Supplementary Materials

Development of a Microwave Assisted Extraction protocol for the simultaneous determination of mycotoxins and pesticide residues in apples by LC-MS/MS

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Table S1. LC-MS/MS parameters.

Analyte	Parent Ion	Product Ion	Polarity	Collision Energy (V)	Cone Voltage	Retention Time (RT)
		305.0	positive	24		
abamectin	890.6	567.0		15	175	28.75
		90.1	positive	32		
acetamiprid	223.0	126.0		22	132	6.46
		180.7	positive	14		
acrinathrin	559.1	207.7		14	145	28.00
		146.8	negative	36		
alternariol	256.9	212.8		25	136	17.16
alternariol monomethyl ether	270.9	212.8	negative	39		
		255.8		24	162	21.07
		139.8	positive	18		
Boscalid	343.0	306.9		19	151	19.81
		108.1	positive	35		
bupirimate	317.1	166.1		33	120	21.72
		132.1	positive	31		
carbendazim	192.2	160.0		18	119	6.98
		96.9	positive	32		
chlorpyrifos	349.8	197.8		21	152	25.55
chlorpyrifos methyl		124.9	positive	26		
	321.8	289.8		19	150	23.52
		204.9	positive	26		
citrinin	251.3	232.9		17	109	15.37
		101.9	positive	33		
clofentezine	303.0	137.9		15	140	23.13
		132.0	positive	17		
clothianidin	250.1	169.1		12	131	5.15
		70.1	positive	25		
cyproconazole	292.0	125.0		32	124	20.58
		77.0	positive	39		22.31

cyprodinil	226.1	93.0		34	129	
		181.0	positive	44		
deltamethrin	522.9	280.7		16	147	27.53
		251.0	positive	29		
difenoconazole	406.0	337.0		14	151	23.43
		107.0	positive	36		
etofenprox	394.2	177.0		14	126	30.12
		70.0	positive	19		
fenbuconazole	337.1	124.9		33	144	21.65
		134.9	positive	33		
fenpyroximate	422.2	366.0		15	139	26.65
		173.9	positive	19		
flonicamid	230.0	202.9		19	160	3.74
		126.1	negative	33		
fludioxonil	247.1	169.1		37	126	19.79
		173.0	positive	29		
fluopyram	397.1	208.1		21	99	20.92
		306.8	positive	28		
fluquinconazole	376.0	348.9		19	154	20.79
		108.9	positive	33		
flutriafol	302.1	122.8		29	91	17.42
		167.9	positive	24		
hexythiazox	353.1	227.9		14	134	25.48
		158.9	positive	32		
imazalil	297.1	200.9		17	134	20.06
		149.8	positive	24		
indoxacarb	528.1	202.8		41	172	23.73
kresoxim methyl		116.0	positive	33		
	314.1	206.1		10	142	22.05
lambda cyhalothrin		141.0	positive	42		
	467.0	224.9		16	142	26.95
		132.9	positive	24		
methoxyfenozide	369.2	148.9		17	141	20.17
		70.1	positive	20		
myclobutanil	289.1	124.9		32	120	20.59
		80.9	negative	14		
patulin	153.1	108.9		12	109	2.63
		70.0	positive	15		
penconazole	284.1	158.9		32	128	22.37
		72.1	positive	22		
pirimicarb	239.1	182.1		16	109	16.39
		162.9	positive	23		
pyraclostrobin	388.1	194.0		12	115	22.84
		82.2	positive	23		
pyrimethanil	200.3	107.2		25	130	19.18

pyriproxyfen		95.9	positive	15		
	322.1	128.9		34	123	25.28
		98.0	positive	40		
spinosin A	732.4	142.0		31	153	24.15
		98.0	positive	40		
spinosin D	746.6	141.9		30	148	25.08
		212.8	positive	32		
spirodiclofen	411.0	312.8		10	165	26.58
		180.8	positive	32		
tau-fluvalinate	520.2	207.8		16	135	28.70
		70.0	positive	20		
tebuconazole	308.2	124.9		35	125	22.41
		132.9	positive	21		
tebufenozide	353.1	296.9		11	136	21.75
		116.9	positive	39		
tebufenpyrad	334.1	144.9		28	153	24.70
		131.1	positive	32		
thiabendazole	202.1	175.1		25	131	10.09
		126.0	positive	23		
thiacloprid	253.0	186.0		15	152	8.89
		181.0	positive	16		
thiamethoxam	291.9	211.0		13	144	3.63
		185.9	positive	20		
trifloxystrobin	409.1	205.9		13	128	23.77

