

APPLICATIONS

Dicamba and Acidic Herbicides in Agricultural Field Samples by LC-MS/MS

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Background

Widespread global use as weed control agents and plant growth regulators for agricultural crops, lawns, and gardens makes the active ingredients in Acid Herbicide (AcH) products account for more use than all the other types of pesticides combined. These predominant herbicide chemicals include the well-characterized 2,4-dichlorophenoxyacetic acid (2,4-D), dicamba, triclopyr, and other AcHs. The US EPA recently ruled in favor of continued use of dicamba despite complaints and concern about drift across plots during spray application. While adjustments in regulation around application patterns were made, these AcHs remain a prevalent concern in environmental monitoring and crop contamination analysis.

Introduction

Historically, the analysis of AcHs has been performed using a complex sample preparation procedure to derivatize the analytes followed by detection with gas chromatography and an electron capture detector. The US EPA Method 8151: CHLORINATED HERBICIDES BY GC USING METHYLATION OR PENTAFLUOROBENZYLATION DERIVATIZATION has been the most common analytical approach for these analytes. This method, however, is extremely difficult to perform correctly, is not rugged, and is time consuming. LC-MS/MS as a replacement technology would eliminate the need for the derivatization step thus making this a more rugged analytical approach. A recent literature review of chlorophenoxy acid herbicide methods demonstrated that LC-MS/MS was the prevalent technology cited. Acidic functional groups are easiest to ionize as their conjugate base, and LC-MS/MS methods can utilize negative mode electrospray ionization (ESI-) with great sensitivity.

LC Method Parameters

Column:	Kinetex® 2.6 µm F5	
Dimensions:	100 x 3.0 mm	
Part No.:	00D-4723-Y0	
Flow Rate:	0.5 mL/min	
Mobile Phase:	A: Water B: 0.2% Formic acid in Methanol	
Gradient:	Time (min)	% B
	0	2
	1	40
	4	52
	12	85
	13.5	90
	15.5	90
	15.6	2
Flow Rate:	1.5 mL/min	
Backpressure:	300 Bar	
Temperature:	30 °C	
Injection Volume:	50 µL	
Detection:	MS/MS – Qtrap® 6500+	

Ion Source Parameters: Electrospray Ionization (ESI) conducted in negative ion mode.

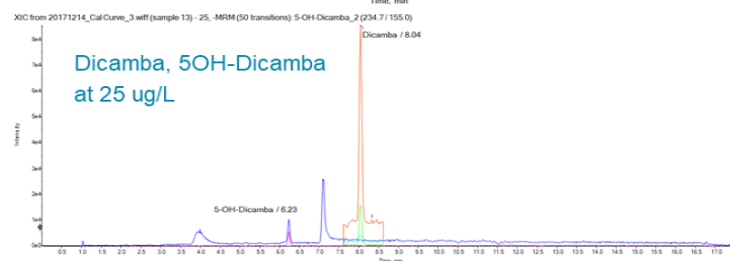
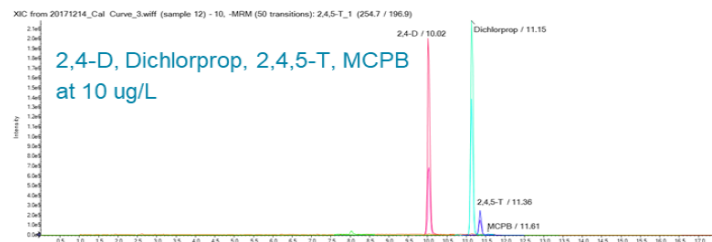
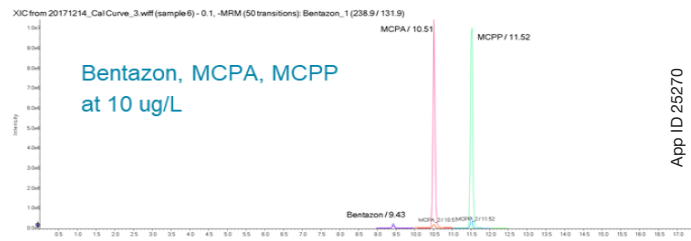
Parameter	Setting
Curtain Gas (CUR)	20
Collision Gas	-2
Ion Spray Voltage (IS)	3000
Temperature (TEM)	600
Nebulizer Gas (GS1)	55
Heater Gas (GS2)	55

Quantitative method performance for acidic herbicides and metabolites

Compound ID	LOD (ng/mL, in vial)	LOQ (ng/mL, in vial)	LOQ (ng/g, in sample)	S/N at 1 ppb	% CV at 1 ppb	% CV at 25 ppb	Cal Range
2,4,-T	0.1	0.25	3.5	132	12	11	0.1 - 50
2,4,5-TP	0.025	0.05	0.7	72	18	6	0.025 - 50
2,4,-D	0.025	0.05	0.7	226	6	7	0.05 - 50
2,4-DB	5	10	140	--	--	3	5 - 50
5OH-Dicamba	1	2.5	35	49	26	3	0.5 - 50
Acifluorfen	<0.1	0.1	1.4	17	10	11	0.1 - 50
Bentazon	<0.01	<0.01	<0.14	1883	5	3	0.1 - 25
DCGA	5	10	140	--	--	7	--
DCSA	1	2.5	1.4	7	7	8	0.05 - 50
Dicamba	0.25	1	14	25	14	11	0.25 - 50
Dichlorprop	0.025	0.05	0.7	586	2	5	0.025 - 50
MCPA	1	2.5	<0.14	4	1	3	0.01 - 100
MCPB	0.5	1	14	384	6	2	0.5 - 50
MCPP	<0.01	<0.01	<0.14	560	3	3	0.01 - 100

APPLICATIONS

Elution profile of some example AcHs using Kinetex[®] F5 column chemistry



Kinetex Ordering Information

2.6 µm MidBore [™] Columns (mm)	SecurityGuard ULTRA Cartridges [†]		
	50 x 3.0	100 x 3.0	150 x 3.0
F5	00B-4723-Y0	00D-4723-Y0	00F-4723-Y0
			AJO-9321 for 3.0 mm ID

[†]SecurityGuard ULTRA Cartridges require holder, Part No.: AJO-9000

Results

The SCIEX[®] QTRAP[®] 6500+ system was coupled with the Exion-LC[™] AD and Phenomenex Kinetex F5 analytical column to attain sensitive quantitation of acid herbicides including dicamba and dicamba metabolites. Quantitation was achieved to ng/L levels for many analytes in neat calibration solutions, corresponding to ng/g levels in the field samples. Spiked and unspiked agricultural samples were analyzed to demonstrate sensitivity, recovery, and precision in complex matrices. Target field samples demonstrated highest frequency of analyte detection compared to samples collected further from fields. Endogenous occurrence of several analytes was reported.

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