction solution is then purified with a multi-mode solid phase extraction cartridge. The compounds are eluted with hexane. The sample is then analyzed by gas chromatography with electron-impact mass spectrometry (GC/MS).

3. SAFETY PRECAUTIONS

- 3.1. 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 Dow AgroSciences LLC 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.
- 3.2. Acetonitrile, methanol and hexane are flammable and should be used in well-ventilated areas away from ignition sources.
- 3.3. Acetonitrile, methanol, and hexane are toxic and may be harmful or fatal if inhaled or absorbed. It is imperative that proper eye and personal protection equipment be worn when handling these reagents.

4. EQUIPMENT (Note 12.1.)

4.1. Laboratory Equipment

- 4.1.1. Balance, analytical, Model AE100, Mettler-Toledo Inc., Columbus, OH 43240.
- 4.1.2. Balance, pan, Model BasBal, Mettler-Toledo Inc.
- 4.1.3. Centrifuge, with rotor to accommodate 4-oz jars, Model CU-5000, International Equipment Company, Needham Heights, MA 02194.
- 4.1.4. Evaporator, N-Evap, Organomation Associates, Inc., Berlin, MA 01503.
- 4.1.5. Hammer mill, with 1/8-inch screen, Model 2001, AGVISE Laboratories, Inc., Northwood, ND 58267.
- 4.1.6. Pipet, positive-displacement, 10  $\mu$ L capacity, catalog number M10, Gilson Inc., Middleton, WI 53562.
- 4.1.7. Pipet, positive-displacement, 50  $\mu$ L capacity, catalog number M50, Gilson Inc.
- 4.1.8. Pipet, positive-displacement, 100  $\mu$ L capacity, catalog number M100, Gilson Inc.
- 4.1.9. Pipet, positive-displacement, 1000  $\mu$ L capacity, catalog number M1000, Gilson Inc.
- 4.1.10. Shaker, variable speed reciprocating with box carrier, Model 6000, Eberbach Corporation, Ann Arbor, MI 48106.
- 4.1.11. Ultrasonic cleaner, Model 1200, Branson Cleaning Equipment Company, Shelton, CT

06484.

4.1.12. Vortex mixer, Model G-560, Scientific Industries Inc., Bohemia, NY 11716.

4.2. Chromatographic System

4.2.1. Column, analytical, DB-5, 30 m x 0.25 mm x 0.25  $\mu$ m, catalog number 122-5032, J&W Scientific, Folsom, CA 95630.

