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Validation Report 36

Determination of pesticide residues in soya cake
by GC-MS/MS and LC-MS/MS

(QuEChERS-EMR method)

Elena Hakme
Mette Erecius Poulsen
Ederina Ninga
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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 soya cake. The method was tried validated for 220 pesticides and metabolites. A total of 140 pesticides were analysed by LC-MSMS and 129 compounds by GC-MSMS in soya cake. Some pesticides were commonly 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 before injection equlibrated with 2% B eluent. 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 220 compounds (pesticides or/and metabolites) in soya cake. The validation was performed on 5-6 replicates in three different spiking levels; 0.005, 0.01 and 0.05 mg/kg.

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). 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 validation results obtained for the 220 pesticides or metabolites using LC-MS/MS and GC-MS/MS are presented in appendix 2. On GC, the lowest LOQs achieved were 0.005 mg/kg for 115 compounds, 0.01 mg/kg for 3 compounds and 0.05 mg/kg for 11 compounds. On LC, the lowest LOQs achieved were 0.005 mg/kg for 125 compounds, 0.01 mg/kg for 2 compounds and 0.05 mg/kg for 14 compounds. The obtained results including recovery, RSD_r, LOQ and number of replicates are shown in appendix 2.

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 for compounds validated by GC-MS/MS

Name	RT	Parent Mass	Product Mass	Collision Energy
2-phenylphenol	9.81	169.1	115.1	25
2-phenylphenol	9.81	169.1	141.1	10
2-phenylphenol	9.81	170.1	169.1	10
Acrinathrin I	24.1	181	152	22
Acrinathrin I	24.1	208.1	180.9	8
Acrinathrin I	24.1	289	93.1	22
Aldrin	15.14	219.9	150	30
Aldrin	15.14	292.9	185.9	30
Aldrin	15.14	292.9	257.9	10
Atrazine	11.97	200.1	104.1	20
Atrazine	11.97	215.1	173.1	10
Atrazine	11.97	215.1	200.1	10
Azoxystrobin	30.33	344.1	172.1	25
Azoxystrobin	30.33	344.1	329.1	20
Azoxystrobin	30.33	388.1	345.1	15
Bifenthrin	22.3	181.1	141	22
Bifenthrin	22.3	181.1	165.1	15
Bifenthrin	22.3	181.1	166.1	15
Bitertanol	25.44	170.1	115.1	25
Bitertanol	25.44	170.1	141.1	20
Bitertanol	25.44	171.2	142.1	20
Boscalid	27.31	342	140	15
Boscalid	27.31	344	142	15
Bromophos-ethyl	16.84	302.8	284.8	14
Bromophos-ethyl	16.84	358.9	302.8	14
Bromophos-ethyl	16.84	358.9	330.9	10
Bromopropylate	22.33	184.9	75.5	30
Bromopropylate	22.33	340.8	185	14
Bromopropylate	22.33	342.7	185	15
Bromuconazole I	22.07	173	109	25
Bromuconazole I	22.07	173	145	15
Bromuconazole I	22.07	294.9	173	10
Bromuconazole II	22.84	172.9	145	16
Bromuconazole II	22.84	293	173	10
Bromuconazole II	22.84	295	175	10
Bupirimate	18.2	273.1	193.1	10
Bupirimate	18.2	316.2	208.1	10
Cadusafos	11.31	159	97	20
Cadusafos	11.31	213.1	89	12
Carboxin	18.25	235.1	87	15
Carboxin	18.25	235.1	143	15

Name	RT	Parent Mass	Product Mass	Collision Energy
Chlorfenapyr	18.52	248.9	112	24
Chlorfenapyr	18.52	363.8	247.2	30
Chlorfenapyr	18.52	363.8	282.1	20
Chlorfenson	17.6	111	75	14
Chlorfenson	17.6	175	75	28
Chlorfenson	17.6	175	111	10
Chlorfenvinphos	16.16	266.9	159	15
Chlorfenvinphos	16.16	268.9	161	12
Chlorfenvinphos	16.16	323	267	15
Chlormephos	9.1	154	121	5
Chlormephos	9.1	234	121	14
Chlorobenzilate	19.06	139	74.9	26
Chlorobenzilate	19.06	139	111	12
Chlorobenzilate	19.06	251	139	14
Chlorpropham	10.97	213.1	127	15
Chlorpropham	10.97	213.1	171	10
Chlorpyrifos	14.94	196.7	168.9	12
Chlorpyrifos	14.94	313.9	257.9	12
Chlorpyrifos	14.94	316.1	260	15
Chlorpyrifos-methyl	13.66	285.9	93	20
Chlorpyrifos-methyl	13.66	285.9	270.9	25
Chlorpyrifos-methyl	13.66	287.9	272.9	25
Clomazone	12.1	125	89	15
Clomazone	12.1	204	107	15
Cyflutrin	26.9	206	151	12
Cyflutrin	26.9	226	206	10
Cyhalothrin-lambda II	24.12	180.9	151.9	22
Cyhalothrin-lambda II	24.12	197	141.1	10
Cyhalothrin-lambda II	24.12	208.1	180.9	8
Cypermethrin	27.45	163	127	10
Cypermethrin	27.45	181	152	20
Cyproconazole	18.68	383	282	20
Cyproconazole	18.68	383.1	254	20
Cyprodinil	15.92	224.1	118	30
Cyprodinil	15.92	224.1	208.1	30
Cyprodinil	15.92	225.1	210.1	25
Demeton-S-methyl	10.66	88	59.8	6
Demeton-S-methyl	10.66	109	79	6
Demeton-S-methyl	10.66	141.9	79	12
Diazinon	12.42	179	137	15
Diazinon	12.42	199	93	15
Diazinon	12.42	304.1	179.1	15
Dichlorvos	7.68	185	93	12
Dichlorvos	7.68	185	109	17
Dichlorvos	7.68	220	185	10
Dicloran	11.82	160	124	10

Name	RT	Parent Mass	Product Mass	Collision Energy
Dicloran	11.82	206	176	10
Dicloran	11.82	208	178	10
Dieldrin	18.2	276.9	240.9	12
Dieldrin	18.2	278.9	242.9	12
Dieldrin	18.2	280.9	244.9	10
Difenoconazole (I+II)	26.59/26.65	323.1	265	15
Difenoconazole (I+II)	26.59/26.65	324.9	267	10
Difenoconazole (I+II)	26.59/26.65	325.1	267	20
Dimethomorph I	30.52	301	139	14
Dimethomorph I	30.52	301.1	165	12
Dimethomorph I	30.52	387.1	301.1	12
Dimethomorph II	31.03	301.1	165	12
Dimethomorph II	31.03	387.1	301.1	12
Diphenylamine	10.75	168.1	139	38
Diphenylamine	10.75	168.1	167.1	14
Diphenylamine	10.75	169.2	167.1	22
Disulfoton	12.73	142	109	10
Disulfoton	12.73	274	88	10
Endosulfan-alpha	17.36	195	160	10
Endosulfan-alpha	17.36	240.9	205.9	10
Endosulfan-alpha	17.36	242.9	207.9	10
Endosulfan-beta	19.19	195	160	10
Endosulfan-beta	19.19	240.9	205.9	10
Endosulfan-beta	19.19	242.9	207.9	10
Endosulfan-sulfate	20.37	269.9	234.9	15
Endosulfan-sulfate	20.37	271.9	234.9	10
Endosulfan-sulfate	20.37	273.9	238.9	10
Endrin	18.87	244.8	173	22
Endrin	18.87	262.8	192.9	30
Endrin	18.87	278.9	242.9	12
EPN	22.25	157	110	15
EPN	22.25	169	77	16
Epoxiconazole	21.53	165	138	8
Epoxiconazole	21.53	192	111	10
Epoxiconazole	21.53	192	138	10
Ethion	19.35	231	129	20
Ethion	19.35	384	231	10
Ethoprophos	10.78	158	97	10
Ethoprophos	10.78	200	158	8
Ethoxyquin	11.83	174.1	131.2	18
Ethoxyquin	11.83	174.1	146.1	12
Ethoxyquin	11.83	202.1	174.1	14
Etofenprox	27.89	163.1	107.1	16
Etofenprox	27.89	163.1	135.1	10
Etofenprox	27.89	376.2	163.1	20
Fenarimol	24.41	139	75	26

