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LCMS™-8060NX High Performance Liquid Chromatograph Mass Spectrometer

Application News

Determination of Regulated Polar Pesticides and Herbicides in Water by LC-MS/MS

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User Benefits

- Replace four techniques with one instrument, one injection, and simplified extraction to analyze 52 polar pesticides and herbicides
- No extractions with methylene chloride and no time-consuming derivatizations
- Rapid polarity switching speed improves throughput

■ Introduction

The concentration of pesticides and herbicides in water is often measured by environmental laboratories. Many of the pesticide and herbicide methods are based on older technologies that require extraction from a large volume of water sample into an immiscible solvent, concentration to a smaller volume, and a solvent exchange prior to injection into a gas chromatograph (GC) with a semi selective or selective detector, such as an electron capture detector (ECD) or a Nitrogen-Phosphorus Detector (NPD). In addition, sample analytes may require a derivatization step, such as the derivatization of acid herbicides using diazomethane prior to analysis on the GC. Other methods may use liquid chromatography (LC) with semi-selective detectors, such as Ultraviolet (UV) absorbance or fluorescence (RF) detectors, allowing direct injection of the aqueous sample (Figure 1) However, to increase sensitivity or improve selectivity, the analytes are often derivatized during the LC process.

This application news describes the development of ASTM D8574, a new method for most regulated water soluble (polar) pesticides and herbicides using the Shimadzu LCMS-8060NX Liquid Chromatography Tandem Mass Spectrometer (LC-MS/MS) (Figure 2), which features rapid polarity switching that enables analysis of both positive and negative mode analytes in one injection. The method enables the direct analysis of 52 targeted analytes (Table 1) after cosolvation of an 8 mL sample with 2 mL methanol.

