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Validation Report 22

Determination of pesticide residues in wheat, rye and oat
by LC-MS/MS and GC-MS/MS

(QuEChERS method)

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CONTENT:

1. Introduction

This report describes the validation of the QuEChERS method combined with GC-MS/MS and LC-MS/MS. The method was validated for 147 pesticides and metabolites on LC-MSMS and 140 on GC-MSMS in wheat, rye and oat. 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].

2. Principle of analysis

Sample preparation: The samples is milled with a sieve at 1 mm.

The extraction procedure is outlines in Appendix 3 and described briefly in the following.

Extraction: The sample is shaken and a salt and buffer mixture is added and the sample is shaken again.

Clean-up: After centrifugation the supernatant is transferred to a clean tube and put in -80 degree freezer. When the extract is almost thawed it is centrifuged and the supernatant is transferred to a tube containing PSA and $MgSO_4$. An aliquot was withdrawn prior to this clean-up step and analysed by LC-MS/MS. After shaking and an additional centrifugation step the final extract is diluted 1:1 with acetonitrile to obtain the same matrix concentration as in the matrix matched calibration standards.

Quantification and qualification: The final extracts are analysed by GC-MS/MS. Crude extract withdrawn before PSA clean-up was analysed by LC-MS/MS.

GC-MS/MS: The pesticide residues were separated on a DB5-MS column and analysed by triple quadrupole operating in the multiple reaction monitoring mode (MRM) with electron energy at 70 eV, source temperature at 180°C and transfer line at 250°C. The injection volume was 1 µl. For each pesticide minimum two sets of precursor and product ions were determined. One for quantification and one for qualification. The MRM transitions for the pesticides and degradation products are given in Appendix 1a.

LC-MS/MS: The pesticide residues are separated on a reversed-phase column and detected by tandem mass spectrometry (MS/MS) by electrospray (ESI). The validation includes pesticides determined in positive mode. All pesticides were detected in the MRM mode. For each pesticide or metabolite a precursor ion and 2 product ions were determined. One product ion for quantification and one for qualification. The MRM transitions for the pesticides and degradation products sought validated are given in Appendix 1b.

3. Validation design

The method was sought validated for over 200 pesticides or metabolites in wheat, rye and oat, see **Appendix 1**. The validation was performed on 5-6 replicates on wheat at each of the two spiking levels; 0.005 and 0.01 mg/kg. A blank sample of each cereal commodity was included. Only two spiking levels were chosen because all of the compounds included in the validation have already been implemented in methods at the laboratory and validation just needed to be verified on new LC-MS/MS and GC-MS/MS systems.

4. Chromatograms and calibration curves

The calibration curve is determined by the analysis of each of the analysts at least 4 calibration levels within the range of 0.03, 1, 3.3, 10, 33.3 and 100 ng/ml. The calibration curves were in generally best fitted to a linear curve. The quantification was performed from the mean of two bracketing calibration curves. The majority of the correlation coefficients (R) were higher or equal to 0.99.

5. Validation parameters

Precision – repeatability and internal reproducibility

Repeatability was calculated for all pesticides and degradation products on all three spiking levels (0.005 mg/kg and 0.01 mg/kg). Repeatability is given as the relative standard deviation on the result from two or more analysis at the same sample, done by the same technician, on the same instrument and within a short period of time.

Repeatability (RSD_r) in this validation was calculated from the 5-6 replicate determinations. Repeatability were calculated as given in ISO 5725-2[2].

Accuracy – Recovery

The accuracy was determined from recovery studies in which samples were spiked at three concentration levels (0.005 mg/kg and 0.01 mg/kg) with the relevant pesticides, isomers and degradation products.

Robustness

The QuEChERS method has, in connection with the development of the method, been shown to be robust by Anastassiades et al. 2003[1].

Limit of quantification, LOQ

The quantification limits (LOQ) was determined as the lowest spike level for which the acceptance criteria (se Section 6) was meet.

The obtained results including recovery, RSD_r, RSD_R, Combined Uncertainty (U_c) and limit of quantification (LOQ) are presented in appendix 2.

6. Criteria for the acceptance of validation results

For the pesticides to be accepted as validated the following criteria for precision and trueness must to be fulfilled:

1. The relative standard deviation of the repeatability should be ≤20%[3].
2. The average relative recovery must be between 70 and 120%[3].

If the above mentioned criteria have been meet, the quantification limits, LOQs is stated.

The expanded uncertainty is calculated to demonstrate that it is less than 50%. The expanded uncertainty is given by:

$$U = \sqrt{RSD^2 + Bias^2 + (RSD^2/n)} * 2$$

Where RSD is the intra-laboratory uncertainty (RSD_R),
Bias is 100 minus the recovery,
RSD^2/n is the uncertainty of the bias,
n is the number of recoveries included in the bias and
2 is the coverage factor corresponding to 95% confidence level.

If the expanded uncertainty is higher than 50%, the analytical results must be corrected for recovery and the combined uncertainty is then given by:

$$U_c = \sqrt{RSD^2 + (RSD^2/n)}$$

Where RSD in this validation is the repetability uncertainty (RSD_r),
RSD^2/n is the uncertainty of the bias,
n is the number of recoveries included in the bias and
2 is the coverage factor corresponding to 95% confidence level.

The bias/recovery used for correction will be the bias/recoveries determined for the individual analytes during the initial validation and/or ongoing method validation. However, if it is evaluated that the type of sample being analysed is significantly different from the matrices employed for the method validation it is possible to correct for bias/recoveries based on recovery from spiked

samples included in the analytical batch in question. However, minimum of 5 recovery samples must be included then.

The obtained results including recovery, RSD_r, RSD_R, expanded uncertainty (Uc and limit of quantification (LOQ) are presented in appendix 2

7. Results and conclusion

The validation results obtained for the 147 pesticides or metabolites using LC-MSMS are presented in appendix 2. For 136 compounds an LOQ of 0.005 mg/kg and for 11 an LOQ of 0.01 mg/kg was achieved.

The validation results obtained for the 140 pesticides or metabolites using GC-MSMS are also presented in appendix 2. For 129 compounds an LOQ of 0.005 mg/kg and for 11 an LOQ of 0.01 mg/kg.

It has been decided at our laboratory that all results shall be corrected for recovery when possible, regardless of the expanded uncertainty, and the uncertainty that applies is therefore the combined uncertainty which are presented in appendix 2 for each compound.

9. 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 SANTE/11813/2017, 21–22 November 2017 rev.0, European Commission, Brussels, 2017.

Appendix 1a. MRM transitions for GC-MS/MS for compounds in mixture ABC.

Pesticide name	RT	Precusor Mass	Product Mass	Collision Energy
2-Phenylphenol	9.42	141	115	15
2-Phenylphenol	9.42	170	115	35
2-Phenylphenol	9.42	170	141	25
2-Phenylphenol	9.42	170	169	10
Acrinathrin I	23.39	181	152	22
Acrinathrin I	23.39	208.1	180.9	8
Acrinathrin I	23.39	289	93.1	8
Acrinathrin II	23.75	181	152	22
Acrinathrin II	23.75	208.1	180.9	8
Acrinathrin II	23.75	289	93.1	22
Aldrin	14.47	262.7	192.9	32
Aldrin	14.47	292.9	257.9	10
Atrazine	11.47	200	122	8
Atrazine	11.47	215	173	10
Atrazine	11.47	215	200	10
Azinphos-ethyl	23.84	132	51	26
Azinphos-ethyl	23.84	132	77	12
Azinphos-ethyl	23.84	160	77	16
Azinphos-methyl	21.37	132	77	12
Azinphos-methyl	21.37	160	50.9	34
Azinphos-methyl	21.37	160	77	22
Azoxystrobin	29.64	344.1	156	34
Azoxystrobin	29.64	344.1	171.9	36
Azoxystrobin	29.64	344.1	329	14
Azoxystrobin	29.64	388	300.9	20
Azoxystrobin-d4	29.66	348	332	30
Bifenthrin	21.54	165.1	163.6	24
Bifenthrin	21.54	181	165.9	10
Bifenthrin	21.54	181	179	12
Bifenthrin	21.54	181.1	153.1	10
Bifenthrin	21.54	181.1	166.1	10
Bitertanol	24.68	170	115.1	34
Bitertanol	24.68	170	141.1	20
Bitertanol	24.68	170	169.1	16
Boscalid	26.52	139.9	76	22
Boscalid	26.52	139.9	112	10
Boscalid	26.52	167	139	20
Boscalid	26.52	341.8	140.2	15
Boscalid	26.52	343.7	139.9	15
Bromophos-ethyl	16.19	96.9	78.9	12
Bromophos-ethyl	16.19	302.7	284.8	14
Bromophos-ethyl	16.19	358.9	302.9	15
Bromophos-ethyl	16.19	358.9	330.9	10

