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Validation Report 35

Determination of pesticide residues in rape seeds
by GC-MS/MS and LC-MS/MS

(QuEChERS-EMR method)

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CONTENT:

1. Introduction

This report describes the validation of the QuEChERS method combined with LC-MS/MS and GC-MS/MS for the analysis of pesticide residues in rape seeds. Rape seeds are difficult matrices with high fat content (>40%). The method was tried validated for 222 pesticides and metabolites by both LC-MS/MS and GC-MS/MS in rape seed (S), rape cake (C), and rape meal (M). Some pesticides were analyzed on both GC and LC. The QuEChERS method is an extraction method which has been developed to be Quick, Easy, Cheap, Efficient, Rugged and Safe. The method is most commonly used on fruit, vegetables and cereals[1]. In this study, the clean-up was made with EMR-Lipid that allow lipid/matrix removal without analyte loss.

2. Principle of analysis

Sample preparation

Two gram of homogenized sample were weighted accurately in a 50 mL polypropylene PP tube. Ceramic homogenizer was inserted in each tube before adding 10 mL of cold water and 10 mL of acetonitrile. Samples were mechanically shaken for 1 minute. Prepared mixture of salts, containing 4 g $MgSO_4$, 1 g NaCl, 1 g Na_3 citrate dihydrate and 0.5 g Na_2H cirate sesquihydrate, was added to the samples. Tubes were shaken mechanically for another minute and then centrifuged for 10 minutes at 4500 rpm. Eight millilitre of supernatant were transferred in a clean tube and placed in -80°C freezer for at least 1 hour. After freezing-out the samples were removed from freezer, thawed and centrifuged at 5 °C for 10 minutes at 4500 rpm. 6 mL extract were transferred to a 15 ml single use centrifuge tube containing 900 mg PSA and 900 mg $MgSO_4$, shaken 30 seconds and centrifuged five minutes at 4500 rpm. Five ml extract solution were transfer to a d-SPE EMR tube which was previously activated with 5 mL of water, shaken and centrifuged. Supernatant was transferred to a 15 mL EMR-Polish tube, shaken 30 seconds and centrifuged five minutes at 4500 rpm. The extract was transferred to a 15 ml centrifuge tube. 10 µl formic acid solution 5% was added for each millilitre extract. Final extract solution was diluted 1:1 with acetonitrile and transferred to 2 mL sample vials appropriate for GC and LC analysis.

GC-MS/MS

For gas chromatographic separation, a Thermo Scientific™ Trace™ 1310 Gas Chromatograph coupled to a Thermo Scientific™ TriPlus™ RSH autosampler was used. The samples were injected in a programmable temperature vaporizer (PTV) mode through a PTV baffle liner 2×2.75×120 mm

for Thermo GCs (Siltek). The injection volume was 1 µL and the injection temperature was set to 70°C. Helium (99.999%) was used as carrier gas at a flow of 1.2 $ml.min^{-1}$. The analytes were separated on a DB5-MS capillary column of 30 m long, 0.25 mm inner diameter and a film thickness of 0.25 µm. The oven temperature program was as follows: 60°C for 1.5 min, up to 90°C at 25°C/min for 1.5 min, up to 180°C at 25°C /min, then up to 280°C at 5 °C/min and finally up to 300°C at 10°C/min and for 12 min. The total runtime was 42 min. For the mass spectrometric analysis, a thermo Scientific™ TSQ™ 8000 Evo was used. The electron ionization (EI) source was used with an electron energy of 70 eV. The analyses were performed by a triple quadrupole operating in the multiple reaction-monitoring mode (MRM). The source temperature was set at 300°C, and the transfer line, at 280°C.

LC-MS/MS

The pesticide residues analysis were also performed by LC-(ESI)MS/MS. The LC system employed was a Thermo Ultimate 3000 and the mass spectrometer was a Bruker EVOQ. The analytes were separated on a Accuity UPLC BEH C18 1.7 µm, 2.1*100 mm reversed-phase column. The injection volumne was 1 µl. The eluents consisted of milli-q water with 0,1% formic acid and 5 mM ammonia solution (A eluent) and methanol (B elutent) and a flow rate of 0.4 ml/min was applied. The analytes were separated using a gradient elution programme. The column is equlibrated with 2% B eluent before injection. At the time of injection the propotion of B elutent is increased to 35% within 0.1 min and then inceased further reaching 98% at a run time of 7 min. The 98% of B eluent is then maintained for 3 minutes before the proportion is lowered again to 2% within 0.1 min and maintained until a total run time of 13 min in order to prepare the column for the next injection. The mass spectrometer was operated in multiple reaction monitoring mode and using both positive and negative electrospray ionisation.

3. Validation

The method was validated for 222 compounds (pesticides or/and metabolites) in in three different matrices (rapeseed, rape cake, and rape meal). The validation was performed on 5-6 replicates of each of the three feed matrices in three different spiking levels; 0.005, 0.01 and 0.05 mg/kg. Blank samples were included for each feed commodity.

Calibration curves and linearity

Linearity study were performed by using matrix-matched calibration curve prepared in 6 different concertation for each one of the compounds within the range of 0.33 to 100 ng/ml. The calibration curves were fitted to linear function and the deviation of the back–calculated concentration of the calibration standards from the true concentrations were within ±20%.

All quantifications were performed using bracketing calibration curves using matrix matched calibration curve.

Recovery and precision

Recovery values were calculated as average recovery of 5-6 replicates for each level (0.005, 0.01, and 0.05 mg/kg) and matrixes. Accepted values for recovery were recoveries in the range 70-120% (following SANTE document)[3]. Values out from this range have been accepted when the precision data were satisfactory. Precision value were calculated as the relative standard deviation of the measurements. RSD ≤ 20% were accepted[3].

Limit of quantification, LOQ

The Limit of quantification (LOQ) was determinate as the lowest spiked level for which the acceptance criteria were meet (average relative recovery in percentage between 70 and 120 and precision lower then or equal 20%)[3].

4. Results and conclusion

The method was validated for 222 pesticides and/ metabolites in three different matrices (rapeseeds, rape cake and rape meal) using QuEChERS based extraction with EMR clean up in LC-MS/MS and GC-MS/MS. 58 compounds were validated both in GC and LC. The validation results are given in Appendix 2. The lowest LOQ achieved in GC/MS/MS was 0,005 mg/kg for 107 compounds and 0.01 mg/kg for 8 compounds and 0.05 mg/kg for 14 compounds. On LC/MS/MS the lowest LOQ 0,005 mg/kg was achieved for 116 compounds, 0.01 mg/kg for 15 compounds and 0.05 mg/kg for 15 compounds. The majority of the combined uncertainties were lower than 50%, indicating that recovery for correction is not needed.

Some compounds, were not successfully validated in the present study on LC; it was the case of aldicarb-sulfoxide, fipronil-sulfide, methomyl, omethoate, paraoxon-methyl, pymetrozine, spinosad_D, thiodicarb, and tolylfluanid. Likewise, some compounds were not successfully validated on GC; it was the case of acrinathrin(II), carbosulfan, clofentezine, dicofol-pp, fenoxycarb,

fluvalinate-tau(I+II), formothion, methamidophos, mevinphos, monocrotophos, oxycarboxin, phosmet, profenofos, and simazine.

Some compounds did not have the same sensitivity with each of the feed matrix e.g fenpropidin. Fenpropidin is marked as S C^1 M in appendix 2, which means that the LOQ for fenpropidin is 0.005 in rape seed (S) and rape meal (M) but he LOQ achieved with rape cake (C) is 0.01 mg/kg.

5. References

1. EN 15662:2008. Foods of plant origin - Determination of pesticide residues using GC-MS and/or LC-MS/MS following acetonitrile extraction/partitioning and clean-up by dispersive SPE - QuEChERS-method
2. ISO 5725-2:1994. Accuracy (trueness and precision) of measurement methods and results – Part2. Basic method for the determination of repeatability and reproducibility of standard measurement method. First edition. December 1994.
3. Guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed, Document Nº SANTE/12682/2019, Implemented by 01/01/2020.

Appendix 1a.
MRM transitions and collision energy for compounds validated by GC-MS/MS.