Figure 2: Nexera™ and LCMS-8060NX™

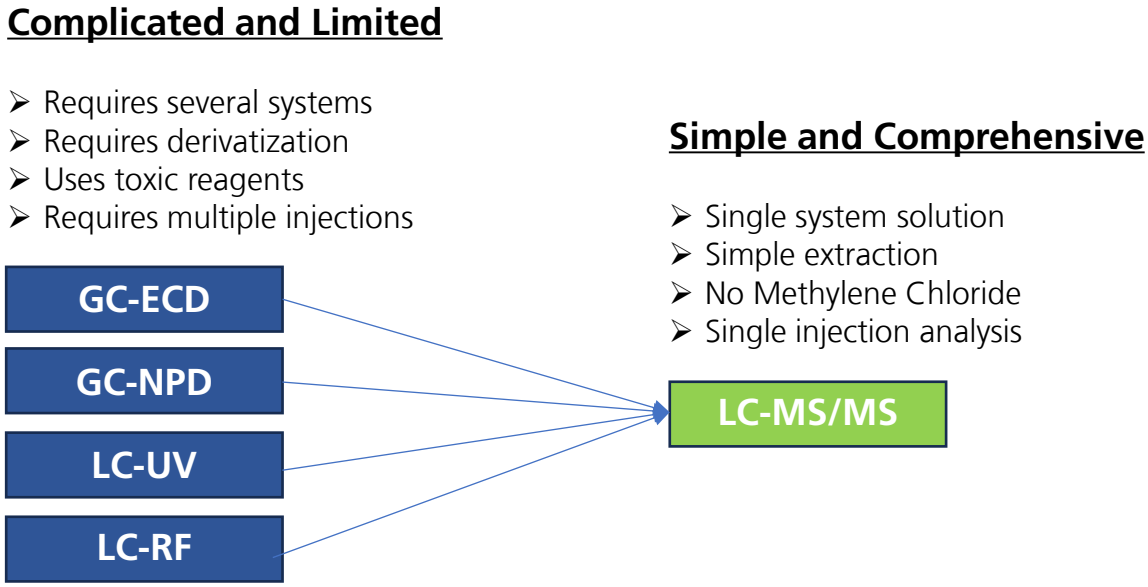

Figure 1: Instrument techniques replaced by one LCMS method

Table 1: Analytes, Polarity, Retention Time, and MS Transitions

Analytes	Polarity	Ret. Time	Primary Ion Transition	Confirmation Ion Transition
Chloramben	negative	3.281	204 > 160.15	204 > 35.05
Dalapon	negative	3.552	141 > 97.1	143 > 99.1
Bentazon	negative	6.863	239 > 132.15	239 > 197.05
Dicamba	negative	7.097	218.9 > 175	221.1 > 177
4-Nitrophenol	negative	8.197	138 > 108.1	138 > 92
3,5-Dichlorobenzoic acid	negative	9.409	188.95 > 145.05	188.95 > 35.05
2,4-D	negative	9.443	218.9 > 161.15	218.9 > 125.15
Clopyralid	negative	9.624	190.05 > 146.1	190.05 > 59
Triclopyr	negative	9.758	256 > 198	254 > 196
Dichlorprop	negative	10.048	233 > 161.05	235 > 163.05
1-Naphthol	negative	10.371	143.05 > 115.1	143.05 > 41
2,4,5-T	negative	10.375	253 > 195	253 > 159.05
Dinoseb	negative	10.449	239.3 > 194.15	239.3 > 134.2
2,4-DB	negative	10.757	247.2 > 161.1	249.1 > 163.1
2,4,5-TP (Silvex, Fenoprop)	negative	10.957	266.9 > 195.05	266.9 > 159.1
Acifluorfen	negative	11.036	360 > 316	360 > 195.05
Pentachlorophenol	negative	11.649	265 > 35.1	263 > 34.9
Fipronil	negative	11.953	435 > 330	435 > 250.05
Methamidophos	positive	3.005	142.2 > 93.95	142.2 > 124.9
Picloram	positive	4.415	240.8 > 194.9	240.8 > 222.9
Aldicarb sulfoxide	positive	4.811	207.1 > 89.1	207.1 > 132.15
Aldicarb sulfone	positive	5.236	240.1 > 86.2	240.1 > 148.15
Oxamyl	positive	5.389	237.1 > 72.1	237.1 > 90
Methomyl	positive	5.854	163 > 87.9	163 > 106.15
Thiamethoxam-d3	positive	6.08	295.05 > 214.1	295.05 > 184.1
Thiamethoxam	positive	6.114	292 > 181.1	292 > 211.1
Desisopropylatrazine	positive	6.798	174.1 > 68.15	174.1 > 104
Quinclorac	positive	6.846	242 > 223.9	242 > 160.9
Imidacloprid	positive	6.981	256.1 > 174.95	256.1 > 209
Clothianidin	positive	7.091	250 > 132.05	250 > 169.1
Mevinphos	positive	7.487	225.1 > 127	225.1 > 193
3-Hydroxycarbofuran	positive	7.512	255 > 163.15	255 > 220.05
Desethylatrazine	positive	8.179	188.1 > 146.1	188.1 > 104.05
Benomyl (carbendazim)	positive	8.27	192 > 160.1	192 > 132.1
Aldicarb	positive	8.631	208.2 > 115.85	208.2 > 89
Cyanazine	positive	9.076	240.8 > 214	240.8 > 104
Propoxur	positive	9.416	209.9 > 93.1	209.9 > 168.15
Carbofuran	positive	9.48	222.1 > 123.15	222.1 > 165
Metribuzin	positive	9.507	215.1 > 187.1	215.1 > 49.1
Simazine	positive	9.568	202.1 > 104	202.1 > 68.05
Carbaryl (NAC)	positive	9.775	202.1 > 145.1	202.1 > 127
Atrazine	positive	10.453	216.1 > 174.1	216.1 > 104.05
Atrazine-d5	positive	10.46	221.15 > 179.1	221.15 > 101.1
Azoxystrobin	positive	10.867	404 > 371.95	404 > 328.95
Methiocarb	positive	11.219	226.1 > 121.1	226.1 > 169.05
Propazine	positive	11.237	230.2 > 146.15	230.2 > 188.1
Malathion	positive	11.38	348.1 > 127.05	348.1 > 99
Acetochlor	positive	11.919	270 > 224	270 > 148
Alachlor	positive	11.933	270.1 > 238	270.1 > 162.15
Metolachlor	positive	11.977	284.1 > 252.05	284.1 > 176.1
Tebuconazole-d9	positive	12.227	317.2 > 70.05	317.2 > 125.05
Tebuconazole	positive	12.251	308.2 > 70.05	308.2 > 125.05
Propiconazole	positive	12.373	342 > 158.9	342 > 69.1
Diazinon	positive	12.435	305.1 > 169.1	305.1 > 153
Chlorpyrifos	positive	13.671	350 > 197.95	350 > 97.05

■ Sample Preparation and Analysis Conditions

Surrogate solution was added to 8 mL samples and mixed. Two ml of methanol was added, the samples were mixed, and filtered or centrifuged, if necessary, then transferred to 1.8 mL vials for analysis (Figure 3). Method blanks, Laboratory Control Samples (LCS), and matrix spikes were also prepared.

