

# Pesticide analysis in teas and chamomile by liquid chromatography and gas chromatography tandem mass spectrometry

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## 1. Aim and scope

This report describes a validation data of 86 pesticides using a multiresidue method by LC-MS/MS and GC-MS/MS in green tea, red tea, black tea and chamomile.

## 2. Short description

Homogenous sample is extracted with acetonitrile according to modified QuEChERS protocol. The obtained extract is analysed by GC-MS/MS and LC-MS/MS.

## 3. Apparatus and consumables

- Automatic pipettes, suitable for handling volumes of 30  $\mu$ L to 500  $\mu$ L and 1 mL to 3 mL.
- 50 ml PTFE centrifuge tubes with screw caps
- 15 ml PTFE centrifuge tubes with screw caps
- Vortex
- Automatic axial extractor
- Centrifuge, suitable for the centrifuge tubes employed in the procedure and capable of achieving at least 3700 rpm
- Concentration workstation
- Syringes, e.g. 2 mL disposable syringes
- Syringe filters, 0.45  $\mu$ m pore size
- Injection vials, 2 ml, suitable for LC and GC auto-sampler
- Volumetric flasks
- Primary secondary amine bonded silica (PSA), bulk material

## 4. Chemicals

- Acetonitrile ultra-gradient grade
- Formic acid
- Trisodium citrate dihydrate
- Sodium chloride
- Disodium hydrogencitrate sesquihydrate
- Calcium chloride
- Anhydrous magnesium sulphate
- Ultra-pure water
- Ethyl acetate HPLC grade
- Pesticides standards

## 5. Procedure

### 5.1. Sample preparation

To obtain representative subsamples, samples should be frozen overnight and after that minced.

### 5.2. Recovery experiments for method validation

The samples employed in validation studies did not contain any of the pesticides analysed.

Individual pesticide stock solutions (1000–2000 mg/L) were prepared in acetonitrile and ethyl acetate and were stored in amber screw-capped glass vials in the dark at -20 °C.

For spiking, 15 g representative portions of previously homogenised tea/chamomile were weighed and transferred to a crystalliser, where they were fortified homogenously with 15 mL of the working standard solution in methanol.

The validation method was performed at four fortification levels (0.010 mg/Kg, 0.025 mg/Kg, 0.050 mg/Kg and 0.100 mg/Kg). Five replicates were analysed at each level.

### 5.3. Extraction

1. Weigh 2 g  $\pm$  0.1 g of sample in 50 mL PTFE centrifuge tube.
2. Add 4 mL of ultra-pure water, shake in a vortex 30 s and leave for 30 minutes.
3. Add 10 mL of acetonitrile and 200  $\mu$ L of 25 mg/L triphenyl phosphate (TPP, internal surrogate standard)
4. Shake in automatic axial extractor for 7 minutes.
5. Add 4 g of magnesium sulphate, 1 g of sodium chloride, 1 g of trisodiumcitrate dehydrate and 0.5 g of disodium hydrogencitrate sesquihydrate.
6. Shake in automatic axial extractor for 7 minutes.
7. Centrifuge for 5 min at 3700 rpm.
8. Transfer 3 mL of supernatant into 15 mL PTFE centrifuge tube containing 150 mg of PSA and 150 mg of calcium chloride and shake in a vortex 30 s.
9. Centrifuge for 5 min at 3700 rpm.
10. Add to the extract 30  $\mu$ L of 5% formic acid in acetonitrile.
11. Evaporate an aliquot under gentle stream of nitrogen and reconstitute:
  - a. for LC analysis with acetonitrile:water (10:90 v/v) and filter the sample thorough 0.45  $\mu$ m PTFE filter

b. for GC analysis with ethyl acetate.

With this treatment, 1 mL of sample extract represents 0.2 g of sample.

#### 5.4. Measurement

Both LC and GC systems were operated in multiple reaction monitoring mode (MRM). Selected reaction monitoring (SRM) experiments were carried out to obtain the maximum sensitivity for the detection of the target molecules. For confirmation of the studied compounds, two SRM transitions and a correct ratio between the abundances of the two optimised SRM transitions (SRM2/SRM1) were used, along with retention time matching. The mass transitions used are presented in Appendix I.

#### 5.5. Instrumentation and analytical conditions for the LC- MS/MS system

##### 5.5.1. Agilent 1200 HPLC

- Column: Agilent Zorbax SB, C8, 4.6 mm x 150 mm x 5 µm
- Mobile phase A: acetonitrile
- Mobile phase B: 0.1% formic acid in ultra-pure water
- Flow rate: 0.6 mL/min
- Injection volume: 10 µL

Mobile phase gradient for pesticides analyse in positive mode

Time [min]	Mobile phase A	Mobile phase B
0	30%	70%
3	30%	70%
5	50%	50%
21	100%	0%
24	100%	0%

Re-equilibration with initial mobile phase: 7 minutes.

Mobile phase gradient for pesticides analyse in negative mode

Time [min]	Mobile phase A	Mobile phase B
0	60%	40%
3	60%	40%
6	80%	20%
8	100%	0%
11	100%	0%

Re-equilibration with initial mobile phase: 7 minutes.