Compound Name	RT	Transition I (CE)			Transition II (CE)			Transition III (CE)		
2-phenylphenol	9.81	169.1	115.1	25	169.1	141.1	10	170.1	169.1	10
Acrinathrin I	24.1	181	152	22	208.1	180.9	8	289	93.1	22
Aldrin	15.14	219.9	150	30	292.9	185.9	30	292.9	257.9	10
Atrazine	11.97	200.1	104.1	20	215.1	173.1	10	215.1	200.1	10
Azoxystrobin	30.33	344.1	172.1	25	344.1	329.1	20	388.1	345.1	15
Bifenthrin	22.3	181.1	141	22	181.1	165.1	15	181.1	166.1	15
Bitertanol	25.44	170.1	115.1	25	170.1	141.1	20	171.2	142.1	20
Boscalid	27.31	342	140	15	344	142	15			
Bromophos-ethyl	16.84	302.8	284.8	14	358.9	302.8	14	358.9	330.9	10
Bromopropylate	22.33	184.9	75.5	30	340.8	185	14	342.7	185	15
Bromuconazole (I+II)	22.07/22.84	173	109	25	173	145	15	294.9	173	10
Bupirimate	18.2	273.1	193.1	10	316.2	208.1	10			
Cadusafos	11.31	159	97	20	213.1	89	12			
Carboxin	18.25	235.1	87	15	235.1	143	15			
Chlorfenapyr	18.52	248.9	112	24	363.8	247.2	30	363.8	282.1	20
Chlorfenson	17.6	111	75	14	175	75	28	175	111	10
Chlorfenvinphos	16.16	266.9	159	15	268.9	161	12	323	267	15
Chlormephos	9.1	154	121	5	234	121	14			
Chlorobenzilate	19.06	139	74.9	26	139	111	12	251	139	14
Chlorpropham	10.97	213.1	127	15	213.1	171	10			
Chlorpyrifos	14.94	196.7	168.9	12	313.9	257.9	12	316.1	260	15
Chlorpyrifos-methyl	13.66	285.9	93	20	285.9	270.9	25	287.9	272.9	25
Clomazone	12.1	125	89	15	204	107	15			
Cyflutrin	26.9	206	151	12	226	206	10			
Cyhalothrin-(I+II)	23.78/24.12	180.9	151.9	22	197	141.1	10	208.1	180.9	8
Cypermethrin	27.45	163	127	10	181	152	20			
Cyproconazole	18.68	383	282	20	383.1	254	20			
Cyprodinil	15.92	224.1	118	30	224.1	208.1	30	225.1	210.1	25
Deltamethrin_cis (I+II)	29.95	181	152.1	22	252.8	92.9	16	252.8	172	8
Demeton-S-methyl	10.66	88	59.8	6	109	79	6	141.9	79	12
Diazinon	12.42	179	137	15	199	93	15	304.1	179.1	15
Dichlorvos	7.68	185	93	12	185	109	17	220	185	10
Dicloran	11.82	160	124	10	206	176	10	208	178	10
Dieldrin	18.2	276.9	240.9	12	278.9	242.9	12	280.9	244.9	10
Difenoconazole (I+II)	26.59/26.65	323.1	265	15	324.9	267	10	325.1	267	20
Dimethomorph (I+II)	30.52/31.03	301	139	14	301.1	165	12	387.1	301.1	12
Diphenylamine	10.75	168.1	139	38	168.1	167.1	14	169.2	167.1	22
Disulfoton	12.73	142	109	10	274	88	10			
Endosulfan-alpha	17.36	195	160	10	240.9	205.9	10	242.9	207.9	10
Endosulfan-beta	19.19	195	160	10	240.9	205.9	10	242.9	207.9	10
Endosulfan-sulfate	20.37	269.9	234.9	15	271.9	234.9	10	273.9	238.9	10
Endrin	18.87	244.8	173	22	262.8	192.9	30	278.9	242.9	12
EPN	22.25	157	110	15	169	77	16			

Compound Name	RT	Transition I (CE)			Transition II (CE)			Transition III (CE)		
Epoxiconazole	21.53	165	138	8	192	111	10	192	138	10
Ethion	19.35	231	129	20	384	231	10			
Ethoprophos	10.78	158	97	10	200	158	8			
Ethoxyquin	11.83	174.1	131.2	18	174.1	146.1	12	202.1	174.1	14
Etofenprox	27.89	163.1	107.1	16	163.1	135.1	10	376.2	163.1	20
Fenarimol	24.41	139	75	26	219	107	15	251	139	15
Fenazaquin	22.9	145.1	117.1	12	160	117.1	20	160	145.1	8
Fenbuconazole	26.53	129	77.8	18	129	102	15	198.1	129	15
Fenitrothion	14.47	277	109	20	277	260	10			
Fenpropathrin	22.59	265.1	89	20	265.1	210.1	15			
Fenpropimorph	15.14	128.1	110.1	15	303.3	128.1	15			
Fenson	15.52	268	77	20	268	141	10			
Fenthion	15.03	278	109	18	278	169	14			
Fenvalerate (I+II)	29.08	125	89	18	167	89	32	419.1	225.1	10
Fluazifop-P-butyl	18.79	383.1	254.1	20	383.1	282.1	15			
Fludioxonil	17.64	248	127	20	248	154	20	248	182	15
Flufenoxuron	12.64	267.9	170	24	267.9	241	12	331	276	15
Fluquinconazole	25.83	340	108.1	36	340	298	22	340	313	14
Flutriafol	17.41	123	75	15	219.1	123	15			
HCH-alpha	11.58	182.9	147	12	216.9	180.9	8	218.9	182.9	8
HCH-beta	12.06	182.9	147	12	216.9	180.9	8	218.7	183	8
Heptenophos	10.16	124	89	10	250	89	25			
Hexaconazole	17.68	213.9	159	18	231.1	175	10	256.1	159	10
Hexythiazox	16.87	184	59	20	184	149	6	227	149.1	8
Indoxacarb	29.91	203	134	20	264	176	20			
Iprodione	21.92	314	245	15	314	271	10	316	247	15
Iprovalicarb (I+II)	18.06/18.37	118.9	117.1	8	134.1	42	20			
Isofenphos-methyl	15.72	199	121	10	241.1	199	8			
Isoprothiolane	17.71	204	85	25	204	118	7	290.1	118	15
Jodofenfos	17.63	125	47	12	376.8	361.8	16	379	364	20
Kresoxim-methyl	18.24	116	63	24	116	89	14	206.1	116.1	15
Lindane	12.28	182.9	147	12	216.9	180.9	8	218.9	182.9	8
Linuron	14.65	248.1	61	15	250.1	61	15			
Metalaxyl	14.01	206.1	132.1	20	234.1	174.1	10	249.1	190.1	10
Methacrifos	9.49	240	180	5	240	208	10			
Methidathion	16.78	145	58	15	145	85	10			
Metribuzin	13.61	198.1	82	17	198.1	89	16	198.1	110.1	10
Myclobutanil	18.08	179.1	125.1	15	179.1	152.1	8	288.1	179.1	10
Nuarimol	20.98	235.1	139	15	314.1	139	15			
Ofurace	19.9	131.9	117	16	232.1	158.1	18	232.1	186.1	8
Oxadixyl	19.25	163	117	30	163.1	132.1	8	233.1	146.1	10
Paclobutrazol	17.07	125	89	18	236.1	125.1	15	238.1	127.1	15
Parathion	15.13	235	139	8	291	81	20	291	109	8
Parathion-methyl	13.78	125	47	12	263	79	22	263	109	11
Penconazole	16.08	248	157	25	248	192	13			
Pencycuron	12.1	125	89	15	125	99	16			