4.2.2. HP 6890 Series Injector, Agilent Technologies, Wilmington, DE 19808

4.2.3. HP 6890 Series GC System, Agilent Technologies.

4.2.4. Mass spectrometer, Model 5973N, Agilent Technologies, Palo Alto, CA 94304

4.2.5. Mass spectrometer data system, Enhanced ChemStation, Agilent Technologies, Santa Clara, CA 95051

5. GLASSWARE AND MATERIALS (Note 12.1.)

5.1. Cylinder, graduated mixing, 50-mL capacity, catalog number 3002-50, Corning Inc., Acton, MA 01720.

5.2. Cylinder, graduated mixing, 500-mL capacity, catalog number 3002-500, Corning Inc.

5.3. Cylinder, graduated mixing, 2000-mL capacity, catalog number 3002-2L, Corning Inc.

5.4. Dish, aluminum weighing, catalog number 08-732, Fisher Scientific.

5.5. Flask, volumetric, 100-mL, catalog number 5640-100, Corning Inc.

5.6. Flask, volumetric, 200-mL, catalog number 5640-200, Corning Inc.

5.7. Pipet, serological, 2-mL, catalog number 7077-2N, Corning Inc.

5.8. Pipet, serological, 10-mL, catalog number 7077-10N, Corning Inc.

5.9. Pipet, serological, 25-mL, catalog number 7077B-25N, Corning Inc.

5.10. Pipet, volumetric, 1.0-mL, catalog number 13-650-3B, Fisher Scientific.

5.11. Pipet, volumetric, 2.0-mL, catalog number 13-650-3C, Fisher Scientific.



- 5.12. Pipet, volumetric, 10-mL, catalog number 13-650-3L, Fisher Scientific.
- 5.13. Pipet, volumetric, 20-mL, catalog number 13-650-3N, Fisher Scientific.
- 5.14. Pipet, volumetric, 30-mL, catalog number 13-650-3Q, Fisher Scientific.
- 5.15. Pipet, volumetric, 50-mL, catalog number 13-650-3S, Fisher Scientific.
- 5.16. Pipet tip, positive-displacement, 100- $\mu$ L capacity, catalog number CP100, Gilson Inc.
- 5.17. Pipet tip, positive-displacement, 1000- $\mu$ L capacity, catalog number CP1000, Gilson Inc.
- 5.18. Vial, autosampler, 2-mL, catalog number C4011-1W, National Scientific Company, Rockwood, TN 37854.
- 5.19. Vial, 8-mL, with PTFE-lined screw cap, catalog number 2503T, Qorpak, Bridgeville, PA 15017.
- 5.20. Vial, 22-mL, with PTFE-lined screw cap, catalog number 2506T, Qorpak.
- 5.21. Vial, 45-mL, catalog number 60958A-11, Kimble Glass Co., Vineland, NJ 08360.
- 5.22. Vial cap, PTFE-lined, for 45-mL vial, catalog number 5205, Qorpak.
- 5.23. Vial cap, for autosampler vial, catalog number C4011-1A, National Scientific Company.
6. REAGENTS, STANDARDS, AND PREPARED SOLUTIONS (Note 12.1.)
  - 6.1. Reagents
    - 6.1.1. Methanol-Anhydrous, ChromAR, catalog number 3041-10, Mallinckrodt Baker Inc., Phillipsburg, NJ 08865.
    - 6.1.2. Acetonitrile, ChromAR HPLC grade, catalog number 2856, Mallinckrodt Baker Inc.
    - 6.1.3. Hexane, OmniSolv grade, catalog number HX0296-1, EMD Chemicals Inc., Gibbstown, NJ 08027.
    - 6.1.4. Peanut Oil, cooking grade, Planters Company, East Hanover, NJ 07936.
    - 6.1.5. Water, OmniSolv grade, catalog number WX-0004-1, EMD Chemicals Inc.

6.2. Standards

6.2.1. Benfluralin, *N*-butyl-*N*-ethyl-2,6-dinitro-4-(trifluoromethyl)benzenamine.

6.2.2. Ethalfluralin, *N*-ethyl-*N*-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl)benzenamine

6.2.3. Trifluralin, 2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)benzenamine

Obtain from the Test Substance Coordinator, Dow AgroSciences LLC, 9330 Zionsville Road, Building 304, Indianapolis, IN 46268.

6.3. Prepared Solutions

6.3.1. hexane + peanut oil

Weigh approximately 0.5 g peanut oil into an 8-mL vial and quantitatively transfer to a 1000-mL graduated mixing cylinder with hexane. Dilute to volume with hexane.

6.3.2. acetonitrile/water (99:1)

Pour 980 mL of acetonitrile into a 1000-mL graduated mixing cylinder. Pipet 10 mL of water into the cylinder, swirl, and allow the solution to equilibrate to room temperature. Dilute to volume with acetonitrile.

7. PREPARATION OF STANDARDS

7.1. Preparation of Fortification Solutions

7.1.1. Individually weigh 0.1000 g of benfluralin, ethalfluralin, and trifluralin analytical standards and quantitatively transfer to separate 100-mL volumetric flasks with methanol. Dilute to volume with methanol to obtain 1000- $\mu\text{g}/\text{mL}$  stock solutions.

7.1.2. Pipet 10.0 mL of each of the 1000- $\mu\text{g}/\text{mL}$  solutions in Section 7.1.1 into a 100-mL volumetric flask and dilute to volume with methanol to obtain a 100.0- $\mu\text{g}/\text{mL}$  mixed stock solution.