### 5.5.2. Agilent 6410 QqQ MS/MS

- ESI source gas temperature: 300 °C
- Gas flow: 9 L/min
- Nebuliser gas: nitrogen
- Nebuliser gas pressure: 40 psi
- Capillary voltage in positive mode: 4000 V
- Capillary voltage in negative mode: -4000 V
- Collision gas: nitrogen

## 5.6. Instrumentation and analytical conditions for the GC- MS/MS system

### 5.6.1. Agilent 7890

- Column: HP-5MS UI 15 m × 0.25 mm × 0.25 µm
- Retention Time Locking compound: trifluralin (retention time 5.81 min)
- Injection mode: splitless
- Ultra inert inlet liner, with a glass wool frit from Agilent
- Injection volume: 2 µl
- Injector temperature:

Time [min]	Temperature	
0	80 °C	solvent evaporation
0.1	80 °C	
0.6	300 °C	
20	300 °C	

- Carrier gas: helium
- Carrier gas purity: 99.999%
- Carrier gas pressure: constant, 14.194 psi
- Quenching gas: helium
- Oven temperature: 70°C for 1 min, programmed to 150°C at 50°C/min, then to 200°C at 6°C/min and finally to 280°C at 16°C/min (4.07 min). The total run time was 20 minutes with 3 additional minutes for backflushing at 280°C.

### 5.6.2. Agilent 7000 QqQ MS/MS

- Ionisation mode: electron impact ionisation
- Temperature of the transfer line: 280 °C
- Temperature of ion source: 280 °C
- Temperature of quadrupole 1 and 2: 150 °C
- Collision gas: nitrogen
- Collision gas purity: 99.999%
- Solvent delay: 2 minutes

## 6. Validation of the method

### 6.1. Recoveries and within-laboratory reproducibility

The results corresponding to the mean recovery (n=5) and within-laboratory reproducibility in terms of relative standard deviation (RSD) at both fortification levels are summarized in Appendix II.

### 6.2. Limits of quantitation

Document N° SANCO/12495/2011 defines limit of quantitation as the lowest validated spike level meeting the method performance acceptability criteria. Due to the high complexity of the matrices and considering the good repeatability of the method, we accepted those recoveries in the range 60–140%, which is the range proposed by the guideline for routine analysis working with multiresidue methods. LOQs are summarized in Appendix II.

### 6.3. Limits of detection

The analytical limit of detection (LOD) for each pesticide was determined as the minimum concentration of analyte providing a spectrum in which the qualifier selected reaction monitoring (SRM2) transition had a signal-to-noise ratio (S/N) of 3. LODs are summarized in Appendix II.

### 6.4. Linearity

Linearity of the (QqQ)MS systems was evaluated by assessing the signal responses of the target analytes from matrix-matched calibration solutions prepared by spiking blank extracts at seven concentration levels, from 0.5 to 200 µg/L, which correspond in the sample to 2.5 to 1000 µg/kg given the 5-times dilution factor. In almost all cases, coefficient of determination ( $r^2$ ) was higher than 0.99. Linearity ranges for all pesticides in all matrices are summarized in Appendix II.

### 6.5. Matrix effects

Matrix effects were assessed by comparison of the slopes of seven-point matrix-matched calibration curves with the slopes of the calibration curves in solvent. Values of matrix effects are summarized in Appendix II.

This report aims to provide information to laboratories that analyse pesticide residues in green tea, red tea, black tea and chamomile or are interested in it.

## 7. References

- **Pesticide analysis in teas and chamomile by liquid chromatography and gas chromatography tandem mass spectrometry using a modified QuEChERS method: Validation and pilot survey in real samples** Ana Lozano, Łukasz Rajski, Noelia Belmonte-Valles, Ana Uclés, Samanta Uclés, Milagros Mezcua, Amadeo R. Fernández-Alba; 2012, Journal of Chromatography A, 1268, 109- 122
- **Comparison of three multiresidue methods to analyse pesticides in green tea with liquid and gas chromatography/tandem mass spectrometry** Łukasz Rajski, Ana Lozano, Noelia Belmonte-Valles, Ana Uclés, Samanta Uclés, Milagros Mezcua and Amadeo R. Fernandez-Alba; 2013, Analyst, 138, 921-931
- **Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed** (Document N° SANCO/12495/2011)
- <http://www.eurl-pesticides.eu>

## APPENDIX I: MASS TRANSITIONS

Table 1. Detection and chromatographic parameters for the selected compounds analysed by LC-MS/MS.

