Application News

No. LCMS-095

Liquid Chromatography Mass Spectrometry

Analysis of Dicamba and 2,4-D by the Triple Quad LCMS-8060

■ Executive Summary

Formulation assay including LOD, LOQ and robustness tests of dicamba and 2,4-D spiked into a commercial brand herbicide.

■ Background

The purpose of this analysis was to demonstrate the sensitivity of the LCMS-8060 when analyzing dicamba and 2,4-D in a solution of 100x diluted glufosinate herbicide that contains a high amount of surfactants and other potential mass spec interferants.

■ Method

The LC/MS/MS method was quickly developed with readily available mobile phases. Dicamba in methanol 0.01 and 0.025 ppb had a S/N of 3/1 and 10/1, respectively. 2,4-D in methanol at 0.0001 and 0.001 ppb had a S/N of 13/1 and 90/1, respectively. See Figures 1-4 for chromatograms

MRM and source conditions were optimized using LabSolutions Connect software and flow injection analyses. Parameters optimized include:

- Collision energy (rough and fine-tuned)
- Q1 Pre-rod voltage
- Q3 Pre-rod voltage
- Interface voltage (probe voltage)
- Collision gas pressure
- Nebulizing gas flow
- Drying gas flow
- Heating gas flow
- Interface temperature
- Desolvation line temperature
- Heating block temperature

LabSolutions Connect software chose the best parameters based upon the intensity of the peak. Only about 40 µL of standard was used in the optimizations. See Figures 5-6 for LabSolutions Connect results.

A calibration curve was prepared in 100x diluted herbicide from 0.1 – 10 ppb dicamba and 0.01 – 1 ppb 2,4-D. An LOD sample at 0.01 ppb dicamba and 0.001 2,4-D was also analyzed. A duplicate curve was analyzed at the beginning and near the end of the analysis along with five sets of QCs (triplicate injections) and 134 injections of the mid-QC over time to show ruggedness. See Figures 7-8 (dicamba) and Figures 9-10 (2,4-D) for the LOD at injection 13 and injection 222, respectively. See Figures 11-12 (dicamba) and Figures 13-14 (2,4-D) for the LOQ at injection 16 and injection 225, respectively.

There were 134 injections of the mid-level QC over time with a % RSD of 1.87 and 3.16 for dicamba and 2,4-D, respectively. See Table 1 for more % RSDs. See Table 2 for curve accuracy values and Figures 15-16 for a graphical representation of the curves and QCs. See Figures 17-20 for a graphical representation of variance in the areas of the MQC injections as well as the LOD injections.

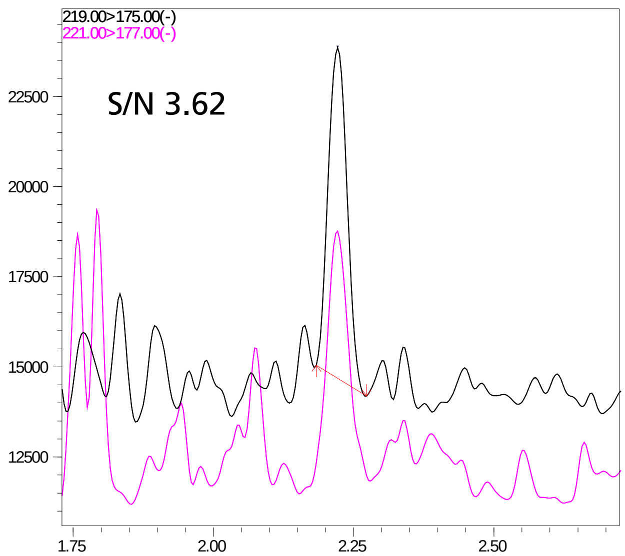


Figure 1: Limit of Detection for Dicamba (0.01 ppb)