The instrument was calibrated using up to 9 concentrations from 0.01 and 100 µg/L, depending on the analyte.

For this method development, Shimadzu first compiled a list of all regulated pesticides and herbicides amenable to Liquid Chromatography (LC). We then determined MRM transitions and collision energies or retrieved them from the Shimadzu LC/MS/MS Method Package for Residual Pesticides Ver. 2 Database, if available. Next, we optimized the chromatography, choosing the best column, gradient, and ionization conditions to enable measurement of all analytes in one injection (Figure 4).

Figure 3: Generalized schematic of sample preparation steps

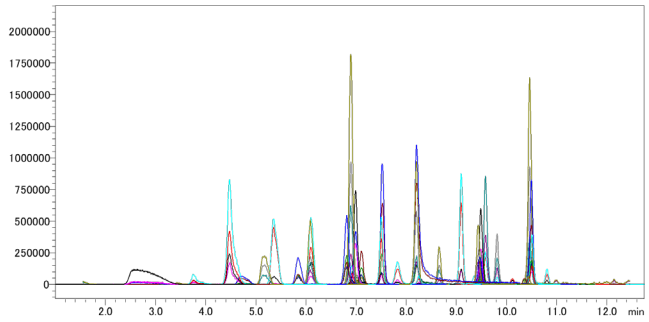

Figure 4: Chromatogram of 52 both positive and negative mode target analytes eluting within 11 minutes

As we expected, not all the original target analytes performed adequately under the chosen conditions, so they were excluded from the method. Finally, dwell times were increased to maximize response. Figure 5 shows MRM chromatograms of three residues at the lowest calibration concentration, or Limit of Quantitation (LOQ). Figure 6 shows the calibration curves of the same three compounds.

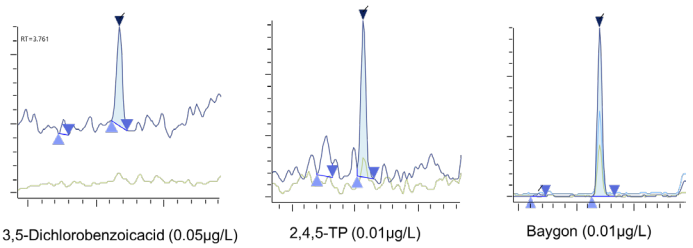

Figure 5: MRM chromatograms of three compounds at the LOQ

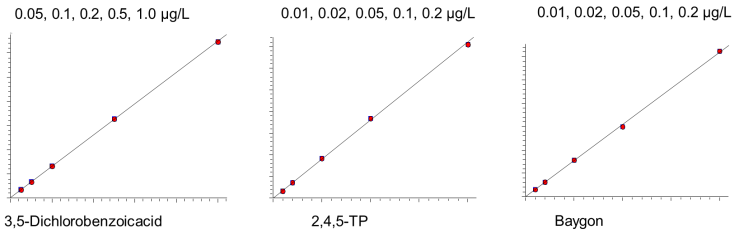

Figure 6: Calibration curve of three selected compounds

■ Quantitative Analysis

A mid-range LCS spike concentration ranging from 0.625 µg/L to 12.5 µg/L was used to verify precision and recovery and establish single laboratory performance criteria of the method (Table 2).

Six aliquots each of four sample matrices (reagent water, tap water, 3000 mg/L total dissolved solids (TDS) synthetic wastewater, and river water) were spiked at the same concentration as the LCS. Recovery and precision were calculated for each sample. Data is shown graphically in Figures 7 and 8.