Compound Name	RT	Transition I (CE)			Transition II (CE)			Transition III (CE)		
Pendimethalin	15.88	252.1	162.1	12	252.1	191.1	12	281.1	252.1	12
Permethrin (I+II)	25.72	183	153	15	183.1	165.1	12	183.1	168.1	12
Phenthoate	16.34	121	77	22	246	121	8	274	121	10
Phosalone	23.38	182	111	15	367	182	10			
Pirimicarb	13.02	166.1	71	25	166.1	96.1	10	238.1	166.1	15
Pirimicarb-desmethyl	13.22	152.1	96.1	15	224.1	152.1	10			
Pirimiphos-methyl	14.39	290.1	125	15	290.1	233.1	10	305.1	180	15
Prochloraz	25.97	180.1	138.1	12	308	266	10	310	268	10
Procymidone	16.5	283	67	15	283	96	10	283	96.1	8
Propiconazole (I+II)	20.47	172.9	74	38	172.9	109	26	259	173	15
Propoxur	8.11	110	62.9	24	110	64.1	16	152.1	110	8
Propyzamide	12.4	172.9	74	38	172.9	109	26	172.9	145	14
Prothiofos	17.73	267	239	10	309	239	5			
Pyrazophos	24.42	232	204	10	265.1	210.1	10	373	232	12
Pyridaben	25.88	147.1	117	10	147.1	132.1	15	309.1	147.1	15
Pyridaphenthion	21.86	340.1	199	10	340.1	203	25			
Pyrimethanil	12.58	198.1	118.1	35	199.1	198.1	10			
Pyriproxyfen	23.75	136.1	78	20	136.1	96	10			
Quinoxyfen	20.4	307	237.1	15	307	272	10	309	237.1	15
Tebuconazole	21.05	125	89	16	250	125	20	252.1	127.1	20
Tebufenpyrad	22.79	276.1	171.1	15	333.2	171	20	333.2	276	10
Tecnazene	10.47	214.8	143.6	20	214.8	178.7	10	214.8	179.9	15
Tefluthrin	12.72	177	127	15	177	137	15			
Tetraconazole	15.18	336	204	20	336	218	20			
Tetradifon	23.18	355.9	159	15	355.9	228.9	10			
Thiometon	11.65	88	45	20	88	60	6	125	47	14
Tolclofos-methyl	13.85	265	220	20	265	250	15	267	252	15
Triadimefon	15.2	208.1	127	10	208.1	181.1	10			
Triadimenol	16.63	112	57.6	8	128	65	18	168.2	70	10
Triallate	12.93	268	184	22	270	186	22			
Triazophos	19.78	161	106	12	161	134	8	257.1	162	10
Trichlorfon	7.68	145	109	10	185	93	12			
Tricyclazole	17.71	162	133.9	8	204.1	118	5	231	189	10
Trifloxystrobin	20.29	190.1	130	10	222.1	130	10	222.1	162.1	10
Trifluralin	10.99	264.1	160.1	15	306.1	206	15	306.1	264.1	15
Triticonazole	23.4	182	75.1	30	182	111	15	235.1	182.1	10
Vinclozolin	13.74	212	145	15	212	172	15	285	212	15

Appendix 1b.
MRM transitions for compounds validated by LC-MS/MS

Compound Name	RT	Polarity	Transition I (CE)			Transition II (CE)			Transition III (CE)		
3-hydroxycarbofuran	2.64	Positive	238	163	13	238	181	9.5			
Acephate	1.78	Positive	183.78	143.01	12						
Acetamiprid	2.67	Positive	223	56	9.5	223	90	29	223	126	17
Aldicarb	3.25	Positive	208.2	116.09	10	208.2	89.09	15	191	89.2	15
Aldicarb-sulfone	1.97	Positive	240.4	148.18	13	240.4	86.3	21	240.09	223.3	20
Atrazine	4.55	Positive	216	96	20	216	104	24.5	216	174	15
Azinphos-ethyl	5.77	Positive	346	137	22	346	233	12			
Azinphos-methyl	4.92	Positive	318	132	11	318	261	5.5			
Azoxystrobin	5.15	Positive	404	344	21	404	372	15	404	328	39
Bifenthrin	8.30	Positive	440	166	35	440	181	10			
Bitertanol	6.54	Positive	338	70	5	338	99	12	338	268	8.5
Boscalid	5.41	Positive	343	271	24	343	307	12.5			
Bromoxynil	4.41	Negative	276	79	20.5	276	80.59	25	276	274.6	5.5
Bromuconazole	5.65	Positive	377.9	70	9	377.9	159	17.5			
Bupirimate	5.62	Positive	317	166	23	317	108	25			
Buprofezin	6.97	Positive	306	116	14	306	201	8			
Cadusafos	6.66	Positive	271	131	20.5	271	159	11.5			
Carbaryl	4.11	Positive	202	127	26.5	202	145	7			
Carbendazim	2.01	Positive	192	105	31.5	192	132	24	192	160	13
Carbofuran	3.86	Positive	222	123	17.5	222	165	9.5			
Carboxin	4.06	Positive	236	87	23.5	236	93	27.5	236	143	11
Chlorpyrifos	7.31	Positive	349.7	198	16	351.7	200	18			
Clethodim	6.86	Positive	360	164	17.5	360	166	24.5			
Clofentezine	6.54	Positive	303	102	30	303	138	11.5			
Clothianidin	2.50	Positive	250	169	13	250	132	50			
Cyazofamid	5.95	Positive	325	108	9.5	325	217	12.5	325	261	6.5
Cypermethrin	7.74	Positive	433	191	14	435	193	14			
Demeton-S-methyl	3.88	Positive	231	61	25	231	89	10			
Demeton-S-methylsulfone	2.11	Positive	263	109	24	263	121	12	263	169	13.5
Diazinon	6.34	Positive	305	97	30	305	153	20	305	169	20
Dichlorprop	5.46	Negative	233	125	26	233	161	10			
Dichlorvos	3.78	Positive	221	109	16	238	221	4			
Difenoconazole	6.69	Positive	406	188	42	406	251	23.5	406	337	14
Diflubenzuron	6.06	Positive	311	141	25	311	158	8			
Dimethoate	2.67	Positive	230	125	19	230	171	14	230	199	8
Dinoterb	6.43	Negative	239	136	34	239	207	23			
Ditalimphos	5.70	Positive	300	130	30	300	148	16			
DMF	3.53	Positive	150	132.2	35	150	106.8	20			
DMPF	2.04	Positive	163	107	25	163	117	20.5	163	122	15
DMST	3.99	Positive	215	77	43	215	106.09	13	215	151	5
DNOC	4.33	Negative	196.95	137	17	196.95	109.09	10			
Epoxiconazole	5.88	Positive	330	101	30	330	121	17.5			

Compound Name	RT	Polarity	Transition I (CE)			Transition II (CE)			Transition III (CE)		
Ethiofencarb	4.26	Positive	226	107	11	226	165	5.5			
Ethion	7.20	Positive	385	199	10	402	199	15	402	385	5
Ethoprophos	5.85	Positive	243.24	97	23	243.24	131	31			
Etofenprox	8.21	Positive	394	135	22.5	394	177	13.5	394	359	10.5
Fenamiphos	6.03	Positive	304	201.7	35	304	216.9	21			
Fenamiphos-sulfone	4.03	Positive	336	188	31	336	266	50			
Fenamiphos-sulfoxide	3.89	Positive	337.2	320.1	5	337.2	171.09	20			
Fenazaquin	7.79	Positive	307	57.4	20	307	147.09	17	307	161.09	14
Fenbuconazole	6.02	Positive	337	70.2	16	337	125	25			
Fenhexamid	5.83	Positive	302	97	18.5	302	302	8.5			
Fenoxycarb	6.12	Positive	302	88	13.5	302	116	8	302	256	12
Fenpropidin	4.28	Positive	274	117	30.5	274	147	23.5			
Fenthion	6.27	Positive	279	105	20.5	279	169	15.5	279	247	10.5
Fenthion-oxon	4.96	Positive	263	231	30	263	216	20			
Fenthion-oxon-sulfone	2.74	Positive	295	217	20	295	104.09	33			
Fenthion-oxon-sulfoxide	2.62	Positive	279.08	264	15	279.08	104	20			
Fenthion-sulfone	4.20	Positive	328	125.09	22	328	279	22	328	311	7
Fenthion-sulfoxide	4.02	Positive	295	109.2	26	295	125	30	295	280	17
Fipronil	6.12	Negative	435.22	330.2	13	435.22	250.09	42			
Fluazifop-p-butyl	7.00	Positive	384	254	17.5	384	282	18	384	328	14
Fluoxastrobin	5.78	Positive	459.19	427.1	17	459.19	188	45			
Fluquinconazole	5.75	Positive	376	307	21.5	376	349	18			
Flusilazole	6.08	Positive	316	165	23.5	316	247	16.5			
Fosthiazate	4.31	Positive	284.4	104.09	25	284.4	228.2	30			
Heptenophos	4.78	Positive	251	125	12	251	127.09	14			
Hexaconazole	6.49	Positive	314	70	12.5	314	159.7	24.5			
Hexythiazox	7.35	Positive	353	168	23.5	353	228	14.5			
Imazalil	3.82	Positive	297	159	16.5	297	201	13			
Imidacloprid	2.44	Positive	256	175	16.5	256	209	13.5			
Indoxacarb	6.75	Positive	528	150	23.5	528	203	32.5	528	293	12
Iodosulfuron-methyl-sodium	4.94	Positive	530.07	163.09	13	530.07	390	21			
Iprodione	6.06	Positive	330	101	25	330	245	12	332	247	16
Iprovalicarb	5.70	Positive	321	119	14	321	203	7			
Isoprothiolane	5.48	Positive	291	145	35	291	189	20	291	231	10
Isoproturon	4.64	Positive	207	72	11.5	207	165	12			
Linuron	5.22	Positive	249	160	16	249	182	13.5			
Lufenuron	7.23	Negative	511	158.09	10	511	141	30	511	176.7	30
Malaoxon	3.88	Positive	315	99	20	315	127	10			
Malathion	5.44	Positive	331	99	18	331	127	10			
Mecarbam	5.80	Positive	330	97	45	330	199	14	330	227	8
Mepanipyrim	5.70	Positive	224	77	49	224	106	20			
Metaflumizone	7.17	Negative	505.1	302.1	25	505.1	328	15	505	116.5	16.5
Metalaxyl	4.65	Positive	280	192	16.5	280	220	12.5			
Metconazole	6.50	Positive	320	70	14.5	320	125	32.5			
Methamidophos	1.64	Positive	142	94	11.5						

