

Automated detection of trace level basic and acidic pesticides and herbicides in drinking water by online SPE LC/MS

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Introduction

The presence of pesticides and herbicides in drinking water poses threats to human health and the environment. As a result, their levels in municipal water supplies are regulated by several government agencies down to part-per-trillion levels (European Union Water Directive 98/83/EC)¹. The diverse range of analyte properties, low analyte concentrations and variable water matrix composition present significant analytical challenges.

We have utilized an automated Agilent FlexCube online SPE solution with an LC/6460 QQQ system for the simultaneous quantitation of basic and acidic pesticides and herbicides at ppt or sub-ppt levels in drinking water. This flexible system features an integrated loading pump and interchangeable valve heads to support large sample volume injections (up

Experimental

Pesticides and herbicides were spiked into tap water (Santa Clara, California) at designated concentrations from a working solution of 1 ppm in acetonitrile. The samples were loaded onto cartridges alternatively via valve control. Figure 1 showed Flexcube system and the hydrolytic pathway of the cartridges loading and eluting in this study.

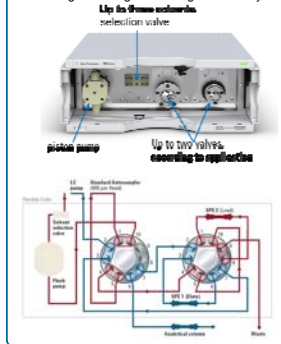


Figure 1: FlexCube and two valve system in this study

Experimental (Cont'd)

Reagents

Acetonitrile were from Honeywell (p/n: 015-4). Ultrapure water was obtained from a Milli-Q Integral system. Formic acid was from Fluka (p/n: 94318). The pesticides and herbicides mixtures were from Agilent (p/n: 5190-0469).

HPLC Method

Agilent HPLC system consisted of an Agilent 1290 Infinity FlexCube (G4227A), Agilent 1260 Binary Pump (G1312B), an Agilent 1260 Infinity Autosampler (G1326B with 900 µL loop), and an Agilent 1290 Infinity Thermostatted Column

Column and Cartridge	Agilent 1290 Infinity FlexCube (G4227A) with 1260 Binary Pump (G1312B) and 1260 Infinity Autosampler (G1326B) with 900 µL loop.
Mobile Phase	0.1% Formic acid in water (pH 3.0) and 0.1% Formic acid in acetonitrile (pH 3.0).
Binary Pump	Agilent 1260 Binary Pump (G1312B) with 1260 Infinity Autosampler (G1326B) with 900 µL loop.
Gradient	0.1% Formic acid in water (pH 3.0) and 0.1% Formic acid in acetonitrile (pH 3.0).
FlexCube	Agilent 1290 Infinity FlexCube (G4227A) with 1260 Binary Pump (G1312B) and 1260 Infinity Autosampler (G1326B) with 900 µL loop.
Time zone	0.1% Formic acid in water (pH 3.0) and 0.1% Formic acid in acetonitrile (pH 3.0).

Table 1: HPLC gradient conditions

Mass Spectrometer Parameters

Detection was carried out with Agilent 6460 triple quadrupole mass spectrometer with the proven Agilent JetStream, electrospray ionization source. The MRM transitions of analytes and source parameters were optimized in an automatic fashion using Agilent Optimizer software. The mass spectrometer parameters listed in Table 2.

Parameter	Value
Modulator	36 psi
Sheath gas temp	300°C
Sheath gas flow	12 L/min
Cup voltage	3000V (-14000V)
Nozzle voltage	90V (-100V)
Data MSV	200 Hz

Table 2: Agilent 6460 Mass Spectrometer and Source Parameters with Agilent JetStream ionization source

Results and Discussion

A: The MRM transitions, collision energies and fragmentor voltages

These compound dependent parameters were optimized in an automatic fashion with Agilent Optimizer software. The values were listed in Table 3.

Compounds	Precursor Ion	Product Ion	Tag (V)	CF (V)	Polarity	Compounds	Precursor Ion	Product Ion	Tag (V)	CF (V)	Polarity
Metolachlor	418.07	175	140	57	-	Carbendazim	229.1	165.1	80	30	-
Metolachlor	418.07	140	140	80	+	Carbendazim	222.1	123.1	80	30	+
Pyridoxaloximin	388.11	163.8	65	8	-	Atrazine	216.1	174.1	175	16	-
Pyridoxaloximin	388.11	163.1	95	20	+	Atrazine	218.1	88	125	40	+
Malathion	331	176.8	80	6	+	Aminocarb	208.1	187.7	106	17	+
Malathion	331	99	80	10	-	Aminocarb	209.1	137.2	106	21	-
Diazinon	306.1	168.1	106	37	+	Thiabendazole	207	176	130	74	+
Diazinon	306.1	97	106	40	-	Thiabendazole	202	131	130	36	-
Imazalil	297.1	201	115	15	+	Hexachlorocyclopentadiene	461	158	120	15	+
Imazalil	297.1	109	115	20	-	Hexachlorocyclopentadiene	461	141	120	45	-
Metolachlor	278.1	216.1	70	4	-	Atrifluorfen	359.99	316	60	5	-
Metolachlor	278.1	124.2	70	15	+	Atrifluorfen	359.99	288	60	6	+
Imazapyr	267.1	217.1	170	20	-	2,4,5-TP	265.94	164.9	80	17	-
Imazapyr	267.1	88.1	170	40	+	2,4,5-TP	268.94	168.9	80	30	+
Dimethoate	230	168.8	70	0	-	2,4,5-TP	264.9	164.9	70	15	-
Dimethoate	230	176	70	18	+	2,4,5-TP	267.9	164.9	70	10	+
Metolachlor	229	77.1	65	16	-	Bentazone	239.1	197	75	20	-
Metolachlor	229	48.1	65	17	+	Bentazone	238.1	137	75	24	+
Malathion	168	176.1	80	25	-	Dinoseb	239.07	209	120	25	-
Malathion	168	83.2	80	18	+	Dinoseb	238.97	183	170	25	-

