Separation of Methyl Ester Derivatives of 3,6-Dichloro-2-Methoxybenzoic Acid, 2,4-Dichlorophenoxyacetic Acid and 2,4,5-Trichlorophenoxyacetic Acid

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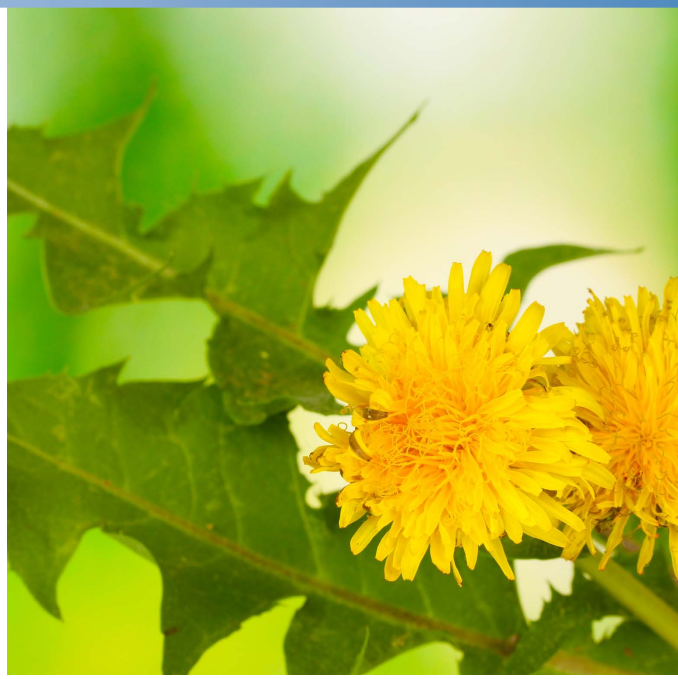
Application Note 20587

Key Words
TG-5MS, methyl esters, dicamba, 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid

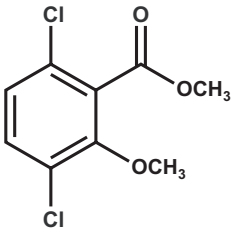
Abstract
This application note demonstrates the analysis of methyl esters of the chlorinated pesticides dicamba, 2,4-D, and 2,4,5-T on a TraceGOLD TG-5MS GC column using SIM mode in GC-MS detection.



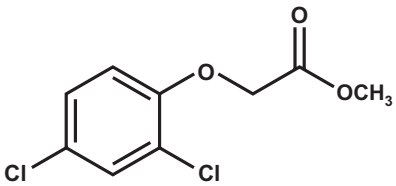
Introduction

Herbicides, also commonly known as weed killers, are toxic to plants and are used to destroy unwanted vegetation. Selective herbicides kill specific targets while leaving the desired crop relatively unharmed. Some act by interfering with the growth of the weed and are often synthetic "imitations" of plant hormones.

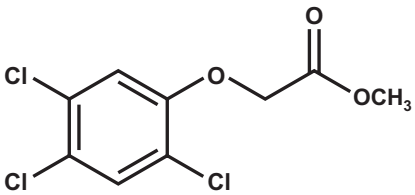
Dicamba (3,6-dichloro-2-methoxybenzoic acid) is a chlorinated derivative of benzoic acid.



Methyl ester of dicamba



Methyl ester of 2,4-Dichlorophenoxyacetic acid



Methyl ester of 2,4,5-Trichlorophenoxyacetic acid

A phenoxyacid herbicide is a member of a family of chemicals related to the growth hormone indole acetic acid (IAA). When sprayed on broad-leaf plants it induces rapid, uncontrolled growth and eventually kills them. Grasses, on the other hand, have a mechanism for deactivating phenoxyacid herbicides. When these herbicides are sprayed on crops such as wheat, tobacco, or corn, the broad-leaf plants in a field are selectively killed, leaving the crops relatively unaffected. The wide variety of phenoxyacid herbicides in use today can be grouped into the phenoxyacetic, phenoxybutyric and phenoxypropionic subtypes. The phenoxypropionic subtype contains the aryloxyphenoxypropionic subtype, which includes the greatest number of commercial variants. Phenoxyacid herbicides are acidic and are typically applied in an ester or salt form.

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The phenoxyacetic acids 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) were used in this application along with 3,6-dichloro-2-methoxybenzoic acid. The Thermo Scientific™ TraceGOLD™ TG-5MS column was able to separate the methyl ester of all the components with excellent peak shape and good resolution.

Experimental Details

Consumables		Part Number
Column:	TraceGOLD TG-5MS, 30 m x 0.25 mm x 0.25 µm	26098-1420
Septum:	BTO, 17 mm	31303211
Liner:	Thermo Scientific FOCUS™ split liner, 3 x 8 x 105 mm	45350031
Column ferrules:	100% graphite ferrules for Thermo Scientific TRACE™ injector 0.1–0.25 mm ID	29053488
MS ferrules:	15% graphite/85% Vespel® ferrules	29033460
Injection syringe:	10 µL fixed needle syringe for Thermo Scientific TriPlus™ Autosampler	36500525
Sample handling vials and closure:	Thermo Scientific Chromacol™ 9 mm screw thread 0.3 mL fixed insert amber Micro+ vials Thermo Scientific Chromacol 9 mm screw thread closure with silicone/PTFE septa	03-FISV (A) 9-SC(B)-ST101
Fisher Scientific™ HPLC grade hexane		H/0403/15

Preparation of Solutions
Dicamba methyl ester (200 µg/mL in n-hexane)
2,4-D methyl ester (200 µg/mL in n-hexane)
2,4,5-T methyl ester (200 µg/mL in n-hexane)

Sample Preparation
A mixture with 1 µg/mL of each of the three components was prepared in n-hexane.

