Determination of Pesticides in Water by SPE and LC/MS/MS in Both Positive and Negative Ion Modes

Application Note

Environmental

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Abstract

Using solid phase extraction (SPE) and liquid chromatography/tandem mass spectrometry (LC/MS/MS), 46 pesticides in positive ion mode and 14 pesticides in negative ion mode were analyzed at low pg level on column without any derivatization. Good linearity was observed for all analytes from 5 pg to 1 ng on column.

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Introduction

To monitor trace pesticide residues in surface and ground water, an effective sample preparation and analysis method is required. In 1996, U.S. Geological Survey National Water Quality Laboratory (NWQL) developed and implemented a graphitized carbon-based SPE and high-performance liquid chromatography (HPLC) method to determine polar pesticide concentrations [1].

Subsequently, the NWQL developed an HPLC-mass spectrometry (MS) method to improve the sensitivity and selectivity. This method is capable of quantifying pesticides and pesticide metabolites in filtered water at concentrations as low as 10 ng/L.

Taking advantage of the Multiple Reaction Monitoring (MRM) technique, any interference and matrix signal from organic matter in the water can be minimized from the target compound signals for better confirmation and quantitation. In this application, SPE and LC/MS/MS methods are described to analyze 46 pesticides in positive ion mode and 14 pesticides in negative ion mode.

Experimental

Sample Preparation Procedure
See reference 1 for more information

1. Filter water samples in the field or laboratory using 0.7-µm glass fiber filters.
2. Pump 1 L of the filtered water sample, at a flow rate of 20 mL/min, through a Carbopak-B SPE cartridge containing 0.5 g of graphitized carbon sorbent.
3. Elute the compounds with 1.5 mL methanol, followed by 13 mL of an 80:20 methylene chloride:methanol mixture that has been acidified with trifluoroacetic acid anhydride (0.2%).
4. Reduce the two fractions to near dryness and then combine. The final volume of the extract is 1 mL.

Calibration Samples

Separate stock solutions of either positive ion mode or negative ion mode analytes were diluted 1 to 10 to make the calibration standard solutions. The concentrations of the seven calibration solutions were 5, 10, 50, 100, 200, 500, and 1,000 pg/µL (ppb).

Instrumentation

Positive Ion Mode

LC:	1200 LC
Column:	ZORBAX Extend-C-18, RRHT, 2.1 mm × 100 mm, 1.8 µm
Column temperature:	40 °C
Mobile phases:	A: 0.1% formic acid in water, add NH_4OH buffer to pH 5.5 B: Acetonitrile (ACN)
Flow rate:	0.3 mL/min

Gradient:

Time	**%B**
0	0
15	100
20	100
21.5	0

Injection volume:	1.0 µL
MS:	G6410A QQQ
Ionization:	ESI (+)
Mass range:	100–500 amu
Scan time:	300 ms
Capillary:	3500 V
Nebulizer P:	40 psi
Drying gas:	9 L/min
Gas temperature:	350 °C
Skimmer:	35 V

Negative Ion Mode

LC:	1200 LC
Column:	ZORBAX Extend-C-18, RRHT, 2.1 mm × 100 mm, 1.8 µm
Column temperature:	60 °C
Mobile phases:	A: 0.04% glacial acetic acid in water B: Acetonitrile (ACN)
Flow rate:	0.3 mL/min

Gradient:

Time	**%B**
0	0
1	40
2	52
3	60
4	100
8	100
9	0

Injection volume:	1.0 µL
MS:	G6410A QQQ
Ionization:	ESI (–)
Mass range:	120–400 amu
Scan time:	300 ms
Capillary:	3500 V
Nebulizer P:	40 psi
Drying gas:	9 L/min
Gas temperature:	200 °C
Skimmer:	35 V

The MRM parameters for positive ion mode and negative ion mode are listed in Tables 1 and 2, respectively.