Compound Name	RT	Polarity	Transition I (CE)			Transition II (CE)			Transition III (CE)		
Methiocarb	5.29	Positive	243.4	169.3	13	243.4	121.2	30			
Methiocarb-sulfone	2.75	Positive	275	107	33.5	275	122	14.5	275	201	7
Methiocarb-sulfoxide	2.51	Positive	242	122	23	242	185	20			
Methoxyfenozide	5.53	Positive	369	149	11.5	369	313	5			
Metsulfuron-methyl	3.82	Positive	382	167	14	382	199	27			
Mevinphos	2.61	Positive	225	127	13	225	193	6			
Monocrotophos	2.19	Positive	224	127	12.5	224	193	7.5	224	98	10
Monolinuron	4.23	Positive	215	126	17	215	148	13			
Ofurace	3.88	Positive	282	160	22	282	236	14			
Oxamyl	2.00	Positive	237	72	9.5	237	90	6.5	237	220	5.5
Oxycarboxin	2.92	Positive	268	147	24	268	175	13			
Oxydemeton-methyl	2.06	Positive	247	109	26	247	169	12			
Parathion	6.12	Positive	292	236	20	292	94	20	291.1	236.2	20
Penconazole	6.28	Positive	284	159	27.5	284	173	16.5			
Pencycuron	6.63	Positive	329	125	20	329	218	13.5			
Pendimethalin	7.37	Positive	282.12	212	10	282.12	194	10			
Phosmet	4.97	Positive	335	133	36	335	160	17			
Phosmet-oxon	3.31	Positive	302	160	21	302	133	31			
Phosphamidon	3.50	Positive	300	174.09	13	300	227	12	300	127	22
Phoxim	6.44	Positive	299	129	9	299	153	6			
Pirimicarb	3.10	Positive	239	72.09	16	239	182.3	25			
Pirimiphos-methyl	6.40	Positive	306	164	20	306	108	20			
Prochloraz	6.34	Positive	376	266	16.5	376	308	10.5			
Propamocarb	1.76	Positive	189	74	23	189	102	13	189	144	7.5
Propargite	7.48	Positive	368	175	15	368	231	9.5			
Propiconazole	6.38	Positive	342	159	20	342	69	20			
Propoxur	3.80	Positive	210.28	111.2	13	210.28	168.3	30			
Propyzamide	5.50	Positive	256	145	35	256	173	21	256	190	13
Prosulfocarb	6.88	Positive	252	91	20	252	128	10			
Prosulfuron	5.27	Positive	420.27	141.09	15	420.27	167	15	420.27	109	15
Prothioconazole-desthio	5.94	Positive	312	70	18	312	125	25			
Pyraclostrobin	6.44	Positive	388	163	18.5	388	194	7.5			
Pyridate	8.07	Positive	379	207	17	379	351	8.5			
Pyrimethanil	4.70	Positive	200	82	20.5	200	107	19.5			
Pyriproxyfen	7.21	Positive	322	96.2	14	322	184.9	22	322	227	13
Quinoxyfen	7.31	Positive	308	161.9	47	308	197	31			
Simazine	3.82	Positive	202	124	17	202	132	32			
Spinosad_A	5.75	Positive	733	142	21.5	733	189	30	733	98	20
Spirodiclofen	7.61	Positive	411	313	20	411	71	20			
Spiroxamine	4.61	Positive	298	100	23	298	144	15			
Tebufenozide	6.09	Positive	353	133	17	353	297	7.5			
Tebufenpyrad	7.09	Positive	334	117	31	334	145	24			
Teflubenzuron	7.23	Negative	379	195	20.5	379	339	9	379	359	5.5
Thiabendazole	2.15	Positive	202	131	27	202	175	19.5			
Thiacloprid	2.94	Positive	253	90	30	253	99	36.5	253	126	17

Compound Name	RT	Polarity	Transition I (CE)			Transition II (CE)			Transition III (CE)		
Thiamethoxam	2.15	Positive	292	132	18.5	292	181	18	292	211	11.5
Thiometon	4.44	Positive	247	61	25	247	89	10			
Thiophanate-methyl	3.76	Positive	342.78	151.12	20	342.78	93.15	50	343	311	8
Triadimenol	5.74	Positive	296	70	7	296	99	11.5			
Triallate	7.41	Positive	306	144.92	23	306	86	24	304	143	20
Triazophos	5.66	Positive	314	119	30	314	162	17			
Trichlorfon	2.71	Positive	274	109	19.5	274	127	18	274	257	8
Tricyclazole	3.09	Positive	190	109	31.5	190	136	25.5			
Trifloxystrobin	6.77	Positive	409	145	36	409	186	11			
Triflumuron	6.50	Positive	359.06	156.09	25	359.06	138.8	20			
Triticonazole	5.85	Positive	318	70	12	318	125	30.5			
Vamidothion	2.59	Positive	288	146	20	288	118	30			
Zoxamide	6.39	Positive	336	132	11	336	159	36.5	336	187	17

Appendix 2.

Recoveries, repeatability (RSDr), internal reproducibility (RSDR), expanded uncertainty (U) and Limit of Quantification (LOQ) for pesticides validated rape seed (S), rape cake (C), and rape meal (M) using QuEChERS-EMR

	Compound	Spiking level 0.005					Spiking level 0.01					Spiking level 0.05					LOQ	Matrices
		Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%		
GC	2-phenylphenol	90	17	18	42	18	91	10	20	45	20	95	8	9	21	9	0.005	S C M
LC	3-hydroxycarbofuran	84	19	16	47	17	78	18	17	56	17	89	18	20	46	20	0.005	S C M^1
LC	Acephate	75	20	18	62	19	70	18	19	71	20	89	20	19	44	20	0.005	S C M
LC	Acetamiprid						81	12	14	48	14	95	16	14	31	15	0.01	S^2 C^1 M^1
GC	Acrinathrin I											59	19	18	89	18	0.05	S^2 M^2
LC	Aldicarb											82	18	22	58	23	0.05	S^2 C^2 M^2
LC	Aldicarb-sulfone	101	35	30	63	31	59					89	11	20	47	21	0.05	S^2 C^2 M^2
GC	Aldrin	57	12	12	90	12	54	10	10	94	10	55	9	20	99	20	0.005	S C M
LC	Atrazine	83	17	21	55	22	81	13	20	56	20	87	16	18	46	19	0.005	S C M
GC	Atrazine	100	7	7	15	8	96	6	8	19	8	103	8	11	23	11	0.005	S C M
LC	Azinphos-ethyl	98	18	37	77	38	82	13	19	52	19	83	17	19	51	19	0.005	S C M
LC	Azinphos-methyl	81	23				66	9				86	20	16	44	17	0.05	S^2 C^2 M^2
LC	Azoxystrobin	90	17	23	52	24	75	17	18	63	19	88	19	19	45	19	0.005	S C M
GC	Azoxystrobin	102	8	17	36	18	94	6	17	37	18	96	6	14	30	15	0.005	S C M
LC	Bifenthrin	78	17	22	64	23	68	14	22	79	22	76	14	20	63	20	0.05	S^2 C^2 M^2
GC	Bifenthrin	72	5	7	57	7	61	5	19	87	19	69	9	9	64	9	0.005	S C M
LC	Bitertanol	92	20	19	43	20	86	13	20	50	20	93	17	21	46	22	0.005	S C M
GC	Bitertanol						100	10	12	24	12	106	8	9	23	10	0.01	S2 C^1 M^1
LC	Boscalid	79	17	19	58	20	76	17	17	60	18	93	17	19	41	19	0.005	S C^1 M
GC	Boscalid	92	5	9	24	9	89	6	8	27	8	92	7	8	24	9	0.005	S C M
GC	Bromophos-ethyl	78	6	9	48	9	74	7	8	55	8	74	10	17	62	18	0.005	S C M
GC	Bromopropylate	88	5	9	29	9	85	8	11	38	12	84	8	16	45	16	0.005	S C M
LC	Bromoxynil	86	13	17	46	18	84	23	21	54	22	82	19	19	54	20	0.05	S^2 C^2 M^2
LC	Bromuconazole	101	19	20	42	21	85	16	15	43	15	90	19	17	41	18	0.005	S C M
GC	Bromuconazole I	95	12	14	31	15	90	10	20	45	20	95	6	20	43	21	0.005	S C M
GC	Bromuconazole II											94	13	29	61	30	0.05	S^2 C^2 M^2
LC	Bupirimate	91	20	21	48	22	80	16	22	59	22	90	19	19	45	20	0.005	S C M