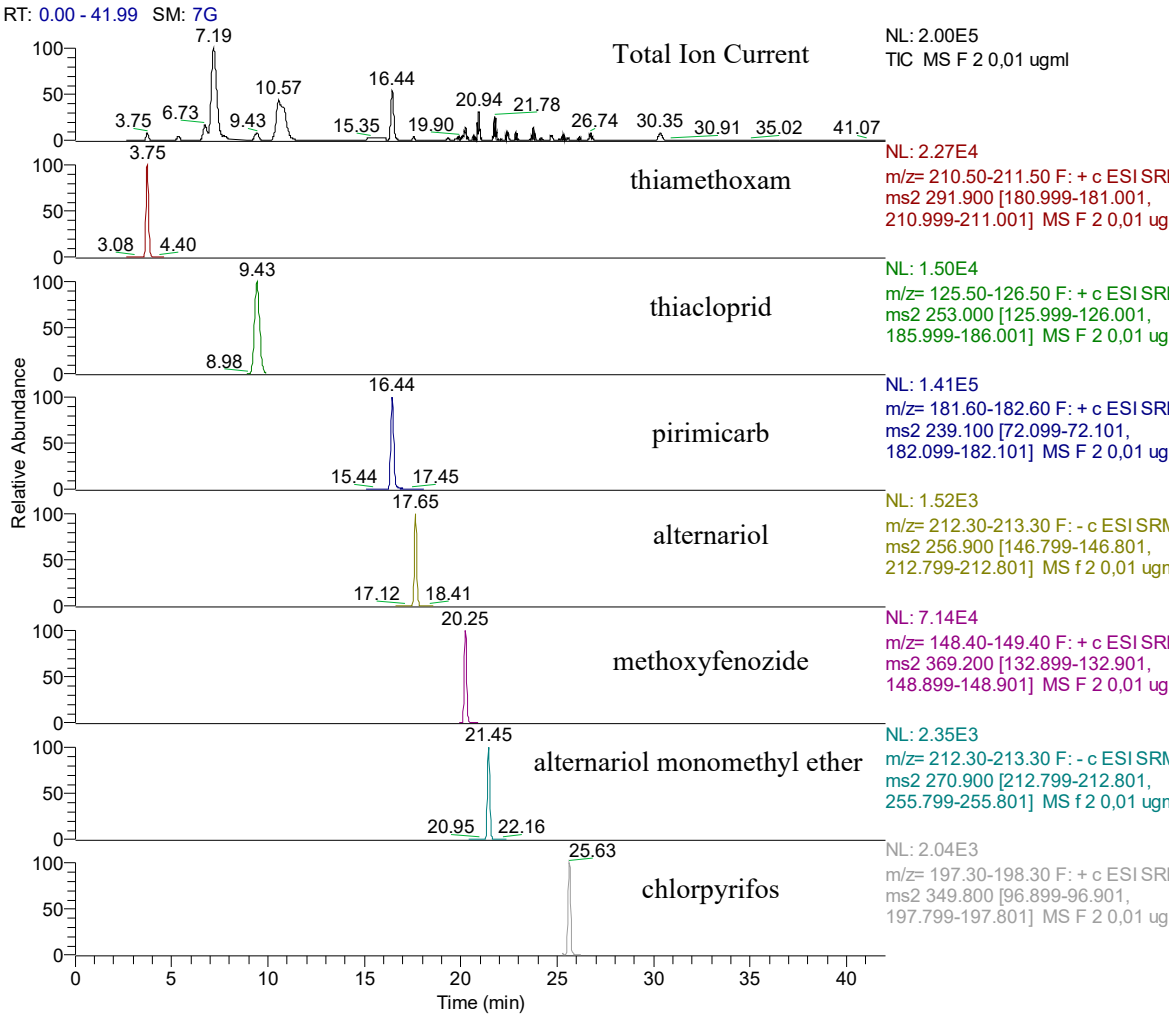

Figure S1. Total Ion Current and selected SRM chromatograms from a 0.01 µg/g level fortified apple sample.