Compound	Rt (min)	Fragmentor (V)	SRM1	CE 1 (V)	SRM2	CE 2 (V)	Ionization mode
Acetamiprid	6.5	120	223.0 / 126.0	20	223.0 / 56.0	15	ESI (+)
Atrazine	10.8	120	216.0 / 174.0	15	216.0 / 146.0	20	ESI (+)
Azoxystrobin	13.2	120	404.0 / 372.0	10	404.0 / 344.0	20	ESI (+)
Buprofezin	16.9	120	306.0 / 201.0	10	306.0 / 116.0	15	ESI (+)
Carbaryl	10.6	140	202.0 / 145.0	10	202.0 / 127.0	20	ESI (+)
Carbendazim	2.8	150	192.0 / 160.0	15	192.0 / 132.0	20	ESI (+)
Carbofuran	10.3	90	222.0 / 123.0	20	222.0 / 165.0	10	ESI (+)
Dimethoate	6.6	90	230.0 / 199.0	5	230.0 / 171.0	10	ESI (+)
Imazalil	8.4	150	297.0 / 159.0	20	297.0 / 255.0	15	ESI (+)
Imidacloprid	5.8	90	256.0 / 175.0	15	256.0 / 209.0	15	ESI (+)
Metalaxyl	10.8	120	280.0 / 220.3	5	280.0 / 192.4	10	ESI (+)
Methiocarb Sulfone	8.2	120	258.0 / 122.0	15	258.0 / 201.1	5	ESI (+)



Compound	Rt (min)	Fragmentor (V)	SRM1	CE 1 (V)	SRM2	CE 2 (V)	Ionization mode
Methiocarb Sulfoxide	4.3	90	242.0 / 185.0	10	242.0 / 170.0	20	ESI (+)
Methiocarb	12.8	90	226.0 / 169.0	5	226.0 / 121.0	20	ESI (+)
Metolachlor	14.9	120	284.0 / 252.0	10	284.0 / 176.0	20	ESI (+)
Methomyl	4.1	60	163.2 / 88.1	20	163.2 / 106.2	20	ESI (+)
Metribuzin	9.8	120	215.2 / 187.2	15	215.2 / 171.2	20	ESI (+)
Monocrotophos	3.2	60	224.0 / 127.0	10	224.0 / 193.0	5	ESI (+)
Myclobutanil	13.4	150	289.2 / 70.2	15	289.2 / 125.1	20	ESI (+)
Omethoate	2.9	90	214.1 / 125.0	20	214.1 / 183.0	5	ESI (+)
Pirimicarb	4.0	150	239.2 / 72.2	20	239.2 / 182.1	15	ESI (+)
Pirimiphos methyl	17.0	150	306.2 / 164.2	20	306.2 / 108.2	20	ESI (+)
Profenofos	17.9	120	373.0 / 302.9	15	373.0 / 344.9	5	ESI (+)
Simazine	9.1	120	202.0 / 132.0	20	202.0 / 124.0	20	ESI (+)
Terbutylazine	12.8	120	230.2 / 174.2	15	230.2 / 132.1	20	ESI (+)
Thiodicarb	9.3	60	355.1 / 108.1	10	355.1 / 163.1	5	ESI (+)
Triadimefon	13.9	150	294.2 / 197.1	10	294.2 / 225.0	10	ESI (+)
Triadimenol	12.2	60	296.2 / 70.2	10	296.2 / 227.0	5	ESI (+)
TPP	16.2	120	327.0 / 77.2	35	327.0 / 152.2	30	ESI (+)
2,4-DP	6.2	90	233.1 / 161.1	5	233.1 / 152.2	20	ESI (-)
2,4 D	5.3	90	218.9 / 160.9	15	220.8 / 162.9	5	ESI (-)
MCPP	6.2	90	213.0 / 141.1	10	213.0 / 70.8	15	ESI (-)

Table 2. Acquisition and chromatographic parameters for the selected compounds analysed by GC-MS/MS.

Pesticide	Rt (min)	Time Segment	SRM1	CE1 (V)	SRM2	CE2 (V)	SRM3	CE3(V)
Alachlor	8.58	2	188 / 160	10	188 / 130	40		
Benalaxyl	13.46	3	148 / 105	20	204 / 176	2		
Bifenthrin	14.45	4	181 / 166	10	181 / 115	50		
Biphenyl	3.56	1	154 / 102	40	154 / 126	40		
Boscalid	16.53	4	140 / 112	10	140 / 76	25		
Chinomethionat	11.18	2	234 / 206	10	206 / 148	15		
Chlorpyrifos	9.73	2	313 / 258	15	313 / 286	5		
Chlorpyrifos Methyl	8.36	2	288 / 93	26	286 / 271	16		
Cypermethrin	16.45-16.62	4	163 / 127	5	209 / 141	20	181 / 152	25
Cyproconazole	12.67	3	139 / 111	14	222 / 125	14		
Cyprodinil	10.53	2	224 / 208	20	224 / 197	21		
Diazinon	7.22	1	304 / 179	15	304 / 137	30		
Dichlofluanid	9.37	2	224 / 123	8	167 / 124	5		
Dichlorvos	2.94	1	185 / 93	15	185 / 109	15		
Dicloran	6.44	1	206 / 176	5	208 / 148	20	206 / 124	22
Endosulfan I	11.38	2	239 / 204	15	241 / 206	25		
Endosulfan II	12.74	3	241 / 206	14	239 / 204	15		
Endosulfan sulfate	13.54	3	387 / 289	5	387 / 206	40		
Ethion	13.05	3	231 / 129	25	231 / 175	5		
Ethoprophos	5.41	1	158 / 97	15	158 / 114	5		
Etofenprox	16.66	4	163 / 107	15	163 / 135	5		
Fenarimol	15.33	4	139 / 111	15	219 / 107	10		
Fenitrothion	9.27	2	277 / 260	5	277 / 109	20		
Fenpropathrin	14.55	4	181 / 152	26	265 / 210	10		