Name	RT	Parent Mass	Product Mass	Collision Energy
Fenarimol	24.41	219	107	15
Fenarimol	24.41	251	139	15
Fenazaquin	22.9	145.1	117.1	12
Fenazaquin	22.9	160	117.1	20
Fenazaquin	22.9	160	145.1	8
Fenbuconazole	26.53	129	77.8	18
Fenbuconazole	26.53	129	102	15
Fenbuconazole	26.53	198.1	129	15
Fenitrothion	14.47	277	109	20
Fenitrothion	14.47	277	260	10
Fenoxycarb	22.37	116	44.1	16
Fenoxycarb	22.37	255.1	186.1	10
Fenpropathrin	22.59	265.1	89	20
Fenpropathrin	22.59	265.1	210.1	15
Fenpropimorph	15.14	128.1	110.1	15
Fenpropimorph	15.14	303.3	128.1	15
Fenson	15.52	268	77	20
Fenson	15.52	268	141	10
Fenthion	15.03	278	109	18
Fenthion	15.03	278	169	14
Fenvalerate (I+II)	29.08	125	89	18
Fenvalerate (I+II)	29.08	167	89	32
Fenvalerate (I+II)	29.08	419.1	225.1	10
Fluazifop-P-butyl	18.79	383.1	254.1	20
Fluazifop-P-butyl	18.79	383.1	282.1	15
Fludioxonil	17.64	248	127	20
Fludioxonil	17.64	248	154	20
Fludioxonil	17.64	248	182	15
Flufenoxuron	12.64	267.9	170	24
Flufenoxuron	12.64	267.9	241	12
Flufenoxuron	12.64	331	276	15
Fluquinconazole	25.83	340	108.1	36
Fluquinconazole	25.83	340	298	22
Fluquinconazole	25.83	340	313	14
Flutriafol	17.41	123	75	15
Flutriafol	17.41	219.1	123	15
Formothion	11.76	125	79	5
Formothion	11.76	126	93	8
HCH-alpha	11.58	182.9	147	12
HCH-alpha	11.58	216.9	180.9	8
HCH-alpha	11.58	218.9	182.9	8
HCH-beta	12.06	182.9	147	12
HCH-beta	12.06	216.9	180.9	8
HCH-beta	12.06	218.7	183	8
Heptenophos	10.16	124	89	10
Heptenophos	10.16	250	89	25

Name	RT	Parent Mass	Product Mass	Collision Energy
Hexaconazole	17.68	213.9	159	18
Hexaconazole	17.68	231.1	175	10
Hexaconazole	17.68	256.1	159	10
Hexythiazox	16.87	184	59	20
Hexythiazox	16.87	184	149	6
Hexythiazox	16.87	227	149.1	8
Iprovalicarb (I+II)	18.06/18.037	118.9	117.1	8
Iprovalicarb (I+II)	18.06/18.037	134.1	42	20
Isofenphos-methyl	15.72	199	121	10
Isofenphos-methyl	15.72	241.1	199	8
Isoprothiolane	17.71	204	85	25
Isoprothiolane	17.71	204	118	7
Isoprothiolane	17.71	290.1	118	15
Jodofenfos	17.63	125	47	12
Jodofenfos	17.63	376.8	361.8	16
Jodofenfos	17.63	379	364	20
Kresoxim-methyl	18.24	116	63	24
Kresoxim-methyl	18.24	116	89	14
Kresoxim-methyl	18.24	206.1	116.1	15
Lindane	12.28	182.9	147	12
Lindane	12.28	216.9	180.9	8
Lindane	12.28	218.9	182.9	8
Linuron	14.65	248.1	61	15
Linuron	14.65	250.1	61	15
Metalaxyl	14.01	206.1	132.1	20
Metalaxyl	14.01	234.1	174.1	10
Metalaxyl	14.01	249.1	190.1	10
Methacrifos	9.49	240	180	5
Methacrifos	9.49	240	208	10
Methamidophos	7.59	141	64	18
Methamidophos	7.59	141	79	20
Methidathion	16.78	145	58	15
Methidathion	16.78	145	85	10
Metribuzin	13.61	198.1	82	17
Metribuzin	13.61	198.1	89	16
Metribuzin	13.61	198.1	110.1	10
Mevinphos	8.94	127	95	14
Mevinphos	8.94	127	109	10
Myclobutanil	18.08	179.1	125.1	15
Myclobutanil	18.08	179.1	152.1	8
Myclobutanil	18.08	288.1	179.1	10
Nuarimol	20.98	235.1	139	15
Nuarimol	20.98	314.1	139	15
Ofurace	19.9	131.9	117	16
Ofurace	19.9	232.1	158.1	18
Ofurace	19.9	232.1	186.1	8

Name	RT	Parent Mass	Product Mass	Collision Energy
Oxadixyl	19.25	163	117	30
Oxadixyl	19.25	163.1	132.1	8
Oxadixyl	19.25	233.1	146.1	10
Paclobutrazol	17.07	125	89	18
Paclobutrazol	17.07	236.1	125.1	15
Paclobutrazol	17.07	238.1	127.1	15
Parathion	15.13	235	139	8
Parathion	15.13	291	81	20
Parathion	15.13	291	109	8
Parathion-methyl	13.78	125	47	12
Parathion-methyl	13.78	263	79	22
Parathion-methyl	13.78	263	109	11
Penconazole	16.08	248	157	25
Penconazole	16.08	248	192	13
Pencycuron	12.1	125	89	15
Pencycuron	12.1	125	99	16
Pendimethalin	15.88	252.1	162.1	12
Pendimethalin	15.88	252.1	191.1	12
Pendimethalin	15.88	281.1	252.1	12
Permethrin (I+II)	25.72	183	153	15
Permethrin (I+II)	25.72	183.1	165.1	12
Permethrin (I+II)	25.72	183.1	168.1	12
Phenthoate	16.34	121	77	22
Phenthoate	16.34	246	121	8
Phenthoate	16.34	274	121	10
Phosalone	23.38	182	111	15
Phosalone	23.38	367	182	10
Pirimicarb	13.02	166.1	71	25
Pirimicarb	13.02	166.1	96.1	10
Pirimicarb	13.02	238.1	166.1	15
Pirimicarb-desmethyl	13.22	152.1	96.1	15
Pirimicarb-desmethyl	13.22	224.1	152.1	10
Pirimiphos-methyl	14.39	290.1	125	15
Pirimiphos-methyl	14.39	290.1	233.1	10
Pirimiphos-methyl	14.39	305.1	180	15
Prochloraz	25.97	180.1	138.1	12
Prochloraz	25.97	308	266	10
Prochloraz	25.97	310	268	10
Procymidone	16.5	283	67	15
Procymidone	16.5	283	96	10
Procymidone	16.5	283	96.1	8
Propiconazole (I+II)	20.47	172.9	74	38
Propiconazole (I+II)	20.47	172.9	109	26
Propiconazole (I+II)	20.47	259	173	15
Propoxur	8.11	110	62.9	24
Propoxur	8.11	110	64.1	16