Table S2. Recoveries (%) obtained using acetonitrile, ethyl acetate, methanol, and water as extraction solvents.

	RE%			
Compound	**ACN**	**AcOEt**	**MeOH**	**Water**
abamectin (B1a)	63	28	45	20
acetamiprid	73	89	55	98
acrinathrin	77	28	30	28
alternariol	72	89	44	41
alternariol monomethyl ether	76	77	43	29
boscalid	81	82	54	58
bupirimate	84	89	52	71
carbendazim	83	109	60	101
chlorpyrifos	57	34	26	29
chlorpyrifos-methyl	45	42	20	16

citrinin	12	63	26	30
clofentezine	73	54	28	21
clothianidin	70	91	53	108
cyproconazole	77	87	50	71
cyprodinil	77	83	44	60
deltamethrin	69	24	33	19
difenoconazole	74	60	37	30
etofenprox	80	28	40	24
fenbuconazole	82	71	45	47
fenpyroximate	82	31	40	31
flonicamid	56	86	51	96
fludioxonil	77	73	50	35
fluopyram	81	76	53	65
fluquinconazole	81	75	52	58
flutriafol	79	91	49	128
hexythiazox	81	37	36	21
imazalil	75	101	50	84
indoxacarb	77	28	36	29
kresoxym-methyl	79	68	48	59
lambda-cyhalothrin	70	25	37	26
methoxyfenozide	84	79	54	77
myclobutanil	79	83	50	60
patulin	53	28	25	5
penconazole	78	83	47	50
pirimicarb	82	90	51	75
pyraclostrobin	91	48	42	31
pyrimethanil	73	88	46	79
pyriproxyfen	80	33	35	23
spinosyn A	74	93	48	44
spinosyn D	73	90	46	28
spirodiclofen	89	30	38	27
tau-fluvalinate	53	23	35	23
tebuconazole	80	83	47	51
tebufenozide	84	72	56	63
tebufenpyrad	81	47	40	26
thiabendazole	63	85	49	97
thiacloprid	74	90	54	94
thiamethoxam	61	75	51	100
trifloxystrobin	86	35	44	45

Table S3. Recoveries (%) obtained using acetonitrile as extraction solvent at different temperatures (60°C, 80°C, 100°C).

Compounds	RE (%)		
	60 °C	80 °C	100 °C
abamectin (B1a)	63	54	5
acetamiprid	73	71	14
acrinathrin	77	22	7
alternariol	72	13	12
alternariol monomethyl ether	76	11	12
boscalid	81	70	12
bupirimate	84	62	9
carbendazim	83	77	16
chlorpyrifos	57	29	6
chlorpyrifos-methyl	45	23	9
citrinin	12	3	3
clofentezine	73	24	5
clothianidin	70	76	14
cyproconazole	77	70	11
cyprodinil	77	57	9
deltamethrin	69	38	9
difenoconazole	74	46	8
etofenprox	80	34	4
fenbuconazole	82	64	11
fenpyroximate	82	33	4
flonicamid	56	84	12
fludioxonil	77	11	10
fluopyram	81	70	10
fluquinconazole	81	62	12
flutriafol	79	70	20
hexythiazox	81	35	7
imazalil	75	58	15
indoxacarb	77	43	10
kresoxym-methyl	79	70	10
lambda-cyhalothrin	70	32	9
methoxyfenozide	84	75	12
myclobutanil	79	70	12
patulin	53	6	8
penconazole	78	61	9

pirimicarb	82	70	11
pyraclostrobin	91	51	10
pyrimethanil	73	70	11
pyriproxyfen	80	37	6
spinosyn A	74	50	12
spinosyn D	73	34	5
spirodiclofen	89	30	3
tau-fluvalinate	53	38	2
tebuconazole	80	59	11
tebufenozide	84	73	11
tebufenpyrad	81	43	9
thiabendazole	63	43	12
thiacloprid	74	70	14
thiamethoxam	61	112	14
trifloxystrobin	86	53	10

Table S4. Recoveries (%) obtained using ethyl acetate as extraction solvent at different temperatures (60°C, 80°C, 100°C).

