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Comparison of matrix effects in multi-residue pesticide analysis when using online SPE or direct injection in Liquid Chromatography-tandem Mass Spectrometry

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Introduction

The multi-residue determination of pesticides is extremely challenging due to the uncertainty concerning adverse effects that those residues may have on human health after a lengthy exposure at low levels. Consequently, stricter food safety regulations are being enforced around the world, placing pesticide analysis laboratories under increasing pressure to expand the list of targeted pesticides, to detect analytes at lower levels and with greater precision, to reduce analysis turnaround times, and all the while maintaining or reducing costs. Most pesticides are generally analyzed by gas chromatography but this technique however, is not suitable for polar pesticides or thermolabile. A well established tool for the determination of residues of such pesticides is liquid chromatography combined with tandem mass spectrometry.

The aim of this study was to develop and compare two fast, sensitive and simple methodologies for the multi-residue of pesticides, that require the online SPE or direct injection in Liquid Chromatography-tandem Mass Spectrometry, thus the limits of quantification and matrix effects can be compared.

Materials and Methods

Sample preparation

Samples of 94 pesticides spiked at different concentrations (5 to 300ng/L) in spring water and different environmental waters were prepared adding ascorbic acid (800 mg/L) and phosphoric acid (0.2% v/v) and three internal standards (d5-Atrazine, d6-Bentazone, d6-Diuron).

LC-MS/MS analysis

Sample were analyzed using Nexera X2 UHPLC system (Shimadzu Corp.) with or without online SPE. Detection was performed using a highly sensitive triple quadrupole mass spectrometer (LCMS-8050, Shimadzu Corp.) in MRM mode. Thanks to the high speed polarity switching capability of the MS, measurements were made in positive and negative electrospray ionization in one injection. Electrospray parameters (gas flows and temperatures) were optimized to find the optimal combination. The whole acquisition method lasted 15 min.

Table 1 – Direct injection conditions

Analytical column	: Zorbax Eclipse Plus C18 2.1*150 mm, 3.5 µm.
Mobile phases	: A = Water + 0.05% acetic acid B = Acetonitrile + 0.05% acetic acid
Gradient	: 10% B (0-1.5min), 50% B (3.5 min), 100% B (9.5 min), 100% B (13.4 min), 10%B (13.5 min), Stop (15.0min)
Column temperature	: 40 °C
Injection volume	: 100 µL
Flow rate	: 0.4 mL/min

Table 2 – online SPE conditions

Analytical column	: Restek Raptor ARC-18 100*2.1 mm 2.7 µm
SPE cartridge	: Spark holland PLRP-S 10x2mm 15µm
Mobile phases	: A = Water + 0.05 % acetic acid B = Methanol
SPE Mobile phases	: Loading (A'): Water + 1% acetic acid Elution/Wash (B'): Methanol
Gradient	: 0% B (0-1.55), 100% B (1.6), 100% B (9.95 min), 10% B (10 min), Stop (15.0min)
Column temperature	: 30 °C
Injection volume	: 1000 µL
Flow rate	: 0.6 mL/min
Flow rate SPE	: 0.2 to 2 mL/min

