Application Note: 10041

Determination of Phenoxy-acid Herbicides in Various Matrices

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Key Words

- PolarisQ
- Environmental
- GC-MS/MS
- Herbicides
- Ion Trap
- Water Quality

Introduction

Phenoxy-acid herbicides are often used mixed with fertilizers and applied to lawns and gardens to remove dandelions, thistles, and ragweed. The herbicides are toxic to these broadleaf plants, which are absorbed through the plant surface and transported throughout the circulatory system to all parts of the plant. The plant dies due to root starvation caused by abnormal cell growth that blocks the movement of liquids and nutrients. The herbicides will exist in the garden for up to three weeks exposing other animals to the effects of this poison. Also, the runoff of the lawns and gardens can pose a threat to the animals of nearby rivers and lakes. Since the long-term effects of these compounds are not completely known, monitoring for the presence of phenoxy acid herbicides is important.[1]

The Thermo Scientific PolarisQ external source ion trap mass spectrometer operated in EI-MS/MS will be used to demonstrate a sensitive and robust methodology for the analysis of phenoxy acid herbicides in various matrices. This is accomplished by coupling the splitless injection technique with MS/MS. This ensures that both sensitivity and confirmation can be achieved in pure standards as well as matrix.

Instrument Conditions

PolarisQ Ion Trap

Ion Source temperature: 250 °C
Ionization Mode: +EI; 70 eV
AGC: 50
Injection Waveforms: On (default)
Buffer Gas Flow: 2.0 mL/min
MS/MS Parameters: See Table 1 on page 3.

TRACE GC Ultra Gas Chromatograph

Column: Restek Rtx™-5; 0.18 mm ID x 40 m; 0.2 µ film thickness
Oven: 100 °C (1 min); 10 °C/min
300 °C (4 min); 25 min run time
Split/Splitless injector: Splitless mode
Injector temperature: 250 °C
Column flow: 1.5 mL/min
Splitless time: 1.0 min
Injection port liner: 5 mm Focus Liner; splitless; packed with glass wool

Autosampler

Injection Volume: 2 microliters

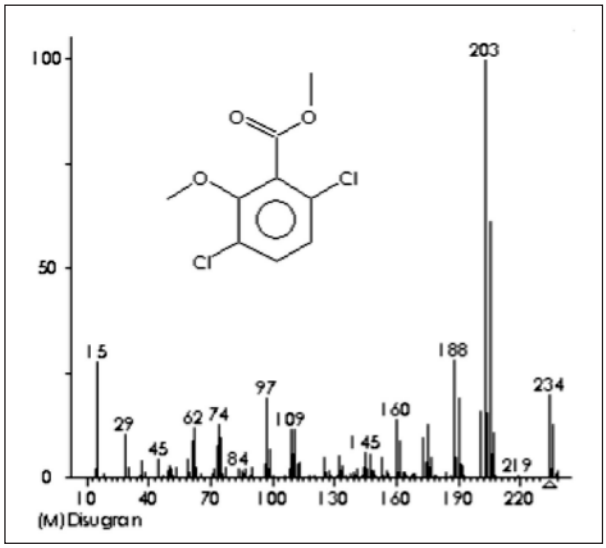

Figure 1: Full scan EI spectrum of dicamba methyl ester from NIST library.

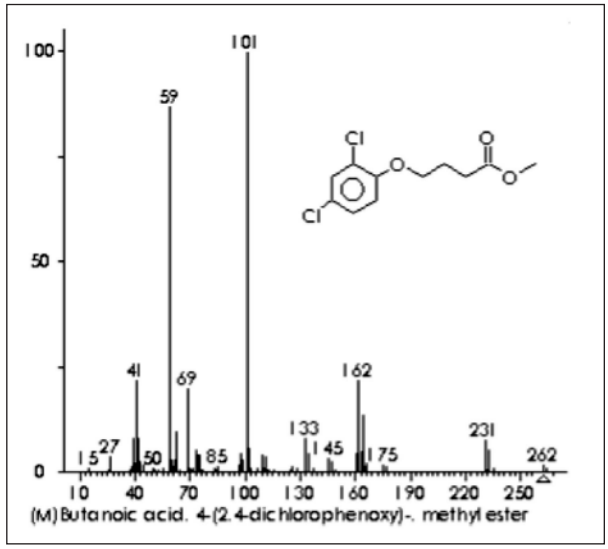

Figure 2: Full scan EI spectrum of 2,4-DB methyl ester from NIST library.