7.1.3. Pipet 10.0 mL of the 100.0- $\mu\text{g}/\text{mL}$  solution in Section 7.1.2 into a 100-mL volumetric flask and dilute to volume with methanol to obtain a 10.0- $\mu\text{g}/\text{mL}$  fortification solution.

7.1.4. Pipet 10.0 mL of the 10.0- $\mu\text{g}/\text{mL}$  solution in Section 7.1.3 into a 100-mL volumetric flask and dilute to volume with methanol to obtain a 1.0- $\mu\text{g}/\text{mL}$  fortification solution.

7.2. Preparation of Calibration Standards for Quantitation

7.2.1. Prepare calibration standards by pipetting 1 mL of the 100- $\mu\text{g/mL}$  mixed fortification solution from Section 7.1.2 into a 100 mL volumetric flask.

7.2.2. Evaporate the methanol to incipient dryness using an N-Evap set at 25 °C and a nitrogen pressure of approximately 15 psi.

7.2.3. Reconstitute the standard with 100.0 mL of a hexane/peanut oil (0.5 g/L) solution. Mix thoroughly and prepare calibration solutions according to the following table:

Concentration of Spiking Soln. $\mu\text{g/mL}$	Aliquot of Spkg. Soln. mL	Final Soln. Volume mL	Calib Soln. Final Conc. $\mu\text{g/mL}$	Equivalent Sample Conc. $\mu\text{g/g}$
100	1.0	100.0	1.0	2.0
1.00	20.0	100.0	0.20	0.40
1.00	10.0	100.0	0.10	0.20
1.00	5.0	100.0	0.05	0.10
1.00	2.0	100.0	0.02	0.04
1.00	1.0	100.0	0.01	0.02
1.00	0.5	100.0	0.005	0.01
0.2	1.0	100.0	0.002	0.004
0.1	1.0	100.0	0.001	0.002

8. INSTRUMENTAL CONDITIONS

8.1. Typical GC/MS Operating Conditions (Note 12.2.)

Instrumentation: Agilent Model 6890 gas chromatograph  
 Agilent Model 6890 autoinjector  
 Agilent Model 5973N mass spectrometer  
 Agilent G1701CA data system

Column: J & W fused silica capillary  
 Durabond-5 liquid phase  
 30 m x 0.25 mm i.d.  
 0.25- $\mu\text{m}$  film thickness

Oven Method:  
 Column 100 °C for 1.5 min  
 100 °C to 140 °C at 5 °C/min hold 0 min  
 140 °C to 150 °C at 1 °C/min hold 3 min  
 150 °C to 280 °C at 50 °C/min hold 5 min

Transfer Line	280 °C
Carrier Gas Method:	helium
Constant Flow	1.4 mL/min
Vacuum Compensation	on
Initial Head Pressure	~15 psi
Linear Velocity	~44 cm/s
Injection Method:	splitless
Injector Temperature	250 °C
Purge Delay	0.9 min
Splitter Flow	50 mL/min
Septum Purge	on
Injection Volume	5 µL
Detector Mode:	Electron impact
Source Temperature	230 °C
Quad Temperature	150 °C
Calibration Program	Electron impact autotune
Electron Multiplier	1906 volts
SIM Resolution	high
Dwell Time	50 msec
Ions Monitored:	
benfluralin	m/z 292 (quantitation ion) m/z 264 (confirmation ion) m/z 276 (confirmation ion)
ethalfluralin	m/z 276 (quantitation ion) m/z 316 (confirmation ion) m/z 292 (confirmation ion)
trifluralin	m/z 306 (quantitation ion) m/z 264 (confirmation ion) m/z 290 (confirmation ion)

### 8.3. Mass Spectra

Full-scan mass spectra of benfluralin, ethalfluralin, and trifluralin are illustrated in Figures 1-3, respectively.

8.4. Typical Calibration Curve

Typical calibration curves for the determination of benfluralin, ethalfluralin, and trifluralin in soil are shown in Figures 4-6, respectively.

8.5. Typical Chromatograms

Typical chromatograms of a standard, a control sample, a 0.01- $\mu\text{g/g}$  (LOQ) recovery sample, and a 2.0  $\mu\text{g/g}$  recovery sample for the determination of benfluralin, ethalfluralin, and trifluralin in soil are illustrated in Figures 7-9, respectively.