	Recoveries (%)		
Compounds	**60 °C**	**80 °C**	**100 °C**
abamectin (B1a)	28	25	31
acetamiprid	89	77	68
acrinathrin	28	6	23
alternariol	89	78	74
alternariol monomethyl ether	77	72	71
boscalid	82	82	88
bupirimate	89	74	88
carbendazim	109	89	91
chlorpyrifos	34	31	60
chlorpyrifos-methyl	42	43	55
citrinin	63	48	11
clofentezine	54	45	55
clothianidin	91	82	90
cyproconazole	87	81	81
cyprodinil	83	72	81
deltamethrin	24	25	55
difenoconazole	60	55	64

etofenprox	28	25	52
fenbuconazole	71	72	75
fenpyroximate	31	30	56
flonicamid	86	85	85
fludioxonil	73	77	72
fluopyram	76	76	84
fluquinconazole	75	75	78
flutriafol	91	83	87
hexythiazox	37	37	63
imazalil	101	70	96
indoxacarb	28	25	51
kresoxym-methyl	68	73	78
lambda-cyhalothrin	25	23	55
methoxyfenozide	79	80	84
myclobutanil	83	84	84
patulin	28	55	24
penconazole	83	80	77
pirimicarb	90	81	107
pyraclostrobin	48	50	65
pyrimethanil	88	84	86
pyriproxyfen	33	37	71
spinosyn A	93	54	57
spinosyn D	90	74	41
spirodiclofen	30	26	52
tau-fluvalinate	23	25	54
tebuconazole	83	83	78
tebufenozide	72	76	77
tebufenpyrad	47	43	63
thiabendazole	85	75	111
thiacloprid	90	83	81
thiamethoxam	75	73	76
trifloxystrobin	35	33	59

Table S5. Recoveries (%) obtained in the absence of acids, and after the addition of 1% CH_3COOH, 5% CH_3COOH, and 1% HCOOH.

Compounds	Recoveries (%)			
	No Added Acid	**1% CH_3COOH**	**5% CH_3COOH**	**1% HCOOH**
abamectin (B1a)	50	98	21	64
acetamiprid	72	87	33	83
acrinathrin	30	87	31	58
alternariol	59	80	65	80
alternariol monomethyl ether	53	82	75	80
boscalid	67	82	25	94
bupirimate	67	90	32	80
carbendazim	72	91	34	87
chlorpyrifos	38	61	19	60
chlorpyrifos-methyl	35	37	13	30
clofentezine	38	64	28	60
clothianidin	74	86	33	83
cyproconazole	69	83	34	82
cyprodinil	62	83	33	71
deltamethrin	41	88	29	72
difenoconazole	54	75	29	75
etofenprox	43	82	31	70
fenbuconazole	63	84	32	80
fenpyroximate	50	90	28	79
flonicamid	75	84	33	80
fludioxonil	52	76	70	66
fluopyram	74	86	36	80
fluquinconazole	70	83	38	81
flutriafol	72	84	33	79
hexythiazox	50	82	27	77

imazalil	65	89	32	74
indoxacarb	50	80	31	78
kresoxym-methyl	70	85	32	75
lambda-cyhalothrin	44	78	31	59
methoxyfenozide	77	91	37	92
myclobutanil	70	85	36	76
penconazole	64	84	32	76
pirimicarb	72	86	33	80
pyraclostrobin	58	83	35	84
pyrimethanil	70	81	33	71
pyriproxyfen	50	90	29	90
spinosyn A	45	91	37	80
spinosyn D	45	90	27	74
spirodiclofen	49	83	29	67
tau-fluvalinate	46	89	29	73
tebuconazole	68	81	35	77
tebufenozide	79	93	40	90
tebufenpyrad	56	85	31	73
thiabendazole	72	89	32	74
thiacloprid	73	87	36	84
thiamethoxam	77	91	35	90
trifloxystrobin	64	80	33	81

Table S6. Regression equation and correlation coefficients of pure standards and spiked extracts.