Bromopropylate	21.57	184.9	75.5	30
Bromopropylate	21.57	340.8	185	14
Bromopropylate	21.57	342.7	185	15
Bromuconazole I	21.3	172.9	144.9	16
Bromuconazole I	21.3	293	173	10
Bromuconazole I	21.3	295	175	10
Bromuconazole I	22.06	293	173	10
Bromuconazole I	22.06	295	175	10
Bromuconazole II	22.05	172.9	145	16
Bromuconazole II	22.05	293	173	10
Bromuconazole II	22.05	295	175	10
Bupirimate	17.57	208.1	165	12
Bupirimate	17.57	273.1	193.2	8
Bupirimate	17.57	316.2	208.2	10
Cadusafos	10.83	159	96.9	16
Cadusafos	10.83	159	130.9	8
Cadusafos	10.83	213	89.1	12
Carbosulfan	21.34	160	50.9	34
Carbosulfan	21.34	160	77	22
Carbosulfan	21.34	160	133	10
Carboxin	17.57	87	43	6
Carboxin	17.57	143	43	16
Carboxin	17.57	143	87	8
Carboxin	17.57	235	143	5
Chlorfenapyr	17.8	136.9	102	12
Chlorfenapyr	17.8	247	227	15
Chlorfenapyr	17.8	248.9	112	24
Chlorfenapyr	17.8	248.9	137.1	18
Chlorfenapyr	17.8	328	247	15
Chlorfenson	16.95	174.9	111	10
Chlorfenson	16.95	248	154	10
Chlorfenson	16.95	302	175	10
Chlorfenvinphos	15.51	266.9	159	16
Chlorfenvinphos	15.51	266.9	203	10
Chlorfenvinphos	15.51	269	161	15
Chlorfenvinphos	15.51	323	266.9	14
Chlorobenzilate	18.37	111	75.1	14
Chlorobenzilate	18.37	139	74.9	26
Chlorobenzilate	18.37	139	111	12
Chlorobenzilate	18.37	251	111	15
Chlorobenzilate	18.37	251	139	14
Chlorobenzilate	18.37	253	139	20
Chlorpropham	10.56	171	127	8
Chlorpropham	10.56	213	171	10
Chlorpropham	10.56	264	206	10
Chlorpyrifos	14.3	196.7	107	36
Chlorpyrifos	14.3	196.7	168.9	12

Chlorpyrifos	14.3	313.9	257.9	12
Chlorpyrifos	14.3	316.1	260	15
Chlorpyrifos-d10	14.32	200	109	36
Chlorpyrifos-d10	14.32	200	172	12
Chlorpyrifos-methyl	13.09	127	99	6
Chlorpyrifos-methyl	13.09	285.9	93	20
Chlorpyrifos-methyl	13.09	286	271	15
Clomazone	11.59	125	89	16
Clomazone	11.59	138	74.9	24
Clomazone	11.59	204	107	15
Cyflutrin	26.1	206	151	12
Cyflutrin	26.1	226	206	10
Cyhalothrin, lambda R	23.37	180.9	151.9	22
Cyhalothrin, lambda R	23.37	197	141.1	10
Cyhalothrin, lambda R	23.37	208.1	180.9	8
Cyhalothrin, lambda S	23.8	181	151.9	22
Cyhalothrin, lambda S	23.8	208.1	151.8	28
Cyhalothrin, lambda S	23.8	208.1	180.9	8
Cypermethrin	26.79	163	127	10
Cypermethrin	26.79	181	152	20
Cyproconazole	18.13	383	254	20
Cyproconazole	18.13	383	282	20
Cyprodinil	15.25	224.1	196.9	20
Cyprodinil	15.25	224.1	208	18
Cyprodinil	15.25	225.1	209.7	16
Cyprodinil	15.25	226	225	15
Deltamethrin I=II	29.38	181	152.1	22
Deltamethrin I=II	29.38	252.8	92.9	16
Deltamethrin I=II	29.38	252.8	172	8
Demeton-S-methyl	10.23	88	59.8	6
Demeton-S-methyl	10.23	109	79	6
Demeton-S-methyl	10.23	141.9	79	12
Diazinon	11.89	137.1	84.1	12
Diazinon	11.89	199	93	15
Diazinon	11.89	304.1	179.1	10
Dichlorvos	7.36	109	79	6
Dichlorvos	7.36	185	93	12
Dichlorvos	7.36	220	185	10
Dicloran	11.33	160	124.1	8
Dicloran	11.33	176	148	12
Dicloran	11.33	206	176	10
Difenoconazole I+II	28.92	265	138.9	60
Difenoconazole I+II	28.92	324.9	267	10
Dimethomorph I	29.88	301	139	14
Dimethomorph I	29.88	301	165.1	10
Dimethomorph I	29.88	387.1	301.1	10
Dimethomorph II	30.32	301	139	14

Dimethomorph II	30.32	301	165.1	10
Dimethomorph II	30.32	387.1	301.1	10
Diphenylamine	10.35	168.1	139	38
Endosulfan sulfate	19.68	238.7	203.9	12
Endosulfan sulfate	19.68	271.7	234.9	12
Endosulfan sulfate	19.68	271.7	236.8	12
Endosulfan sulfate	19.68	387	252	10
Endosulfan, -beta	18.44	158.9	123	12
Endosulfan, -beta	18.44	194.7	125	22
Endosulfan, -beta	18.44	194.7	159.4	8
Endosulfan, -beta	18.44	240.6	205.9	14
Endosulfan, -beta	18.44	339	159	20
Endrin	18.12	245	173	22
Endrin	18.12	262.8	192.9	30
Endrin	18.12	280.8	245.3	8
EPN	21.48	157	77	22
EPN	21.48	169	77	22
EPN	21.48	169	141	8
Epoxiconazole	20.78	165	138	8
Epoxiconazole	20.78	192	111	22
Epoxiconazole	20.78	192	138	12
Ethion	18.65	153	97	10
Ethion	18.65	230.9	128.9	22
Ethion	18.65	230.9	174.9	12
Ethoprophos	10.35	157.9	96.9	16
Ethoprophos	10.35	157.9	113.9	6
Ethoprophos	10.35	200	158	6
Etofenprox	27.16	163.1	77.1	32
Etofenprox	27.16	163.1	107.1	16
Etofenprox	27.16	163.1	135.1	10
Etofenprox-d5	27.1	168	108	10
Etofenprox-d5	27.1	168	136	20
Fenamiphos	16.83	154	139	10
Fenamiphos	16.83	216.9	202	12
Fenamiphos	16.83	303.1	195.2	8
Fenamiphos sulfone	21.11	320	213.9	14
Fenamiphos sulfone	21.11	320	249.1	18
Fenamiphos sulfone	21.11	320	292.1	8
Fenarimol	23.61	139	74.9	26
Fenarimol	23.61	139	111	14
Fenarimol	23.61	219	107	10
Fenazaquin	22.16	145.1	91	24
Fenazaquin	22.16	145.1	117.1	12
Fenazaquin	22.16	160.1	145.1	8
Fenbuconazole	25.73	129	77.8	18
Fenbuconazole	25.73	129	102	14
Fenbuconazole	25.73	198.1	129.1	8

Fenitrotion	13.88	125	79	8
Fenitrotion	13.88	277	109	16
Fenitrotion	13.88	277	260	6
Fenoxycarb	21.64	116	44.1	16
Fenoxycarb	21.64	116	88	8
Fenoxycarb	21.64	255.1	186.1	10
Fenpropathrin	21.85	181	126.8	28
Fenpropathrin	21.85	181	151.9	22
Fenpropathrin	21.85	208	181	5
Fenpropidin	13.76	98.2	41.5	18
Fenpropidin	13.76	98.2	55.1	14
Fenpropidin	13.76	98.2	70	10
Fenpropidin	13.76	99	71	10
Fenpropimorph	14.49	128.1	70.1	12
Fenpropimorph	14.49	128.1	110.1	8
Fenpropimorph	14.49	303	128	5
Fenson	14.87	141	77	8
Fenson	14.87	268	77	20
Fenson	14.87	268	141	10
Fenthion	14.42	245.3	125	12
Fenthion	14.42	278	109	15
Fenthion	14.42	278	169	10
Fenvalerate I+II	28.38	125	89	18
Fenvalerate I+II	28.38	167	89	32
Fenvalerate I+II	28.38	167	125	10
Fipronil	15.33	366.9	212.9	28
Fipronil	15.33	366.9	244.9	20
Fipronil	15.33	368.8	214.9	30
Fluazifop-P-butyl	18.13	282	91.1	18
Fluazifop-P-butyl	18.13	282	238.1	16
Fluazifop-P-butyl	18.13	383.1	282.1	14
Fludioxonil	16.94	153.7	127	8
Fludioxonil	16.94	248	127	26
Fludioxonil	16.94	248	153.8	10
Flufenoxuron	12.09	268	241	15
Flufenoxuron	12.09	331	268	15
Fluquinconazole	25.08	340	108.1	36
Fluquinconazole	25.08	340	298	16
Fluquinconazole	25.08	340	313	14
Flusilazole	17.46	206	151.3	14
Flusilazole	17.46	233	151.9	14
Flusilazole	17.46	233	164.9	16
Flutriafol	16.7	123	75	24
Flutriafol	16.7	123	95	12
Flutriafol	16.7	219	123	12
Fluvalinate I +II	28.4	180.8	152.1	22
Fluvalinate I +II	28.4	208	181	15