8.6 Typical Confirmation Results

Typical confirmation results are illustrated in Figures 10-12.

9. DETERMINATION OF RECOVERY OF BENFLURALIN, ETHALFLURALIN AND TRIFLURALIN FROM SOIL

9.1. Sample Preparation

Prepare soil samples for analysis by freezing with dry ice or liquid nitrogen and then grinding or chopping using a hammer mill with a 1/8-inch screen size. Prepared soil samples should be stored frozen at approximately -10 to -20 °C until analysis.

9.2. Sample Analysis

9.2.1. Weigh  $10.0 \pm 0.05$  g of sample into a 4 oz jar.

9.2.2. For preparing fortified samples, add the required aliquot of the appropriate spiking solutions to obtain concentrations ranging from 0.010 to 2.00  $\mu\text{g/g}$ .

9.2.3. Add 20.0 mL of the acetonitrile/water (99:1 v/v) extraction solution into the sample jar.

9.2.4. Cap the sample vial with a PTFE-lined cap, and shake the sample for a minimum of 30 minutes on a reciprocating shaker at approximately 180 excursions/minute.

9.2.5. Centrifuge the sample jar for 5 minutes at approximately 2000 rpm.

9.2.6. Transfer a 5.0-mL portion of the extraction solution into a clean 30 mL vial. Add 10 mL of water and mix thoroughly.

9.2.7. Prepare a 300 mg multi mode (C18, SAX, SCX) solid phase extraction cartridge by conditioning with 3 mL of methanol followed by 5 mL of water.

9.2.8. Apply the extract from step 9.2.6 to the cartridge at a rate of approximately 5 mL/min. Discard the eluate. Apply full vacuum (15-20 inches Hg) to the cartridge and dry for

10 minutes.

- 9.2.9. Elute the benfluralin, ethalfluralin, and trifluralin residues from the cartridge slowly (~ 1 mL/min) by adding 2 mL of hexane. Allow the hexane to soak into the bed of the cartridge for 1 minute before collecting the eluate in a 16 x 100 screw top vial. Repeat the step with a second 2 mL portion of hexane.
- 9.2.10. On collection of the second hexane eluate, add approximately 0.003 gram peanut oil to each sample and adjust the volume to 5 mL with hexane. Cap and vortex for approximately 1 minute.
- 9.2.11. Transfer an aliquot of the extract from Step 9.2.10 to a 2 mL autosampler vial and chromatograph the samples using the conditions given in Section 8.1.
- 9.2.12. For sample extracts which contain either benfluralin, ethalfluralin, and trifluralin concentrations of greater than 0.10 µg/mL, dilute with hexane containing peanut oil to give an appropriate concentration in the range 0.001 – 0.10 µg/mL.
- 9.2.13. Determine the suitability of the chromatographic system using the following performance criteria:
- a. Standard curve linearity: Determine that the coefficient of determination equals or exceeds 0.995 for the least squares equation which describes the detector response as a function of standard curve concentration.
  - b. Peak resolution: Visually determine that sufficient resolution has been achieved for the analyte relative to background interferences.
  - c. Appearance of chromatograms: Visually determine that the chromatograms resemble those shown in Figures 7-9 with respect to peak response, baseline noise, and background interference. Visually determine that a minimum signal-to-noise ratio of 10:1 has been attained for each peak in the 0.005-µg/mL calibration standard.

## 10. CALCULATIONS

### 10.1. Calculation of Standard Calibration Curve

- 10.1.1. Inject the series of calibration standards described in Section 7.2.3 and determine the peak areas for the analyte as indicated below.

benfluralin	m/z 292 (quantitation)
	m/z 264 (confirmation)
	m/z 276 (confirmation)

Ethalfluralin	m/z 276 (quantitation)
	m/z 316(confirmation)

Trifluralin      *m/z* 292(confirmation)  
                    *m/z* 306(quantitation)  
                    *m/z* 264 (confirmation)  
                    *m/z* 290 (confirmation)

10.1.2. Prepare a standard curve by plotting the analyte concentration on the abscissa (x-axis) and the respective peak area on the ordinate (y-axis) as shown in Figure 4. Using regression analysis, determine the equation for the curve with respect to the abscissa.