Name	RT	Parent Mass	Product Mass	Collision Energy
Propoxur	8.11	152.1	110	8
Propyzamide	12.4	172.9	74	38
Propyzamide	12.4	172.9	109	26
Propyzamide	12.4	172.9	145	14
Prothiofos	17.73	267	239	10
Prothiofos	17.73	309	239	5
Pyrazophos	24.42	232	204	10
Pyrazophos	24.42	265.1	210.1	10
Pyrazophos	24.42	373	232	12
Pyridaben	25.88	147.1	117	10
Pyridaben	25.88	147.1	132.1	15
Pyridaben	25.88	309.1	147.1	15
Pyridaphenthion	21.86	340.1	199	10
Pyridaphenthion	21.86	340.1	203	25
Pyrimethanil	12.58	198.1	118.1	35
Pyrimethanil	12.58	199.1	198.1	10
Pyriproxyfen	23.75	136.1	78	20
Pyriproxyfen	23.75	136.1	96	10
Quinoxyfen	20.4	307	237.1	15
Quinoxyfen	20.4	307	272	10
Quinoxyfen	20.4	309	237.1	15
Simazine	11.83	172.7	138	6
Simazine	11.83	186	91	8
Tebuconazole	21.05	125	89	16
Tebuconazole	21.05	250	125	20
Tebuconazole	21.05	252.1	127.1	20
Tebufenpyrad	22.79	276.1	171.1	15
Tebufenpyrad	22.79	333.2	171	20
Tebufenpyrad	22.79	333.2	276	10
Tecnazene	10.47	214.8	143.6	20
Tecnazene	10.47	214.8	178.7	10
Tecnazene	10.47	214.8	179.9	15
Tefluthrin	12.72	177	127	15
Tefluthrin	12.72	177	137	15
Tetraconazole	15.18	336	204	20
Tetraconazole	15.18	336	218	20
Tetradifon	23.18	355.9	159	15
Tetradifon	23.18	355.9	228.9	10
Thiometon	11.65	88	45	20
Thiometon	11.65	88	60	6
Thiometon	11.65	125	47	14
Tolclofos-methyl	13.85	265	220	20
Tolclofos-methyl	13.85	265	250	15
Tolclofos-methyl	13.85	267	252	15
Triadimefon	15.2	208.1	127	10
Triadimefon	15.2	208.1	181.1	10

Name	RT	Parent Mass	Product Mass	Collision Energy
Triadimenol	16.63	112	57.6	8
Triadimenol	16.63	118	65	18
Triadimenol	16.63	168.2	70	10
Triallate	12.93	268	14	22
Triallate	12.93	270	186	22
Triazophos	19.78	161	106	12
Triazophos	19.78	161	134	8
Triazophos	19.78	257.1	162	10
Tricyclazole	17.71	162	133.9	8
Tricyclazole	17.71	204.1	118	5
Tricyclazole	17.71	231	189	10
Trifloxystrobin	20.29	190.1	130	10
Trifloxystrobin	20.29	222.1	130	10
Trifloxystrobin	20.29	222.1	162.1	10
Trifluralin	10.99	264.1	160.1	15
Trifluralin	10.99	306.1	206	15
Trifluralin	10.99	306.1	264.1	15
Triticonazole	23.4	182	75.1	30
Triticonazole	23.4	182	111	15
Triticonazole	23.4	235.1	182.1	10
Vinclozolin	13.74	212	145	15
Vinclozolin	13.74	212	172	15
Vinclozolin	13.74	285	212	15

Appendix 1b.

MRM transitions for compounds validated by LC-MS/MS

Compound Name	Retention Time	ESI Mode	Parent mass	Product mass	Collision Energy
3-hydroxycarbofuran	2.64	Positive	238	163	13
3-hydroxycarbofuran	2.64	Positive	238	181	9.5
Acephate	1.78	Positive	183.78	143.01	12
Acetamiprid	2.67	Positive	223	56	9.5
Acetamiprid	2.67	Positive	223	90	29
Acetamiprid	2.67	Positive	223	126	17
Aldicarb	3.25	Positive	208.2	116.09	10
Aldicarb	3.25	Positive	208.2	89.09	15
Aldicarb	3.25	Positive	191	89.2	15
Aldicarb-sulfone	1.97	Positive	240.4	148.18	13
Aldicarb-sulfone	1.97	Positive	240.4	86.3	21
Aldicarb-sulfone	1.97	Positive	240.09	223.3	20
Aldicarb-sulfoxide	1.90	Positive	223.95	131.98	10
Aldicarb-sulfoxide	1.90	Positive	223.95	89.2	21
Amitraz	2.03	Positive	163	107	26
Amitraz	2.03	Positive	163	122	17
Amitraz	2.03	Positive	163	132	17
Atrazine	4.55	Positive	216	96	20
Atrazine	4.55	Positive	216	104	24.5
Atrazine	4.55	Positive	216	174	15
Azinphos-ethyl	5.77	Positive	346	137	22
Azinphos-ethyl	5.77	Positive	346	233	12
Azinphos-methyl	4.92	Positive	318	132	11
Azinphos-methyl	4.92	Positive	318	261	5.5
Azoxystrobin	5.15	Positive	404	344	21
Azoxystrobin	5.15	Positive	404	372	15
Azoxystrobin	5.15	Positive	404	328	39
Bifenthrin	8.30	Positive	440	166	35
Bifenthrin	8.30	Positive	440	181	10
Bitertanol	6.54	Positive	338	70	5
Bitertanol	6.54	Positive	338	99	12
Bitertanol	6.54	Positive	338	268	8.5
Boscalid	5.41	Positive	343	271	24
Boscalid	5.41	Positive	343	307	12.5
Bromoxynil	4.41	Negative	276	79	20.5
Bromoxynil	4.41	Negative	276	80.59	25
Bromoxynil	4.41	Negative	276	274.6	5.5
Bromuconazole	5.65	Positive	377.9	70	9
Bromuconazole	5.65	Positive	377.9	159	17.5
Bupirimate	5.62	Positive	317	166	23
Bupirimate	5.62	Positive	317	108	25