Fluvalinate I +II	28.4	250	199.9	18
Fluvalinate II	28.53	180.8	152.1	22
Fluvalinate II	28.53	208	181	15
Fluvalinate II	28.53	250	199.9	18
Fosthiazate	14.95	194.9	102.9	8
Fosthiazate	14.95	194.9	139	6
Fosthiazate	14.95	283	103	15
HCH	alpha	0	182.8	146.7
HCH	alpha	0	218.8	146.6
HCH,-beta	11.56	180.9	145	14
HCH,-beta	11.56	218.7	146.6	18
HCH,-beta	11.56	218.7	183	8
Heptenophos	9.79	124	62.9	28
Heptenophos	9.79	124	89	12
Heptenophos	9.79	215	200	10
Heptenophos	9.79	250	124	10
Heptenophos	9.79	250	215	5
Hexythiozox	16.27	184	59	20
Hexythiozox	16.27	184	149	6
Hexythiozox	16.27	227	149.1	8
Indoxacarb	29.26	133.9	106	15
Indoxacarb	29.26	203	106.1	22
Indoxacarb	29.26	203	134	20
Iodofenfos	16.93	125	47	12
Iodofenfos	16.93	125	79	6
Iodofenfos	16.93	376.8	361.8	16
Iodofenfos	16.93	379	364	20
Iprodione	21.19	314	245	10
Iprodione	21.19	315.7	247	10
Iprodione	21.19	315.7	273	8
Iprovalicarb I	17.41	118.9	91	12
Iprovalicarb I	17.41	118.9	117.1	8
Iprovalicarb I	17.41	134.1	42	20
Iprovalicarb II	17.72	118.9	91.1	12
Iprovalicarb II	17.72	118.9	117.1	8
Iprovalicarb II	17.72	134.1	42	20
Isofenphos-methyl	15.03	199	65	34
Isofenphos-methyl	15.03	199	121	10
Isofenphos-methyl	15.03	214.1	121.1	20
Isoprothiolane	17.09	204	85	28
Isoprothiolane	17.09	204	118	8
Isoprothiolane	17.09	290	118	12
Kresoxim-methyl	17.59	116	62.9	24
Kresoxim-methyl	17.59	130.9	130.1	10
Kresoxim-methyl	17.59	206	116	4
Kresoxim-methyl	17.59	206	131	10
Lindane	11.77	180.9	109	26

Lindane	11.77	180.9	145	14
Lindane	11.77	218.7	183	8
Linuron	13.93	159.8	133	12
Linuron	13.93	187	124	20
Linuron	13.93	248	61.1	8
Malathion	14.08	125	79	8
Malathion	14.08	173	127	5
Malathion	14.08	173.1	99	12
Mecarbam	15.55	131	42	12
Mecarbam	15.55	131	86	10
Mecarbam	15.55	159	131	6
Mecarbam	15.55	226	198	5
Mecarbam	15.55	329	131	10
Metalaxyl	13.44	131.9	117	12
Metalaxyl	13.44	160.1	130	18
Metalaxyl	13.44	160.1	144.8	10
Methacrifos	9.14	125	79	8
Methacrifos	9.14	180	93	10
Methacrifos	9.14	240	180	10
Methamidophos	7.26	141	64	18
Methamidophos	7.26	141	79	20
Methamidophos	7.26	141	94.8	8
Methidathion	16.12	145	58	14
Methidathion	16.12	145	85	6
Methidathion	16.12	302	145	5
Methidathion	16.12	302.6	284.9	14
Metribuzin	13.02	198	82.1	16
Metribuzin	13.02	198	110	10
Metribuzin	13.02	214	198	5
Myclobutanil	17.48	179	90	28
Myclobutanil	17.48	179	125	14
Myclobutanil	17.48	179	151.7	8
Nuarimol	20.24	107	79	6
Nuarimol	20.24	139	111	12
Nuarimol	20.24	235	139	14
Ofurace	19.15	131.9	117	16
Ofurace	19.15	232.1	158.1	18
Ofurace	19.15	232.1	186.1	8
Omethoate	10.05	109.8	62.9	24
Omethoate	10.05	109.8	64	16
Oxadixyl	18.53	131.9	117	16
Oxadixyl	18.53	163.1	117	24
Oxadixyl	18.53	163.1	132.1	8
Paclobutrazol	16.37	125	89	18
Paclobutrazol	16.37	236	125	12
Paclobutrazol	16.37	236	167	10
Parathion	14.5	109	81	10

Parathion	14.5	291	81	20
Parathion	14.5	291	109	12
Parathion-methyl	13.24	124.9	47	12
Parathion-methyl	13.24	124.9	79	6
Parathion-methyl	13.24	263	109	12
Penconazole	15.4	158.9	89	28
Penconazole	15.4	248	157	22
Penconazole	15.4	248	192	12
Pencycuron	11.59	125	89	16
Pencycuron	11.59	125	99	16
Permethrin I	24.82	163	91	12
Permethrin I	24.82	183.1	153	12
Permethrin I	24.82	183.1	165.1	12
Permethrin I	24.82	183.1	168.1	12
Permethrin II	25.1	163	91	12
Permethrin II	25.1	183.1	153	12
Permethrin II	25.1	183.1	165.1	12
Permethrin II	25.1	183.1	168.1	12
Phenthoate	15.68	121	77	22
Phenthoate	15.68	246	121	8
Phenthoate	15.68	274	121	10
Phosalone	22.62	182	74.8	30
Phosalone	22.62	182	111	14
Phosalone	22.62	367	182	5
Phosmet	21.34	160	50.9	34
Phosmet	21.34	160	76.9	22
Phosmet	21.34	160	133	10
Phosphamidon	12.79	127	94.9	16
Phosphamidon	12.79	127	109	25
Phosphamidon	12.79	264.1	127	12
Pirimicarb	12.48	166.1	55	18
Pirimicarb	12.48	166.1	96	12
Pirimicarb	12.48	238.1	166.1	10
Pirimicarb desmetyl	12.71	152.1	42	25
Pirimicarb desmetyl	12.71	152.1	96	10
Pirimicarb desmetyl	12.71	224.1	152.1	10
Pirimiphos methyl	13.79	290.1	125	20
Pirimiphos methyl	13.79	290.1	233	8
Pirimiphos methyl	13.79	305.1	180.1	8
Prochloraz	25.19	180.1	138.1	12
Prochloraz	25.19	308	147.1	12
Prochloraz	25.19	310	268	5
Procymidone	15.85	95.9	67.1	8
Procymidone	15.85	283	96.1	8
Procymidone	15.85	283	254	10
Profenofos	17.14	296.7	268.9	10
Profenofos	17.14	336.9	266.9	12

Profenofos	17.14	336.9	308.9	8
Propiconazole I	19.61	172.9	74	38
Propiconazole I	19.61	172.9	109	26
Propiconazole I	19.61	259	173	15
Propiconazole II	19.81	172.9	74	38
Propiconazole II	19.81	172.9	109	26
Propiconazole II	19.81	259	173	15
Propoxur	10.05	110	62.9	24
Propoxur	10.05	110	64.1	16
Propoxur	10.05	152.1	110	8
Propyzamide	11.87	172.9	74	38
Propyzamide	11.87	172.9	109	26
Propyzamide	11.87	172.9	145	14
Prosulfocarb	13.7	128.1	43.1	10
Prosulfocarb	13.7	160.1	100.1	10
Prosulfocarb	13.7	251.1	128.1	5
Prothiofos	17.03	266.7	220.9	18
Prothiofos	17.03	266.7	238.9	8
Prothiofos	17.03	308.9	239	14
Pyrazophos	23.65	221	148.7	14
Pyrazophos	23.65	221	193.1	8
Pyrazophos	23.65	231.9	204.1	10
Pyridaben	25.08	147.1	117.1	20
Pyridaben	25.08	147.1	119.1	8
Pyridaben	25.08	147.1	132.1	12
Pyridaphenthion	21.12	199	77.1	24
Pyridaphenthion	21.12	199	92.1	14
Pyridaphenthion	21.12	340	199.1	8
Pyrimethanil	12.03	198.1	117.9	30
Pyrimethanil	12.03	198.1	157.6	18
Pyrimethanil	12.03	198.1	182.9	14
Pyriproxyfen	23	136.1	78	20
Pyriproxyfen	23	136.1	96	10
Pyriproxyfen	23	226.1	186.1	12
Quinoxyfen	19.64	237	208	26
Quinoxyfen	19.64	271.8	237.1	12
Quinoxyfen	19.64	307	237	18
Simazine	11.38	172.7	138	6
Simazine	11.38	172.7	172.2	8
Simazine	11.38	186	91	8
Tebuconazole	20.32	125	89	16
Tebuconazole	20.32	125	99	16
Tebuconazole	20.32	250	125	20
Tebufenpyrad	21.99	276.1	171	10
Tebufenpyrad	21.99	318.1	131.1	14
Tebufenpyrad	21.99	318.1	145.1	14
Tecnazene	10.04	214.8	143.6	20