Table 3: Optimized MRM transitions for analytes in this method

B: Linearity, LOD and LLOQ of pesticides and herbicides in drinking water

The analytes were spiked into drinking water from a concentration of 0.1 to 100 ppt in positive mode and 10 ppt to 10 ppb in negative mode. Figure 2 showed the signal intensity of analytes. Linearity was evaluated covering at least 2 orders of magnitude with excellent correlation coefficient. Chromatographic separation was shown in figure 2. Method precision and an example of linear calibration curve was illustrated in figure 3. Summary of performance was listed in Table 4.

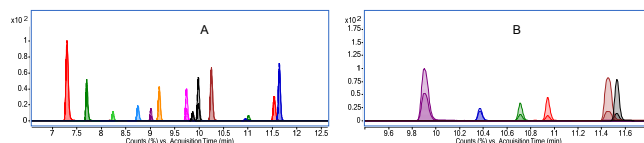


Figure 2: 10 ppt of 14 pesticides and herbicides in positive ion mode (A) and 1 ppb of 6 pesticides and herbicides in negative ion mode (B)

Results and Discussion

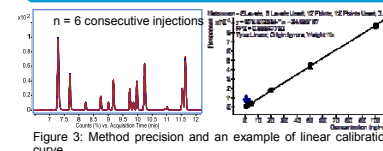


Figure 3: Method precision and an example of linear calibration curve

Compound	RI	HI	HSU (%)	Area	HSU (%)	R ²	LOU (ppt)	LOQ (ppt)
Aminocarb	7.288	0.03	8.42	0.9996	0.125	0.038		
Thiabendazole	7.704	0.02	15.40	0.9970	0.273	0.081		
Imazapyr	8.237	0.06	7.18	0.9990	0.886	0.200		
Dimethoate	8.756	0.02	7.88	0.9992	0.666	0.200		
Imazalil	9.032	0.02	7.83	0.9990	5.000	2.000		
Metolachlor	9.188	0.04	8.30	0.9998	0.150	0.053		
Carbendazim	9.749	0.03	6.62	0.9995	0.200	0.050		
Metolachlor	9.875	0.03	5.76	0.9990	0.500	0.700		
Atrazine	9.965	0.04	8.21	0.9995	0.050	0.015		
Metolachlor	10.259	0.05	5.94	0.9990	0.110	0.048		
Malathion	10.950	0.05	10.72	0.9980	5.000	2.000		
Malathion	11.021	0.04	9.53	0.9990	1.750	0.400		
Diazinon	11.543	0.06	8.83	0.9960	1.000	0.500		
Diazinon	11.644	0.06	6.33	0.9975	4.166	0.125		
Bentazone	8.898	0.03	1.04	0.9968	0.75	0.08		
2,4,5-TP	10.388	0.03	2.20	0.9995	6.8	2.0		
2,4,5-TP	10.769	0.02	4.05	0.9996	5.13	1.54		
Atrifluorfen	10.942	0.00	5.68	0.9983	10.3	3.1		
Dinoseb	11.450	0.02	1.41	0.9991	3.84	1.15		
Hexachlorocyclopentadiene	11.526	0.02	7.04	0.9995	10	50		

Table 4: Summary of detection sensitivity and precision

Conclusions

The analysis of basic and acidic pesticides and herbicides in drinking water by online SPE LC/6460 triple quadrupole MS delivers a method applicable for an available kit containing compounds of both acid and basic classes. Their performance is demonstrated. All compound delivered excellent linearity, LLOQs and LODs at low level. Peak area RSDs and retention time RSDs as well as recoveries were excellent for the applied online SPE method. Automatic online SPE is superior to tedious offline SPE with much less solvent consumption and labor cost for water quality analysis. All components are controlled under one software package and this makes method development much easier to conduct.

C Carryover and Recovery

Carryover was evaluated by injecting 100 ppt (positive) or 10 ppb (negative) of analytes followed by a blank. Atrazine and Bentazone showed the highest carryover at 0.5% and 0.3% respectively. Most of the analytes are undetectable in blank. Figure 4 showed the carryover for Atrazine.

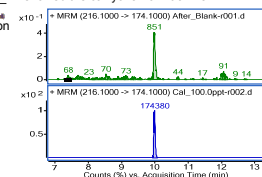


Figure 4: Atrazine showed the highest carryover at 0.5%

Recovery was evaluated by comparing direct injection of analytes to analytical column vs. trapping the analytes on online SPE cartridges. Most of the recoveries range from 80-120% as shown in figure 5.



Figure 5: examples of recovery of selected analytes

References

- European Union Drinking Water Directive 98/83/EC http://ec.europa.eu/environment/water/water-drink/index_en.htm
- "Quantification of trace-level herbicides in drinking water by online enrichment with the Agilent 1200 Infinity Series Online-SPE Solution and Triple Quadrupole MS Detection," Agilent Application Note, Publication Number 5991-1738EN, 2013.
- "Comparison of Direct Injection and Online SPE for Quantification by LC/MS of Trace-Level Herbicides in Water," Agilent Technical Note, Publication Number 5991-2140EN, 2013.