Pesticide	Rt (min)	Time Segment	SRM1	CE1 (V)	SRM2	CE2 (V)	SRM3	CE3(V)
Fenvalerate/Esfenvalerate RR/SS	17.50	4	167 / 125	12	125 / 89	22		
Fenvalerate/Esfenvalerate SR/RS	17.29	4	167 / 125	12	125 / 89	22		
Flucythrinate	16.6-16.8	4	199 / 157	5	157 / 107	15		
Fludioxonil	12.46	3	248 / 127	30	248 / 154	25		
Fonofos	6.96	1	137 / 109	5	246 / 137	5		
Iprodione	14.35	4	314 / 56	20	314 / 245	10		
Isocarbophos	10.12	2	136 / 108	14	230 / 212	8		
Isofenphos Methyl	10.48	2	199 / 121	10	199 / 167	10		
Kresoxim Methyl	12.52	3	206 / 116	5	206 / 131	10		
Lindane	6.79	1	219 / 183	5	181 / 145	12		
Malathion	9.55	2	173 / 99	15	158 / 125	8		
Methidathion	11.32	2	145 / 85	5	145 / 58	15		
Mevinphos	3.85	1	127 / 109	10	127 / 95	15		
Oxadixyl	13.15	3	163 / 132	15	163 / 117	25		
Parathion Ethyl	9.82	2	291 / 109	10	291 / 81	10		
Parathion Methyl	8.44	2	263 / 109	10	233 / 124	10		
Penconazole	10.74	2	248 / 157	25	248 / 192	15		
Permethrin	15.58-15.8	4	163 / 127	5	183 / 153	15		
Phorate	5.97	1	231 / 129	20	231 / 175	20		
Phosmet	14.40	4	160 / 77	30	160 / 133	15		
Propargite	13.91	3	135 / 107	15	135 / 77	25		
Propyzamide	7.07	1	173 / 145	16	173 / 109	32		
Pyridaben	15.84	4	147 / 117	20	147 / 132	10		
Pyrimethanil	7.19	1	198 / 118	25	198 / 156	25		
Pyriproxyfen	14.99	4	136 / 78	18	136 / 96	8		
Quinalphos	10.96	2	146 / 91	30	157 / 129	15		
Terbufos	6.88	1	231 / 129	25	231 / 175	10		
Tetrachlorvinphos	11.64	2	329 / 109	25	329 / 79	35		
TPP	13.96	3	326 / 233	10	326 / 169	35		
Triazophos	13.38	3	161 / 134	5	161 / 106	10		
Trifluralin	5.80	1	306 / 264	10	264 / 160	15		
Vinclozolin	8.41	2	212 / 172	15	212 / 109	40		

**APPENDIX II: VALIDATION RESULTS**

Table 3. Recoveries % (RSD) at 10, 25, 50 and 100 µg/kg (n=5) in the four matrices.