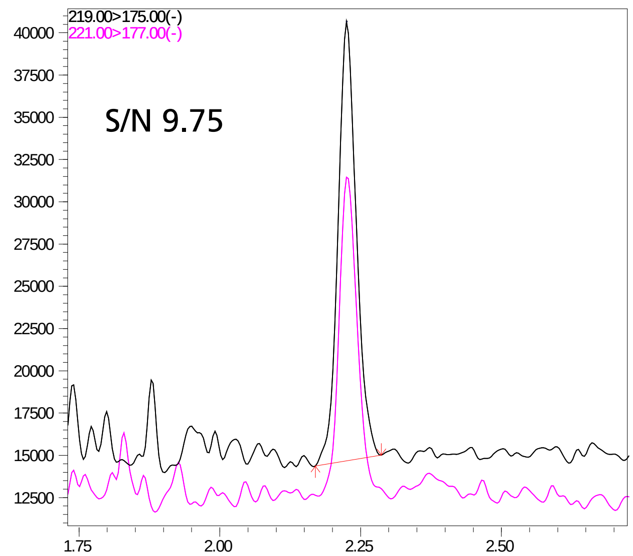


Figure 2: Dicamba, 0.025 ppb

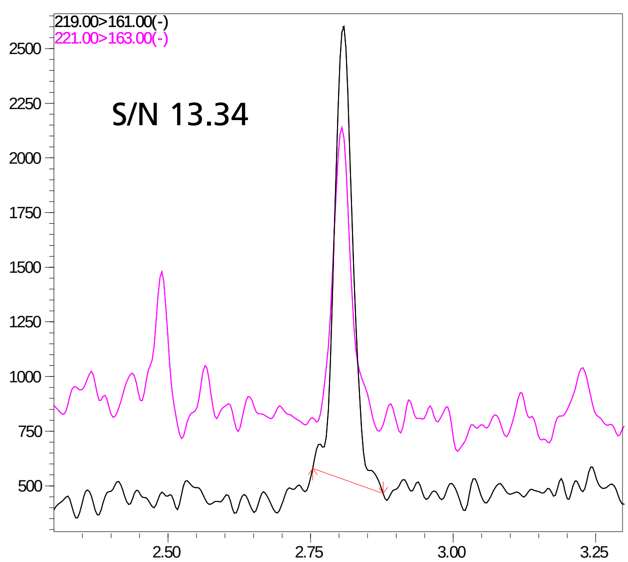


Figure 3: 2,4-D, 0.0001 ppb

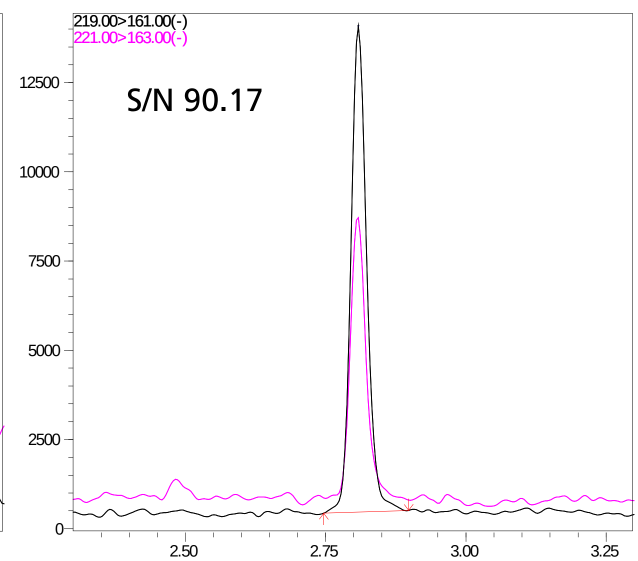
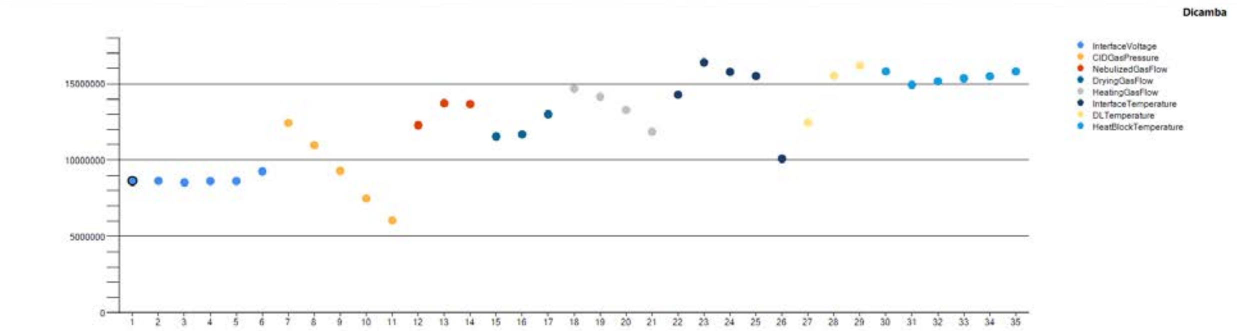


Figure 4: 2,4-D, 0.001 ppb

		Compound Name	Polarity	Precursor m/z	m/z1	CE1	Message	Interface Voltage	CID Gas	Nebulizing Gas	Drying Gas	Heating Gas	Interface Temp	DL Temp	Heat Block Temp	User Name
	1	Dicamba	-	219	175	7	The boundary v...	-5	210	2.5	8	6	200	250	200	System Administrator