	Compound	Spiking level 0.005					Spiking level 0.01					Spiking level 0.05					LOQ	Matrices
		Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%		
GC	Bupirimate	104	5	9	20	9	100	6	9	19	10	102	7	16	33	17	0.005	S C M
LC	Buprofezin	83	19	23	58	23	79	17	21	61	22	90	13	22	49	22	0.005	S C M
LC	Cadusafos	90	16	23	52	24	88	13	20	49	21	106	9	22	48	23	0.005	S C^1 M
GC	Cadusafos	100	5	6	13	6	98	8	8	17	8	99	8	11	23	11	0.005	S C M
LC	Carbaryl	95	18	22	47	23	77	14	19	61	19	85	18	17	47	18	0.005	S C M
LC	Carbendazim	78	18				76	8	19	62	19	83	14	19	52	20	0.005	S^2 C^1 M
LC	Carbofuran	83	20	19	52	20	84	17	15	45	16	97	18	17	35	17	0.005	S C M
LC	Carboxin	87	18	21	51	22	79	8	18	56	19	82	17	18	52	19	0.005	S C M
GC	Carboxin	98	7	10	21	11	93	5	5	18	5	94	7	9	22	9	0.005	S C M
GC	Chlorfenapyr	116	11	20	51	20	99	10	15	32	16	97	8	19	39	19	0.005	S C M
GC	Chlorfenson	90	5	7	25	7	85	4	4	31	5	87	8	14	39	15	0.005	S C M
GC	Chlorfenvinphos	82	12	20	55	21	86	15	25	59	26	87	13	20	50	21	0.005	S C M
GC	Chlormephos	105	10	19	40	20	91	8	18	42	19	99	7	21	43	21	0.005	S C M
GC	Chlorobenzilate	97	5	12	25	12	95	7	12	27	13	94	7	17	37	17	0.005	S C M
GC	Chlorpropham	95	10	16	34	16	97	10	10	22	11	99	8	10	22	11	0.005	S C M
LC	Chlorpyrifos	96	17	20	44	22	67	21	23	82	24	80	18	19	56	20	0.05	S^2 C^2 M^2
GC	Chlorpyrifos	88	9	9	30	9	87	4	5	27	5	83	10	12	42	12	0.005	S C M^2
GC	Chlorpyrifos-methyl	86	8	9	34	9	82	18	18	52	19	82	12	13	45	13	0.005	S C M
LC	Clethodim	93	23	22	49	23	80	16	25	66	26	99	15	18	38	19	0.01	S^1 C^1 M^1
LC	Clofentezine	110	27	31	70	34	112	11	23	54	24	88	18	20	49	21	0.01	S^2 C^1 M^1
GC	Clomazone	106	4	5	17	6	101	3	4	8	4	108	7	10	26	11	0.005	S C M
LC	Clothianidin	86	19	20	50	21	84	19	18	50	19	87	19	20	49	21	0.005	S C M
LC	Cyazofamid	92	19	20	45	21	77	14	16	57	16	92	17	17	38	18	0.005	S C M
GC	Cyflutrin	89	8	13	35	14	71	15	19	69	19	76	12	20	63	20	0.005	S C M
GC	Cyhalothrin-lambda (I+II)						68	11	26	84	27	77	17	18	59	18	0.01	S^1 C^1 M^1
LC	Cypermethrin	78	25	22	64	24	74	19	19	66	20	84	11	13	42	13	0.01	S^2 C^1 M^1
GC	Cypermethrin											79	10				0.05	S^2
GC	Cyproconazole	86	13	17	46	18	91	6	6	22	6	88	12	18	45	19	0.005	S C M
GC	Cyprodinil	88	14	15	39	15	86	9	13	39	13	83	8	18	51	19	0.005	S C M
GC	Deltamethrin_cis (I+II)											51	17	46	136	47	0.05	S^2 C^2 M^2
LC	Demeton-S-methyl	88	16	20	47	20	76	16	16	59	17	86	20	18	47	19	0.005	S C M

	Compound	Spiking level 0.005					Spiking level 0.01					Spiking level 0.05					LOQ	Matrices
		Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%		
GC	Demeton-S-methyl	99	15	14	29	14	93	17	18	40	19	93	12	14	32	14	0.005	S C M
LC	Demeton-S-methylsulfone	84	20	18	49	18	80	13	16	52	17	87	19	21	50	22	0.005	S C M
LC	Diazinon	86	18	23	55	23	79	16	22	61	22	95	13	12	28	13	0.005	S C M
GC	Diazinon	105	6	9	21	9	100	6	7	14	7	103	8	14	28	14	0.005	S C M
LC	Dichlorprop	121	13	13	50	14	97	13	13	28	13	85	18	19	48	19	0.01	S1 C1 M[1]
LC	Dichlorvos	98	12	12	25	12	74	13	13	59	14	80	20	18	54	18	0.005	S C M[1]
GC	Dichlorvos	90	8	12	33	13	88	13	14	37	14	90	14	19	44	20	0.005	S C M
GC	Dicloran	91	6	14	35	15	90	10	12	31	12	89	8	14	36	14	0.005	S C M
GC	Dieldrin	77	14	20	62	21	74	7	8	55	8	75	9	19	63	19	0.005	S C M
LC	Difenoconazole	99	16	32	66	33	78	13	31	78	32	103	15	21	44	22	0.005	S C M
GC	Difenoconazole (I+II)	86	8	9	34	9	79	7	17	55	18	88	8	10	31	10	0.005	S C M
LC	Diflubenzuron	79	11				81	12	26	67	28	91	17	20	45	21	0.005	S C[2] M[1]
LC	Dimethoate	92	17	20	45	21	79	14	15	52	16	88	20	21	50	22	0.005	S C M
GC	Dimethomorph I	108	5	7	22	7	99	7	7	14	7	98	6	8	17	8	0.005	S C M
GC	Dimethomorph II	107	8	8	21	8	99	7	10	21	10	94	7	13	30	14	0.005	S C M
LC	Dinoterb	98	22	19	40	20	82	21	18	52	19	78	16	15	54	15	0.05	S[2] C[2] M[2]
GC	Diphenylamine	90	7	18	43	19	96	7	16	34	17	98	8	12	26	13	0.005	S C[2] M
GC	Disulfoton	98	8	10	21	10	93	7	8	22	8	94	7	12	28	12	0.005	S C M
LC	Ditalimphos	88	18	21	49	22	76	16	16	58	17	85	16	21	52	21	0.005	S C M
LC	DMF	90	14	19	43	19	78	17	18	57	18	86	18	19	49	20	0.005	S C M
LC	DMPF	96	15	14	31	15	84	18	27	65	28	76	19	18	62	19	0.005	S C M[1]
LC	DMST	107	12	29	62	30	105	18	19	41	20	115	18	25	60	26	0.005	S C[1] M
LC	DNOC											79	17	18	57	19	0.05	S[2] C[2] M[2]
GC	Endosulfan-alpha	72	13	12	62	12	73	6	7	56	7	72	10	16	65	16	0.005	S C M
GC	Endosulfan-beta	80	7	10	44	10	81	6	11	44	11	81	8	19	55	20	0.005	S C M
GC	Endosulfan-sulfate											55	20	59	151	60	0.05	S[2] C[2] M[2]
GC	Endrin	78	14	17	56	17	70	9	11	64	12	69	9	18	73	19	0.005	S C M
GC	EPN											79	10	10	46	10	0.05	S[2] C[2] M[2]
LC	Epoxiconazole	99	18	17	36	18	89	18	18	43	18	93	17	18	39	18	0.005	S C M
GC	Epoxiconazole	100	6	6	12	6	95	7	8	20	9	98	8	9	20	10	0.005	S C M
LC	Ethiofencarb	85	13	20	52	21	75	15	19	64	20	86	13	14	39	14	0.005	S C[1] M