Table 1. Positive Ion Mode MRM Method Parameters

Name	RT	Precursor	Quant ion	Qual ion	Collision V	Dwell	Segment
3(4 chlorophenyl) methyl/urea	8.05	185	128	93	10	30	4
3-Keto Carbofuran	8.24	236	179	151	10	30	4
3-OH Carbofuran	6.90	238	163	181	10	40	3
Aldicarb	8.20	116	89	70	5	30	4
Aldicarb sulfone	5.52	223	76	86	5	50	2
Aldicarb sulfoxide	4.99	207	89	132	5	150	1
Atrazine	9.86	216	174	96	20	40	5
Bendiocarb (Ficam)	9.32	224	167	109	5	40	5
Benomyl	6.61	192	160	132	30	40	3
Bensulfuron	10.86	411	149	182	15	60	7
Bromacil	8.44	261	205	162	20	30	4
Caffeine	5.48	195	138	110	15	50	2
Carbaryl	9.69	202	145	127	15	40	5
Carbofuran	9.36	222	165	123	10	40	5
Chlorimuron ethyl	11.57	415	186	213	10	60	8
Cycloate	14.52	216	83	154	15	60	8
Desethyl atrazine	7.06	188	146	79	15	40	3
Desisopropyl atrazine	5.94	174	68	104	30	50	2
Desisopropyl desethyl atrazine	1.76	142	86	57	15	150	1
Diphenamid	10.82	240	134	167	20	60	7
Diuron	10.02	233	72	160	20	75	6
Fenuron	6.90	165	72	92	15	40	3
Flumetsulam	7.49	326	129	262	20	30	4
Fluometuron	9.70	233	72	168	20	40	5
Hydroxy-atrazine	6.82	198	156	114	20	40	3
Imazaquin	7.68	312	267	252	20	30	4
Imazethapyr	6.99	290	177	69	30	40	3
Imidacloprid	7.01	256	175	209	15	40	3
Linuron	11.45	249	160	182	15	60	7
Metalaxyl (Apron)	10.15	280	220	192	10	75	6
Methiocarb	11.28	226	169	121	5	60	7
Methomyl	5.77	163	88	106	5	50	2
Metsulfuron methyl	8.43	382	167	199	15	30	4
Neburon	12.99	275	57	88	20	60	8
Nicosulfuron (Accent)	7.97	411	182	213	15	30	4
Norflurazon	10.51	304	284	160	30	75	6
Oryzalin	12.58	347	288	305	10	60	8
Oxamyl (Vydate)	5.59	237	72	90	10	50	2
Propham	10.68	138	120	92	10	75	6
Propiconazole (Tilt)	12.89	342	156	69	20	60	8
Propoxur (Baygon)	9.26	210	111	168	5	40	5
Siduron	11.12	233	137	94	15	60	7
Siduron isomer	11.28	233	137	94	15	60	7
Sulfometuron, methyl ester	9.25	365	150	199	15	40	5
Tebuthiuron	8.14	229	127	116	15	30	4
Terbacil	8.69	161	144	88	15	30	4

Table 2. Negative Ion Mode MRM Method Parameters

Name	RT	MW	Quant	Qual	Frag V	Collision V	Dwell	Segment
Clopyralid	3.47	191	190 > 146	192 > 148	80	5	70	1
Picloram	3.69	240	239 > 195	241 > 198	80	5	70	1
Dicamba	4.31	220	219 > 175	219 > 145	60	0	50	2
DCPA	4.49	330	273 > 215	271 > 213	100	5	50	2
Bentazone	4.69	240	239 > 132	239 > 197	120	25	50	2
2,4-D	5.02	220	219 > 161	221 > 163	80	15	25	3
Bromoxynil	5.06	275	274 > 79	274 > 81	120	25	25	3
MCPA	5.09	200	199 > 141	201 > 143	100	10	25	3
Triclopyr	5.26	255	254 > 196	256 > 198	80	10	25	3
2,4-DP	5.42	234	233 > 161	235 > 163	80	5	25	3
2,4-DB	5.66	248	247 > 161	249 > 163	80	10	40	4
MCPB	5.70	228	227 > 141	229 > 143	80	5	40	4
Acifluorofen	5.89	361	360 > 316	360 > 286	60	5	40	4
Dinoseb	6.50	240	239 > 193	239 > 163	120	25	40	4

Results and Discussion

Figure 1 shows the total ion chromatogram (TIC) for the positive ion mode. As seen in Figure 1, the analysis time is less than 15 minutes for the 46 analytes. Using a 1.8 µm particle size column, the peak widths of these analytes are about 0.1 minute. The narrower peak width helps to achieve a higher signal-to-noise (s/n) ratio.

Analysis time in negative ion mode is less than 7 minutes for the 11 analytes, as seen in Figure 2.