	Data File Name	Interface Voltage	CID Gas	Nebulizing Gas	Drying Gas	Heating Gas	Interface Temp	DL Temp	Heat Block Temp	User Name	Date Acquired
1	C:\LabSolutions\Data\Dicamba 2-4 D\Optimization -connect\20171017_160752\Data\Dica...	-1	270	2	10	10	300	250	400	System Administrator	2017/10/17 16:09
2	C:\LabSolutions\Data\Dicamba 2-4 D\Optimization -connect\20171017_160752\Data\Dica...	-1.5	270	2	10	10	300	250	400	System Administrator	2017/10/17 16:10
3	C:\LabSolutions\Data\Dicamba 2-4 D\Optimization -connect\20171017_160752\Data\Dica...	-2	270	2	10	10	300	250	400	System Administrator	2017/10/17 16:12
4	C:\LabSolutions\Data\Dicamba 2-4 D\Optimization -connect\20171017_160752\Data\Dica...	-3	270	2	10	10	300	250	400	System Administrator	2017/10/17 16:14
5	C:\LabSolutions\Data\Dicamba 2-4 D\Optimization -connect\20171017_160752\Data\Dica...	-4	270	2	10	10	300	250	400	System Administrator	2017/10/17 16:15
6	C:\LabSolutions\Data\Dicamba 2-4 D\Optimization -connect\20171017_160752\Data\Dica...	-5	270	2	10	10	300	250	400	System Administrator	2017/10/17 16:17
7	C:\LabSolutions\Data\Dicamba 2-4 D\Optimization -connect\20171017_160752\Data\Dica...	-5	210	2	10	10	300	250	400	System Administrator	2017/10/17 16:19
8	C:\LabSolutions\Data\Dicamba 2-4 D\Optimization -connect\20171017_160752\Data\Dica...	-5	240	2	10	10	300	250	400	System Administrator	2017/10/17 16:20
9	C:\LabSolutions\Data\Dicamba 2-4 D\Optimization -connect\20171017_160752\Data\Dica...	-5	270	2	10	10	300	250	400	System Administrator	2017/10/17 16:22
10	C:\LabSolutions\Data\Dicamba 2-4 D\Optimization -connect\20171017_160752\Data\Dica...	-5	300	2	10	10	300	250	400	System Administrator	2017/10/17 16:23
11	C:\LabSolutions\Data\Dicamba 2-4 D\Optimization -connect\20171017_160752\Data\Dica...	-5	330	2	10	10	300	250	400	System Administrator	2017/10/17 16:25
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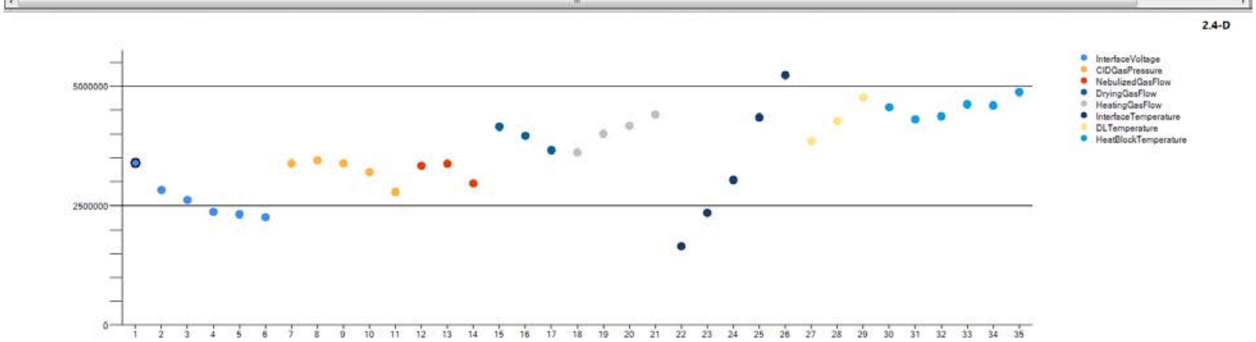
14	C:\LabSolutions\Data\Dicamba 2-4 D\Optimization -connect\20171017_160752\Data\Dica...	-5	210	3	10	10	300	250	400	System Administrator	2017/10/17 16:30
15	C:\LabSolutions\Data\Dicamba 2-4 D\Optimization -connect\20171017_160752\Data\Dica...	-5	210	2.5	4	10	300	250	400	System Administrator	2017/10/17 16:32

Figure 5: LabSolutions Connect Source Optimization Results – Dicamba

		Compound Name	Polarity	Precursor m/z	m/z1	CE1	Message	Interface Voltage	CID Gas	Nebulizing Gas	Drying Gas	Heating Gas	Interface Temp	DL Temp	Heat Block Temp	User Name
	1	2,4-D	-	219	161	13		-1	240	2.5	4	12	350	250	450	System Administrator