Objective

The purpose of this study was to develop a robust and sensitive method for the determination of methylated phenoxy acid herbicides by GC-MS/MS. Utilizing USEPA Method 8151 as the starting point, a calibration curve containing herbicides was purchased from AccuStandard. The method was evaluated for three matrices, soil, pond water, and lawn clippings. Each matrix was injected multiple times to validate detectivity and reproducibility.

Sample Preparation

500 mL of pond water was extracted twice with 60 mL of methylene chloride. 50 grams of soil was mixed with 50 grams of sodium sulfate and sonicated for 15 minutes with 100 mL methylene chloride. 10 grams of lawn clippings were mixed with 15 grams sodium sulfate and sonicated with 150 mL methylene chloride for 15 minutes. The methylene chloride extracts were dried with sodium sulfate and the resulting extracts were evaporated to dryness with nitrogen. The prepared extracts were reconstituted with 2000 µL of isooctane. 900 µL of the isooctane was transferred into two vials. 100 µL of iso-octane was added to the blank vial and 100 µL of the methylated standard "Level 6" was added to the "spike" vial.

Results and Discussion

Electron impact was chosen because of the consistent response of all compounds. The MS/MS parameters for each compound are listed in Table 1 and the fragmentation pathways for two of the compounds are shown in Figures 3 and 4. In each case the base peak was chosen to be the precursor ion. See Figures 1 and 2 on page 1 for dicamba methyl ester and 2,4-DB methyl ester.

A calibration curve was prepared by injecting each standard in triplicate. See Figures 5 and 7 for the mass chromatograms and Figures 6 and 8 for linearity graphs of dicamba methyl ester and 2,4-DB methyl ester respectively. The chromatograms in Figure 9 show the total ion chromatograms from the full scan analysis of the various extracts before spiking. Table 1 summarizes the calibration range and correlation coefficients for all compounds. Each of the three matrices was injected 12 times for reproducibility. External standardization was used for calibration purposes to emulate a worst-case scenario from the standpoint of system robustness, since it will not compensate for the loss of signal due to ion source or any other contamination. By injecting spiked matrix samples repetitively and plotting the resulting areas over time one can surmise how well a particular GC-MS system will perform a given method. In this case we have chosen to extract and inject soil, lawn clippings, and pond water without regard to any sample clean-up. The confirmation of peaks was performed by forward library searching against a spectrum obtained from a standard (see Table 2).

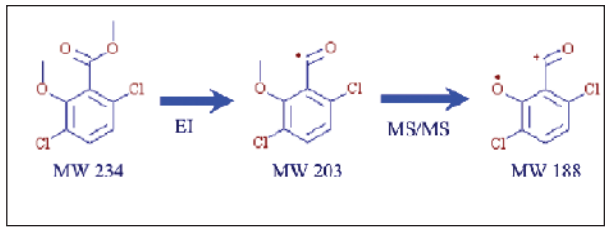

Figure 3: The EI and subsequent MS/MS fragmentation of dicamba methyl ester.

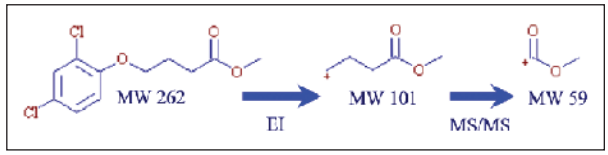

Figure 4: The EI and subsequent MS/MS fragmentation of 2,4-DB methyl ester.

COMPOUND	RETENTION TIME	PRECURSOR ION	QUAN.ION	CONC.RANGE (pg/µL)	CORRELATION COEFF.
Dicamba	10.15	203	188	10-350	0.9974
MCPP	10.49	228	169	2000-100,000	0.9935
MCPA	10.70	214	182	2000-100,000	0.9948
Dichlorprop	11.21	162	126	20-700	0.9963
2,4-D	11.45	199	125	20-700	0.9950
2,4,5-TP	12.83	196	132	5-175	0.9977
2,4,5-T	13.14	232	159	5-175	0.9990
2,4-DB	13.82	101	59	20-700	0.9963
Dinoseb	19.90	225	195	5-175	0.9937