Results and discussion

Comparison between direct injection and online SPE

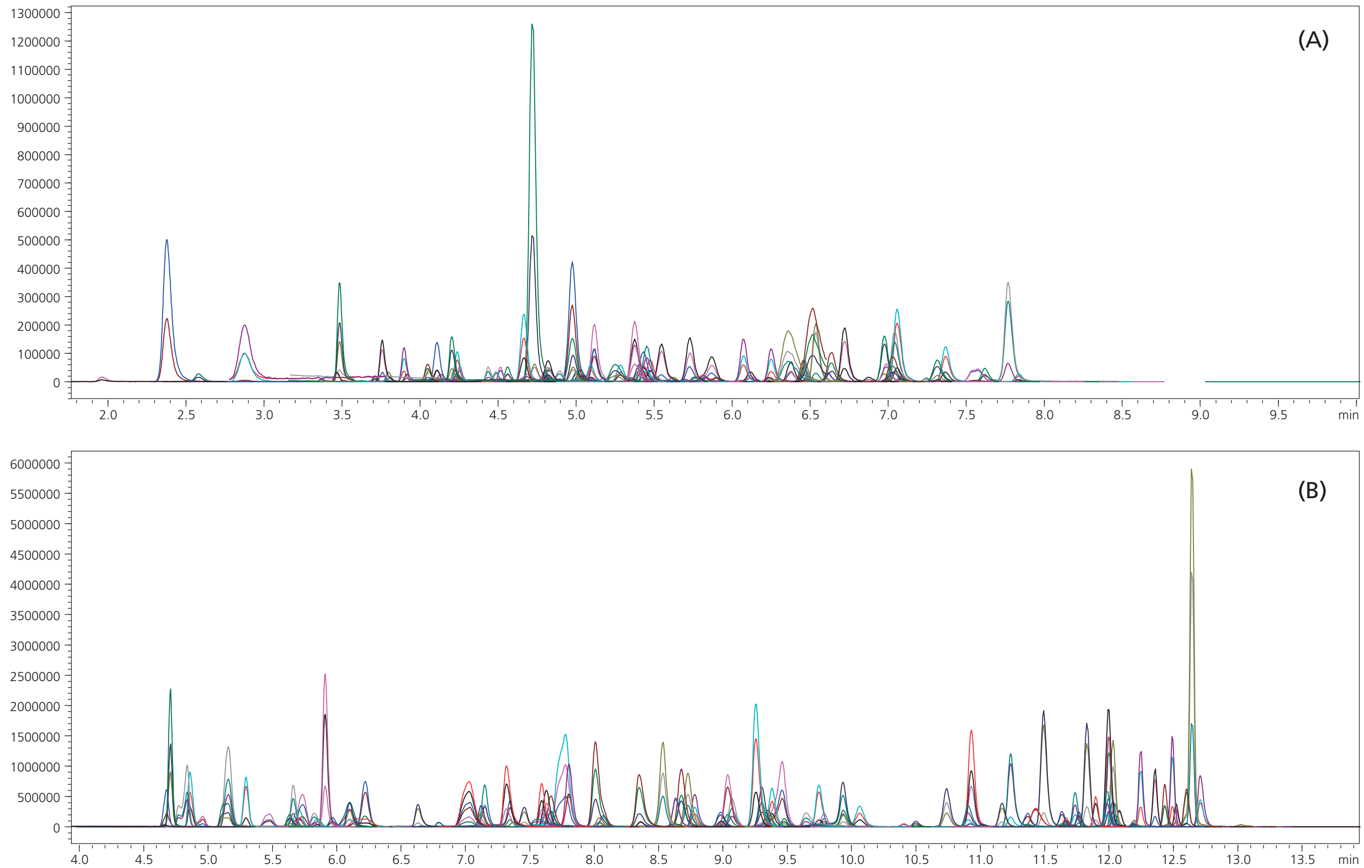

Figure 1 – Chromatograms of the 94 pesticides in spring water at 200 ng/L using (A) Direct injection or (B) online SPE.