	Data File Name	Interface Voltage	CID Gas	Nebulizing Gas	Drying Gas	Heating Gas	Interface Temp	DL Temp	Heat Block Temp	User Name	Date Acquired
1	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_IfsVoltage_1.lcd	-1	270	2	10	10	300	250	400	System Administrator	2017/10/18 15:56
2	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_IfsVoltage_2.lcd	-1.5	270	2	10	10	300	250	400	System Administrator	2017/10/18 15:57
3	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_IfsVoltage_3.lcd	-2	270	2	10	10	300	250	400	System Administrator	2017/10/18 15:59
4	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_IfsVoltage_4.lcd	-3	270	2	10	10	300	250	400	System Administrator	2017/10/18 16:00
5	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_IfsVoltage_5.lcd	-4	270	2	10	10	300	250	400	System Administrator	2017/10/18 16:02
6	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_IfsVoltage_6.lcd	-5	270	2	10	10	300	250	400	System Administrator	2017/10/18 16:03
7	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_CIDGas_7.lcd	-1	210	2	10	10	300	250	400	System Administrator	2017/10/18 16:05
8	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_CIDGas_8.lcd	-1	240	2	10	10	300	250	400	System Administrator	2017/10/18 16:07
9	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_CIDGas_9.lcd	-1	270	2	10	10	300	250	400	System Administrator	2017/10/18 16:08
10	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_CIDGas_10.lcd	-1	300	2	10	10	300	250	400	System Administrator	2017/10/18 16:10
11	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_CIDGas_11.lcd	-1	330	2	10	10	300	250	400	System Administrator	2017/10/18 16:11
12	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_NebulizedGas_12....	-1	240	2	10	10	300	250	400	System Administrator	2017/10/18 16:13
13	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_NebulizedGas_13....	-1	240	2.5	10	10	300	250	400	System Administrator	2017/10/18 16:15
14	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_NebulizedGas_14....	-1	240	3	10	10	300	250	400	System Administrator	2017/10/18 16:16
15	C:\LabSolutions\Data\Dicamba 2-4 D\2,4-D\20171018_155458\Data\2,4-D_DryingGas_15.lcd	-1	240	2.5	4	10	300	250	400	System Administrator	2017/10/18 16:18