Separation Conditions	
Instrumentation:	Thermo Scientific TRACE GC Ultra™ gas chromatograph
Carrier gas:	Helium
Splitless time:	1 min
Column flow:	1.2 mL/min, constant flow
Oven temperature:	100 °C (0.0 min), 25 °C/min, 330 °C (1 min)
Injector type:	Splitless
Injector mode:	Constant flow
Injector temperature:	250 °C
Detector type:	MS
Detector temperature:	240 °C
MS transfer line temperature:	280 °C
Ion source temperature:	220 °C
Ionization mode:	EI
Ions in selected ion monitoring (SIM) mode:	Dicamba: (205, 203, 188) amu 2,4-D: (199, 155) amu 2,4,5-T: (268, 233, 196) amu

Injection Conditions	
Instrumentation:	Thermo Scientific TriPlus Autosampler
Injection volume:	3.0 µL

Results

The analysis performed on the TraceGOLD TG-5MS column using SIM mode gave excellent separation and good peak shape for methyl esters of dicamba, 2,4-,D, and 2,4,5-T compounds (Figures 1 and 2). Table 1 shows the retention time and level of detection of 1 µg/mL.

Conclusion

The TraceGOLD TG-5MS GC column separated all compounds with excellent peak shape and resolution.

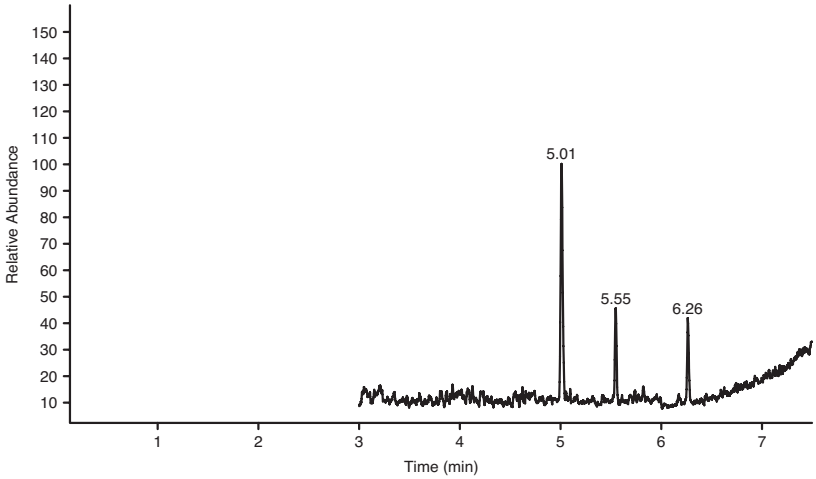

Figure 1: SIM mode chromatogram of a mixture of three herbicide methyl ester components (reference standard) separated on a TraceGOLD TG-5MS, 30 m x 0.25 mm x 0.25 µm, GC column

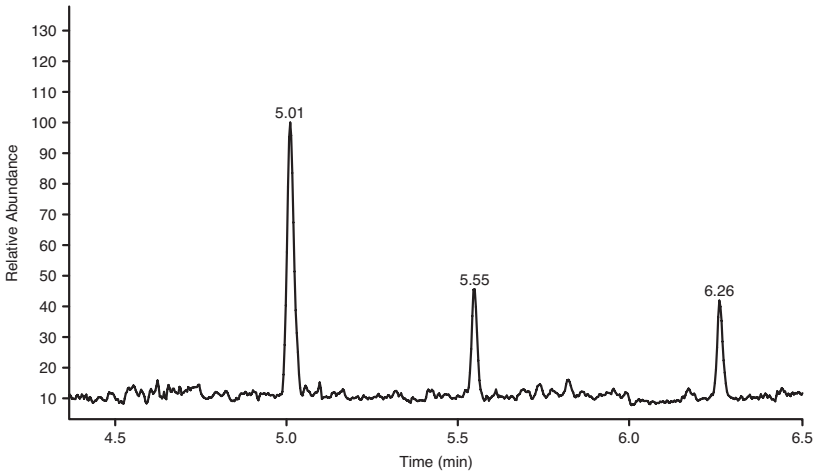

Figure 2: Expanded chromatogram for dicamba, 2,4-D, and 2,4,5-T methyl ester

Elution order	Compound	Concentration (µg/mL)	t_R (min)
1	Dicamba methyl ester	1.0	5.01
2	2,4-Dichlorophenoxyacetic acid methyl ester	1.0	5.55
3	2,4,5-Trichlorophenoxyacetic acid methyl ester	1.0	6.26

Table 1: Retention time (t_R) of methyl esters of dicamba, 2,4-D, and 2,4,5-T

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