Compound Name	Retention Time	ESI Mode	Parent mass	Product mass	Collision Energy
Buprofezin	6.97	Positive	306	116	14
Buprofezin	6.97	Positive	306	201	8
Cadusafos	6.66	Positive	271	131	20.5
Cadusafos	6.66	Positive	271	159	11.5
Carbaryl	4.11	Positive	202	127	26.5
Carbaryl	4.11	Positive	202	145	7
Carbendazim	2.01	Positive	192	105	31.5
Carbendazim	2.01	Positive	192	132	24
Carbendazim	2.01	Positive	192	160	13
Carbofuran	3.86	Positive	222	123	17.5
Carbofuran	3.86	Positive	222	165	9.5
Carboxin	4.06	Positive	236	87	23.5
Carboxin	4.06	Positive	236	93	27.5
Carboxin	4.06	Positive	236	143	11
Chlorpyrifos	7.31	Positive	349.7	198	16
Chlorpyrifos	7.31	Positive	351.7	200	18
Clethodim	6.86	Positive	360	164	17.5
Clethodim	6.86	Positive	360	166	24.5
Clofentezine	6.54	Positive	303	102	30
Clofentezine	6.54	Positive	303	138	11.5
Clothianidin	2.50	Positive	250	169	13
Clothianidin	2.50	Positive	250	132	50
Cyazofamid	5.95	Positive	325	108	9.5
Cyazofamid	5.95	Positive	325	217	12.5
Cyazofamid	5.95	Positive	325	261	6.5
Cypermethrin	7.74	Positive	433	191	14
Cypermethrin	7.74	Positive	435	193	14
Demeton-S-methyl	3.88	Positive	231	61	25
Demeton-S-methyl	3.88	Positive	231	89	10
Demeton-S-methylsulfone	2.11	Positive	263	109	24
Demeton-S-methylsulfone	2.11	Positive	263	121	12
Demeton-S-methylsulfone	2.11	Positive	263	169	13.5
Diazinon	6.34	Positive	305	97	30
Diazinon	6.34	Positive	305	153	20
Diazinon	6.34	Positive	305	169	20
Dichlorprop	5.46	Negative	233	125	26
Dichlorprop	5.46	Negative	233	161	10
Dichlorvos	3.78	Positive	221	109	16
Dichlorvos	3.78	Positive	238	221	4
Difenoconazole	6.69	Positive	406	188	42
Difenoconazole	6.69	Positive	406	251	23.5
Difenoconazole	6.69	Positive	406	337	14
Diflubenzuron	6.06	Positive	311	141	25
Diflubenzuron	6.06	Positive	311	158	8
Dimethoate	2.67	Positive	230	125	19
Dimethoate	2.67	Positive	230	171	14

Compound Name	Retention Time	ESI Mode	Parent mass	Product mass	Collision Energy
Dimethoate	2.67	Positive	230	199	8
Dinoterb	6.43	Negative	239	136	34
Dinoterb	6.43	Negative	239	207	23
Ditalimphos	5.70	Positive	300	130	30
Ditalimphos	5.70	Positive	300	148	16
DMF	3.53	Positive	150	132.2	35
DMF	3.53	Positive	150	106.8	20
DMPF	2.04	Positive	163	107	25
DMPF	2.04	Positive	163	117	20.5
DMPF	2.04	Positive	163	122	15
DMPF	2.04	Positive	163	132	15
DMST	3.99	Positive	215	77	43
DMST	3.99	Positive	215	106.09	13
DMST	3.99	Positive	215	151	5
DMST	3.99	Positive	215	77	43
DMST	3.99	Positive	215	106.09	13
DMST	3.99	Positive	215	151	5
DNOC	4.33	Negative	196.95	137	17
DNOC	4.33	Negative	196.95	109.09	10
Epoxiconazole	5.88	Positive	330	101	30
Epoxiconazole	5.88	Positive	330	121	17.5
Ethiofencarb	4.26	Positive	226	107	11
Ethiofencarb	4.26	Positive	226	165	5.5
Ethion	7.20	Positive	385	199	10
Ethion	7.20	Positive	402	199	15
Ethion	7.20	Positive	402	385	5
Ethoprophos	5.85	Positive	243.24	97	23
Ethoprophos	5.85	Positive	243.24	131	31
Etofenprox	8.21	Positive	394	135	22.5
Etofenprox	8.21	Positive	394	177	13.5
Etofenprox	8.21	Positive	394	359	10.5
Fenamiphos	6.03	Positive	304	201.7	35
Fenamiphos	6.03	Positive	304	216.9	21
Fenamiphos-sulfone	4.03	Positive	336	188	31
Fenamiphos-sulfone	4.03	Positive	336	266	50
Fenamiphos-sulfoxide	3.89	Positive	337.2	320.1	5
Fenamiphos-sulfoxide	3.89	Positive	337.2	171.09	20
Fenazaquin	7.79	Positive	307	57.4	20
Fenazaquin	7.79	Positive	307	147.09	17
Fenazaquin	7.79	Positive	307	161.09	14
Fenbuconazole	6.02	Positive	337	70.2	16
Fenbuconazole	6.02	Positive	337	125	25
Fenhexamid	5.83	Positive	302	97	18.5
Fenhexamid	5.83	Positive	302	302	8.5
Fenoxycarb	6.12	Positive	302	88	13.5
Fenoxycarb	6.12	Positive	302	116	8

Compound Name	Retention Time	ESI Mode	Parent mass	Product mass	Collision Energy
Fenoxycarb	6.12	Positive	302	256	12
Fenpropidin	4.28	Positive	274	117	30.5
Fenpropidin	4.28	Positive	274	147	23.5
Fenthion	6.27	Positive	279	105	20.5
Fenthion	6.27	Positive	279	169	15.5
Fenthion	6.27	Positive	279	247	10.5
Fenthion-oxon	4.96	Positive	263	231	30
Fenthion-oxon	4.96	Positive	263	216	20
Fenthion-oxon-sulfone	2.74	Positive	295	217	20
Fenthion-oxon-sulfone	2.74	Positive	295	104.09	33
Fenthion-oxon-sulfoxide	2.62	Positive	279.08	264	15
Fenthion-oxon-sulfoxide	2.62	Positive	279.08	104	20
Fenthion-sulfone	4.20	Positive	328	125.09	22
Fenthion-sulfone	4.20	Positive	328	279	22
Fenthion-sulfone	4.20	Positive	328	311	7
Fenthion-sulfoxide	4.02	Positive	295	109.2	26
Fenthion-sulfoxide	4.02	Positive	295	125	30
Fenthion-sulfoxide	4.02	Positive	295	280	17
Fipronil	6.12	Negative	435.22	330.2	13
Fipronil	6.12	Negative	435.22	250.09	42
Fipronil-sulfide	6.22	Negative	419	383	10
Fipronil-sulfide	6.22	Negative	419	262	30
Fipronil-sulfide	6.22	Negative	421	385	10
Fluazifop-p-butyl	7.00	Positive	384	254	17.5
Fluazifop-p-butyl	7.00	Positive	384	282	18
Fluazifop-p-butyl	7.00	Positive	384	328	14
Fluoxastrobin	5.78	Positive	459.19	427.1	17
Fluoxastrobin	5.78	Positive	459.19	188	45
Fluquinconazole	5.75	Positive	376	307	21.5
Fluquinconazole	5.75	Positive	376	349	18
Flusilazole	6.08	Positive	316	165	23.5
Flusilazole	6.08	Positive	316	247	16.5
Fosthiazate	4.31	Positive	284.4	104.09	25
Fosthiazate	4.31	Positive	284.4	228.2	30
Heptenophos	4.78	Positive	251	125	12
Heptenophos	4.78	Positive	251	127.09	14
Hexaconazole	6.49	Positive	314	70	12.5
Hexaconazole	6.49	Positive	314	159.7	24.5
Hexythiazox	7.35	Positive	353	168	23.5
Hexythiazox	7.35	Positive	353	228	14.5
Imazalil	3.82	Positive	297	159	16.5
Imazalil	3.82	Positive	297	201	13
Imidacloprid	2.44	Positive	256	175	16.5
Imidacloprid	2.44	Positive	256	209	13.5
Indoxacarb	6.75	Positive	528	150	23.5
Indoxacarb	6.75	Positive	528	203	32.5