Tecnazene	10.04	214.8	178.7	10
Tecnazene	10.04	214.8	179.9	15
Tefluthrin	12.19	177	127	14
Tefluthrin	12.19	177	137	16
Tefluthrin	12.19	197	141.1	10
Tetraconazole	14.57	100.9	51	10
Tetraconazole	14.57	159	123.4	16
Tetraconazole	14.57	171	136	10
Tetraconazole	14.57	336	204	28
Tetradifon	22.41	159	74.8	32
Tetradifon	22.41	159	111	20
Tetradifon	22.41	159	131	10
Thiamethoxam	15.05	212	125	10
Thiamethoxam	15.05	212	139	12
Thiamethoxam	15.05	247	182.1	10
Thiometon	11.15	125	79	8
Thiometon	11.15	158	125	10
Tolclofos-methyl	13.29	265	219.9	20
Tolclofos-methyl	13.29	265	250	12
Tolclofos-methyl	13.29	266.8	252	12
TPP	20.42	325.07	169.04	25
TPP	20.42	326	169	35
TPP	20.42	326.07	215.05	25
TPP	20.42	326.07	233.05	10
TPP	20.42	326.07	325.07	10
Triadimefon	14.59	208	111	20
Triadimefon	14.59	208	126.7	12
Triadimefon	14.59	208	180.8	8
Triallate	12.41	86.1	43.3	6
Triallate	12.41	268	183.9	18
Triallate	12.41	268	226	12
Triazophos	19.11	161	105.7	12
Triazophos	19.11	161	134.1	8
Triazophos	19.11	257	162	5
Triazophos	19.11	285	162	10
Trichlorfon	7.38	145	109	10
Trichlorfon	7.38	185	93	12
Tricyclazole	17.09	162	84.9	18
Tricyclazole	17.09	162	133.9	8
Trifloxystrobin	19.61	116.1	89	8
Trifloxystrobin	19.61	145	95	8
Trifloxystrobin	19.61	186	145	10
Trifloxystrobin	19.61	222	190	5
Trifluralin	10.57	306.1	159.7	20
Trifluralin	10.57	306.1	206	10
Trifluralin	10.57	306.1	264.1	8
Triticonazole	22.6	217	167	18

Triticonazole	22.6	235.1	181.9	12
Triticonazole	22.6	235.1	217.1	8
Vamidothion	16.31	87.1	44.4	10
Vinclozolin	13.16	198	145	15
Vinclozolin	13.16	285	212	5
Zoxamide	20.82	186.9	123	22
Zoxamide	20.82	186.9	159	14
Zoxamide	20.82	258	187	10

Appendix 1b. MRM transitions for LC-MS/MS for compounds in mixture ABC.

LC-MS/MS	Mode	Retention time	Precursor ion-1	Product ion-1	CE	Precursor ion-2	Product ion-2	CE
Acephate	Positive	1.76	183.8	143.0	-12			
Acetamiprid	Positive	2.65	223.0	126.0	-17	223.0	56.0	-9.5
Aldicarb Sulfone	Positive	1.95	240.4	148.2	-13	240.4	86.3	-21
Aldicarb Sulfoxide	Positive	1.88	224.0	132.0	-10	224.0	89.2	-21
Amitraz	Positive	2.07	163.0	107.0	-26	163.0	122.0	-17
Atrazine	Positive	4.54	216.0	174.0	-15	216.0	104.0	-24.5
Azinphos-ethyl	Positive	5.75	346.0	233.0	-12	346.0	137.0	-22
Azinphos-methyl	Positive	4.90	318.0	261.0	-5.5	318.0	132.0	-11
Azoxystrobin	Positive	5.14	404.0	372.0	-15	404.0	344.0	-21
Bifenthrin	Positive	8.30	440.0	181.0	-10	440.0	166.0	-35
Bitertanol	Positive	6.53	338.0	70.0	-5	338.0	268.0	-8.5
Boscalid	Positive	5.39	343.0	271.0	-24	343.0	307.0	-12.5
Bromoxynil	Negative	4.38	276.0	79.0	20.5	276.0	80.6	25
Bromuconazole	Positive	5.63	377.9	159.0	-17.5	377.9	70.0	-9
Bupirimate	Positive	5.62	317.0	166.0	-23	317.0	108.0	-25
Buprofezin	Positive	6.97	306.0	116.0	-14	306.0	201.0	-8
Cadusafos	Positive	6.66	271.0	159.0	-11.5	271.0	131.0	-20.5
Carbaryl	Positive	4.09	202.0	145.0	-7	202.0	127.0	-26.5
Carbendazim	Positive	2.01	192.0	160.0	-13	192.0	105.0	-31.5
Carbofuran	Positive	3.85	222.0	165.0	-9.5	222.0	123.0	-17.5
Carbofuran, 3-hydroxy	Positive	2.63	238.0	163.0	-13	238.0	181.0	-9.5
Carboxin	Positive	4.04	236.0	143.0	-11	236.0	93.0	-27.5
Chlorpyrifos	Positive	7.32	351.7	200.0	-18	349.7	198.0	-16
Chlorpyrifos-methyl	Positive	6.66	322.0	125.0	-15	324.0	292.0	-15
Clethodim	Positive	6.87	360.0	166.0	-24.5	360.0	164.0	-17.5
Clomazone	Positive	4.99	240.0	125.1	-29	240.0	100.0	-20
Clothianidin	Positive	2.47	250.0	169.0	-13	250.0	132.0	-50
Cyazofamid	Positive	5.92	325.0	108.0	-9.5	325.0	217.0	-12.5

LC-MS/MS	Mode	Retention time	Precursor ion-1	Product ion-1	CE	Precursor ion-2	Product ion-2	CE
Cypermethrin	Positive	7.78	433.0	191.0	-14	435.0	193.0	-14
Cyproconazole	Positive	5.55	292.0	125.0	-25.5	292.0	70.0	-12
Deltamethrin	Positive	7.78	523.0	281.0	-14	521.0	279.0	-14
Demeton-S-methyl	Positive	3.88	231.0	89.0	-10	231.0	61.0	-25
Demeton-S-methyl sulfone	Positive	2.12	263.0	169.0	-13.5	263.0	109.0	-24
Demeton-S-methyl sulfoxide (oxydemeton-s-methyl)	Positive	2.05	247.0	169.0	-12	247.0	109.0	-26
Diazinon	Positive	6.33	305.0	169.0	-20	305.0	97.0	-30
Dichlorprop	Negative	5.40	233.0	161.0	10	233.0	125.0	26
Difenoconazole	Positive	6.70	406.0	251.0	-23.5	406.0	188.0	-42
Diflubenzuron	Positive	6.03	311.0	141.0	-25	311.0	158.0	-8
Dimethoate	Positive	2.67	230.0	199.0	-8	230.0	125.0	-19
Dimethomorph	Positive	5.29	388.0	301.0	-17.5	388.0	139.0	-30.5
Dinoterb	Negative	6.41	239.0	207.0	23	239.0	136.0	34
Ditalimfos	Positive	5.69	300.0	148.0	-16	300.0	130.0	-30
DMF	Positive	3.52	150.0	106.8	-20	150.0	132.2	-35
DMPF	Positive	2.07	163.0	122.0	-15	163.0	107.0	-25
DNOC	Negative	4.31	197.0	137.0	17	197.0	109.1	10
Epoxiconazole	Positive	5.86	330.0	121.0	-17.5	330.0	101.0	-30
Ethiofencarb	Positive	4.25	226.0	107.0	-11	226.0	165.0	-5.5
Ethion	Positive	7.20	385.0	199.0	-10	402.0	199.0	-15
Ethoprophos	Positive	5.85	243.2	97.0	-23	243.2	131.0	-31
Etofenprox	Positive	8.21	394.0	177.0	-13.5	394.0	135.0	-22.5
Fenamiphos	Positive	6.02	304.0	216.9	-21	304.0	201.7	-35
Fenamiphos sulfone	Positive	4.02	336.0	188.0	-31	336.0	266.0	-50
Fenarimol	Positive	5.83	331.0	268.0	-18	331.0	189.0	-38
Fenazaquin	Positive	7.80	307.0	161.1	-14	307.0	57.4	-20
Fenbuconazole	Positive	6.00	337.0	125.0	-25	337.0	70.2	-16
Fenhexamid	Positive	5.80	302.0	302.0	-8.5	302.0	97.0	-18.5
Fenoxycarb	Positive	6.09	302.0	116.0	-8	302.0	88.0	-13.5