Compounds	Standard Solution in Solvent		Matrix Matched	
	Calibration Curve	R^2	Calibration Curve	R^2
abamectin (B1a)	y=2.977e2 x-3.972e^3	0.9926	y =3.317e2 x-4.893e3	0.9918
acetamiprid	y=3.435e4 x+ 3.735e^5	0.9903	y =3.449e4 x+2.734e5	0.9945
acrinathrin	y=2.865e2 x-8.143e^3	0.9909	y =3.291e2 x-1.068e3	0.9901
alternariol	y=1.454e3 x+1.043e4	0.9914	y =1.992e3 x+5.127e3	0.9902
alternariol monomethyl ether	y=1.054e4 x+2.058e5	0.9929	y =1.466e4 x+2.414e5	0.9904
boscalid	y=1.01e4 x+3.656e4	0.9941	y =9.995e3 x+8.54e3	0.9938
bupirimate	y= 1.342e4 x+1.618e5	0.9915	y =1.325e4 x+2.001e5	0.9902

carbendazim	y= 1.118e5 x+5.775e5	0.9911	y =2.067e5 x+4.217e6	0.9928
chlorpyrifos	y=8.586e2 x+1.96e4	0.9911	y =9.361e2 x+4.582e1	0.9905
chlorpyrifos methyl	y=2.775e2 x-3.668e3	0.9914	y =3.426e2 x-6.883e2	0.9906
clofentezine	y=3.925e3 x+1.303e4	0.9924	y =2.728e3 x+8.353e3	0.9902
clothianidin	y =4.507e3 x+1.957e4	0.9908	y =6.183e3 x-3.514e3	0.9905
cyproconazole	y =8.288e3 x+1.596e4	0.9920	y =8.19e3 x+4.103e4	0.9940
cyprodinil	y =7.479e3 x+1.06e4	0.9912	y =7.577e3 x+4.565e4	0.9906
deltamethrin	y =2.983e2 x-6.906e3	0.9904	y =6.169e2 x-5.886e3	0.9906
difenoconazole	y =1.019e4 x+1.132e5	0.9925	y =1.221e4 x+2.93e4	0.9906
etofenprox	y =2.316e3 x+2.143e4	0.9966	y =9.119e3 x-4.378e4	0.9942
fenbuconazole	y =5.119e3 x+3.844e4	0.9903	y =5.873e3 x+1.989e3	0.9901
fenpyroximate	y =9.995e3 x+1.591e5	0.9914	y=2.614e4 x-2.238e5	0.9912
flonicamid	y =3.375e3 x+2.027e4	0.9909	y =2.649e3 x-1.331e4	0.9952
fludioxonil	y =2.172e3 x+7.735e4	0.9924	y =2.742e3 x+5.014e4	0.9908
fluopyram	y =4.09e4 x +1.979e5	0.9903	y =4.232e4 x+3.669e5	0.9963
fluquinconazole	y =3.968e3 x +2.778e3	0.9962	y =3.327e3 x+6.612e3	0.9979
flutriafol	y =6.202e3 x -4.518e3	0.9922	y =5.649e3 x+4.074e4	0.9914
hexythiazox	y =4.855e3 x +3.766e4	0.9904	y =5.268e3 x-1.176e4	0.9904
imazalil	y =8.084e3 x+1.034e5	0.9916	y =1.005e4 x+1.271e4	0.9924
indoxacarb	y =9.104e2 x+1.165e4	0.9914	y =1.093e3 x+9.942e3	0.9904
kresoxym-methyl	y =1.451e3 x+8.419e3	0.9909	y =1.472e3 x+4.097e3	0.9901
lambda-cyhalothrin	y =1.849e2 x-4.726e3	0.9968	y =3.717e2 x-3.972e3	0.9906
methoxyfenozide	y =1.52e4 x+2.698e5	0.9930	y =1.954e4 x+2.191e5	0.9903
myclobutanil	y =9.711e3 x-1.587e4	0.9937	y =9.166e3 x+2.55e4	0.9981
penconazole	y =1.088e4 x+7.269e4	0.9929	y =1.049e4 x+3.471e4	0.9907
pirimicarb	y =8.883e4 x+8.844e5	0.9909	y =8.105e4 x+7.413e5	0.9930
pyraclostrobin	y =6.192e3 x+2.461e4	0.9917	y =9.155e3 x-3.709e4	0.9902
pyrimethanil	y =4.684e3 x+2.389e4	0.9927	y =4.66e3 x+7.508e3	0.9954
pyriproxyfen	y =3.688e3 x+1.019e5	0.9908	y =8.726e3 x-5.447e4	0.9912
spinosyn A	y =2.622e3 x-1.271e4	0.9925	y =3.944e3 x+3.554e4	0.9902
spinosyn D	y =1.568e3 x-6.469e3	0.9909	y =3.016e3 x2.066e4	0.9905
spirodiclofen	y =2.19e2 x-1.196e3	0.9908	y =2.778e2 x-5.617e3	0.9905
tau-fluvalinate	y =6.292e2 x-1.522e4	0.9901	y =8.966e2 x-3.867e3	0.9920
tebuconazole	y =6.567e3 x+2.219e4	0.9941	y =4.737e3 x+5.593e4	0.9903
tebufenozide	y =1.583e4 x+3.251e5	0.9913	y =1.806e4 x+3.079e5	0.9912
tebufenpyrad	y =9.106e3 x+1.59e4	0.9903	y =7.469e3 x+8.691e3	0.9908
thiabendazole	y =6.728e4 x-3.907e5	0.9953	y =1.185e5 x+9.159e5	0.9996
thiacloprid	y =1.585e4 x+3.961e5	0.9952	y =1.719e4 x+7.731e4	0.9952
thiamethoxam	y =5.791e3 x+6.562e4	0.9903	y =1.214e4 x+5.024e3	0.9969
trifloxystrobin	y =1.615e4 x+1.557e5	0.9905	y =1.626e4 x+6.562e4	0.9901