Compound Name	Retention Time	ESI Mode	Parent mass	Product mass	Collision Energy
Indoxacarb	6.75	Positive	528	293	12
Iodosulfuron-methyl-sodium	4.94	Positive	530.07	163.09	13
Iodosulfuron-methyl-sodium	4.94	Positive	530.07	390	21
Iprodione	6.06	Positive	330	101	25
Iprodione	6.06	Positive	330	245	12
Iprodione	6.06	Positive	332	247	16
Iprovalicarb	5.70	Positive	321	119	14
Iprovalicarb	5.70	Positive	321	203	7
Isoprothiolane	5.48	Positive	291	145	35
Isoprothiolane	5.48	Positive	291	189	20
Isoprothiolane	5.48	Positive	291	231	10
Isoproturon	4.64	Positive	207	72	11.5
Isoproturon	4.64	Positive	207	165	12
Linuron	5.22	Positive	249	160	16
Linuron	5.22	Positive	249	182	13.5
Lufenuron	7.23	Negative	511	158.09	10
Lufenuron	7.23	Negative	511	141	30
Lufenuron	7.23	Negative	511	176.7	30
Lufenuron	7.23	Negative	511	328.4	20
Malaoxon	3.88	Positive	315	99	20
Malaoxon	3.88	Positive	315	127	10
Malathion	5.44	Positive	331	99	18
Malathion	5.44	Positive	331	127	10
Mecarbam	5.80	Positive	330	97	45
Mecarbam	5.80	Positive	330	199	14
Mecarbam	5.80	Positive	330	227	8
Mepanipyrim	5.70	Positive	224	77	49
Mepanipyrim	5.70	Positive	224	106	20
Metaflumizone	7.17	Negative	505.1	302.1	25
Metaflumizone	7.17	Negative	505.1	328	15
Metaflumizone	7.17	Negative	505	116.5	16.5
Metalaxyl	4.65	Positive	280	192	16.5
Metalaxyl	4.65	Positive	280	220	12.5
Metconazole	6.50	Positive	320	70	14.5
Metconazole	6.50	Positive	320	125	32.5
Methamidophos	1.64	Positive	142	94	11.5
Methamidophos	1.64	Positive	142	125	12
Methiocarb	5.29	Positive	243.4	169.3	13
Methiocarb	5.29	Positive	243.4	121.2	30
Methiocarb-sulfone	2.75	Positive	275	107	33.5
Methiocarb-sulfone	2.75	Positive	275	122	14.5
Methiocarb-sulfone	2.75	Positive	275	201	7
Methiocarb-sulfoxide	2.51	Positive	242	122	23
Methiocarb-sulfoxide	2.51	Positive	242	185	20
Methoxyfenozide	5.53	Positive	369	149	11.5
Methoxyfenozide	5.53	Positive	369	313	5

Compound Name	Retention Time	ESI Mode	Parent mass	Product mass	Collision Energy
Metsulfuron-methyl	3.82	Positive	382	167	14
Metsulfuron-methyl	3.82	Positive	382	199	27
Mevinphos	2.61	Positive	225	127	13
Mevinphos	2.61	Positive	225	193	6
Monocrotophos	2.19	Positive	224	127	12.5
Monocrotophos	2.19	Positive	224	193	7.5
Monocrotophos	2.19	Positive	224	98	10
Monolinuron	4.23	Positive	215	126	17
Monolinuron	4.23	Positive	215	148	13
Ofurace	3.88	Positive	282	160	22
Ofurace	3.88	Positive	282	236	14
Omethoate	1.84	Positive	214	125	20
Omethoate	1.84	Positive	214	155	14.5
Omethoate	1.84	Positive	214	183	10
Oxamyl	2.00	Positive	237	72	9.5
Oxamyl	2.00	Positive	237	90	6.5
Oxamyl	2.00	Positive	237	220	5.5
Oxycarboxin	2.92	Positive	268	147	24
Oxycarboxin	2.92	Positive	268	175	13
Paraoxon-methyl	3.34	Positive	265	202	35
Paraoxon-methyl	3.34	Positive	265	127	40
Oxydemeton-methyl	2.06	Positive	247	109	26
Oxydemeton-methyl	2.06	Positive	247	169	12
Parathion	6.12	Positive	292	236	20
Parathion	6.12	Positive	292	94	20
Parathion	6.12	Positive	291.1	236.2	20
Parathion	6.12	Positive	291.1	94.09	20
Penconazole	6.28	Positive	284	159	27.5
Penconazole	6.28	Positive	284	173	16.5
Pencycuron	6.63	Positive	329	125	20
Pencycuron	6.63	Positive	329	218	13.5
Pendimethalin	7.37	Positive	282.12	212	10
Pendimethalin	7.37	Positive	282.12	194	10
Phosmet	4.97	Positive	335	133	36
Phosmet	4.97	Positive	335	160	17
Phosmet-oxon	3.31	Positive	302	160	21
Phosmet-oxon	3.31	Positive	302	133	31
Phosphamidon	3.50	Positive	300	174.09	13
Phosphamidon	3.50	Positive	300	227	12
Phosphamidon	3.50	Positive	300	127	22
Phoxim	6.44	Positive	299	129	9
Phoxim	6.44	Positive	299	153	6
Pirimicarb	3.10	Positive	239	72.09	16
Pirimicarb	3.10	Positive	239	182.3	25
Pirimiphos-methyl	6.40	Positive	306	164	20
Pirimiphos-methyl	6.40	Positive	306	108	20

Compound Name	Retention Time	ESI Mode	Parent mass	Product mass	Collision Energy
Prochloraz	6.34	Positive	376	266	16.5
Prochloraz	6.34	Positive	376	308	10.5
Propamocarb	1.76	Positive	189	74	23
Propamocarb	1.76	Positive	189	102	13
Propamocarb	1.76	Positive	189	144	7.5
Propargite	7.48	Positive	368	175	15
Propargite	7.48	Positive	368	231	9.5
Propiconazole	6.38	Positive	342	159	20
Propiconazole	6.38	Positive	342	69	20
Propoxur	3.80	Positive	210.28	111.2	13
Propoxur	3.80	Positive	210.28	168.3	30
Propyzamide	5.50	Positive	256	145	35
Propyzamide	5.50	Positive	256	173	21
Propyzamide	5.50	Positive	256	190	13
Prosulfocarb	6.88	Positive	252	91	20
Prosulfocarb	6.88	Positive	252	128	10
Prosulfuron	5.27	Positive	420.27	141.09	15
Prosulfuron	5.27	Positive	420.27	167	15
Prosulfuron	5.27	Positive	420.27	109	15
Prothioconazole-desthio	5.94	Positive	312	70	18
Prothioconazole-desthio	5.94	Positive	312	125	25
Pyraclostrobin	6.44	Positive	388	163	18.5
Pyraclostrobin	6.44	Positive	388	194	7.5
Pyridate	8.07	Positive	379	207	17
Pyridate	8.07	Positive	379	351	8.5
Pyrimethanil	4.70	Positive	200	82	20.5
Pyrimethanil	4.70	Positive	200	107	19.5
Pyriproxyfen	7.21	Positive	322	96.2	14
Pyriproxyfen	7.21	Positive	322	184.9	22
Pyriproxyfen	7.21	Positive	322	227	13
Quinoxyfen	7.31	Positive	308	161.9	47
Quinoxyfen	7.31	Positive	308	197	31
Simazine	3.82	Positive	202	124	17
Simazine	3.82	Positive	202	132	32
Spinosad_A	5.75	Positive	733	142	21.5
Spinosad_A	5.75	Positive	733	189	30
Spinosad_A	5.75	Positive	733	98	20
Spinosad_A	5.75	Positive	732.6	142.09	10
Spinosad_D	5.95	Positive	747	142	22
Spinosad_D	5.95	Positive	747	189	27.5
Spinosad_D	5.95	Positive	747	89.2	40
Spinosad_D	5.95	Positive	746.6	142.1	10
Spirodiclofen	7.61	Positive	411	313	20
Spirodiclofen	7.61	Positive	411	71	20
Spiroxamine	4.61	Positive	298	100	23
Spiroxamine	4.61	Positive	298	144	15