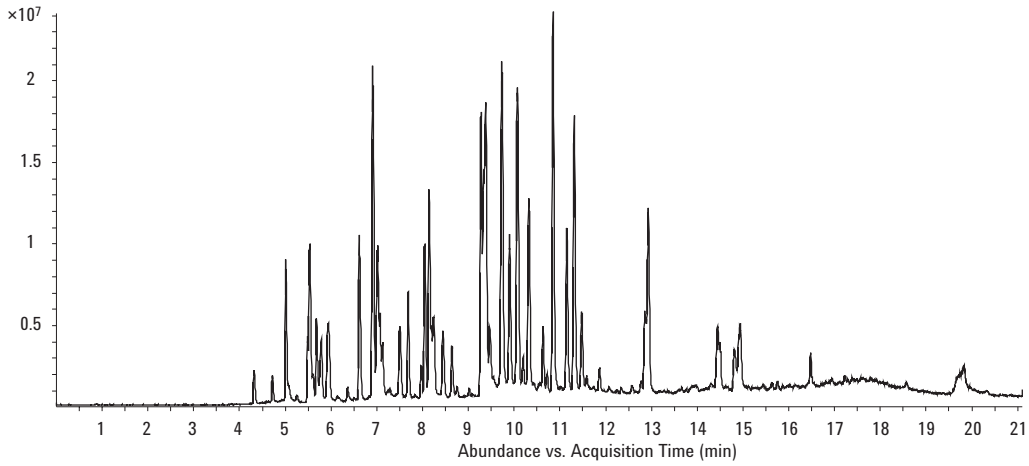

Figure 1. Positive ion mode TIC of 46 pesticides.

A few compounds, for example, Dicamba, MCPB and 2,4-DB, are sensitive to heat from the drying gas. Higher drying gas temperature (350 °C) will lower the intensity of the precursor ion.

Therefore, in the negative ion mode, the drying gas temperature was set to 200 °C. Figure 3 shows the overlaid chromatograms of all 14 pesticides, each at 5 pg on column, from the negative ion mode MRM analysis.

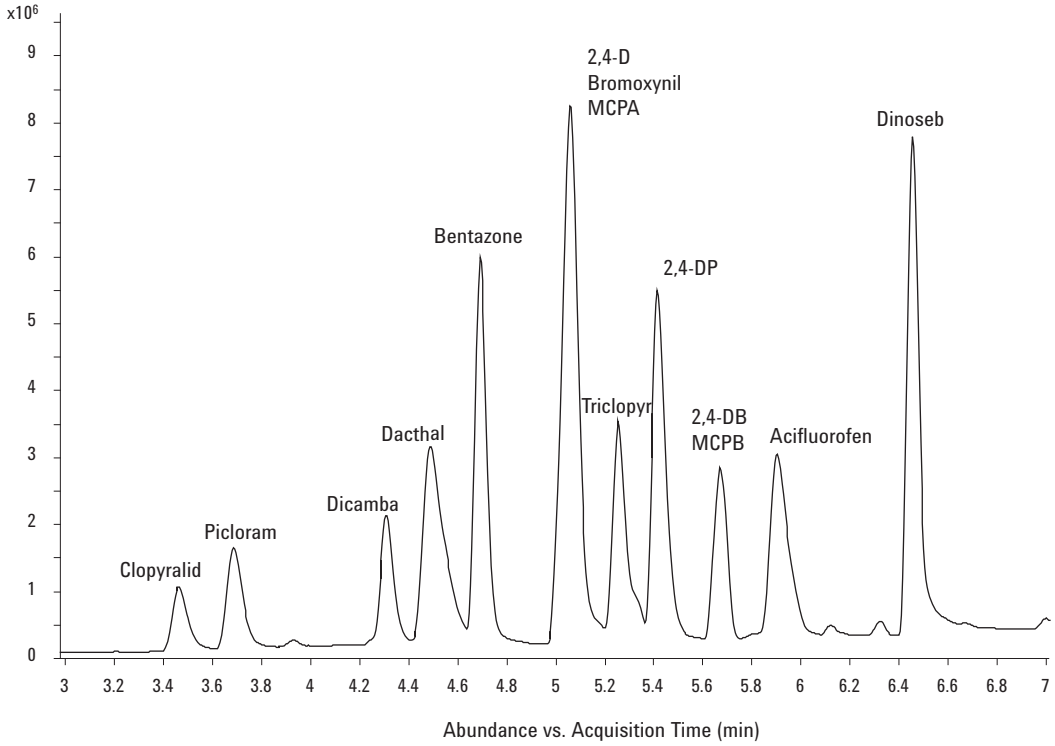

Figure 2. Negative ion mode TIC of 14 pesticides.