	Compound	Spiking level 0.005					Spiking level 0.01					Spiking level 0.05					LOQ	Matrices
		Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%		
LC	Ethion	87	19	22	52	23	76	14	21	66	22	92	13	19	43	20	0.005	S C M
GC	Ethion	97	6	8	17	8	85	14	14	42	14	77	12	17	58	17	0.005	S C M
LC	Ethoprophos	90	17	16	38	16	78	19	19	59	20	88	16	19	47	20	0.005	S C M
GC	Ethoprophos	110	5	12	32	13	108	14	16	36	16	110	8	16	40	17	0.005	S C M
GC	Ethoxyquin	124	6	20	63	20	93	9	32	67	33	96	7	19	41	20	0.005	S C M
LC	Etofenprox	75	20	20	64	20	70	15	19	72	19	80	9	12	47	12	0.005	S C M
GC	Etofenprox	74	4	7	54	8	71	7	11	62	11	75	10	20	65	20	0.005	S C M
LC	Fenamiphos	90	19	19	44	19	83	14	20	53	20	90	15	20	45	20	0.005	S C M
LC	Fenamiphos-sulfone	86	19	17	45	18	82	16	17	49	17	96	18	16	33	16	0.005	S C^{1} M
LC	Fenamiphos-sulfoxide											91	14	17	41	18	0.05	C^{2} M^{2}
GC	Fenarimol	89	8	11	31	11	92	6	7	21	7	92	8	11	28	11	0.005	S C M
LC	Fenazaquin	83	15	21	55	22	77	14	22	64	23	84	11	20	52	21	0.005	S C M
GC	Fenazaquin	80	14	14	49	14	76	10	13	55	13	76	14	20	64	21	0.005	S C M
LC	Fenbuconazole	114	15	17	46	18	89	18	16	39	17	95	18	17	37	18	0.005	S C M
GC	Fenbuconazole	95	7	13	30	14	95	9	9	21	9	96	7	10	22	10	0.005	S C M
LC	Fenhexamid	109	7				82	15				93	20	20	43	20	0.005	S^{2} M
GC	Fenitrothion	102	15	18	38	19	99	8	16	32	16	102	10	15	30	15	0.005	S C M
LC	Fenoxycarb	91	17	23	51	24	78	13	19	59	19	88	20	21	50	21	0.005	S C M
GC	Fenpropathrin											103	10	12	26	13	0.05	S^{2} M^{2}
LC	Fenpropidin	90	16	23	52	24	83	13	17	48	17	88	19	17	43	18	0.005	S C^{1} M
GC	Fenpropimorph	95	4	4	13	4	90	5	5	22	5	91	8	12	31	13	0.005	S C M
GC	Fenson	98	4	5	10	5	94	4	5	16	5	97	8	13	27	13	0.005	S C M
LC	Fenthion	103	15	19	41	20	83	14	14	45	15	94	14	16	35	16	0.005	S C M
GC	Fenthion	100	7	10	20	10	101	13	17	34	17	102	9	20	41	20	0.005	S C M
LC	Fenthion-oxon	87	13	23	53	24	79	16	20	58	20	87	19	21	51	22	0.005	S C^{1} M
LC	Fenthion-oxon-sulfone	101	20	20	40	20	86	15	14	41	15	87	19	20	48	20	0.005	S C M
LC	Fenthion-oxon-sulfoxide	96	9	17	36	18	84	14	15	45	15	95	11	10	23	10	0.005	C M
LC	Fenthion-sulfone	105	15	23	48	24	86	14	13	38	13	88	17	18	45	19	0.005	S C M
LC	Fenthion-sulfoxide	93	20	19	42	20	81	16	21	57	22	91	18	18	41	19	0.005	S C M
GC	Fenvalerate (I+II)	99	14	19	40	20	76	17	18	61	18	69	12	19	73	20	0.005	S M
LC	Fipronil	98	19	17	37	18	88	19	20	47	20	89	17	18	44	19	0.005	S C M

	Compound	Spiking level 0.005					Spiking level 0.01					Spiking level 0.05					LOQ	Matrices
		Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%		
LC	Fluazifop-p-butyl	86	19	23	54	23	75	19	20	65	21	95	13	17	36	17	0.005	S C M
GC	Fluazifop-p-butyl	99	5	7	14	7	95	5	5	15	5	97	7	13	27	13	0.005	S C M
GC	Fludioxonil	99	5	6	12	6	98	6	5	12	5	100	6	9	19	9	0.005	S C M
GC	Flufenoxuron	101	17	17	35	17	90	13	17	40	18	91	10	20	44	20	0.005	S C M
LC	Fluoxastrobin	93	15	21	46	22	77	15	14	55	14	95	15	16	35	17	0.005	S C M
LC	Fluquinconazole	93	20	23	50	24	87	15	15	40	15	88	16	20	47	20	0.005	S C M
GC	Fluquinconazole	98	7	12	25	12	92	4	9	25	10	95	7	12	27	12	0.005	S C M
LC	Flusilazole	86	19	17	45	18	82	16	17	51	18	87	18	18	46	19	0.005	S C^1 M
GC	Flutriafol	99	6	7	14	7	99	5	5	10	5	102	7	8	17	8	0.005	S C M
LC	Fosthiazate	93	18	20	44	21	81	16	19	55	19	85	19	21	52	21	0.005	S C M
GC	HCH-alpha	90	5	19	44	20	87	6	19	47	20	91	8	20	46	21	0.005	S C M
GC	HCH-beta	89	8	12	34	13	86	6	10	34	10	88	8	16	41	17	0.005	S C M
LC	Heptenophos	82	18	20	54	20	76	15	19	62	19	89	19	20	46	20	0.005	S C M
GC	Heptenophos	97	11	12	25	12	94	16	19	40	19	96	14	15	31	15	0.005	S C M
LC	Hexaconazole											111	18	22	52	23	0.05	S^2 M^2
GC	Hexaconazole											98	13	20	42	21	0.05	S^2 C^2 M^2
LC	Hexythiazox	80	21	26	67	27	75	15	22	68	23	82	13	22	58	23	0.01	S^1 C^1 M^1
GC	Hexythiazox	78	7	19	58	19	86	11	13	39	13	90	8	20	45	20	0.005	S C M
LC	Imazalil	84	13	16	46	17	75	17	16	60	17	82	18	16	49	17	0.005	S C M
LC	Imidacloprid	89	16	21	49	22	79	16	17	54	17	89	17	20	47	21	0.005	S C1 M
LC	Indoxacarb	87	17	23	55	24	97	15	24	50	25	101	15	28	57	29	0.005	S C1 M^1
GC	Indoxacarb	94	19	18	39	19	82	18	16	50	17	75	12	19	63	19	0.005	S C M^2
LC	Iodosulfuron-methyl-sodium	85	14	16	46	17	80	17	18	55	19	89	18	19	45	19	0.005	S^1 C M
LC	Iprodione	80	24	23	61	23	79	19	19	58	20	83	19	22	56	22	0.01	S^1 C^1 M^1
GC	Iprodione						58	20	19	94	20	51	15	20	108	21	0.01	S^1 C^1 M^2
LC	Iprovalicarb	93	20	20	44	21	80	15	18	55	19	87	20	21	50	21	0.005	S C M
GC	Iprovalicarb I	111	16	19	45	20	104	11	14	29	14	103	10	17	36	18	0.005	S C M
GC	Iprovalicarb II	111	12	14	37	15	105	13	14	31	15	103	9	20	41	20	0.005	S C M
GC	Isofenphos-methyl	109	4	12	30	12	106	11	13	29	13	108	9	19	42	20	0.005	S C M
LC	Isoprothiolane	90	20	20	46	21	80	16	20	58	21	90	14	16	38	16	0.005	S C M
GC	Isoprothiolane	103	7	9	21	10	102	4	4	10	4	106	7	11	26	11	0.005	S C M