Compound	Green Tea				Red Tea				Black Tea				Chamomille			
	10 µg/kg	25 µg/kg	50 µg/kg	100 µg/kg	10 µg/kg	25 µg/kg	50 µg/kg	100 µg/kg	10 µg/kg	25 µg/kg	50 µg/kg	100 µg/kg	10 µg/kg	25 µg/kg	50 µg/kg	100 µg/kg
2,4-D <sup>a</sup>	41.7 (16)	42.6 (18)	47.3 (15)	49.4 (18)	<LOD	32.2 (9)	39.5 (8)	42.9 (6)	55.7 (13)	52.2 (10)	52.1 (11)	51.5 (10)	49.8 (17)	40.4 (10)	42.5 (11)	43.7 (18)
2,4-DP <sup>a</sup>	55.5 (10)	57.8 (13)	58.2 (14)	61.1 (11)	<LOD	43.7 (3)	55.3 (6)	59.6 (7)	62.0 (11)	62.7 (5)	59.8 (15)	56.2 (16)	49.2 (15)	61.0 (9)	55.2 (10)	38.3 (8)
Acetamiprid <sup>a</sup>	104.9 (13)	119.4 (16)	96.8 (7)	89.7 (3)	88.7 (10)	92.0 (5)	92.8 (7)	93.1 (5)	81.2 (18)	77.6 (17)	99.1 (17)	112.4 (13)	98.3 (9)	115.8 (4)	101.7 (6)	105.7 (7)
Alachlor <sup>b</sup>	<LOD	93.7 (8)	88.3 (8)	76.1 (9)	69.2 (8)	72.8 (3)	84.9 (10)	81.3 (9)	<LOD	72.4 (3)	92.1 (7)	91.3 (5)	<LOD	65.8 (4)	83.9 (8)	88.4 (9)
Atrazine <sup>a</sup>	88.3 (7)	93.0 (4)	86.4 (6)	80.6 (5)	75.1 (14)	81.3 (5)	84.8 (5)	79.4 (3)	73.3 (12)	68.7 (1)	71.1 (2)	75.1 (12)	82.5 (12)	111.8 (5)	78.6 (9)	74.7 (10)
Azoxystrobin <sup>a</sup>	71.5 (7)	72.4 (9)	76.3 (6)	81.0 (4)	80.0 (9)	83.1 (4)	84.8 (3)	75.9 (1)	79.2 (9)	72.2 (4)	75.2 (7)	62.8 (11)	108.3 (6)	103.3 (3)	75.9 (10)	79.3 (19)
Benalaxyl <sup>b</sup>	<LOD	87.3 (3)	86.7 (8)	84.7 (7)	<LOD	<LOD	<LOD	76.5 (5)	<LOD	<LOD	<LOD	87.9 (3)	<LOD	<LOD	<LOD	<LOD
Bifenthrin <sup>b</sup>	97.4 (13)	112.0 (16)	99.4 (12)	101.4 (10)	92.3 (6)	107.1 (1)	108.3 (3)	98.6 (2)	97.2 (8)	102.7 (5)	95.4 (4)	98.9 (2)	112.3 (16)	115.1 (18)	105.4 (13)	109.2 (14)
Biphenyl <sup>b</sup>	88.3 (15)	91.4 (14)	92.5 (13)	95.2 (11)	75.8 (10)	81.1 (10)	87.7 (8)	84.8 (8)	79.3 (10)	88.1 (4)	95.3 (2)	91.2 (2)	91.9 (8)	96.4 (4)	97.8 (4)	92.6 (3)
Boscalid <sup>b</sup>	<LOD	<LOD	<LOD	119.2 (19)	66.6 (7)	70.0 (5)	73.9 (5)	78.9 (4)	79.3 (7)	73.7 (8)	92.9 (5)	90.0 (4)	72.1 (6)	72.6 (2)	77.4 (4)	84.5 (5)
Buprofezin <sup>a</sup>	101.3 (7)	105.2 (3)	104.7 (5)	102.2 (3)	78.9 (8)	85.2 (5)	90.0 (5)	90.3 (3)	81.9 (18)	73.1 (18)	82.9 (10)	80.8 (11)	45.2 (11)	37.5 (7)	40.4 (11)	48.0 (11)
Carbaryl <sup>a</sup>	96.5 (8)	98.7(4)	93.0 (7)	81.5 (10)	86.7 (10)	90.4 (6)	93.4 (3)	95.8 (2)	82.4 (11)	85.5 (8)	89.8 (9)	92.9 (9)	108.8 (18)	115.6 (8)	98.8 (14)	99.6 (14)
Carbendazim <sup>a</sup>	46.2 (15)	50.9 (16)	53.3 (13)	56.9 (17)	58.2 (9)	61.3 (3)	63.9 (6)	68.8 (8)	49.1 (16)	48.2 (6)	48.3 (7)	49.6 (7)	95.1 (11)	90.7 (3)	91.8 (10)	96.6 (9)