Compound Name	Retention Time	ESI Mode	Parent mass	Product mass	Collision Energy
Tebufenozide	6.09	Positive	353	133	17
Tebufenozide	6.09	Positive	353	297	7.5
Tebufenpyrad	7.09	Positive	334	117	31
Tebufenpyrad	7.09	Positive	334	145	24
Teflubenzuron	7.23	Negative	379	195	20.5
Teflubenzuron	7.23	Negative	379	339	9
Teflubenzuron	7.23	Negative	379	359	5.5
Thiabendazole	2.15	Positive	202	131	27
Thiabendazole	2.15	Positive	202	175	19.5
Thiacloprid	2.94	Positive	253	90	30
Thiacloprid	2.94	Positive	253	99	36.5
Thiacloprid	2.94	Positive	253	126	17
Thiamethoxam	2.15	Positive	292	132	18.5
Thiamethoxam	2.15	Positive	292	181	18
Thiamethoxam	2.15	Positive	292	211	11.5
Thiometon	4.44	Positive	247	61	25
Thiometon	4.44	Positive	247	89	10
Thiophanate-methyl	3.76	Positive	342.78	151.12	20
Thiophanate-methyl	3.76	Positive	342.78	93.15	50
Thiophanate-methyl	3.76	Positive	343	311	8
Triadimenol	5.74	Positive	296	70	7
Triadimenol	5.74	Positive	296	99	11.5
Triallate	7.41	Positive	306	144.92	23
Triallate	7.41	Positive	306	86	24
Triallate	7.41	Positive	304	143	20
Triallate	7.41	Positive	304	86	20
Triazophos	5.66	Positive	314	119	30
Triazophos	5.66	Positive	314	162	17
Trichlorfon	2.71	Positive	274	109	19.5
Trichlorfon	2.71	Positive	274	127	18
Trichlorfon	2.71	Positive	274	257	8
Tricyclazole	3.09	Positive	190	109	31.5
Tricyclazole	3.09	Positive	190	136	25.5
Trifloxystrobin	6.77	Positive	409	145	36
Trifloxystrobin	6.77	Positive	409	186	11
Triflumuron	6.50	Positive	359.06	156.09	25
Triflumuron	6.50	Positive	359.06	138.8	20
Triticonazole	5.85	Positive	318	70	12
Triticonazole	5.85	Positive	318	125	30.5
Vamidothion	2.59	Positive	288	146	20
Vamidothion	2.59	Positive	288	118	30
Zoxamide	6.39	Positive	336	132	11
Zoxamide	6.39	Positive	336	159	36.5
Zoxamide	6.39	Positive	336	187	17

Appendix 2.

Recoveries, repeatability (RSDr), number of replicates and Limit of Quantification (LOQ) for pesticides validated on soya cake using QuEChERS-EMR method.

Compound		0.005 mg/kg		0.01 mg/kg		0.05 mg/kg		
		Recovery%	RSDr %	Recovery%	RSDr %	Recovery %	RSDr %	LOQ
GC	2-phenylphenol	86	12	89	4	101	3	0.005
LC	3-hydroxycarbofuran	40	94	61	25	84	20	0.05
LC	Acephate	83	10	62	9	75	11	0.05
LC	Acetamiprid	84	8	88	15	89	20	0.005
GC	Acrinathrin(I)					74	16	0.05
LC	Aldicarb					95	6	0.05
LC	Aldicarb-sulfone	87	17	96	13	89	17	0.005
LC	Aldicarb-sulfoxide	98	15	85	16	89	17	0.005
GC	Aldrin	48	18	48	6	59	8	0.005
GC	Atrazine	93	10	94	8	113	4	0.005
LC	Atrazine	112	8	94	20	95	15	0.005
LC	Azinphos-ethyl	73	8	74	20	91	18	0.005
LC	Azinphos-methyl	94	11	87	14	100	20	0.005
GC	Azoxystrobin	107	4	73	7	80	6	0.005
LC	Azoxystrobin	104	12	90	20	95	17	0.005
GC	Bifenthrin	70	7	64	5	69	5	0.005
LC	Bifenthrin	84	9	70	18	72	17	0.005
GC	Bitertanol	91	16	73	28	87	15	0.005
LC	Bitertanol	87	20	94	16	85	7	0.005
GC	Boscalid	79	6	87	4	99	3	0.005
LC	Boscalid	99	8	94	17	95	20	0.005
GC	Bromophos-ethyl	73	2	75	6	89	4	0.005
GC	Bromopropylate	68	7	93	16	98	10	0.005
LC	Bromoxynil	101	11	98	13	99	15	0.005
LC	Bromuconazole	96	19	94	20	101	18	0.005
GC	Bromuconazole(I)	72	16	79	12	83	5	0.005