LC-MS/MS	Mode	Retention time	Precursor ion-1	Product ion-1	CE	Precursor ion-2	Product ion-2	CE
Fenpropathrin	Positive	7.57	367.0	125.0	-15	367.0	97.0	-27.5
Fenpropidin	Positive	4.40	274.0	147.0	-23.5	274.0	117.0	-30.5
Fenpropimorph	Positive	4.55	304.0	147.0	-24	304.0	130.0	-19
Fenthion	Positive	6.26	279.0	169.0	-15.5	279.0	105.0	-20.5
Fenthion oxon sulfone	Positive	2.73	295.0	217.0	-20	295.0	104.1	-33
Fenthion oxon sulfoxide	Positive	2.61	279.1	264.0	-15	279.1	104.0	-20
Fenthion sulfone	Positive	4.18	328.0	311.0	-7	328.0	125.1	-22
Fipronil	Negative	6.10	435.2	330.2	13	435.2	250.1	42
Fluazifop-p-butyl	Positive	7.01	384.0	282.0	-18	384.0	254.0	-17.5
Flufenoxuron	Positive	7.52	489.6	158.1	-13	489.6	141.0	-22
Fluoxastrobin	Positive	5.76	459.2	427.1	-17	459.2	188.0	-45
Fluquinconazole	Positive	5.73	376.0	307.0	-21.5	376.0	349.0	-18
Flusilazole	Positive	6.07	316.0	247.0	-16.5	316.0	165.0	-23.5
Fosthiazate	Positive	4.31	284.4	104.1	-25	284.4	228.2	-30
Heptenophos	Positive	4.78	251.0	127.1	-14	251.0	125.0	-12
Hexythiazox	Positive	7.35	353.0	228.0	-14.5	353.0	168.0	-23.5
Imazalil	Positive	3.93	297.0	159.0	-16.5	297.0	201.0	-13
Imidacloprid	Positive	2.42	256.0	209.0	-13.5	256.0	175.0	-16.5
Indoxacarb	Positive	6.75	528.0	293.0	-12	528.0	150.0	-23.5
Iodosulfuron-methyl	Positive	4.92	530.1	163.1	-13	530.1	390.0	-21
Iprodione	Positive	6.05	330.0	245.0	-12	330.0	101.0	-25
Iprovalicarb	Positive	5.70	321.0	119.0	-14	321.0	203.0	-7
Isoprothiolane	Positive	5.46	291.0	231.0	-10	291.0	189.0	-20
Isoproturon	Positive	4.64	207.0	72.0	-11.5	207.0	165.0	-12
Kresoxim-methyl	Positive	6.19	314.0	116.0	-30	314.0	131.0	-20
Linuron	Positive	5.19	249.0	160.0	-13.5	249.0	160.0	-16
Malaoxon	Positive	3.88	315.0	127.0	-10	315.0	99.0	-20
Malathion	Positive	5.44	331.0	127.0	-10	331.0	99.0	-18
Mecarbam	Positive	5.79	330.0	227.0	-8	330.0	97.0	-45
Mepanipyrim	Positive	5.68	224.0	106.0	-20	224.0	77.0	-49

LC-MS/MS	Mode	Retention time	Precursor ion-1	Product ion-1	CE	Precursor ion-2	Product ion-2	CE
Metaflumizone	Negative	7.15	505.1	302.1	25	505.1	328.0	15
Metalaxyl	Positive	4.66	280.0	192.0	-16.5	280.0	220.0	-12.5
Metconazole	Positive	6.49	320.0	125.0	-32.5	320.0	70.0	-14.5
Methacrifos	Positive	4.87	258.1	125.0	-21	258.1	209.0	-11
Methamidophos	Positive	1.63	142.0	94.0	-11.5	142.0	125.0	-12
Methiocarb	Positive	5.27	243.4	121.2	-30	243.4	169.3	-13
Methiocarb sulfone	Positive	2.73	275.0	122.0	-14.5	275.0	107.0	-33.5
Methiocarb sulfoxide	Positive	2.50	242.0	185.0	-20	242.0	122.0	-23
Methoxyfenozide	Positive	5.51	369.0	149.0	-11.5	369.0	313.0	-5
Metribuzin	Positive	3.79	215.0	187.0	-16	215.0	84.0	-16
Metsulfuron-methyl	Positive	3.79	382.0	167.0	-14	382.0	199.0	-27
Mevinphos	Positive	2.62	225.0	127.0	-13	225.0	193.0	-6
Monolinuron	Positive	4.21	215.0	126.0	-17	215.0	148.0	-13
Ofurace	Positive	3.87	282.0	160.0	-22	282.0	236.0	-14
Omethoate	Positive	1.83	214.0	183.0	-10	214.0	125.0	-20
Oxamyl	Positive	1.98	237.0	72.0	-9.5	237.0	90.0	-6.5
Oxycarboxin	Positive	2.91	268.0	175.0	-13	268.0	147.0	-24
Paclobutrazol	Positive	5.44	294.0	125.0	-35	294.0	70.0	-15
Parathion-ethyl	Positive	6.10	292.0	236.0	-20	292.0	94.0	-20
Penconazole	Positive	6.27	284.0	159.0	-27.5	284.0	173.0	-16.5
Pencycuron	Positive	6.62	329.0	125.0	-20	329.0	218.0	-13.5
Pendimethalin	Positive	7.37	282.1	212.0	-10	282.1	194.0	-10
Phosphamidon	Positive	3.44	300.0	127.0	-22	300.0	174.1	-13
Phoxim	Positive	6.43	299.0	129.0	-9	299.0	153.0	-6
Pirimicarb	Positive	3.11	239.0	72.1	-16	239.0	182.3	-25
Pirimiphos-methyl	Positive	6.39	306.0	164.0	-20	306.0	108.0	-20
Prochloraz	Positive	6.33	376.0	308.0	-10.5	376.0	266.0	-16.5
Propamocarb	Positive	1.78	189.0	102.0	-13	189.0	74.0	-23
Propargite	Positive	7.48	368.0	231.0	-9.5	368.0	175.0	-15
Propiconazole	Positive	6.38	342.0	159.0	-20	342.0	69.0	-20

LC-MS/MS	Mode	Retention time	Precursor ion-1	Product ion-1	CE	Precursor ion-2	Product ion-2	CE
Propoxur	Positive	3.80	210.3	111.2	-13	210.3	168.3	-30
Propyzamide	Positive	5.48	256.0	190.0	-13	256.0	145.0	-35
Prosulfocarb	Positive	6.89	252.0	91.0	-20	252.0	128.0	-10
Prosulfuron	Positive	5.24	420.3	141.1	-15	420.3	167.0	-15
Prothioconazole-desthio	Positive	5.92	312.0	125.0	-25	312.0	70.0	-18
Pyraclostrobin	Positive	6.44	388.0	163.0	-18.5	388.0	194.0	-7.5
Pyrimethanil	Positive	4.69	200.0	107.0	-19.5	200.0	82.0	-20.5
Pyriproxyfen	Positive	7.22	322.0	96.2	-14	322.0	184.9	-22
Quinoxyfen	Positive	7.31	308.0	161.9	-47	308.0	197.0	-31
Simazine	Positive	3.81	202.0	124.0	-17	202.0	132.0	-32
Spirodiclofen	Positive	7.63	411.0	313.0	-20	411.0	71.0	-20
Spiroxamine	Positive	4.76	298.0	144.0	-15	298.0	100.0	-23
Tebuconazole	Positive	6.28	308.0	70.0	-13	308.0	125.0	-32
Tebufenozide	Positive	6.07	353.0	133.0	-17	353.0	297.0	-7.5
Tebufenpyrad	Positive	7.09	334.0	145.0	-24	334.0	117.0	-31
Teflubenzuron	Negative	7.22	379.0	339.0	9	379.0	195.0	20.5
Thiabendazole	Positive	2.16	202.0	175.0	-19.5	202.0	131.0	-27
Thiacloprid	Positive	2.92	253.0	126.0	-17	253.0	90.0	-30
Thiamethoxam	Positive	2.16	292.0	211.0	-11.5	292.0	132.0	-18.5
Tolclofos-methyl	Positive	6.51	301.0	269.0	-14	301.0	125.0	-16
Triadimefon	Positive	5.55	294.0	197.0	-16	294.0	225.0	-12
Triadimenol	Positive	5.74	296.0	70.0	-7	296.0	99.0	-11.5
Triallate	Positive	6.98	306.0	144.9	-23	306.0	86.0	-24
Triazophos	Positive	5.64	314.0	162.0	-17	314.0	119.0	-30
Tricyclazole	Positive	3.08	190.0	136.0	-25.5	190.0	109.0	-31.5
Trifloxystrobin	Positive	6.77	409.0	186.0	-11	409.0	145.0	-36
Triflumuron	Positive	6.48	359.1	156.1	-25	359.1	138.8	-20
Triticonazole	Positive	5.84	318.0	70.0	-12	318.0	125.0	-30.5
Vamidothion	Positive	2.59	288.0	146.0	-20	288.0	118.0	-30
Zoxamide	Positive	6.38	336.0	187.0	-17	336.0	132.0	-11

Appendix 2. Recoveries, repeatability (RSD_r), internal reproducibility (RSDR) and Limit of Quantification (LOQ) for pesticides validated on three cereal commodities, oat, rye and wheat using QuEChERS.

Numbers in italic is outside 70-120% recovery or above 20% RSD.