Carbofuran <sup>a</sup>	97.4 (8)	100.0 (6)	95.4 (9)	83.4 (8)	101.1 (15)	103.4 (10)	105.8 (18)	106.5 (16)	91.2 (9)	94.0 (3)	93.5 (5)	101.1 (9)	102.7 (10)	130.5 (2)	115.8 (4)	111.9 (2)
Chinomethionat <sup>b</sup>	<LOD	68.2 (12)	67.2 (9)	70.0 (7)	<LOD	73.7 (3)	71.2 (3)	39.6 (11)	<LOD	59.0 (5)	60.1 (5)	61.0 (2)	72.9 (19)	57.7 (3)	74.3 (6)	73.3 (6)
Chlorpyrifos <sup>b</sup>	86.3 (5)	91.9 (2)	88.4 (6)	86.9 (7)	62.9 (6)	68.2 (2)	72.8 (4)	81.4 (3)	70.4 (13)	74.1 (5)	88.6 (5)	84.0 (2)	81.3 (8)	78.5 (5)	82.1 (6)	87.1 (6)
Chlorpyrifos Methyl <sup>b</sup>	<LOD	89.4 (3)	90.1 (9)	82.4 (8)	<LOD	73.2 (9)	71.5 (7)	83.6 (3)	<LOD	76.4 (3)	79.8 (3)	82.4 (1)	77.3 (10)	73.4 (3)	83.6 (6)	80.9 (6)
Cypermethrin <sup>b</sup>	<LOD	<LOD	78.9 (6)	87.3 (5)	<LOD	<LOD	85.2 (14)	98.4 (7)	<LOD	<LOD	91.2 (8)	99.9 (6)	<LOD	<LOD	<LOD	101.3 (2)
Cyproconazole <sup>b</sup>	<LOD	<LOD	76.5 (9)	81.6 (10)	<LOD	69.1 (2)	79.3 (6)	82.9 (4)	<LOD	<LOD	73.9 (7)	81.0 (2)	<LOD	74.4 (1)	88.0 (3)	91.2 (3)
Cyprodinil <sup>b</sup>	70.1 (16)	72.7 (18)	80.2 (16)	84.7 (15)	60.8 (4)	65.4 (3)	72.7 (8)	76.0 (4)	71.4 (14)	68.2 (3)	77.1 (3)	78.8 (2)	79.2 (8)	75.0 (2)	83.1 (5)	86.0 (7)
Diazinon <sup>b</sup>	<LOD	85.7 (19)	83.7 (16)	93.9 (15)	<LOD	74.2 (4)	83.0 (3)	83.9 (3)	69.1 (10)	72.8 (5)	82.1 (3)	86.7 (2)	69.3 (7)	72.7 (3)	75.9 (5)	85.8 (6)
Dichlofluanid <sup>b</sup>	<LOD	<LOD	<LOD	49.4 (8)	<LOD	<LOD	66.1 (18)	65.7 (20)	<LOD	109.5 (4)	88.2 (5)	82.5 (4)	<LOD	<LOD	<LOD	65.5 (7)
Dichlorvos <sup>b</sup>	76.4 (5)	78.8 (3)	77.1 (5)	71.6 (9)	62.7 (8)	67.9 (4)	63.7 (4)	76.1 (3)	61.2 (5)	71.6 (3)	81.9 (4)	80.7 (3)	69.2 (13)	64.5 (5)	72.3 (11)	70.4 (11)
Dicloran <sup>b</sup>	<LOD	<LOD	84.5 (11)	81.7 (7)	<LOD	<LOD	81.9 (8)	85.7 (5)	<LOD	<LOD	71.0 (5)	76.2 (4)	<LOD	<LOD	76.3 (15)	81.7 (11)
Dimethoate <sup>a</sup>	91.7 (6)	101.1 (2)	89.4 (4)	85.0 (5)	87.3 (6)	92.9 (4)	96.9 (3)	96.1 (4)	103.7 (17)	92.3 (8)	105.9 (9)	109.4 (8)	103.5 (8)	113.9 (6)	110.7 (5)	109.7 (5)
Endosulfan I <sup>b</sup>	82.2 (7)	85.3 (4)	83.8 (7)	79.6 (8)	67.4 (12)	68.5 (11)	72.4 (8)	75.7 (2)	63.9 (8)	68.4 (2)	84.5 (4)	87.8 (4)	79.2 (9)	70.8 (3)	72.1 (4)	83.5 (3)
Endosulfan II <sup>b</sup>	<LOD	83.8 (5)	87.2 (7)	85.3 (6)	<LOD	69.0 (10)	72.8 (7)	76.6 (5)	<LOD	68.5 (6)	74.8 (4)	76.2 (4)	<LOD	78.1 (13)	83.6 (8)	85.9 (6)