Figure 6: LabSolutions Connect Source Optimization Results - 2,4-D

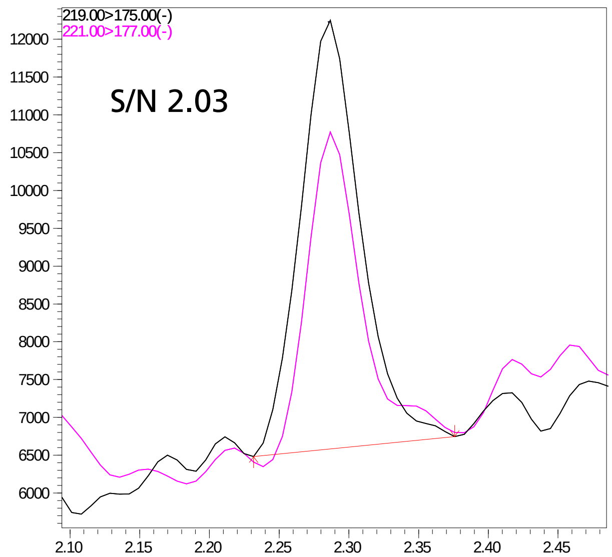


Figure 7: Limit of Detection for Dicamba (0.01 ppb), Injection 13

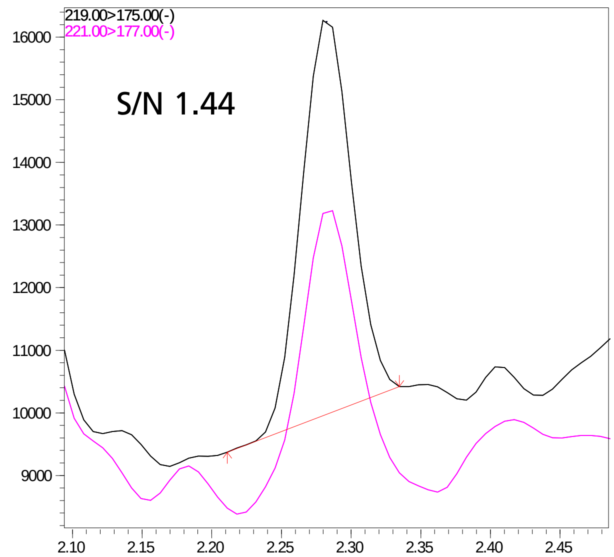


Figure 8: Limit of Detection for Dicamba (0.01 ppb), Injection 222

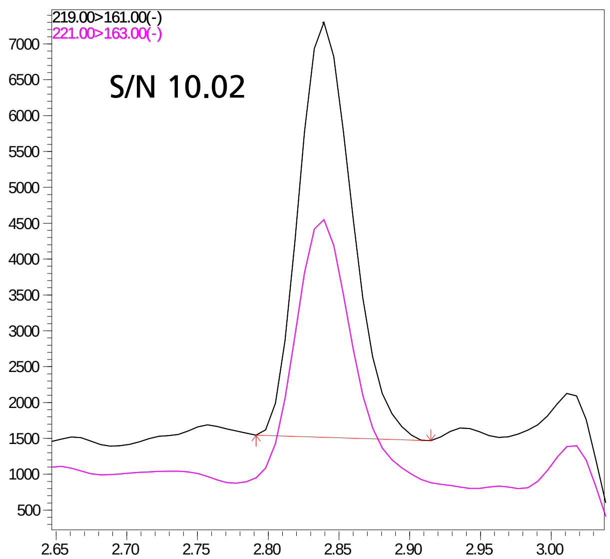


Figure 9: Limit of Detection for 2,4-D (0.001 ppb), Injection 13

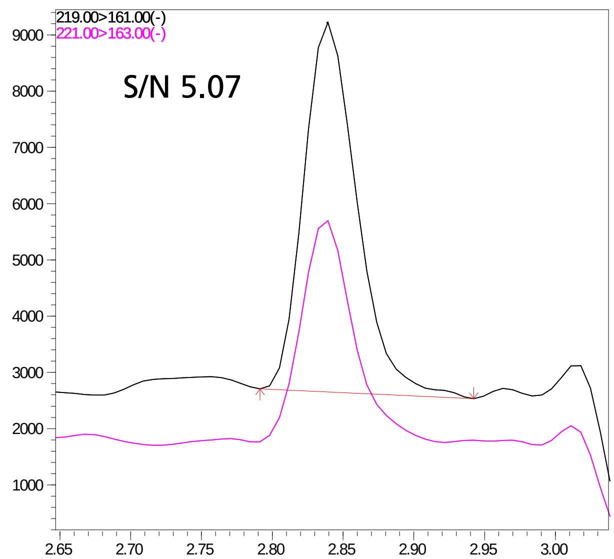


Figure 10: Limit of Detection for 2,4-D (0.001 ppb), Injection 222

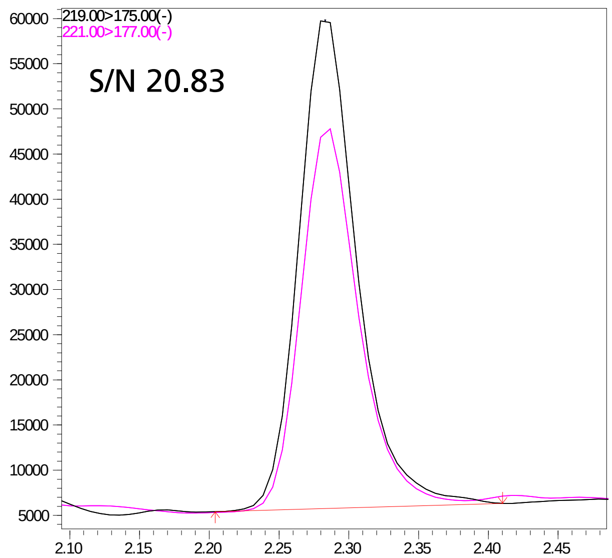


Figure 11: Limit of Quantitation for Dicamba (0.1 ppb), Injection 16

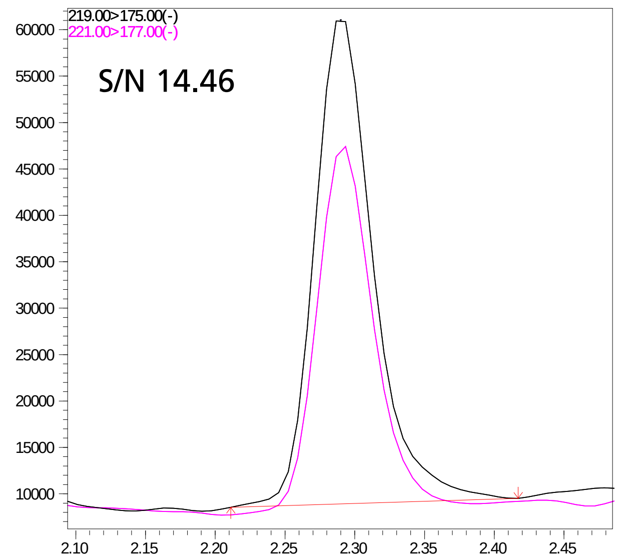


Figure 12: Limit of Quantitation for Dicamba (0.1 ppb), Injection 225

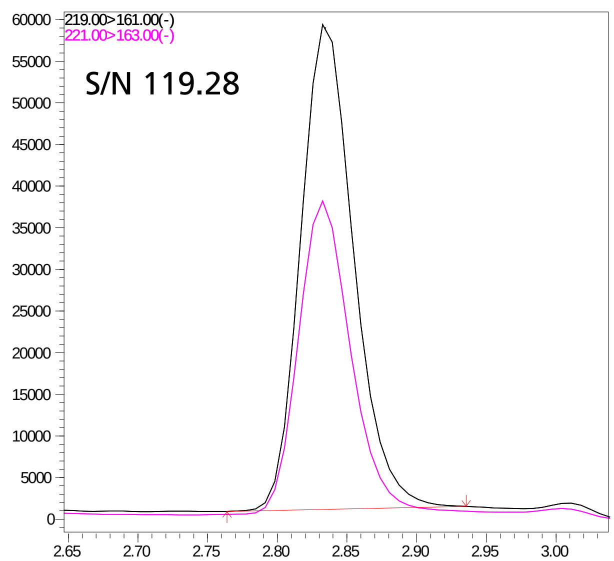


Figure 13: Limit of Quantitation for 2,4-D (0.01 ppb), Injection 16

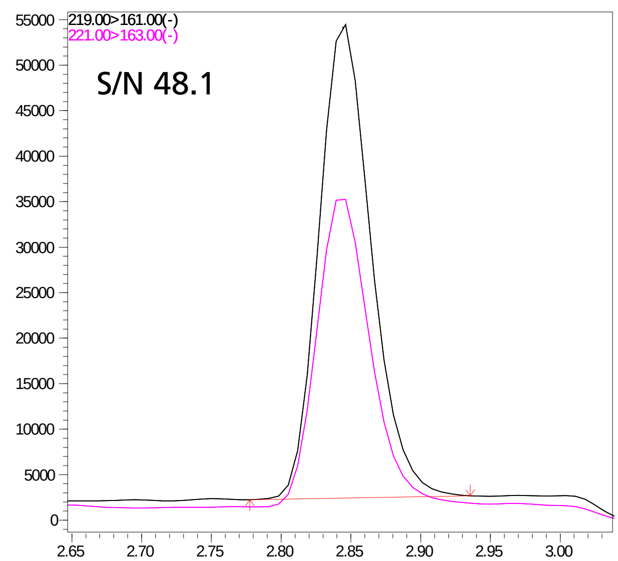


Figure 14: Limit of Quantitation for 2,4-D (0.01 ppb), Injection 225

Table 1: % RSD of Spiked Formulation Injections