For example, using power regression (13.1) with the benfluralin data from Figure 4:

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

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

$$\text{benfluralin} \quad (\mu\text{g/mL}) = \left( \frac{\text{benfluralin peak area}}{\text{constant}} \right)^{1/\text{exponent}}$$

$$\text{benfluralin} \quad (\mu\text{g/mL}) = \left( \frac{\text{benfluralin peak area}}{19035852} \right)^{1/1.1814}$$

## 10.2. Calculation of Percent Recovery

10.2.1. Determine the gross concentration in each recovery sample by substituting the peak area obtained into the above equation and solving for the concentration.

For example, using the data for benfluralin from injection 10, Figure 10:

$$\text{benfluralin} \quad (\text{gross } \mu\text{g/mL}) = \left( \frac{\text{benfluralin peak area}}{19035852} \right)^{1/1.1814}$$

$$\text{benfluralin} \quad (\text{gross } \mu\text{g/mL}) = \left( \frac{34796}{19035852} \right)^{1/1.1814}$$

$$\text{benfluralin} \quad (\text{gross}) = 0.0048 \mu\text{g/mL}$$

10.2.2. Convert the concentration ( $\mu\text{g/mL}$ ) of the analyte found in the prepared extract to the

concentration ( $\mu\text{g/g}$ ) of the analyte found in the original sample as follows (where DF=dilution factor):

$$\begin{aligned} \text{benfluralin} & & \text{benfluralin} \\ (\text{gross } \mu\text{g/g}) & = & (\text{gross } \mu\text{g/mL}) \times \text{MF} \times \text{DF} \\ \\ \text{benfluralin} & = & \text{benfluralin} \times \left( \frac{\text{extract volume}}{\text{aliquot volume}} \times \frac{\text{final volume}}{\text{sample weight}} \right) \times \text{DF} \\ (\text{gross } \mu\text{g/g}) & & (\text{gross } \mu\text{g/mL}) \\ \\ \text{benfluralin} & = & \text{benfluralin} \times \left( \frac{20.0 \text{ mL}}{5.00 \text{ mL}} \times \frac{5.00 \text{ mL}}{10 \text{ gram}} \right) \times 1 \\ (\text{gross } \mu\text{g/g}) & & (\text{gross } \mu\text{g/mL}) \\ \\ \text{benfluralin} & = & 0.0048 \mu\text{g/mL} \times 2.0 \frac{\text{mL} \times \mu\text{g}}{\text{g} \times \text{ng}} \times 1 \\ (\text{gross } \mu\text{g/g}) & & \\ \\ \text{benfluralin} & = & 0.0096 \mu\text{g/g} \\ (\text{gross}) & & \end{aligned}$$

- 10.2.3. Determine the net concentration in each recovery sample by subtracting the analyte concentration in the control sample from that of the gross analyte concentration in the recovery sample.

For example, using the data for benfluralin from Figure 10:

$$\begin{aligned} \text{benfluralin} & & \text{benfluralin} & & \text{benfluralin} \\ (\text{net } \mu\text{g/g}) & = & (\text{gross } \mu\text{g/g}) & - & (\text{control } \mu\text{g/g}) \\ \\ \text{benfluralin} & = & 0.0096 \mu\text{g/g} & - & 0.0000 \mu\text{g/g} \\ (\text{net } \mu\text{g/g}) & & \\ \\ \text{benfluralin} & = & 0.0096 \mu\text{g/g} \\ (\text{net}) & & \end{aligned}$$

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

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



$$\text{Recovery} = \frac{0.0096 \mu\text{g/g}}{0.0100 \mu\text{g/g}} \times 100\%$$

$$\text{Recovery} = 96\%$$

10.3. Determination of Benfluralin, ethalfluralin, and trifluralin in Soil

- 10.3.1. Determine the gross concentration of the analyte in the treated sample by substituting the peak area obtained into the equation for the standard calibration curve and calculating the uncorrected residue result as described in Section 10.2.1-10.2.3.
- 10.3.2. For those analyses that require correction for method recovery, use the average recovery of all the recovery samples fortified at or above the limit of quantitation from a given sample set to correct for method efficiency.