Table 2: Experimentally determined LCS Recovery and Precision limits

Analytes	Spike Concentration, µg/L)	Average % Recovery	Lower Control Limit	Upper Control Limit	Maximum %RSD
Chloramben	12.5	84.7	60	120	25
Dalapon	12.5	84.7	70	130	25
Bentazon	0.625	79.1	50	110	25
Dicamba	12.5	86.2	60	120	25
4-Nitrophenol	0.625	96.2	70	130	25
3,5-Dichlorobenzoic acid	6.25	68.6	50	110	25
2,4-D	1.25	83.2	70	130	25
Clopyralid	1.25	86.1	50	110	25
Triclopyr	1.25	91.2	60	120	25
Dichlorprop	0.625	76.8	60	120	25
1-Naphthol	12.5	78.9	60	120	25
2,4,5-T	1.25	98.6	70	130	25
Dinoseb	0.625	86.8	70	130	25
2,4-DB	6.25	100	70	130	25
2,4,5-TP (Silvex, Fenoprop)	0.625	90	70	130	25
Acifluorfen	1.25	115	70	130	25
Pentachlorophenol	6.25	82.7	60	120	25
Fipronil	0.625	94	70	130	25
Methamidophos	0.625	77.7	60	120	25
Picloram	6.25	77.3	60	120	25
Aldicarb sulfoxide	0.625	82.2	70	130	25
Aldicarb sulfone	0.625	89.7	70	130	25
Oxamyl	0.625	92.1	70	130	25
Methomyl	0.625	94.8	70	130	25
Thiamethoxam-D3	0.625	81.4	60	120	25
Thiamethoxam	0.625	78.5	60	120	25
Desisopropylatrazine	0.625	97.2	70	130	25
Quinclorac	0.625	80	60	120	25
Imidacloprid	0.625	78.5	60	120	25
Clothianidin	0.625	87.5	60	120	25
Mevinphos	0.625	88.6	70	130	25
3-Hydroxycarbofuran	0.625	98.4	70	130	25
Desethylatrazine	0.625	95.4	70	130	25
Benomyl (carbendazim)	0.625	155	70	170	25
Aldicarb	0.625	116	70	130	25
Cyanazine	0.625	91.3	70	130	25
Propoxur	0.625	89.9	70	130	25
Carbofuran	0.625	95.1	70	130	25
Metribuzin	0.625	89.2	70	130	25
Simazine	0.625	95.7	70	130	25
Carbaryl (NAC)	0.625	94.6	70	130	25
Atrazine	0.625	105	70	130	25
Atrazine-D5	0.625	101	70	130	25
Azoxystrobin	0.625	88.8	70	130	25
Methiocarb	0.625	91.5	70	130	25
Propazine	0.625	97.8	70	130	25
Malathion	0.625	96	70	130	25
Acetochlor	1.25	110	70	130	25
Alachlor	0.625	96.8	70	130	25
Metolachlor	0.625	96.7	70	130	25
Tebuconazole-D9	0.625	92	70	130	25
Tebuconazole	0.625	92.4	70	130	25
Propiconazole	0.625	91.5	70	130	25
Diazinon	0.625	91.4	70	130	25
Chlorpyrifos	0.625	80.1	70	130	25