Standard/QC	Dicamba Conc. (ppb)	2,4-D Conc. (ppb)	Number of Injections	Dicamba % RSD	2,4-D % RSD
STD 1	10	1	2	6.72	8.77
STD 2	8	0.8	2	6.59	8.75
HQC	7.5	0.75	15	2.06	3.32
STD 3	5	0.5	2	6.22	6.40
MQC	5	0.5	134	1.87	3.16
STD 4	2.5	0.25	2	5.94	7.80
STD 5	0.5	0.05	2	7.41	10.92
LQC	0.3	0.03	15	3.13	5.78
STD 6	0.1	0.01	2	5.79	10.07
LOQ	0.1	0.01	15	3.23	5.73
LOD	0.01	0.001	15	10.5	5.80

Table 2: % Accuracy of both Dicamba and 2,4-D in Two Curves

Injection Number	Standard	Dicamba Area	Dicamba % Accuracy	2,4-D Area	2,4-D % Accuracy
5	STD 6	157720	105.68	155675	106.57
6	STD 5	848221	91.81	750810	119.08
7	STD 4	4822282	99.71	3248143	105.87
8	STD 3	10205788	104.96	6165049	100.85
9	STD 2	17256649	110.70	10058179	103.01
10	STD 1	22038727	113.04	12691910	104.04
178	STD 6	145319	99.34	134981	89.57
179	STD 5	763722	83.16	643179	101.40
180	STD 4	4433748	91.76	2908383	94.70
181	STD 3	9346019	96.16	5631124	92.08
182	STD 2	15720144	100.87	8886042	90.97
183	STD 1	20038771	102.80	11209539	91.86