For example, using the data for benfluralin from Table 2 for the samples analyzed on 23-Apr-2007:

$$\text{benfluralin (corrected } \mu\text{g/g)} = \frac{\text{benfluralin (gross } \mu\text{g/g)}}{\left(\frac{100}{\% \text{ Recovery}}\right)}$$

$$\text{benfluralin (corrected } \mu\text{g/g)} = 0.0096 \mu\text{g/g} \times \frac{100}{99}$$

$$\text{benfluralin (corrected)} = 0.0097 \mu\text{g/g}$$

10.4. Determination of Soil Moisture

- 10.4.1. Accurately weigh a 10-g portion of soil into a tared aluminum weighing dish.
- 10.4.2. Place the sample in an oven at 110 °C and allow to dry for a minimum of 16 hours.
- 10.4.3. Remove the sample from the oven and place in a desiccator containing Drierite<sup>®</sup> adsorbent. Re-weigh the sample when it has cooled to room temperature.
- 10.4.4. Calculate the percent moisture (dry weight basis) as follows:

$$\text{Percent Moisture (dry weight basis)} = \frac{\text{water, g}}{\text{dry soil, g}} \times 100$$

$$\text{Percent Moisture (dry weight basis)} = \frac{\left( \text{sample weight before drying, g} \right) - \left( \text{sample weight after drying, g} \right)}{\text{sample weight after drying, g}} \times 100$$

10.5. Determination of Dry Weight Concentrations of Benfluralin, ethalfluralin, and trifluralin in Soil

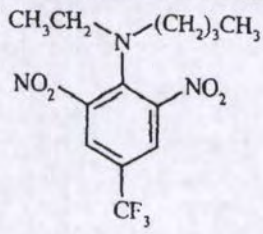
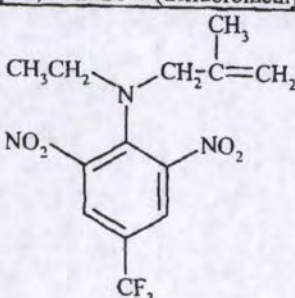
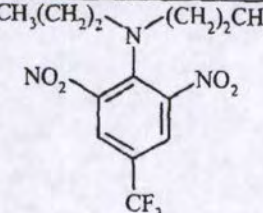
10.5.1. Determine the analyte concentration in the sample as described in Section 10.3.

10.5.2. Determine the soil moisture as described in Section 10.4.

10.5.3. Determine the dry weight analyte concentration in the sample as follows:

$$\text{benfluralin (dry weight } \mu\text{g/g)} = \text{benfluralin } (\mu\text{g/g)} \times \left( 1 + \frac{\% \text{ Moisture}}{100} \right)$$

Table 1. Identity and Structure of Benfluralin, ethalfluralin, and trifluralin

Common Name of Compound	Structural Formula and Chemical Name
Benfluralin Molecular Formula: $C_{13}H_{16}F_3N_3O_4$ Formula Weight: 335.3 Nominal Mass: 335 CAS Number: 1861-40-1	 <p style="text-align: center;">N-butyl-N-ethyl-2,6-dinitro-4-(trifluoromethyl)benzenamine</p>
Ethalfluralin Molecular Formula: $C_{13}H_{14}F_3N_3O_4$ Formula Weight: 333.2694 Nominal Mass: 333 CAS Number: 55283-68-6	 <p style="text-align: center;">N-ethyl-N-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl)benzenamine</p>
Trifluralin Molecular Formula: $C_{13}H_{16}F_3N_3O_4$ Formula Weight: 335.2854 Nominal Mass: 335 CAS Number: 1582-09-8	 <p style="text-align: center;">N-butyl-N-ethyl-2,6-dinitro-4-(trifluoromethyl)benzenamine</p>