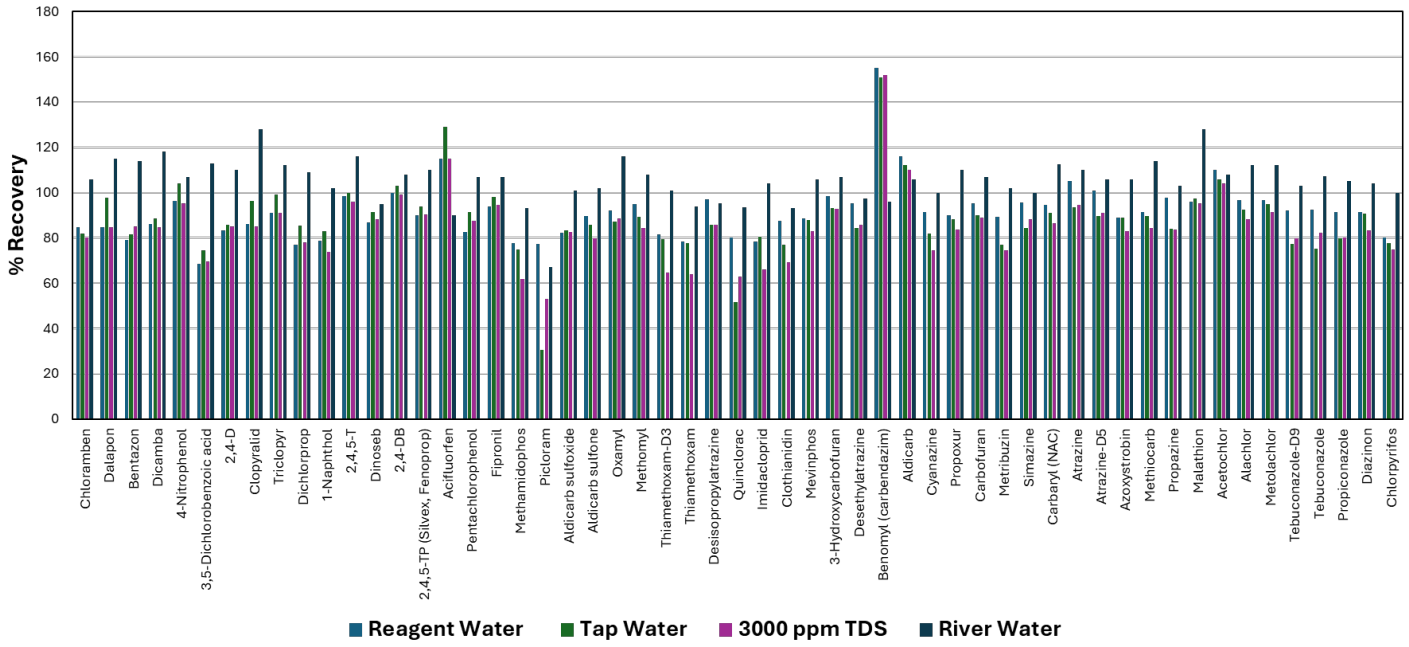

Figure 7: Recovery of mid-level spiked target compounds in various matrices

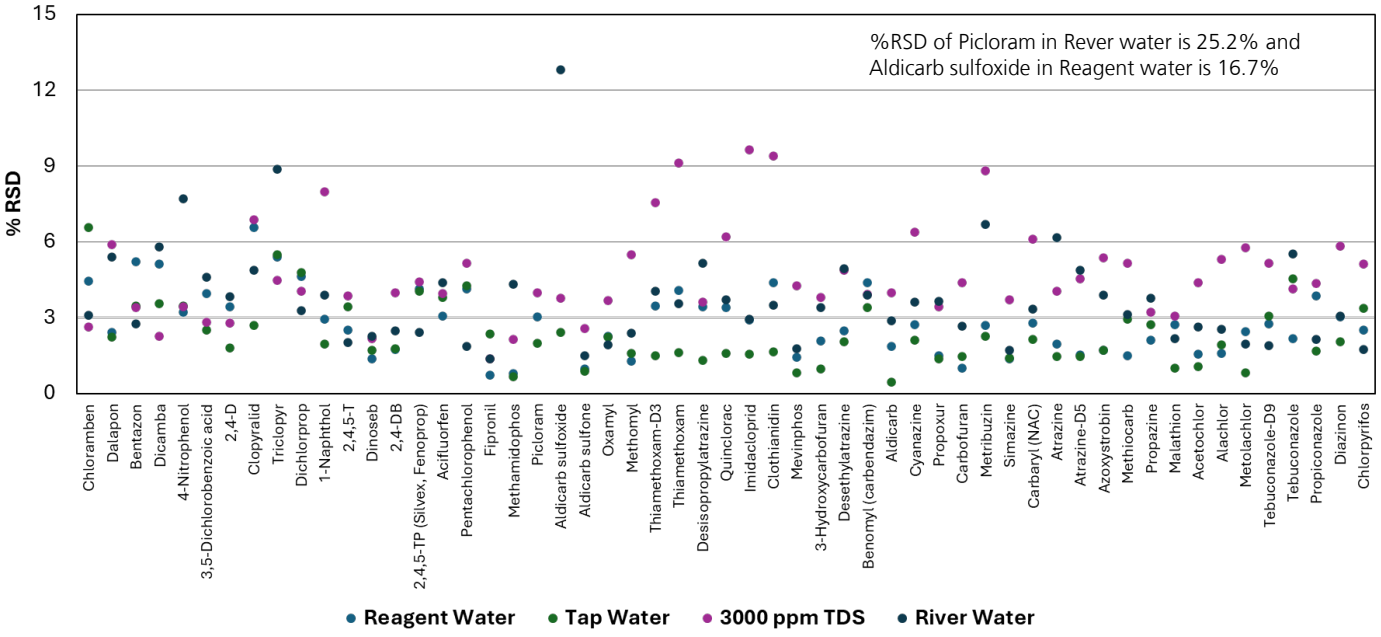

Figure 8: % RSD of Mid-level spiked target compounds in various matrices

■ Conclusion

A new ASTM D8574 method was developed by Shimadzu and validated in four matrices. The method analyzes polar pesticides and herbicides that are regulated in the United States using a single injection into the Shimadzu LCMS-8060NX, or equivalent, replacing other methods that require liquid-liquid extractions or derivatizations. Fifty-two target analytes, of both positive and negative mode, are separated in one chromatogram within 11 minutes.

■ Reference

ASTM D8574

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