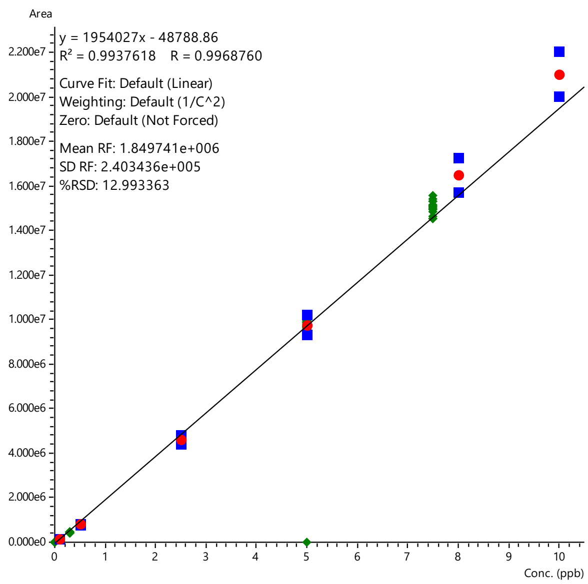


Figure 15: Dicamba Curve and QCs

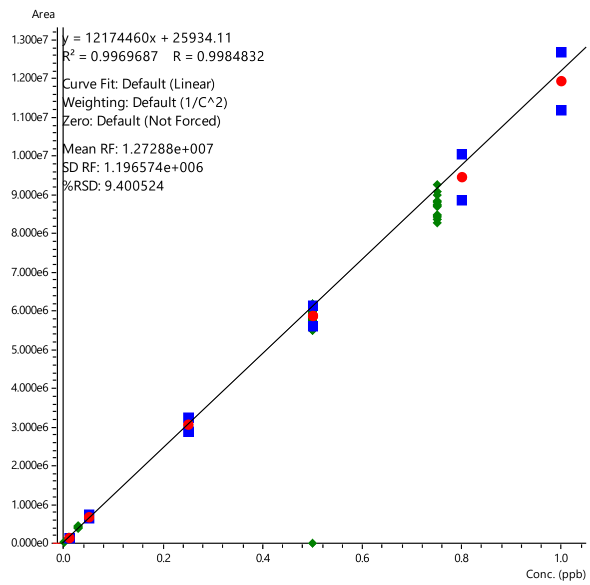


Figure 16: 2,4-D Curve and QCs

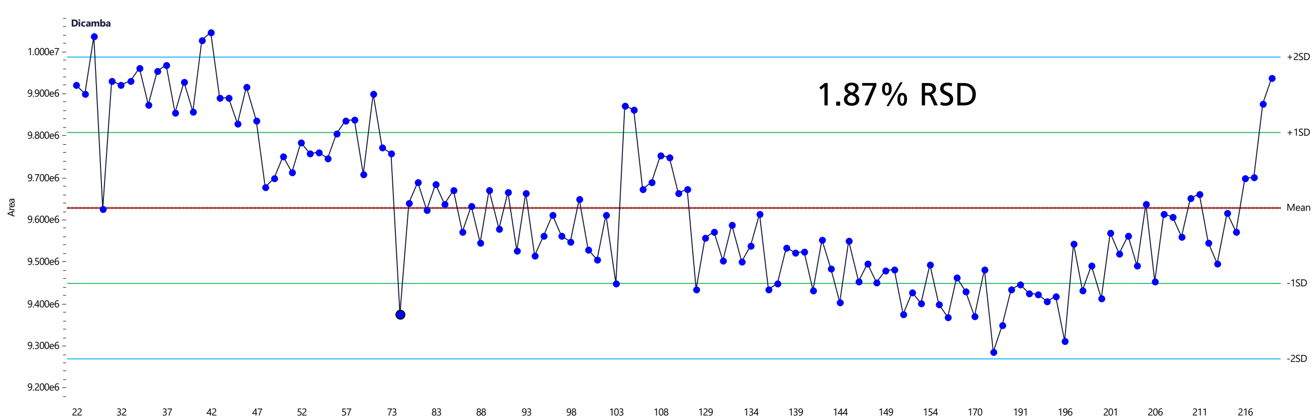


Figure 17: Dicamba Mid QC Areas, 134 Injections

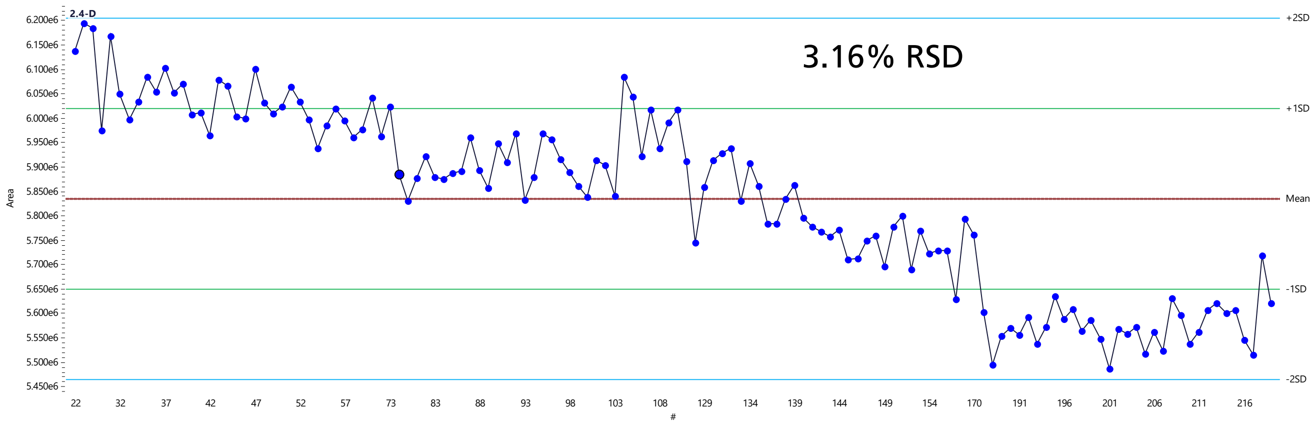


Figure 18: 2,4-D Mid QC Areas, 134 Injections

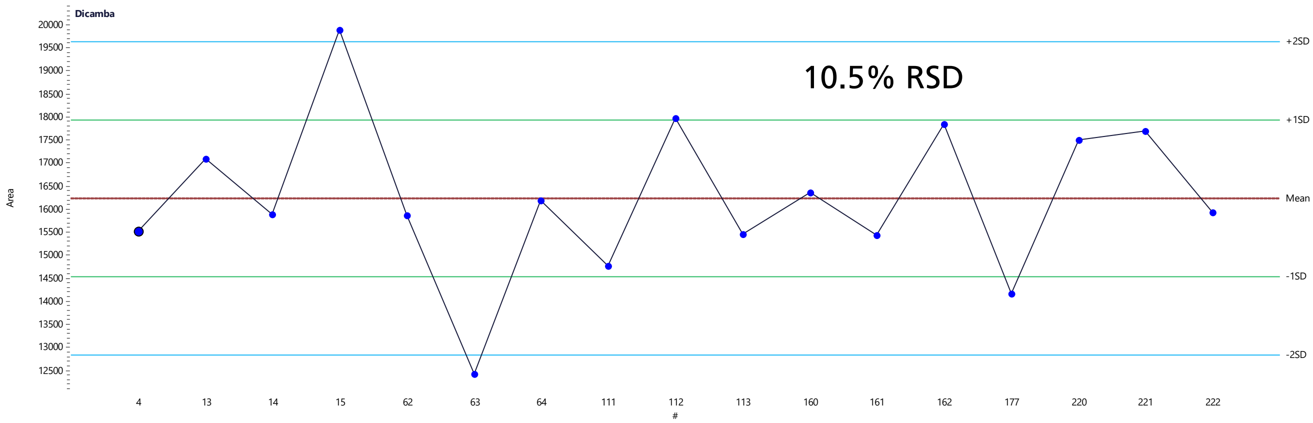


Figure 19: Dicamba LOD Areas, Injection 4 through 222

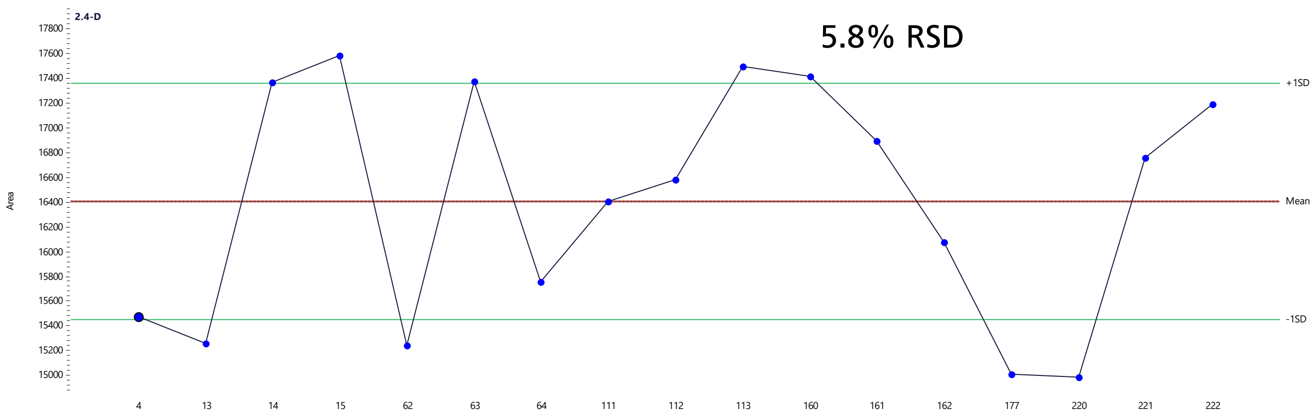


Figure 20: 2,4-D LOD Areas, Injection 4 through 222

■ Results and Discussion

The Shimadzu LCMS-8060 showed sufficient S/N at ultralow detection limits of 0.01 ppb and 0.0001 ppb for dicamba and 2,4-D, respectively. The area counts of four replicate injections of 0.1 ppb dicamba had a %RSD of 4.04.

The Shimadzu LCMS-8060 showed good repeatability and sensitivity over approximately 24 hours of continuous injections. The % RSD was below 11% across all levels including the LOD. The mid-QC areas range from 9.3 to 10.0 million for dicamba and 5.5 to 6.2 million for 2,4-D. These areas are from injection 22 to 230 (5 minute run time). Even the LOD injections have great % RSDs from 10.5 to 5.8% for dicamba and 2,4-D, respectively.

Even with a 100x dilution, it is apparent that the samples are still quite dirty upon injection. The robust interface design of the LCMS-8060 with its removable Desolvation Line will allow analysts to perform routine source cleanings, without breaking vacuum, in order to maintain the instrument's peak operating condition for this ultra-sensitive analysis.

■ Conclusion

The LCMS-8060 has proven to be a very sensitive and robust platform for this application. The method as it stands appears sufficient for routine herbicide analysis.

ULTRA FAST MASS SPECTROMETRY

LCMS-8040

LCMS-8045

LCMS-8050

LCMS-8060

LCMS-2020

LCMS-IT-TOF

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