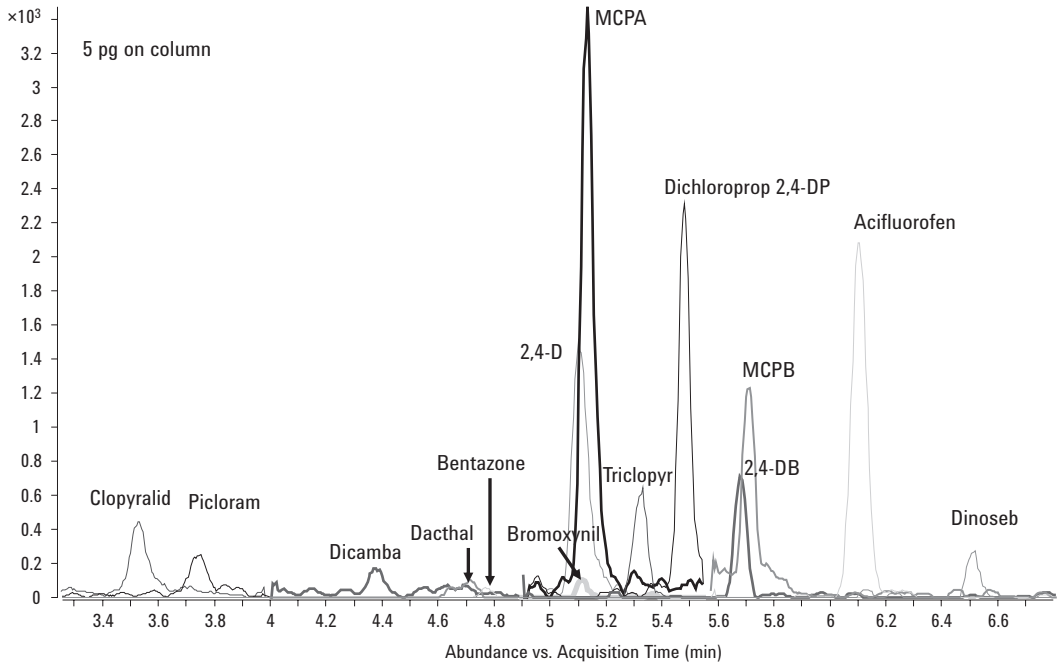

Figure 3. Overlay of the MRM results from 14 pesticides in negative ion mode.

Table 3 shows the linearity results for 14 pesticides over the range of 5, 10, 50, 100, 200, 500, and 1,000 pg on column. The calibration model used was a linear model that included origin with no weighting. All analytes showed excellent linearity.

Table 3. Pesticide Linearity: 5, 10, 50, 100, 200, 500, 1,000 pg on Column

Pesticide	R^2 (linear fit, include origin, no weighting)
Clopyralid	0.9976
Picloram	0.9993
Dicamba	0.9975
DCPA	0.9994
Bentazone	0.9975
2,4-D	0.9990
Bromoxynil	0.9999
MCPA	0.9980
Triclopyr	0.9990
2,4-DP	0.9948
2,4-DB	0.9887
MCPB	0.9847
Acifluorofen	0.9969
Dinoseb	0.9905

Conclusions

Using SPE and LC/MS/MS, 46 pesticides in positive ion mode and 14 pesticides in negative ion mode were analyzed at low pg level on column without any derivatization. Good linearity of responses was observed from 5 pg to 1 ng of analytes on column.

Reference

1. U.S. Geological Survey Water-Resources Investigations Report 01-4134, http://nwql.usgs.gov/Public/pubs/WRIR01-4134.html

Acknowledgments

The author gratefully acknowledges the assistance of Stephen Werner and Ed Furlong of the National Water Quality Lab – United States Geological Survey (Lakewood, CO) for providing the sample preparation procedures and extracts used in this work.

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Published in the USA
September 18, 2008
5989-5320EN

Agilent Technologies