Compound	Green Tea				Red Tea				Black Tea				Chamomille			
	10 µg/kg	25 µg/kg	50 µg/kg	100 µg/kg	10 µg/kg	25 µg/kg	50 µg/kg	100 µg/kg	10 µg/kg	25 µg/kg	50 µg/kg	100 µg/kg	10 µg/kg	25 µg/kg	50 µg/kg	100 µg/kg
Endosulfan sulfate <sup>b</sup>	100.7 (6)	107.1 (5)	94.9 (5)	99.2 (3)	102.3 (8)	108.4 (6)	101.7 (5)	107.9 (6)	117.1 (16)	110.7 (15)	113.8 (13)	112.3 (9)	107.4 (17)	116.2 (13)	110.0 (9)	109.4 (9)
Ethion <sup>b</sup>	77.4 (8)	82.7 (2)	79.1 (6)	81.0 (9)	72.1 (9)	73.8 (6)	75.7 (5)	79.9 (2)	88.5 (9)	79.5 (2)	80.7 (3)	82.0 (3)	<LOD	73.8 (2)	81.2 (8)	81.9 (7)
Ethoprophos <sup>b</sup>	83.7 (7)	89.5 (5)	85.4 (9)	83.3 (7)	<LOD	74.0 (2)	81.3 (4)	83.3 (3)	89.2 (10)	73.5 (2)	83.2 (1)	85.5 (2)	83.9 (12)	73.2 (1)	76.9 (6)	84.1 (5)
Etofenprox <sup>b</sup>	78.2 (9)	89.9 (5)	81.6 (10)	79.1 (8)	70.9 (5)	75.1 (2)	80.2 (5)	79.8 (3)	<LOD	69.8 (3)	68.1 (3)	82.9 (4)	<LOD	77.4 (3)	76.2 (4)	87.3 (4)
Fenarimol <sup>b</sup>	79.5 (7)	83.4 (8)	89.3 (13)	92.7 (15)	68.5 (8)	72.9 (8)	79.3 (6)	78.8 (3)	78.3 (8)	73.7 (5)	79.9 (3)	82.7 (3)	83.2 (9)	77.6 (3)	86.8 (3)	84.4 (5)
Fenitrothion <sup>b</sup>	96.7 (7)	99.2 (4)	83.8 (5)	80.9 (8)	60.1 (19)	64.3 (15)	61.3 (11)	53.0 (5)	76.9 (7)	73.8 (1)	74.3 (3)	79.9 (3)	79.3 (8)	70.7 (2)	71.6 (7)	77.5 (11)
Fenpropathrin <sup>b</sup>	94.6 (9)	108.0 (7)	91.5 (10)	87.8 (10)	59.6 (13)	65.4 (6)	72.4 (7)	77.1 (5)	97.4 (12)	88.2 (7)	91.1 (6)	90.0 (4)	72.1 (15)	51.6 (4)	78.1 (6)	84.2 (6)
Fenvalerate/ Esfenvalerate RR/SS <sup>b</sup>	90.2 (11)	96.8 (8)	92.0 (8)	93.5 (6)	<LOD	97.2 (9)	97.2 (7)	101.6 (6)	<LOD	100.5 (5)	91.1 (6)	88.3 (5)	<LOD	78.8 (12)	91.7 (5)	93.5 (6)
Fenvalerate/ Esfenvalerate SR/RS <sup>b</sup>	84.3 (9)	90.5 (8)	92.4 (5)	87.4 (8)	<LOD	95.1 (7)	97.8 (7)	98.5 (4)	98.3 (17)	101.2 (7)	90.0 (8)	91.9 (8)	<LOD	69.8 (10)	89.8 (7)	87.4 (8)
Flucythrinate <sup>b</sup>	85.9 (8)	88.2 (6)	85.7 (8)	78.3 (7)	77.6 (18)	80.6 (14)	81.2 (5)	83.7 (1)	79.5 (14)	72.6 (12)	73.2 (9)	79.4 (3)	77.3 (10)	69.1 (2)	72.2 (4)	80.8 (8)
Fludioxonil <sup>b</sup>	86.6 (12)	90.2 (7)	93.8 (12)	82.5 (7)	65.5 (7)	70.7 (3)	78.9 (3)	80.1 (2)	78.9 (8)	70.1 (4)	72.7 (4)	76.2 (2)	<LOD	72.2 (2)	77.5 (4)	83.4 (6)
Fonofos <sup>b</sup>	<LOD	<LOD	<LOD	98.8 (14)	<LOD	<LOD	<LOD	78.6 (9)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	90.0 (6)
Imazalil <sup>a</sup>	73.8 (6)	96.0 (7)	73.8 (8)	71.4 (5)	82.1 (19)	85.6 (19)	77.2 (15)	79.5 (12)	59.3 (18)	65.5 (17)	74.3 (14)	72.0 (10)	117.6 (13)	113.9 (4)	103.8 (12)	106.3 (15)
Imidacloprid <sup>a</sup>	85.6 (9)	106.7 (14)	88.4 (13)	73.8 (6)	96.8 (6)	99.9 (4)	100.0 (4)	101.0 (5)	<LOD	51.0 (16)	78.4 (11)	81.7 (10)	<LOD	119.6 (8)	118.1 (12)	117.8 (12)
Iprodione <sup>b</sup>	83.4 (9)	87.7 (5)	85.1 (8)	82.0 (8)	72.4 (10)	77.0 (7)	75.2 (5)	78.7 (4)	63.8 (13)	72.4 (3)	75.9 (5)	78.5 (3)	79.3 (13)	72.5 (3)	78.1 (9)	77.8 (8)
Isocarbophos <sup>b</sup>	<LOD	64.6 (11)	72.7 (10)	87.9 (8)	<LOD	<LOD	71.6 (16)	74.4 (11)	<LOD	<LOD	78.3 (6)	86.0 (1)	<LOD	81.9 (5)	82.1 (7)	81.4 (5)