Table S7. Matrix effect results.

Compound	ME%	Signal Response
abamectin (B1a)	111	-
acetamiprid	100	-
acrinathrin	115	-
alternariol	137	-
alternariol monomethyl ether	139	-
boscalid	99	-
bupirimate	99	-
carbendazim	185	Signal enhancement
chlorpyrifos	109	-
chlorpyrifos methyl	123	-
clofentezine	70	-
clothianidin	137	-
cyproconazole	99	-
cyprodinil	101	-
deltamethrin	207	Signal enhancement
difenoconazole	120	-
etofenprox	394	Signal enhancement
fenbuconazole	115	-
fenpyroximate	262	Signal enhancement
flonicamid	78	-
fludioxonil	126	-
fluopyram	103	-
fluquinconazole	84	-
flutriafol	91	-
hexythiazox	109	-
imazalil	124	-
indoxacarb	120	-
kresoxym-methyl	101	-
lambda-cyhalothrin	201	Signal enhancement
methoxyfenozide	129	-
myclobutanil	94	-
penconazole	96	-
pirimicarb	91	-
pyraclostrobin	148	Signal enhancement
pyrimethanil	99	-
pyriproxyfen	237	Signal enhancement
spinosyn A	150	Signal enhancement
spinosyn D	192	Signal enhancement
spirodiclofen	127	-

tau-fluvalinate	142	Signal enhancement
tebuconazole	72	-
tebufenozide	114	-
tebufenpyrad	82	-
thiabendazole	176	Signal enhancement
thiacloprid	108	-
thiamethoxam	210	Signal enhancement
trifloxystrobin	101	-