GC	Bromuconazole(II)	55	17	63	16	69	7	0.005
GC	Bupirimate	92	6	91	6	111	3	0.005
LC	Bupirimate	105	9	87	18	99	18	0.005
LC	Buprofezin	92	7	81	15	82	13	0.005
GC	Cadusafos	82	6	107	9	108	6	0.005
LC	Cadusafos	105	7	88	20	92	15	0.005
LC	Carbaryl	111	6	85	18	95	19	0.005
LC	Carbendazim	96	6	82	16	90	16	0.005
LC	Carbofuran	109	6	112	18	107	19	0.005
GC	Carboxin	100	6	84	6	101	3	0.005
LC	Carboxin	104	5	95	20	94	18	0.005
GC	Chlorfenapyr	89	13	88	16	108	8	0.005
GC	Chlorfenson	86	4	86	3	104	2	0.005
GC	Chlorfenvinphos					83	12	0.05
GC	Chlormephos					103	5	0.05
GC	Chlorobenzilate	89	5	96	8	108	4	0.005
GC	Chlorpropham	95	7	96	5	113	3	0.005
GC	Chlorpyrifos	80	12	81	8	100	3	0.005
LC	Chlorpyrifos	90	17	72	15	76	16	0.005
GC	Chlorpyrifos-methyl	76	10	78	6	93	6	0.005
LC	Clethodim	109	10	98	20	82	15	0.005
LC	Clofentezine	112	6	76	19	78	15	0.005
GC	Clomazone	98	5	101	4	118	3	0.005
LC	Clothianidin	83	11	88	19	98	18	0.005
LC	Cyazofamid	100	11	81	18	93	18	0.005
GC	Cyflutrin	89	11	86	20	81	16	0.005
GC	Cyhalothrin-lambda(II)			76	20	74	16	0.01
GC	Cypermethrin					77	13	0.05
GC	Cyproconazole	81	13	88	4	99	2	0.005
GC	Cyprodinil	98	9	82	5	105	2	0.005
GC	Demeton-S-methyl					71	19	0.05
LC	Demeton-S-methyl	110	10	96	16	103	19	0.005
LC	Demeton-S-methylsulfone	83	11	98	12	94	16	0.005
GC	Diazinon	94	6	102	6	117	4	0.005
LC	Diazinon	101	15	82	20	79	20	0.005
LC	Dichlorprop	102	17	76	10	104	18	0.005
GC	Dichlorvos	68	9	125	12	122	11	0.005
LC	Dichlorvos	98	12	94	17	99	18	0.005
GC	Dicloran	79	9	73	10	97	2	0.005
GC	Dieldrin	87	18	72	7	87	7	0.005
LC	Difenoconazole	101	12	97	19	83	18	0.005
GC	Difenoconazole(I+II)	71	10	85	6	88	3	0.005
LC	Diflubenzuron	78	16	93	17	92	15	0.005
LC	Dimethoate	90	5	82	20	93	20	0.005

GC	Dimethomorph(I)	73	11	87	7	85	5	0.005
GC	Dimethomorph(II)	64	13	88	7	87	5	0.005
LC	Dinoterb	104	17	84	15	74	16	0.005
GC	Diphenylamine	85	11	89	3	107	3	0.005
GC	Disulfoton	89	4	89	6	100	2	0.005
LC	Ditalimphos	97	13	92	19	92	18	0.005
LC	DMF	105	4	90	19	83	17	0.005
LC	DMPF					80	18	0.05
LC	DNOC					92	7	0.05
GC	Endosulfan-alpha	73	9	68	16	79	3	0.005
GC	Endosulfan-beta	75	13	74	8	99	6	0.005
GC	Endosulfan-sulfate	99	5	72	14	85	6	0.005
GC	Endrin	75	6	67	10	76	4	0.005
GC	EPN	81	5	73	9	94	7	0.005
GC	Epoxiconazole	82	10	104	8	105	3	0.005
LC	Epoxiconazole	85	8	78	20	90	17	0.005
LC	Ethiofencarb	105	10	85	16	98	17	0.005
GC	Ethion	81	4	83	6	96	3	0.005
LC	Ethion	97	8	84	16	80	18	0.005
GC	Ethoprophos	74	8	107	7	105	8	0.005
LC	Ethoprophos	93	12	84	20	85	17	0.005
GC	Ethoxyquin			88	11	101	4	0.01
GC	Etofenprox	66	7	66	3	73	4	0.005
LC	Fenamiphos	103	15	100	15	99	8	0.005
LC	Fenamiphos-sulfone	83	19	94	15	96	19	0.005
GC	Fenarimol	81	5	85	7	97	3	0.005
GC	Fenazaquin	84	2	75	5	85	3	0.005
LC	Fenazaquin	94	10	82	18	79	18	0.005
GC	Fenbuconazole	86	8	94	3	104	3	0.005
LC	Fenbuconazole	108	17	90	20	94	20	0.005
LC	Fenhexamid	102	15	96	12	84	17	0.005
GC	Fenitrothion	84	6	87	4	102	6	0.005
GC	Fenoxycarb	101	4	112	14	87	10	0.005
LC	Fenoxycarb	98	14	95	18	88	18	0.005
GC	Fenpropathrin	97	15	82	17	99	5	0.005
LC	Fenpropidin	101	10	105	19	100	18	0.005
GC	Fenpropimorph	93	6	94	5	109	1	0.005
GC	Fenson	94	3	95	3	114	3	0.005
GC	Fenthion	94	8	94	4	107	4	0.005
LC	Fenthion	100	15	93	14	86	15	0.005
LC	Fenthion-oxon	99	7	91	19	96	15	0.005
LC	Fenthion-oxon-sulfone	88	13	85	17	80	18	0.005
LC	Fenthion-oxon-sulfoxide	93	7	87	19	96	17	0.005
LC	Fenthion-sulfone	107	9	87	14	103	18	0.005

LC	Fenthion-sulfoxide	105	13	90	20	104	19	0.005
GC	Fenvalerate(I+II)	73	12	75	19	65	20	0.005
LC	Fipronil	119	18	95	19	109	15	0.005
LC	Fipronil-sulfide					93	14	0.05
GC	Fluazifop-p-butyl	100	7	95	5	112	5	0.005
LC	Fluazifop-p-butyl	100	12	82	18	82	17	0.005
GC	Fludioxonil	92	7	96	5	110	3	0.005
GC	Flufenoxuron	83	9	82	11	99	3	0.005
LC	Fluoxastrobin	89	17	100	13	83	19	0.005
GC	Fluquinconazole	83	5	89	5	105	3	0.005
LC	Fluquinconazole	88	9	103	7	102	19	0.005
LC	Flusilazole	96	10	92	16	88	20	0.005
GC	Flutriafol	89	5	94	6	114	4	0.005
GC	Formothion					71	17	0.05
LC	Fosthiazate	108	8	93	20	95	16	0.005
GC	HCH-alpha	85	3	84	6	102	4	0.005
GC	HCH-beta	90	5	91	4	104	2	0.005
GC	Heptenophos	53	7	103	16	88	15	0.005
LC	Heptenophos	105	3	91	20	99	17	0.005
GC	Hexaconazole					91	6	0.05
LC	Hexaconazole					85	18	0.05
GC	Hexythiazox	70	5	86	7	96	4	0.005
LC	Hexythiazox	87	10	79	20	79	19	0.005
LC	Imazalil	105	18	96	19	107	16	0.005
LC	Imidacloprid	94	6	85	12	95	16	0.005
LC	Indoxacarb	87	20	93	15	79	17	0.005
LC	Iodosulfuron-methyl-sodium	101	9	68	13	98	20	0.005
LC	Iprodione	102	10	94	18	86	16	0.005
LC	Iprovalicarb	102	17	97	18	96	19	0.005
GC	Iprovalicarb Sum	78	12	110	20	94	19	0.005
GC	Isofenphos-methyl	95	2	100	4	118	3	0.005
GC	Isoprothiolane	91	8	104	4	117	4	0.005
LC	Isoprothiolane	109	7	94	16	99	19	0.005
LC	Isoproturon	110	8	90	19	96	16	0.005
GC	Jodofenfos	69	8	67	7	77	6	0.005
GC	Kresoxim-methyl	139	10	108	10	119	2	0.005
GC	Lindane	88	10	89	4	107	4	0.005
GC	Linuron	103	15	91	17	83	6	0.005
LC	Linuron	84	7	111	16	95	17	0.005
LC	Lufenuron					101	8	0.05
LC	Malaoxon	103	8	107	16	102	20	0.005
LC	Mecarbam	96	15	93	17	99	17	0.005
LC	Mepanipyrim	108	20	105	17	92	17	0.005
LC	Metaflumizone	88	18	94	8	89	19	0.005