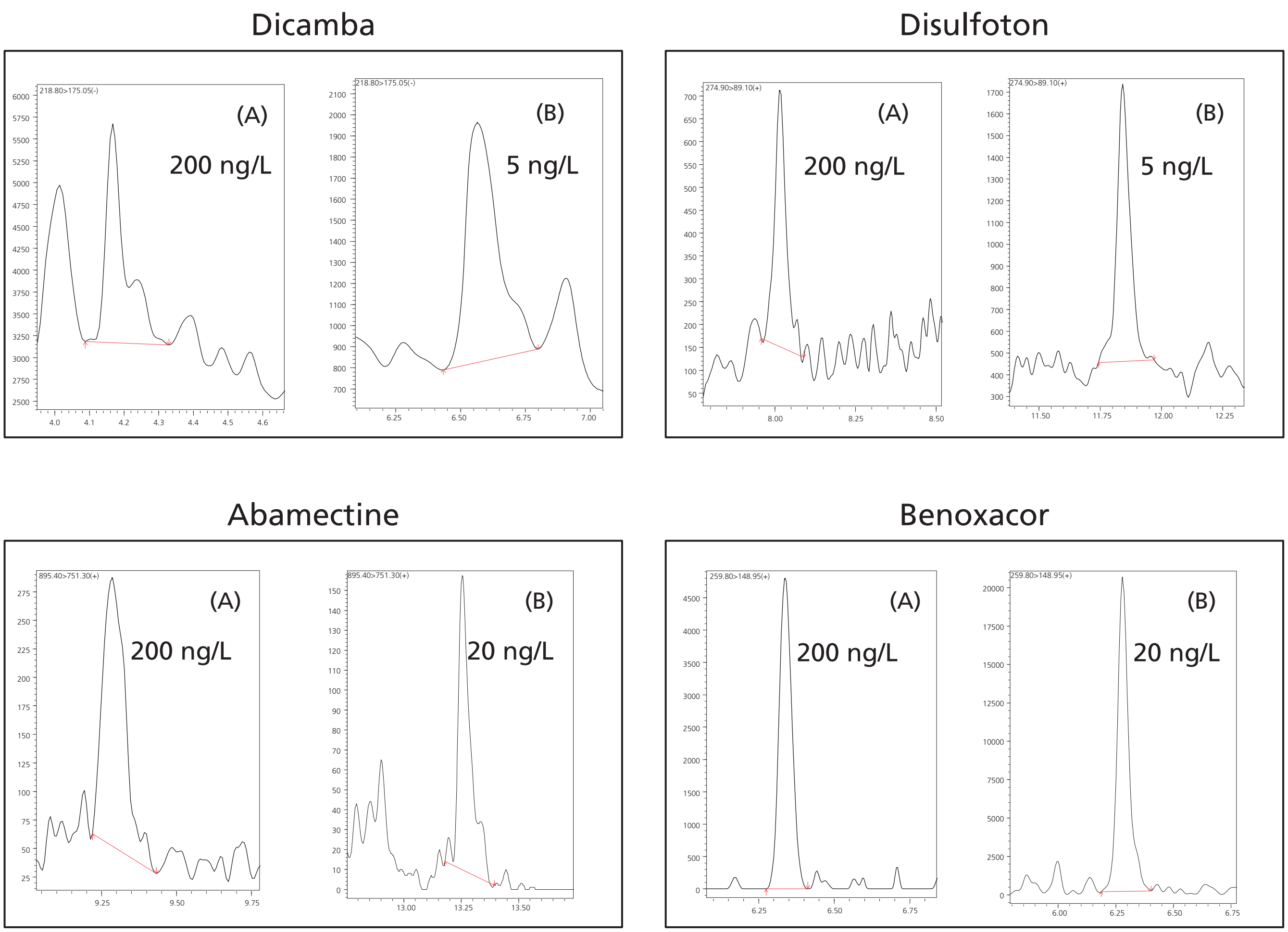

Figure 2 – Chromatogram of selected compounds at their LOQ using (A) Direction injection or (B) online SPE.

Evaluation of matrix effect

Table 3 – Limits of Quantification in spring water

Target compound	Direct Injection		SPE	
	LOQ (ng/L)	S/N	LOQ (ng/L)	S/N
2,4-D	20	5	5	95
2.4.5T	50	9	5	29
Abamectine	100	14	20	7
Acetamiprid	10	58	5	127
Acetochlor	10	29	5	18
Aldicarb sulfone	20	10	5	7
Amidosulfuron	10	45	5	190
Atrazine	10	27	5	92
Atrazine hydroxy	20	26	5	104
Azamethiphos	20	11	5	57
Azoxystrobin	10	15	5	109
Benoxacor	100	8	5	8
Bromuconazole 1	100	5	5	30
Bromuconazole 2	10	5	5	48
Buturon	100	13	5	43
Carbetamide	20	140	5	98
Carbofuran	20	20	5	107
Chlorbromuron	50	22	5	28
Chloridazon	50	5	5	19
Chloroxuron	200	7	5	57
Chlortholuron	50	15	5	11
Clopyralid	>200	...	10	10
Cymoxanil	200	5	5	55
Cyprodinil	10	11	5	152
DCPMU	50	15	5	28
Desethylatrazine	10	16	5	65
Desisopropylatrazine	20	6	5	8
Dicamba	100	4	5	5
Difenoconazole	20	20	5	900
Dimefluron	100	13	5	25
Dimethachlor	20	500	5	14
Dimethoate	10	480	5	56
Dimethomorph	50	5	5	900
Disulfoton	200	3	5	8
Diuron	10	3	5	99
Epoxiconazole	10	6	5	285
Ethidimuron	20	5	5	154
Fenbuconazole	20	10	5	10
Fenpropidin	20	30	5	92
Fenpropimorph	10	20	5	133
Fenuron	10	25	5	100
Flazasulfuron	100	9	5	35
Flupyrsulfuron mepthyl	50	10	5	171