		Spike level 0.005 mg/kg				Spike level 0.01 mg/kg					
	Compound	Recovery %	RSD_r, %	RSDR, %	Comb. Uncer-tainty (%)	Recovery %	RSD_r, %	RSDR, %	Comb. Uncer-tainty (%)	LOQ	Correction for recov. needed
GC	2-Phenylphenol	77	10	18	25	77	13	20	26	0.005	Yes
LC	Acephate	84	13	12	*21*	86	20	*23*	*24*	0.005	Yes
LC	Acetamiprid	109	9	14	13	114	17	*21*	*22*	0.005	No
GC	Acrinathrin I	89	10	20	14	107	14	14	15	0.005	No
GC	Acrinathrin II	85	*23*	*49*	28	101	14	20	14	0.01	Yes
LC	Aldicarb Sulfone	115	14	17	20	118	16	16	*24*	0.005	No
LC	Aldicarb Sulfoxide	96	13	14	14	102	18	18	18	0.005	No
GC	Aldrin	*61*	16	14	42	72	14	15	32	0.005	Yes
LC	Amitraz	91	14	13	16	99	15	15	15	0.005	No
GC	Atrazine	98	18	19	18	103	20	20	20	0.005	No
LC	Atrazine	117	13	17	*21*	118	17	19	*25*	0.005	Yes
GC	Azinphos-ethyl	103	16	20	16	114	16	18	21	0.005	No
LC	Azinphos-ethyl	105	19	20	19	119	15	18	*24*	0.005	No
GC	Azinphos-methyl	84	10	9	18	105	15	19	16	0.005	No
LC	Azinphos-methyl	113	15	18	20	110	14	18	17	0.005	No
GC	Azoxystrobin	112	11	14	16	106	9	*21*	11	0.005	No
LC	Azoxystrobin	*121*	12	16	*24*	112	*21*	20	*25*	0.005	Yes
GC	Bifenthrin	79	4	6	21	88	14	14	18	0.005	Yes
LC	Bifenthrin	94	11	14	13	106	20	20	*21*	0.005	No
GC	Bitertanol	101	11	13	11	111	16	15	20	0.005	No
LC	Bitertanol	113	12	12	18	118	17	19	*25*	0.005	No
GC	Boscalid	103	6	11	7	107	13	14	15	0.005	No

		Spike level 0.005 mg/kg				Spike level 0.01 mg/kg					
	Compound	**Recovery %**	**RSD$_r$, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**Recovery %**	**RSD$_r$, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**LOQ**	**Correction for recov. needed**
LC	Boscalid	111	11	18	16	115	17	18	*22*	0.005	No
GC	Bromophos-ethyl	83	10	10	20	91	12	14	15	0.005	No
GC	Bromopropylate	90	9	14	14	96	15	14	15	0.005	No
LC	Bromoxynil	114	11	16	18	116	18	20	*24*	0.005	No
LC	Bromuconazole	109	14	16	17	*122*	16	17	*27*	0.005	No
GC	Bromuconazole I+II	96	15	18	16	103	14	14	14	0.005	No
GC	Bupirimate	99	12	12	12	102	13	13	13	0.005	No
LC	Bupirimate	118	9	8	20	*124*	18	16	*30*	0.005	No
LC	Buprofezin	103	10	11	10	107	18	18	19	0.005	No
GC	Cadusafos	90	12	13	15	102	15	15	15	0.005	No
LC	Cadusafos	100	15	15	15	111	13	15	17	0.005	No
LC	Carbaryl	112	9	11	15	111	12	17	16	0.005	No
LC	Carbendazim	101	12	14	13	106	11	15	13	0.005	No
LC	Carbofuran	120	4	6	20	119	13	17	*23*	0.005	No
LC	Carbofuran, 3-hydroxy	106	11	14	12	107	17	*21*	19	0.005	No
GC	Carbosulfan	94	7	*21*	9	108	15	19	17	0.005	No
GC	Carboxin	89	18	20	22	96	20	20	20	0.005	Yes
LC	Carboxin	85	16	19	*22*	90	11	15	15	0.005	Yes
GC	Chlorfenapyr	91	*40*	*38*	41	104	*21*	*21*	21	0.01	Yes
GC	Chlorfenson	90	9	9	14	95	17	17	18	0.005	No
GC	Chlorfenvinphos	101	11	20	11	101	15	18	15	0.005	No
GC	Chlorobenzilate	92	7	9	10	101	15	15	15	0.005	No
GC	Chlorpropham	91	16	*21*	18	104	13	12	14	0.005	No
GC	Chlorpyrifos	91	12	20	15	97	18	17	18	0.005	No
LC	Chlorpyrifos	99	11	12	11	104	13	14	14	0.005	No
GC	Chlorpyrifos-methyl	87	14	14	19	100	17	17	17	0.005	No
LC	Chlorpyrifos-methyl	109	14	20	16	114	16	16	*21*	0.005	No

		Spike level 0.005 mg/kg				Spike level 0.01 mg/kg					
	Compound	**Recovery %**	**RSD$_r$, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**Recovery %**	**RSD$_r$, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**LOQ**	**Correction for recov. needed**
LC	Clethodim	92	20	19	*21*	103	18	20	18	0.005	Yes
GC	Clomazone	90	11	11	14	100	18	18	18	0.005	No
LC	Clomazone	108	18	19	20	110	13	17	17	0.005	No
LC	Clothianidin	114	6	12	15	113	11	18	17	0.005	No
LC	Cyazofamid	111	10	18	15	111	13	*21*	17	0.005	No
GC	Cyflutrin	98	7	13	7	102	16	17	16	0.005	No
GC	Cyhalothrin, lambda R	89	9	20	14	102	14	14	14	0.005	No
GC	Cypermethrin	100	18	19	18	105	13	19	14	0.005	No
LC	Cypermethrin	84	12	15	20	94	18	18	19	0.005	No
GC	Cyproconazole	96	18	20	18	98	18	17	18	0.005	No
LC	Cyproconazole	112	15	17	20	109	17	20	20	0.005	No
GC	Cyprodinil	88	11	11	16	97	15	17	15	0.005	No
LC	Deltamethrin	119	11	11	*22*	104	15	16	15	0.005	Yes
GC	Deltamethrin I+II	86	18	20	23	90	15	17	18	0.005	Yes
GC	Demeton-S-methyl	*59*	*42*	*52*	59	80	18	19	27	0.01	Yes
LC	Demeton-S-methyl	*64*	*52*	*57*	*63*	97	14	15	15	0.01	No
LC	Demeton-S-methyl sulfone	105	12	17	13	117	18	16	*24*	0.005	No
LC	Demeton-S-methyl sulfoxid (oxydemeton-s-methyl)	120	8	8	*22*	116	17	16	*24*	0.005	Yes
GC	Diazinon	91	12	18	15	106	15	14	16	0.005	No
LC	Diazinon	96	15	16	16	106	12	14	14	0.005	No
LC	Dichlorprop	111	12	13	17	112	17	18	*21*	0.005	No
GC	Dichlorvos	*69*	10	19	33	72	13	*21*	30	0.005	Yes
GC	Dicloran	95	11	14	12	101	15	14	15	0.005	No
LC	Difenoconazole	115	9	8	17	115	19	*21*	*24*	0.005	No
GC	Difenoconazole I+II	104	6	17	8	112	15	19	19	0.005	No
LC	Diflubenzuron	118	11	11	*21*	117	11	14	20	0.005	Yes
LC	Dimethoate	112	7	11	14	115	11	18	19	0.005	No

		Spike level 0.005 mg/kg				Spike level 0.01 mg/kg					
	Compound	**Recovery %**	**RSD_r, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**Recovery %**	**RSD_r, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**LOQ**	**Correction for recov. needed**
LC	Dimethomorph	119	10	12	*22*	118	13	15	*22*	0.005	Yes
GC	Dimethomorph I+II	102	6	15	6	109	13	17	16	0.005	No
LC	Dinoterb	116	11	11	20	116	14	16	22	0.005	No
LC	Ditalimfos	109	12	13	15	116	14	17	21	0.005	No
LC	DMF	114	9	10	16	115	11	15	19	0.005	No
LC	DMPF	90	13	14	17	97	15	15	15	0.005	No
LC	DNOC	117	10	12	20	113	12	21	18	0.005	No
GC	Endosulfan sulfate	101	11	18	11	104	17	17	18	0.005	No
GC	Endosulfan, beta	111	19	20	22	98	16	17	16	0.005	Yes
GC	Endrin	71	*36*	*37*	46	88	20	19	23	0.01	Yes
GC	EPN	85	*29*	*30*	32	97	15	16	15	0.01	Yes
GC	Epoxiconazole	100	13	14	13	103	15	15	16	0.005	No
LC	Epoxiconazole	113	12	13	18	117	17	19	*24*	0.005	No
LC	Ethiofencarb	76	*35*	*37*	*43*	93	11	15	14	0.01	No
GC	Ethion	93	8	12	10	104	15	15	15	0.005	No
LC	Ethion	109	10	11	13	117	13	19	*21*	0.005	No
GC	Ethoprophos	97	15	15	16	104	14	14	15	0.005	No
LC	Ethoprophos	100	17	15	17	111	12	12	16	0.005	No
GC	Etofenprox	85	8	9	17	90	13	13	17	0.005	No
LC	Etofenprox	98	8	17	8	101	12	19	12	0.005	No
GC	Fenamiphos	97	20	19	21	99	19	17	19	0.005	Yes
LC	Fenamiphos	104	13	16	14	113	14	18	19	0.005	No
GC	Fenamiphos sulfone	100	15	20	15	115	14	14	20	0.005	No
LC	Fenamiphos sulfone	120	9	10	*22*	120	14	19	*24*	0.005	Yes
GC	Fenarimol	94	11	13	12	105	12	12	13	0.005	No
LC	Fenarimol	108	15	18	17	111	16	20	19	0.005	No
GC	Fenazaquin	86	8	9	16	92	14	15	16	0.005	No