Table 1: MS/MS Parameters and Calibration Results

COMPOUND	SPIKE		GRASS			POND WATER			SOIL		
	pg/µL	FIT STD.	pg/µL	%RSD	FIT STD.	pg/µL	%RSD	FIT STD.	pg/µL	%RSD	FIT STD.
Dicamba	35	987	31	3.2%	911	31	2.2%	922	32	4.3%	916
MCPP	6000	937	5034	4.6%	880	5367	3.5%	887	5292	5.1%	877
MCPA	6000	973	4809	2.6%	917	5131	3.5%	920	5024	5.4%	917
Dichlorprop	70	995	66	3.1%	902	64	3.5%	925	65	4.5%	914
2,4-D	70	987	69	2.5%	897	65	3.2%	896	66	4.4%	896
2,4,5-TP	17	992	17	3.5%	750	17	4.0%	853	17	6.0%	777
2,4,5-T	17	995	18	4.6%	690	18	4.9%	777	18	6.8%	695
2,4-DB	70	1000	68	3.7%	892	69	3.9%	918	69	5.1%	911
Dinoseb	17	979	28	8.0%	820	24	8.3%	921	27	13.7%	899

Table 2: Matrix Spike Recovery Data

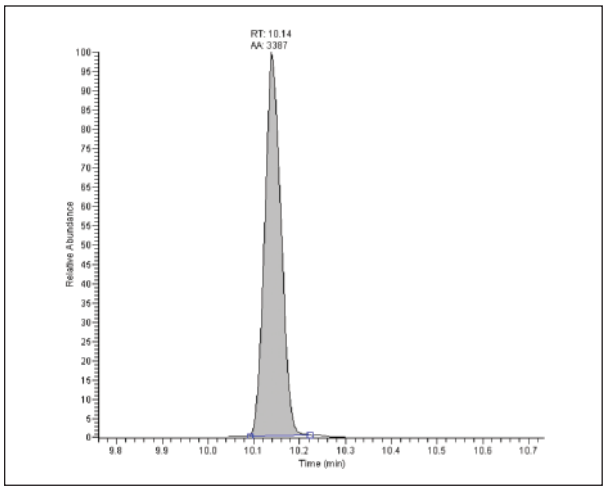

Figure 5: Mass chromatogram of MS/MS product ion for dicamba methyl ester at 10 pg/µL

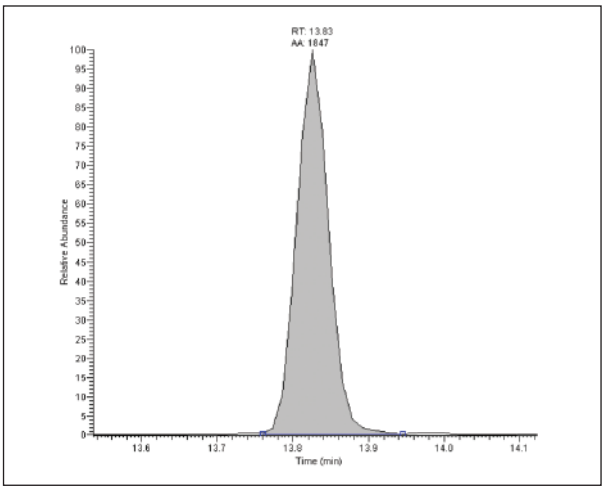

Figure 7: Mass chromatogram of MS/MS product ion for 2,4-DB methyl ester at 20 pg/µL