Fluquinconazole	50	6	5	75
Flurtamone	10	11	5	272
Foramsulfuron	10	9	5	4500
Hexaconazole	10	8	5	500
Imazalil	10	3	5	18
Imazamethabenz	10	40	5	344
Imazaquin	10	5	5	189
Imidacloprid	100	12	5	47
Iodosulfuron methyl	20	14	5	44
Isoproturon	10	14	5	121
Isoxaben	20	20	5	92
Kresoxim-ethyl	50	15	5	107
Mesosulfuron methyl	10	100	5	209
Metalaxyl	10	5	5	20
Metamitron	10	5	5	5
Metazachlor	10	14	5	114
Methabenzthiazuron	10	6	5	205
Methiocarb	10	80	5	111
Methomyl	20	15	5	171
Metolachlor	10	100	5	37
Metosulam	10	160	5	118
Metoxuron	20	25	5	7
Metribuzin	10	10	5	22
Metsulfuron methyl	10	36	5	141
Nicosulfuron	20	10	5	2900
Omethoate	20	34	5	84
Oxadixyl	20	15	5	9
Oxydemethon methyl	20	20	5	20
Phosphate de tributyl	10	80	5	78
Picloram	50	10	10	4
Pirimicarb	10	26	5	132
Prochloraz	10	40	5	444
Propoxur	50	25	5	66
Pyraclostrobin	10	15	5	1400
Pyrifenox 1	20	5	5	10
Pyrifenox 2	20	5	5	10
Pyrimethanil	50	200	5	29
Quinmerac	10	15	5	42
Simazine	10	182	5	70
Simazine hydroxy	50	60	5	340
Sulcotrione	100	16	5	6
Sulfosulfuron	50	20	5	43
Tebuconazole	10	32	5	329
Tebutam	10	11	5	168
Terbuthylazine desethyl 2 hydroxy	10	62	5	300
Tetraconazole	20	10	5	900
Thiacloprid	10	10	5	33
Thifensulfuron methyl	10	40	5	129
Thiodicarb	20	8	5	109
Triazamate	10	20	5	6200
Trichlorphon	100	8	5	13
Trinexapac-ethyl	100	10	5	10
Vamidothion	10	20	5	88