		Spike level 0.005 mg/kg				Spike level 0.01 mg/kg					
	Compound	**Recovery %**	**RSD_r, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**Recovery %**	**RSD_r, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**LOQ**	**Correction for recov. needed**
LC	Fenazaquin	90	7	9	12	95	15	19	16	0.005	No
GC	Fenbuconazole	102	8	12	8	107	14	14	16	0.005	No
LC	Fenbuconazole	116	8	8	18	117	14	15	*22*	0.005	No
LC	Fenhexamid	*122*	*22*	*27*	*31*	113	12	14	18	0.01	No
GC	Fenitrotion	89	*27*	*31*	29	109	20	20	22	0.01	Yes
GC	Fenoxycarb	96	13	17	14	107	13	13	15	0.005	No
LC	Fenoxycarb	110	10	11	14	114	13	16	19	0.005	No
GC	Fenpropathrin	94	16	20	17	103	18	20	18	0.005	No
LC	Fenpropathrin	102	10	*22*	10	101	16	*21*	16	0.01	No
GC	Fenpropidin	*34*	*368*	*422*	374	95	14	14	15	0.01	Yes
LC	Fenpropidin	97	19	19	19	111	11	15	15	0.005	No
GC	Fenpropimorph	80	15	16	25	92	16	16	18	0.005	Yes
LC	Fenpropimorph	97	19	*21*	19	105	13	15	14	0.01	No
GC	Fenson	96	9	10	10	102	16	16	16	0.005	No
GC	Fenthion	77	15	18	28	97	18	18	19	0.005	Yes
LC	Fenthion	92	16	17	18	92	11	19	14	0.005	No
LC	Fenthion oxon sulfone	115	9	11	17	120	12	19	*23*	0.005	No
LC	Fenthion oxon sulfoxide	112	8	10	14	117	13	18	*21*	0.005	No
LC	Fenthion sulfone	105	13	13	14	106	13	13	14	0.005	No
GC	Fenvalerate I+II	99	9	19	9	104	13	13	14	0.005	No
GC	Fipronil	87	*25*	*29*	29	99	13	20	13	0.01	Yes
LC	Fipronil	108	15	19	18	119	14	17	*23*	0.005	No
GC	Fluazifop-P-butyl	93	11	15	13	104	14	14	15	0.005	No
LC	Fluazifop-p-butyl	107	9	9	11	110	14	16	17	0.005	No
GC	Fludioxonil	99	7	9	7	102	16	16	16	0.005	No
GC	Flufenoxuron	94	18	17	18	98	19	19	19	0.005	No
LC	Flufenoxuron	112	11	17	16	117	16	17	*23*	0.005	No

		Spike level 0.005 mg/kg				Spike level 0.01 mg/kg					
	Compound	**Recovery %**	**RSD_r, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**Recovery %**	**RSD_r, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**LOQ**	**Correction for recov. needed**
LC	Fluoxastrobin	116	10	11	19	116	13	16	*21*	0.005	No
GC	Fluquinconazole	102	7	13	8	105	16	16	17	0.005	No
LC	Fluquinconazole	108	10	13	13	110	13	16	17	0.005	No
GC	Flusilazole	106	19	*27*	20	105	14	14	14	0.005	No
LC	Flusilazole	114	10	13	18	118	13	16	*22*	0.005	No
GC	Flutriafol	92	9	11	12	101	17	17	17	0.005	No
GC	Fluvalinate I+II	109	14	20	16	96	10	20	11	0.005	No
GC	Fosthiazate	107	17	20	18	94	*21*	*21*	22	0.005	No
LC	Fosthiazate	119	12	14	*22*	119	14	19	*23*	0.005	Yes
GC	HCH, alpha	88	12	12	17	93	12	16	14	0.005	No
GC	HCH, beta	93	9	10	12	96	16	16	16	0.005	No
GC	Heptenophos	86	10	19	17	93	14	14	15	0.005	No
LC	Heptenophos	96	19	*21*	19	99	15	18	15	0.005	No
LC	Hexythiazox	118	7	16	19	111	14	19	18	0.005	No
GC	Hexythiozox	92	13	13	15	102	16	17	16	0.005	No
LC	Imazalil	102	10	11	10	103	14	14	15	0.005	No
LC	Imidacloprid	114	8	13	16	117	12	18	*21*	0.005	No
GC	Indoxacarb	104	10	10	11	104	16	18	17	0.005	No
LC	Indoxacarb	116	9	11	19	*121*	17	*22*	*27*	0.005	No
GC	Iodofenfos	81	12	16	22	89	16	16	20	0.005	Yes
LC	Iodosulfuron-methyl	116	8	19	18	118	11	16	*21*	0.005	No
GC	Iprodione	97	15	18	16	93	16	16	18	0.005	No
LC	Iprodione	*122*	8	11	*23*	115	10	10	18	0.01	No
LC	Iprovalicarb	117	9	10	19	120	13	17	*24*	0.005	No
GC	Iprovalicarb I+II	93	15	15	16	107	18	20	20	0.005	No
GC	Isofenphos-methyl	95	9	12	11	104	14	14	14	0.005	No
GC	Isoprothiolane	100	10	11	10	106	17	17	18	0.005	No

		Spike level 0.005 mg/kg				Spike level 0.01 mg/kg					
	Compound	**Recovery %**	**RSD$_r$, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**Recovery %**	**RSD$_r$, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**LOQ**	**Correction for recov. needed**
LC	Isoprothiolane	110	11	11	15	113	12	14	18	0.005	No
LC	Isoproturon	119	7	10	20	117	16	19	*24*	0.005	No
GC	Kresoxim-methyl	97	11	12	11	110	14	14	17	0.005	No
LC	Kresoxim-methyl	104	14	15	15	112	15	16	19	0.005	No
GC	Lindane	76	11	18	27	92	17	17	19	0.005	Yes
GC	Linuron	102	16	16	16	91	15	20	18	0.005	No
LC	Linuron	112	20	19	*23*	109	13	15	16	0.005	Yes
LC	Malaoxon	112	7	12	14	120	13	*21*	*24*	0.005	No
GC	Malathion	78	17	19	28	107	16	16	18	0.005	Yes
LC	Malathion	105	14	15	15	107	13	16	15	0.005	No
GC	Mecarbam	98	18	*33*	18	104	13	18	14	0.005	No
LC	Mecarbam	108	12	11	14	108	12	14	15	0.005	No
LC	Mepanipyrim	111	14	17	18	119	16	16	*25*	0.005	No
LC	Metaflumizone	114	7	11	16	113	13	12	19	0.005	No
GC	Metalaxyl	97	17	17	17	114	18	19	23	0.005	No
LC	Metalaxyl	118	12	16	*22*	119	15	20	*24*	0.005	Yes
LC	Metconazole	112	15	18	19	112	16	16	20	0.005	No
GC	Methacrifos	87	17	18	22	95	16	17	17	0.005	Yes
LC	Methacrifos	103	*25*	*24*	*25*	106	17	16	18	0.01	No
GC	Methamidophos	78	14	*21*	26	75	17	17	31	0.005	Yes
LC	Methamidophos	76	13	19	*27*	83	16	20	*24*	0.005	Yes
GC	Methidathion	98	9	19	10	107	16	17	18	0.005	No
LC	Methiocarb	98	19	17	19	109	17	15	19	0.005	No
LC	Methiocarb sulfone	117	7	9	19	*121*	11	18	*24*	0.005	No
LC	Methiocarb sulfoxide	120	7	12	*21*	117	12	17	20	0.005	Yes
LC	Methoxyfenozide	110	14	13	17	118	*21*	18	27	0.005	No
GC	Metribuzin	94	15	14	16	110	16	17	19	0.005	No

		Spike level 0.005 mg/kg				Spike level 0.01 mg/kg					
	Compound	**Recovery %**	**RSD$_r$, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**Recovery %**	**RSD$_r$, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**LOQ**	**Correction for recov. needed**
LC	Metribuzin	95	14	14	15	99	11	16	11	0.005	No
LC	Metsulfuron-methyl	120	7	7	*21*	111	17	15	20	0.005	Yes
LC	Mevinphos	108	15	15	17	113	10	15	17	0.005	No
LC	Monolinuron	111	14	15	18	115	12	16	19	0.005	No
GC	Myclobutanil	99	8	8	8	107	16	16	17	0.005	No
GC	Nuarimol	97	9	12	9	102	12	12	13	0.005	No
GC	Ofurace	102	6	18	6	106	15	17	16	0.005	No
LC	Ofurace	117	10	15	19	119	12	20	*22*	0.01	Yes
GC	Omethoate	96	16	18	17	83	10		19	0.005	No
LC	Omethoate	87	15	15	20	88	14	17	18	0.005	No
GC	Oxadixyl	102	6	9	6	106	14	14	16	0.005	No
LC	Oxamyl	106	11	15	12	116	16	17	*22*	0.005	No
LC	Oxycarboxin	117	7	10	18	118	11	17	*21*	0.005	No
GC	Paclobutrazol	99	10	20	10	102	14	16	14	0.005	No
LC	Paclobutrazol	104	13	*21*	14	106	19	*22*	20	0.005	No
GC	Parathion	98	14	20	15	102	18	20	18	0.005	No
LC	Parathion-ethyl	83	*42*	*39*	*45*	108	9	15	12	0.01	No
GC	Parathion-methyl	93	11	19	13	106	16	17	17	0.005	No
GC	Penconazole	102	5	13	6	103	16	16	16	0.005	No
LC	Penconazole	116	10	10	19	120	13	15	*24*	0.005	No
GC	Pencycuron	90	11	11	14	100	18	18	18	0.005	No
LC	Pencycuron	111	11	16	16	115	14	18	20	0.005	No
LC	Pendimethalin	103	10	12	11	106	12	15	14	0.005	No
GC	Permethrin I+II	88	18	*21*	22	93	20	20	22	0.005	Yes
GC	Phenthoate	94	13	14	14	102	12	13	13	0.005	No
GC	Phosalone	106	11	17	12	110	13	13	17	0.005	No
GC	Phosmet	84	9	11	18	106	17	19	17	0.005	No