GC	Metalaxyl	105	13	108	5	118	5	0.005
LC	Metalaxyl	108	8	95	16	102	18	0.005
LC	Metconazole	100	10	81	18	79	16	0.005
GC	Methacrifos	48	9	90	4	114	5	0.005
GC	Methamidophos	100	19	83	20	53	9	0.005
LC	Methamidophos	84	8	72	13	70	18	0.005
GC	Methidathion	85	6	65	6	71	11	0.005
LC	Methiocarb					85	17	0.05
LC	Methiocarb-sulfone	84	7	86	17	77	19	0.005
LC	Methiocarb-sulfoxide	84	7	80	18	86	20	0.005
LC	Methoxyfenozide	102	8	84	12	117	14	0.005
GC	Metribuzin	93	9	94	5	115	3	0.005
LC	Metsulfuron-methyl	102	10	104	5	95	17	0.005
GC	Mevinphos					83	18	0.05
LC	Mevinphos	98	8	87	18	92	20	0.005
LC	Monocrotophos	87	6	86	15	87	16	0.005
LC	Monolinuron	103	18	77	9	100	17	0.005
GC	Myclobutanil	86	3	96	7	114	3	0.005
GC	Nuarimol	81	4	89	8	101	3	0.005
GC	Ofurace	65	16	90	19	110	17	0.005
LC	Ofurace	102	18	82	1	109	17	0.005
LC	Omethoate	87	9	73	19	85	17	0.005
GC	Oxadixyl	87	9	95	9	112	3	0.005
LC	Oxamyl	109	8	110	19	100	16	0.005
LC	Oxycarboxin	95	9	89	18	63	11	0.005
LC	Oxydemeton-methyl	98	5	86	19	94	16	0.005
GC	Paclobutrazol	76	7	90	9	108	3	0.005
LC	Paraoxon-methyl	60	140	21	149	84	32	0.005
GC	Parathion	96	20	83	17	105	3	0.005
LC	Parathion					98	20	0.05
GC	Parathion-methyl	80	15	82	8	98	8	0.005
GC	Penconazole	86	8	88	4	104	1	0.005
LC	Penconazole	99	12	92	19	86	18	0.005
GC	Pencycuron	98	5	101	4	118	3	0.005
LC	Pencycuron	102	11	84	20	81	13	0.005
GC	Pendimethalin	79	8	86	7	98	3	0.005
LC	Pendimethalin	96	5	78	20	78	18	0.005
GC	Permethrin(I+II)	69	13	66	23	70	4	0.005
GC	Phenthoate	77	10	77	8	95	4	0.005
GC	Phosalone			89	2	53	7	0.01
LC	Phosmet	105	11	99	18	96	15	0.005
LC	Phosmet-oxon	102	7	91	19	74	19	0.005
LC	Phosphamidon	102	8	88	18	76	18	0.005
LC	Phoxim	104	8	85	19	85	18	0.005

GC	Pirimicarb	97	5	100	4	117	4	0.005
LC	Pirimicarb	101	9	86	17	74	19	0.005
GC	Pirimicarb-desmethyl	71	9	106	7	103	5	0.005
GC	Pirimiphos-methyl	92	6	97	6	113	5	0.005
LC	Pirimiphos-methyl	96	13	91	11	80	19	0.005
GC	Prochloraz					92	11	0.05
LC	Prochloraz	105	13	79	19	83	15	0.005
GC	Procymidone	97	8	105	2	123	3	0.005
LC	Propamocarb	93	11	84	18	89	16	0.005
LC	Propargite	101	12	87	19	86	19	0.005
LC	Propiconazole	102	14	84	18	87	18	0.005
GC	Propiconazole(I+II)	83	9	88	4	104	3	0.005
GC	Propoxur					115	6	0.05
LC	Propoxur	110	10	93	30	96	17	0.05
GC	Propyzamide	102	5	95	5	113	4	0.005
LC	Propyzamide	109	12	94	19	97	16	0.005
LC	Prosulfocarb	109	13	79	18	83	19	0.005
LC	Prosulfuron	89	18	101	11	85	20	0.005
LC	Prothioconazole-desthio	96	11	81	20	91	15	0.005
GC	Prothiofos	82	3	68	6	80	5	0.005
LC	Pyraclostrobin	104	12	88	20	83	20	0.005
GC	Pyrazophos					69	9	0.05
GC	Pyridaben	72	4	71	4	79	3	0.005
GC	Pyridaphenthion	88	13	110	9	75	10	0.005
GC	Pyrimethanil	91	6	96	6	111	3	0.005
LC	Pyrimethanil	96	4	90	20	95	17	0.005
GC	Pyriproxyfen	80	7	81	6	89	4	0.005
LC	Pyriproxyfen	95	8	80	20	76	19	0.005
GC	Quinoxyfen	67	2	68	3	77	4	0.005
LC	Quinoxyfen	92	10	77	16	76	18	0.005
GC	Simazine	90	11	90	11	110	4	0.005
LC	Simazine	96	9	64	5	93	20	0.05
LC	Spinosad_A	88	18	102	19	85	16	0.005
LC	Spinosad_D	85	58	96	10	86	6	0.01
LC	Spirodiclofen	67	14	74	18	65	16	0.01
LC	Spiroxamine	114	9	91	19	108	15	0.005
GC	Tebuconazole	79	5	88	7	95	6	0.005
LC	Tebufenozide	115	15	87	18	86	16	0.005
GC	Tebufenpyrad	90	4	90	5	107	3	0.005
LC	Tebufenpyrad	105	17	90	20	82	17	0.005
GC	Tecnazene	76	13	77	9	88	7	0.005
LC	Teflubenzuron	100	19	84	20	107	10	0.005
GC	Tefluthrin	85	5	84	3	101	4	0.005
GC	Tetraconazole	94	7	98	6	115	3	0.005

GC	Tetradifon	72	8	68	7	83	2	0.005
LC	Thiabendazole	85	8	85	19	86	18	0.005
GC	Thiometon	60	12	66	10	73	8	0.005
LC	Thiometon			74	30	74	13	0.05
LC	Thiophanate-methyl	117	7	118	16	111	19	0.005
GC	Tolclofos-methyl	86	2	92	4	110	3	0.005
GC	Triadimefon	98	8	99	7	113	2	0.005
GC	Triadimenol	82	16	76	9	100	4	0.005
GC	Triallate	84	19	68	19	96	5	0.005
LC	Triallate	85	7	88	19	74	20	0.005
GC	Triazophos	60	12	73	17	62	13	0.005
LC	Triazophos	107	10	115	12	102	16	0.005
LC	Trichlorfon			78		88	20	0.05
GC	Tricyclazole	96	6	96	7	114	2	0.005
GC	Trifloxystrobin	106	13	106	5	118	4	0.005
LC	Trifloxystrobin	109	8	84	16	86	16	0.005
LC	Triflumuron	101	13	83	20	80	17	0.005
GC	Trifluralin	94	7	91	6	109	3	0.005
GC	Triticonazole	79	7	78	11	86	10	0.005
LC	Triticonazole	90	18	90	15	90	19	0.005
LC	Vamidothion	90	10	80	17	87	17	0.005
GC	Vinclozolin	87	6	86	4	108	4	0.005
LC	Zoxamide	98	17	84	19	85	17	0.005

Appendix 3.

QuEChERS-EMR method 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.