Table 4 – Comparison of accuracy between direct injection and online SPE for several water samples

Target compound	Direct Injection		Online SPE					
	Surface water spiked at 200 ng/L				Deep water spiked at 150 ng/L		Tap water spiked at 300 ng/L	
	Accuracy (%)	%RSD	Accuracy (%)	%RSD	Accuracy (%)	%RSD	Accuracy (%)	%RSD
2,4-D	90	8	201	8	92	5	105	6
2.4.5T	87	2	160	1	92	11	86	7
Abamectine	122	27	109	27	148	8	118	6
Acetamiprid	112	5	100	7	96	5	98	1
Acetochlor	86	10	109	11	95	2	96	3
Aldicarb sulfone	71	27	75	9	100	7	90	7
Amidosulfuron	91	7	104	8	95	6	94	4
Atrazine	112	21	101	5	106	4	104	2
Atrazine hydroxy	151	20	130	7	103	5	119	6
Azamethiphos	112	3	107	6	100	6	108	3
Azoxystrobin	118	7	115	4	112	4	115	4
Benoxacor	115	23	92	6	98	6	99	4
Bromuconazole 1	103	6	97	5	109	5	110	3
Bromuconazole 2	108	12	97	6	117	6	129	4
Buturon	99	11	99	5	100	4	107	2
Carbetamide	117	4	100	7	96	3	96	4
Carbofuran	112	4	95	7	100	6	102	3
Chlorbromuron	99	13	101	8	96	6	101	6
Chloridazon	90	16	107	7	101	5	105	3
Chloroxuron	100	29	101	7	99	5	103	4
Chlortholuron	105	5	107	9	96	6	103	5
Clopyralid	…..	…..	93	12	104	4	100	2
Cymoxanil	61	17	144	5	89	2	85	2
Cyprodinil	95	2	80	9	85	8	97	3
DCPMU	121	10	94	6	100	2	106	3
Desethylatrazine	108	19	134	10	98	8	104	3
Desisopropylatrazine	100	19	88	7	90	4	84	6
Dicamba	74	16	72	5	100	2	96	3
Difenoconazole	98	5	180	12	103	9	124	15
Dimefluron	126	12	105	14	103	4	109	1
Dimethachlor	110	7	100	6	101	4	106	1
Dimethoate	104	3	93	9	101	5	101	3
Dimethomorph	113	6	96	4	102	3	103	3
Disulfoton	118	20	124	4	112	4	84	2
Diuron	97	3	102	10	106	6	108	3
Epoxiconazole	102	3	88	10	98	3	102	5
Ethidimuron	95	3	66	7	82	3	78	3
Fenbuconazole	112	5	71	13	86	12	88	3
Fenpropidin	106	5	106	13	99	4	108	3
Fenpropimorph	N/A	N/A	107	2	97	6	104	4
Fenuron	102	2	109	10	94	6	98	2
Flazasulfuron	89	17	109	2	99	10	92	8
Flupyrsulfuron mepthyl	99	4	133	3	100	3	106	7
Fluquinconazole	122	8	91	3	93	6	94	6
Flurtamone	108	2	109	4	101	3	104	2
Foramsulfuron	104	4	119	6	121	11	167	9
Hexaconazole	109	3	96	5	102	2	103	5
Imazalil	93	6	114	6	105	5	113	2
Imazamethabenz	91	3	110	8	102	6	113	3
Imazaquin	91	6	120	7	100	8	110	5
Imidacloprid	104	6	92	10	99	2	107	3
Iodosulfuron methyl	113	6	100	5	100	9	95	6
Isoproturon	115	7	116	8	116	8	109	3
Isoxaben	113	3	106	4	102	4	104	4
Kresoxim-ethyl	111	2	109	5	113	8	116	2
Mesosulfuron methyl	104	7	141	3	92	4	99	9
Metalaxyl	112	7	123	12	122	11	140	3
Metamitron	97	6	102	8	94	5	100	3
Metazachlor	112	2	103	5	97	2	102	4
Methabenzthiazuron	97	3	103	6	88	4	92	4
Methiocarb	108	5	98	6	101	4	104	4
Methomyl	96	7	107	3	97	2	89	2
Metolachlor	116	5	106	8	96	3	103	4
Metosulam	126	11	105	4	92	3	97	6
Metoxuron	121	35	136	13	133	9	148	7
Metribuzin	108	3	101	6	98	0	98	8
Metsulfuron methyl	117	1	124	9	106	9	115	3
Nicosulfuron	101	2	128	7	93	7	96	8
Omethoate	94	2	87	10	83	4	58	4
Oxadixyl	112	2	103	6	105	7	107	6
Oxydemethon methyl	111	6	97	5	93	3	94	2
Phosphate de tributyl	141	6	105	18	93	6	98	4
Picloram	100	2	88	7	97	7	113	2
Pirimicarb	100	2	100	7	92	4	100	4
Prochloraz	97	2	96	3	104	4	101	4
Propoxur	115	0	98	11	97	7	104	1
Pyraclostrobin	117	1	94	5	101	6	108	4
Pyrifenox 1	105	5	115	12	111	10	130	6
Pyrifenox 2	99	2	103	8	99	5	104	7
Pyrimethanil	100	1	111	2	99	5	107	3
Quinmerac	83	3	102	10	94	4	96	2
Simazine	103	23	105	6	96	4	96	5
Simazine hydroxy	124	22	89	3	101	4	107	2
Sulcotrione	136	9	74	4	91	8	92	6
Sulfosulfuron	126	7	94	1	97	1	90	5
Tebuconazole	111	2	81	28	105	2	109	2
Tebutam	121	1	94	6	90	7	104	6
Terbuthylazine desethyl 2 hydroxy	88	21	108	7	104	5	93	2
Tetraconazole	113	2	73	9	97	11	85	14
Thiacloprid	105	4	79	9	110	4	102	4
Thifensulfuron methyl	111	3	102	7	97	9	104	7
Thiodicarb	128	4	92	7	98	6	103	5
Triazamate	124	4	105	12	107	9	101	9
Trichlorphon	129	7	92	9	106	4	101	2
Trinexapac-ethyl	118	19	97	3	98	6	107	4
Vamidothion	97	1	122	9	92	3	90	4

Comparison of matrix effects in multi-residue pesticide analysis when using online SPE or direct injection in Liquid Chromatography-tandem Mass Spectrometry

Conclusion

Linearity of response in LCMS quality water of the multi-residue pesticides was demonstrated (r > 0.99). Limits of quantification (LOQ) for 97 % of pesticides were less than 5 ng/L for SPE and 70% less than 20 ng/L for the direct injection. During the validation process the methods were tested for matrix effect with several environmental waters (tap, surface and deep waters). A difference of matrix effect were highlighted between the two injection modes (SPE and direction injection), which helped to set up an analytical strategy based on these effects and the sensitivity of pesticides.

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