	Compound	Spiking level 0.005					Spiking level 0.01					Spiking level 0.05					LOQ	Matrices
		Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%		
LC	Isoproturon	95	17	24	51	25	84	9	21	54	21	85	20	21	52	21	0.005	S C M
GC	Jodofenfos	72	11	11	59	11	74	7	13	59	14	73	17	20	68	20	0.005	S C M
GC	Kresoxim-methyl	95	15	20	43	21	102	12	20	42	21	105	6	11	24	11	0.005	S C M
GC	Lindane						80	13	17	53	18	84	5	20	53	21	0.01	S^2 C^1 M^1
LC	Linuron	112	14	19	47	20	95	15	17	36	17	92	17	18	41	19	0.005	S^1 C M
GC	Linuron	96	12	20	43	21	88	13	16	41	16	91	12	19	43	19	0.005	S C M
LC	Lufenuron											85	20	20	52	21	0.05	S^2 C^2 M^2
LC	Malaoxon	93	16	21	46	22	80	14	19	55	19	90	17	17	40	17	0.005	S C M
LC	Malathion	91	20	20	45	21	78	16	19	59	19	89	17	18	43	18	0.005	S C M
LC	Mecarbam	96	13	20	43	21	77	16	17	58	18	92	13	15	35	16	0.005	S C M
LC	Mepanipyrim	87	7				92	14	23	52	25	94	17	19	40	19	0.005	S^1 C M^1
LC	Metaflumizone	94	19	21	46	22	85	18	24	58	25	91	16	14	34	15	0.005	S C M
LC	Metalaxyl	101	14	23	48	24	82	16	20	55	21	91	18	19	43	20	0.005	S C M
GC	Metalaxyl	113	10	16	41	16	110	9	13	34	14	113	7	13	38	14	0.005	S C M
LC	Metconazole	91	20	22	48	22	84	17	20	52	20	95	19	18	39	19	0.005	S C M
GC	Methacrifos											98	9	19	40	20	0.05	S^2 C^2 M^2
LC	Methamidophos	85	20	23	56	24	73	13	17	65	18	74	18	18	64	19	0.005	S C M
GC	Methidathion											102	11	15	32	16	0.05	S^2 C^2 M^2
LC	Methiocarb	113	17	20	49	21	88	20	19	46	19	90	19	19	43	19	0.005	S C M
LC	Methiocarb-sulfone	86	19	20	49	20	83	14	16	48	17	88	15	20	47	20	0.005	S C M
LC	Methiocarb-sulfoxide	86	20	20	51	21	79	16	17	55	18	90	17	16	38	16	0.005	S C M
LC	Methoxyfenozide	86	15	16	42	16	76	17	18	60	18	89	16	17	42	18	0.005	S C M
GC	Metribuzin	105	8	12	26	12	102	6	7	16	8	109	8	13	32	13	0.005	S C M
LC	Metsulfuron-methyl	88	12	28	63	29	78	15	20	61	21	91	20	19	43	20	0.005	S C M
LC	Mevinphos	91	22	24	54	25	80	15	18	55	18	90	18	21	48	22	0.01	S^1 C^1 M^1
LC	Monocrotophos	85	20	18	48	19	76	10	16	58	17	83	19	21	55	21	0.005	S C M
LC	Monolinuron	89	19	20	48	21	75	17	19	64	19	92	13	14	33	14	0.005	S C M
GC	Myclobutanil	104	8	9	20	10	104	7	8	18	8	106	7	13	28	13	0.005	S C M
GC	Nuarimol	98	4	7	14	7	94	5	4	15	4	99	7	10	20	10	0.005	S C M
LC	Ofurace	94	19	22	46	22	72	14	17	67	18	93	15	15	34	15	0.005	S C M
GC	Ofurace	113	12	14	39	15	92	11	20	44	21	102	9	20	41	20	0.005	S C M

	Compound	Spiking level 0.005					Spiking level 0.01					Spiking level 0.05					LOQ	Matrices
		Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%		
GC	Oxadixyl	110	6	10	29	10	108	7	11	28	11	112	7	12	35	13	0.005	S C M
LC	Oxamyl	91	19	22	49	23	82	15	17	50	17	86	17	19	48	20	0.005	S C M
LC	Oxycarboxin	95	17	21	44	22	81	14	14	48	15	100	14	13	27	14	0.005	S C M
LC	Oxydemeton-methyl	86	20	19	48	19	78	12	13	53	14	81	20	20	56	20	0.005	S C M
GC	Paclobutrazol	98	7	7	14	7	96	5	6	15	6	96	7	8	19	8	0.005	S C M
LC	Parathion	115	19	15	44	16	76	19	22	67	24	92	20	25	55	27	0.005	S C^1 M
GC	Parathion	98	10	18	37	19	100	14	13	28	14	100	9	13	26	13	0.005	S C M
GC	Parathion-methyl	94	14	16	35	16	98	8	11	24	12	96	6	6	15	6	0.005	S C M^2
LC	Penconazole	91	20	18	41	19	81	15	15	48	15	90	15	18	42	19	0.005	S C M
GC	Penconazole	90	6	6	24	7	90	5	5	21	5	93	7	10	25	10	0.005	S C M
LC	Pencycuron	96	20	15	32	15	86	12	19	49	20	101	14	18	36	18	0.005	S^1 C M
GC	Pencycuron	106	4	5	17	6	101	3	4	8	4	108	7	10	26	11	0.005	S C M
LC	Pendimethalin	88	18	25	57	26	76	19	22	66	22	86	11	15	41	15	0.005	S^1 C^1 M
GC	Pendimethalin	79	9	12	48	12	79	10	13	50	13	80	8	17	53	18	0.005	S C M
GC	Permethrin (I+II)											68	13	16	72	16	0.05	S^2 C^2 M^2
GC	Phenthoate	92	15	14	32	14	85	10	10	36	11	87	9	19	48	20	0.005	S C M
GC	Phosalone						74	16	15	61	16	84	18	20	53	21	0.01	S^1 C^1 M^2
LC	Phosmet	88	19	21	49	21	85	17	21	52	21	99	18	21	43	21	0.005	S C M
LC	Phosmet-oxon	96	14	19	40	20	79	14	20	58	20	97	12	15	31	15	0.005	S C M
LC	Phosphamidon	100	16	16	33	17	78	14	21	62	21	92	17	18	40	18	0.005	S^1 C M
LC	Phoxim	93	17	22	47	23	78	14	20	61	21	83	20	21	56	22	0.005	S C M
LC	Pirimicarb	96	20	24	50	25	84	16	22	55	23	96	14	15	33	16	0.005	S C M
GC	Pirimicarb	106	6	6	17	6	102	4	5	11	5	105	7	10	22	10	0.005	S C M
GC	Pirimicarb-desmethyl											98	8	13	27	14	0.05	S^2 C^2 M^2
LC	Pirimiphos-methyl	87	20	31	70	32	73	15	19	67	20	89	14	16	39	16	0.005	S C M
GC	Pirimiphos-methyl	92	7	7	22	7	88	11	10	31	11	94	10	16	36	17	0.005	S C M
LC	Prochloraz	93	18	20	44	20	75	15	19	64	20	88	20	24	54	24	0.005	S C M
GC	Prochloraz						94	16	20	43	21	72	10	15	65	16	0.01	S^1 C^1 M^2
GC	Procymidone	100	6	8	17	9	100	4	6	12	6	104	7	13	28	13	0.005	S C M
LC	Propamocarb	88	20	23	53	24	81	16	21	56	21	90	19	18	42	18	0.005	S C M
LC	Propargite	81	17	20	57	21	74	17	22	69	23	89	14	19	44	19	0.005	S C M