		Spike level 0.005 mg/kg				Spike level 0.01 mg/kg					
	Compound	**Recovery %**	**RSD_r, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**Recovery %**	**RSD_r, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**LOQ**	**Correction for recov. needed**
GC	Phosphamidon	92	15	20	17	96	16	17	16	0.005	No
LC	Phosphamidon	114	8	12	16	*121*	12	19	*24*	0.005	No
LC	Phoxim	101	11	11	11	108	14	16	16	0.005	No
GC	Pirimicarb	95	9	11	11	101	12	12	12	0.005	No
LC	Pirimicarb	111	13	13	17	115	11	15	18	0.005	No
GC	Pirimicarb desmetyl	98	9	11	10	97	17	16	17	0.005	No
GC	Pirimiphos methyl	86	11	14	18	98	20	19	20	0.005	No
LC	Pirimiphos-methyl	96	12	12	13	104	12	15	12	0.005	No
GC	Prochloraz					99	12	14	12	0.010	No
LC	Prochloraz	103	11	19	11	105	12	19	13	0.005	No
GC	Procymidone	97	11	12	12	107	11	11	13	0.005	No
GC	Profenofos	95	15	16	15	95	17	17	18	0.005	No
LC	Propamocarb	85	15	14	*21*	90	18	18	*21*	0.005	Yes
LC	Propargite	115	8	13	17	114	12	19	18	0.005	No
LC	Propiconazole	113	8	10	15	113	13	17	18	0.005	No
GC	Propiconazole I+II	86	18	19	23	91	17	17	19	0.005	Yes
GC	Propoxur	96	8	18	9	97	15	17	15	0.005	No
LC	Propoxur	115	11	16	19	118	10	*22*	*21*	0.005	No
GC	Propyzamide	99	11	11	11	103	13	12	13	0.005	No
LC	Propyzamide	109	12	12	15	114	12	14	18	0.005	No
GC	Prosulfocarb	90	18	18	21	97	12	12	12	0.005	Yes
LC	Prosulfocarb	103	12	13	12	107	13	15	15	0.005	No
LC	Prosulfuron	115	10	12	18	110	16	17	19	0.005	No
LC	Prothioconazole-desthio	108	12	13	14	103	16	17	17	0.005	No
GC	Prothiofos	75	16	20	29	91	13	14	16	0.005	Yes
LC	Pyraclostrobin	113	11	11	17	112	13	16	17	0.005	No
GC	Pyrazophos	101	8	18	8	106	13	17	15	0.005	No

		Spike level 0.005 mg/kg				Spike level 0.01 mg/kg					
	Compound	**Recovery %**	**RSD$_r$, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**Recovery %**	**RSD$_r$, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**LOQ**	**Correction for recov. needed**
GC	Pyridaben	97	13	13	13	101	16	16	16	0.005	No
GC	Pyridaphenthion	98	8	18	8	107	12	18	14	0.005	No
GC	Pyrimethanil	82	9	12	21	89	13	13	17	0.005	Yes
LC	Pyrimethanil	107	17	18	18	107	13	17	15	0.005	No
GC	Pyriproxyfen	89	7	9	13	98	15	15	15	0.005	No
LC	Pyriproxyfen	101	9	10	9	103	14	16	14	0.005	No
GC	Quinoxyfen	83	6	6	18	90	14	14	17	0.005	No
LC	Quinoxyfen	97	11	12	11	101	12	14	12	0.005	No
GC	Simazine	97	11	13	12	100	16	16	16	0.005	No
LC	Simazine	110	7	12	13	117	11	19	20	0.005	No
LC	Spirodiclofen	101	10	11	10	102	15	19	15	0.005	No
LC	Spiroxamine	91	*30*	*30*	*31*	108	11	13	14	0.01	No
GC	Tebuconazole	88	14	*26*	18	99	15	19	15	0.005	No
LC	Tebuconazole	120	7	6	*22*	*127*	13	19	*30*	0.005	Yes
LC	Tebufenozide	115	17	16	*22*	*128*	*30*	*27*	*41*	0.005	Yes
GC	Tebufenpyrad	93	7	15	10	98	12	12	12	0.005	No
LC	Tebufenpyrad	112	9	12	15	115	15	17	*21*	0.005	No
GC	Tecnazene	86	20	20	24	92	15	16	17	0.005	Yes
LC	Teflubenzuron	114	15	16	20	118	14	17	*23*	0.005	No
GC	Tefluthrin	84	10	11	19	92	15	15	17	0.005	No
GC	Tetraconazole	103	18	19	18	103	18	18	18	0.005	No
GC	Tetradifon	91	8	8	12	94	12	12	14	0.005	No
LC	Thiabendazole	111	11	11	16	111	13	18	17	0.005	No
LC	Thiacloprid	114	7	8	15	111	14	18	17	0.005	No
GC	Thiamethoxam	94	16	20	17	111	18	18	21	0.005	No
LC	Thiamethoxam	114	10	11	17	112	11	12	16	0.005	No
GC	Thiometon	*66*	*31*	*44*	46	81	14	14	24	0.01	Yes

		Spike level 0.005 mg/kg				Spike level 0.01 mg/kg					
	Compound	**Recovery %**	**RSD_r, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**Recovery %**	**RSD_r, %**	**RSDR, %**	**Comb. Uncer-tainty (%)**	**LOQ**	**Correction for recov. needed**
GC	Tolclofos-methyl	87	11	12	17	97	13	13	13	0.005	No
LC	Tolclofos-methyl	84	*22*	*23*	*27*	99	16	15	16	0.01	No
GC	Triadimefon	105	12	12	13	111	15	16	18	0.005	No
LC	Triadimefon	*121*	11	11	*24*	116	16	18	*22*	0.005	Yes
LC	Triadimenol	108	15	15	17	112	12	15	17	0.005	No
GC	Triallate	81	12	17	22	89	13	13	17	0.005	Yes
LC	Triallate	101	12	11	12	107	15	17	17	0.005	No
GC	Triazophos	99	8	14	8	108	16	16	18	0.005	No
LC	Triazophos	116	11	10	20	118	11	12	*21*	0.005	No
GC	Trichlorfon	*69*	10	19	33	73	14	*25*	31	0.005	Yes
GC	Tricyclazole	98	17	17	17	103	16	17	16	0.005	No
LC	Tricyclazole	108	7	9	11	110	9	17	13	0.005	No
GC	Trifloxystrobin	99	14	14	14	113	16	16	20	0.005	No
LC	Trifloxystrobin	110	7	7	12	111	12	16	16	0.005	No
LC	Triflumuron	108	9	11	12	107	14	15	16	0.005	No
GC	Trifluralin	79	17	*22*	27	90	12	12	16	0.01	Yes
GC	Triticonazole	105	10	19	11	106	14	16	15	0.005	No
LC	Triticonazole	113	11	13	17	114	13	19	19	0.005	No
LC	Vamidothion	108	9	10	12	111	12	17	16	0.005	No
GC	Vinclozolin	94	9	9	11	99	15	15	16	0.005	No
GC	Zoxamide	99	13	18	13	90	17	*21*	19	0.005	No
LC	Zoxamide	108	11	10	13	112	11	14	16	0.005	No

Appendix 3: Principles of the QuEChERS method for cereal extraction

QuEChERS for cereals (FP417)

Weigh 5 g (±0.05 g) of flour into a 50 ml single use centrifuge tube (red cap). Add internal standard and/or spike standard (maximum 25 µl)

Add a ceramic homogenizer and 10 g of cold water and shake briefly

Add 10 ml acetonitrile and shake vigorously by hand for 1 min. (1. extraction)

Add the prepared mixture of 4 g $MgSO_4$, 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 vigorously 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). When the extract are almost thawed (i.e. About -40 ˚C) centrifugate (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 150 mg PSA and 900 mg $MgSO_4$. Close the tube and shake vigorously for 30 seconds.

Centrifuge for 5 min. at 4500 rpm

Transfer 4 ml of the extract 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.