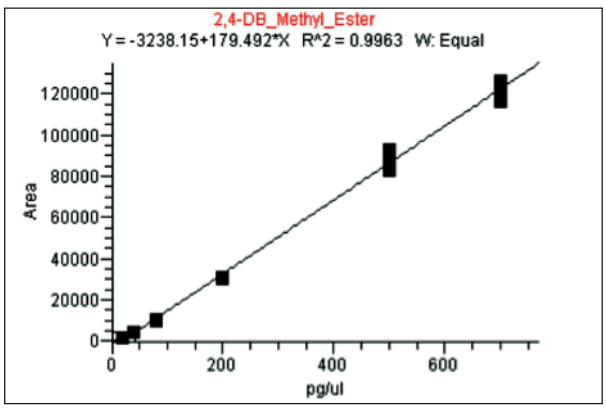

Figure 6: Calibration curve for dicamba methyl ester from 10 pg/µL to 350 pg/µL

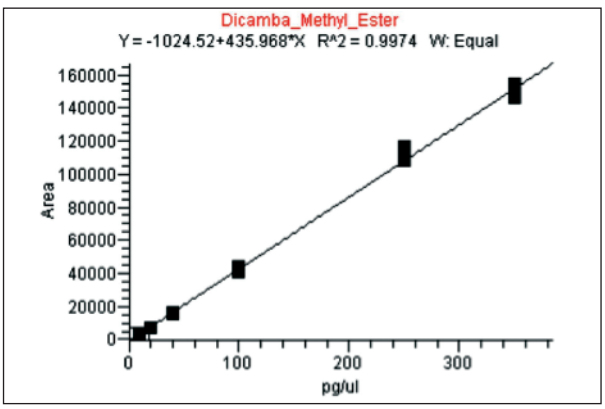

Figure 8: Calibration curve for 2,4-DB methyl ester from 20 pg/µL to 700 pg/µL

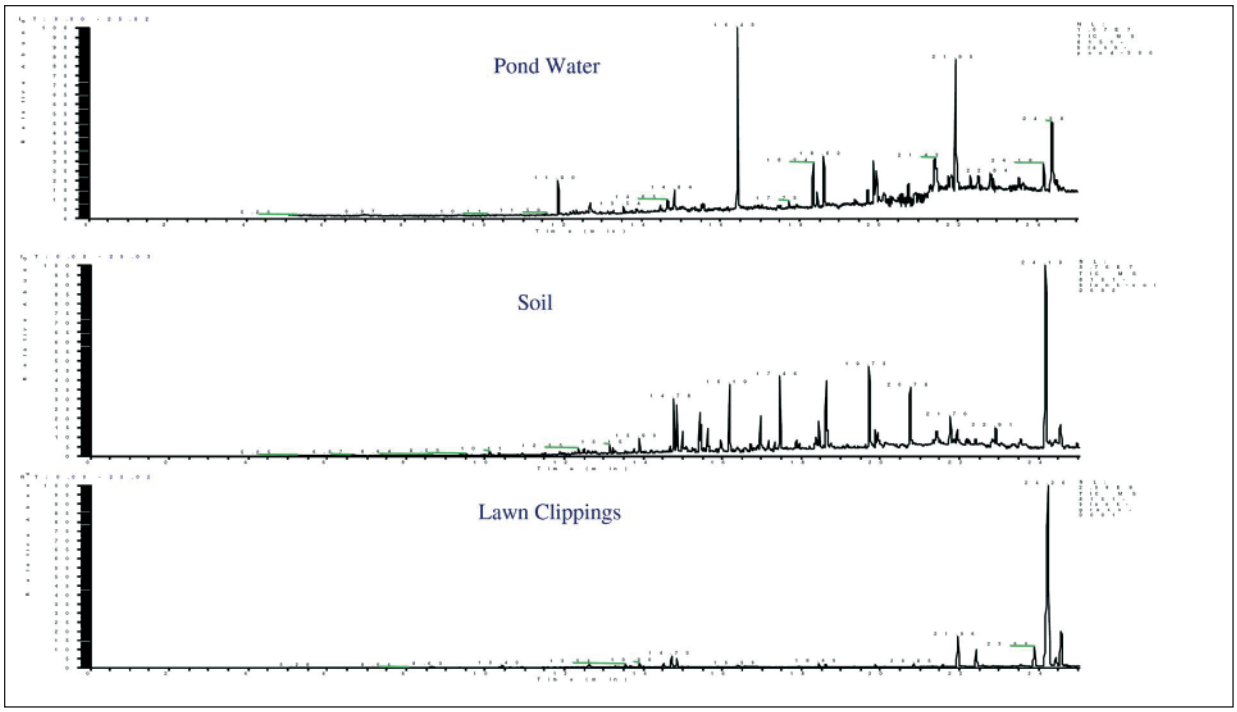

Figure 9: Full scan chromatograms of the pond water, soil, and lawn clippings extracts before spiking.

Conclusion

Although these compounds are normally analyzed by GC-ECD the use of GC-MS/MS eliminates the additional confirmation requirement of a secondary column and/or additional GC-MS analysis[2]. From the results in Table 1 the method is linear and quantitative. This was all performed without significant sample cleanup or any maintenance of the system during the entire method development and sample analysis. The use of MS/MS also provides a level of confirmation not available with conventional GC detectors. From the forward spectral library matching results (Fit - where a value of 1000 is a perfect match) in Table 2 it is clear that the methodology (MS/MS) is not only robust and quantitative but it is sensitive and provides confirmation in a single injection without the need for extensive sample preparation.

References

1. http://www.mb.ec.gc.ca/pollution/pesticides/ec00s10en.html

2. Method 8151A, Chlorinated Herbicides by GC Using Methylation or Pentfluorobenzylation Derivatization US EPA, Revision 1, December 1994

Acknowledgement

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