	Compound	Spiking level 0.005					Spiking level 0.01					Spiking level 0.05					LOQ	Matrices
		Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%		
LC	Propiconazole	91	19	18	41	18	80	17	17	53	18	88	18	20	47	20	0.005	S C M
GC	Propiconazole (I+II)	93	6	7	20	7	93	6	6	19	6	93	8	12	27	12	0.005	S C M
LC	Propoxur	89	17	31	68	32	77	17	19	60	19	91	20	21	48	22	0.005	S C M
GC	Propoxur											94	11				0.05	M^2
LC	Propyzamide	87	20	18	46	19	80	12	19	55	19	84	20	25	61	26	0.005	S C M
GC	Propyzamide	102	14	18	36	18	120	8	10	44	10	103	8	13	27	13	0.005	S C M
LC	Prosulfocarb	99	22	29	61	30	76	21	29	76	30	99	16	31	65	32	0.05	S^2 C^2 M^2
LC	Prosulfuron	90	20	20	47	21	81	18	21	57	21	91	19	20	45	20	0.005	S C M
LC	Prothioconazole-desthio	101	16	25	52	26	82	19	17	50	18	84	20	21	54	22	0.005	S C M
GC	Prothiofos	67	11	20	79	21	69	12	17	70	17	74	9	20	67	21	0.005	S C M
LC	Pyraclostrobin	93	20	22	47	23	79	14	20	59	20	88	18	19	45	19	0.005	S C M
GC	Pyrazophos						89	17				89	12	17	41	17	0.01	S^1 M^2
GC	Pyridaben	81	4	9	41	9	77	9	12	52	13	86	10	20	51	21	0.005	S C M
GC	Pyridaphenthion	122	12	20	61	21	105	12	13	29	14	105	12	20	42	21	0.005	S C M
LC	Pyridate						73	12	26	77	27	83	11	41	90	42	0.01	S^1 C^1 M^2
LC	Pyrimethanil	99	20	22	45	22	79	18	19	58	19	79	18	19	57	19	0.005	S C M
GC	Pyrimethanil	94	6	8	21	8	90	4	8	26	8	92	8	15	34	15	0.005	S C M
LC	Pyriproxyfen	82	20	27	66	28	70	15	28	84	29	77	20	27	72	28	0.005	S C M
GC	Pyriproxyfen	85	6	10	35	10	83	8	9	39	10	80	8	14	49	14	0.005	S C M
LC	Quinoxyfen	75	16	30	79	31	72	14	22	74	23	79	10	14	51	15	0.005	S C M
GC	Quinoxyfen	67	4	5	67	5	64	6	6	73	6	61	9	19	87	19	0.005	S C M
LC	Simazine	87	18	20	49	21	71	17	18	68	18	86	16	15	41	15	0.005	S C M
LC	Spinosad_A	87	12	19	48	20	77	17	16	56	16	97	19	18	38	19	0.005	S C M
LC	Spirodiclofen	81	21	22	60	23	72	16	25	77	26	84	18	22	57	23	0.01	S^1 C^1 M^1
LC	Spiroxamine	94	21	22	47	22	76	16	20	63	21	85	18	19	48	19	0.01	S^1 C^1 M^1
GC	Tebuconazole	92	9	9	24	9	93	9	9	23	9	94	7	10	23	10	0.005	S C M
LC	Tebufenozide	93	16	15	35	16	79	11	18	57	19	85	18	26	63	27	0.005	S C M
LC	Tebufenpyrad	96	22	25	53	26	85	16	26	61	27	96	15	27	56	28	0.01	S^1 C^1 M^1
GC	Tebufenpyrad	100	6	12	25	12	96	8	11	24	11	94	7	18	39	18	0.005	S C M
GC	Tecnazene	80	9	9	45	9	68	9	18	74	18	73	8	20	69	21	0.005	S^1 C M
LC	Teflubenzuron	101	20	26	55	27	98	19	30	61	31	104	17	20	42	21	0.005	S C M

	Compound	Spiking level 0.005					Spiking level 0.01					Spiking level 0.05					LOQ	Matrices
		Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%	Recovery %	RSDr %	RSD_R %	U%	Cu%		
GC	Tefluthrin	98	4	19	40	20	93	10	19	42	20	89	6	24	54	25	0.005	S C M
GC	Tetraconazole	108	8	13	30	13	110	9	9	27	9	111	7	11	31	12	0.005	S C M
GC	Tetradifon	78	7	7	47	7	74	9	11	56	11	74	10	23	70	24	0.005	S C M
LC	Thiabendazole	73	22	30	83	31	68	10	9	66	9	78	19	20	60	20	0.05	S^2 C^2 M^2
LC	Thiacloprid	90	19	27	59	28	73	16	17	65	18	88	18	18	44	18	0.005	S C M
LC	Thiamethoxam	83	17	20	54	21	76	9	25	70	26	87	18	21	50	21	0.005	S C M
LC	Thiometon	139	22	45	124	48	85	22	18	48	19	94	19	24	50	24	0.05	S^2 C^2 M^2
GC	Thiometon						73	19	18	66	18	66	13	14	75	15	0.01	S^1 C^1 M^1
LC	Thiophanate-methyl	101	14				101	7	21	44	22	116	20	20	54	22	0.005	S C^1
GC	Tolclofos-methyl	100	6	17	35	17	101	12	18	38	19	96	8	17	36	18	0.005	S C M
GC	Triadimefon	105	8	12	26	12	100	9	10	21	10	105	7	9	21	9	0.005	S C M
LC	Triadimenol	89	13	17	41	17	79	12	14	51	15	82	19	24	62	25	0.005	S C^2 M
GC	Triadimenol	98	16	16	33	16	101	8	12	26	13	96	7	8	18	8	0.005	S C M^1
LC	Triallate	78	20	18	58	19	70	8	19	72	20	74	20	30	81	31	0.005	S C M
GC	Triallate	81	5	9	43	9	83	13	15	47	16	85	7	18	48	18	0.005	S C M
LC	Triazophos	92	17	18	41	19	80	16	18	54	19	88	19	21	50	22	0.005	S C M
GC	Triazophos	104	18	20	42	21	99	20	18	37	19	99	15	19	39	20	0.005	S C M
LC	Trichlorfon						78	15				85	20	23	55	23	0.01	S^1 C^2 M^2
GC	Trichlorfon	91	8	10	27	10	91	13	13	32	14	92	14	16	36	16	0.005	S C M
LC	Tricyclazole	85	19	18	48	19	76	13	14	56	15	89	15	14	36	14	0.005	S C M
GC	Tricyclazole	106	7	7	19	7	103	5	6	14	6	105	6	10	23	10	0.005	S C M
LC	Trifloxystrobin	90	25	35	75	36	84	20	31	72	32	97	13	27	56	28	0.01	S^1C^1 M^1
GC	Trifloxystrobin	107	19	20	43	20	101	12	13	26	13	106	7	11	26	11	0.005	S C M
LC	Triflumuron	109	15	21	47	22	84	15	23	57	24	97	19	21	45	22	0.005	S C M
GC	Trifluralin	94	6	6	18	6	87	6	17	45	18	89	9	20	46	20	0.005	S^1 C M
LC	Triticonazole	94	19	20	43	21	76	16	18	60	18	86	20	21	51	21	0.005	S C M
GC	Triticonazole	92	14	19	42	20	86	9	18	47	19	84	9	13	42	14	0.005	S C M
LC	Vamidothion	79	20	23	63	23	69	15	14	68	15	95	20	23	48	23	0.005	S C M
GC	Vinclozolin											90	8	19	44	20	0.05	S^2 M^2
LC	Zoxamide	89	21	22	50	22	76	18	21	64	22	86	18	20	49	21	0.01	S^1 C^1 M^1

[1]LOQ: 0.01 mg/kg [2]LOQ: 0.05 mg/kg

Appendix 3.

QuEChERS with EMR-Lipid cleanup procedural steps

Weigh 2 g (±0.02 g) of homogenized feed into a 50 ml single use centrifuge tube. Add internal standard and/or spike standard.
Add a ceramic homogenizer and 10 ml of cold water and shake briefly
Add 10 ml acetonitrile and shake mechanically for 1 min. (1. extraction)
Add the prepared mixture of 4 g MgSO4, 1 g NaCl, 1 g Na_3 citrate dihydrate and 0.5 g Na_2H cirate sesquihydrate. Shake for a few seconds after each addition to prevent lumps.
Shake mechanically for 1 min. (2. Extraction with phase separation)
Centrifuge for 10 min at 4500 rpm
Transfer at least 8 ml of the extract to a 15 ml single use centrifuge tube and store in the freezer (-80˚C for 1 hour or over night. Centrifuge (should be cold 5°C) for 5 min. at 4500 rpm.
Transfer 6 ml of the cold extract to a 15 ml single use centrifuge tube containing **900 mg PSA** and **900 mg $MgSO_4$**. Close the tube and shake mechanically for 30 seconds.
Centrifuge for 5 min. at 4500 rpm
Activate the **EMR dSPE** with 5 ml of water and transfer supernatant solution into the tube. Shake mechanically for 30 sec.
Centrifuge for 5 min. at 4500 rpm
Transfer **5ml** supernatant solution into **Final-EMR** tube and shake for 30 sec.
Centrifuge for 5 min. at 4500 rpm
Transfer the extract (ca. 1,5 ml) to a 15 ml single use centrifuge tube. Add 40 µl of 5% formic acid solution in acetonitrile (10 µl/ml extract). Dilute the extract 1:1 with acetonitrile
Transfer the final extract into auto sampler vials and analyse by GC and LC.