Isofenphos Methyl <sup>b</sup>	85.7 (10)	90.0 (3)	89.6 (3)	82.5 (8)	71.4 (8)	72.3 (2)	79.7 (8)	81.8 (4)	81.2 (7)	73.1 (3)	78.7 (3)	83.6 (3)	<LOD	<LOD	<LOD	83.4 (6)
Kresoxim Methyl <sup>b</sup>	<LOD	86.2 (3)	86.9 (5)	80.4 (8)	67.7 (13)	70.8 (8)	87.3 (8)	83.3 (3)	78.9 (12)	73.7 (1)	81.3 (5)	84.7 (2)	<LOD	71.7 (3)	79.6 (4)	88.4 (6)
Lindane <sup>b</sup>	84.3 (7)	88.5 (4)	82.6 (4)	83.9 (8)	65.8 (7)	69.3 (5)	82.9 (7)	81.4 (4)	88.4 (5)	78.7 (1)	76.2 (6)	83.0 (5)	<LOD	71.6 (3)	82.9 (6)	84.6 (4)
Malathion <sup>b</sup>	95.0 (8)	101.1 (3)	94.7 (2)	81.8 (7)	72.6 (8)	74.4 (5)	79.9 (3)	83.2 (3)	72.8 (10)	77.8 (4)	86.1 (4)	84.9 (3)	<LOD	<LOD	89.3 (12)	84.7 (6)
MCPP <sup>a</sup>	<LOD	89.0 (2)	59.2 (4)	64.2 (9)	<LOD	45.9 (6)	42.9 (15)	59.4 (12)	<LOD	65.9 (10)	52.8 (12)	57.4 (15)	<LOD	66.3 (10)	41.3 (11)	39.7 (7)
Metalaxyl <sup>a</sup>	82.1 (6)	88.3 (4)	83.8 (8)	79.6 (6)	84.7 (9)	86.1 (4)	89.0 (9)	93.5 (4)	76.1 (14)	80.9 (2)	81.8 (11)	82.0 (11)	109.3 (14)	102.7 (1)	92.1 (8)	95.2 (9)
Methidathion <sup>b</sup>	94.6 (9)	100.6 (5)	97.3 (3)	85.4 (10)	70.6 (11)	73.8 (7)	74.7 (7)	84.3 (4)	76.1 (8)	72.2 (3)	78.9 (3)	83.1 (2)	82.9 (10)	70.1 (3)	79.9 (12)	77.4 (10)
Methiocarb sulfone <sup>a</sup>	84.6 (7)	93.1 (6)	82.8 (10)	79.0 (8)	86.9 (9)	90.0 (8)	98.3 (8)	96.3 (4)	89.4 (9)	82.7 (5)	85.7 (6)	81.5 (3)	117.9 (8)	113.8 (3)	105.3 (5)	103.4 (4)
Methiocarb sulfoxide <sup>a</sup>	99.2 (5)	105.3 (3)	85.3 (7)	81.6 (9)	76.3 (19)	78.4 (16)	83.6 (18)	87.4 (11)	65.4 (17)	77.5 (9)	81.9 (9)	83.4 (6)	98.3 (15)	105.9 (9)	92.8 (5)	97.5 (6)
Methiocarb <sup>a</sup>	86.4 (6)	95.8 (5)	86.9 (6)	88.1 (3)	89.3 (9)	91.6 (6)	94.1 (5)	94.5 (5)	<LOD	60.1 (10)	70.4 (8)	71.6 (10)	97.2 (7)	104.6 (2)	101.9 (2)	96.7 (1)
Methomyl <sup>a</sup>	85.7 (9)	107.0 (8)	88.6 (9)	86.1 (7)	87.4 (13)	91.3 (9)	92.9 (8)	94.1 (7)	73.2 (13)	87.3 (8)	92.2 (7)	120.0 (5)	114.6 (7)	115.9 (4)	110.8 (4)	114.3 (1)
Metolachlor <sup>a</sup>	93.3 (8)	92.5 (6)	79.7 (8)	81.3 (6)	76.8 (5)	80.0 (3)	77.2 (10)	80.2 (5)	69.1 (8)	62.1 (2)	67.2 (5)	73.5 (19)	85.9 (12)	93.4 (6)	75.7 (7)	66.8 (10)
Metribuzin <sup>a</sup>	91.5 (7)	101.1 (2)	85.9 (5)	80.5 (4)	84.7 (9)	87.2 (5)	88.3 (8)	93.3 (5)	63.8 (10)	76.2 (3)	78.6 (4)	81.3 (8)	114.5 (16)	119.0 (5)	105.4 (9)	106.6 (8)
Mevinphos <sup>b</sup>	<LOD	<LOD	<LOD	<LOD	<LOD	77.1 (11)	85.9 (7)	86.2 (3)	<LOD	<LOD	<LOD	<LOD	61.9 (11)	66.5 (6)	63.7 (8)	69.1 (14)

Compound	Green Tea				Red Tea				Black Tea				Chamomille			
	10 µg/kg	25 µg/kg	50 µg/kg	100 µg/kg	10 µg/kg	25 µg/kg	50 µg/kg	100 µg/kg	10 µg/kg	25 µg/kg	50 µg/kg	100 µg/kg	10 µg/kg	25 µg/kg	50 µg/kg	100 µg/kg
Monocrotophos <sup>a</sup>	32.6 (15)	57.6 (7)	38.4 (10)	34.0 (13)	54.6 (12)	56.1 (9)	58.1 (4)	58.7 (3)	41.5 (6)	46.5 (1)	49.8 (5)	48.7 (5)	81.2 (9)	83.4 (3)	78.0 (3)	71.8 (6)
Myclobutanil <sup>a</sup>	85.2 (8)	102.3 (7)	72.7 (8)	74.9 (6)	62.2 (8)	65.1 (6)	69.2 (8)	62.4 (6)	67.2 (14)	63.4 (3)	66.4 (13)	59.9 (16)	89.3 (16)	91.2 (7)	68.5 (15)	60.6 (13)
Omethoate <sup>a</sup>	n.d.	n.d.	n.d.	19.8 (15)	<LOD	38.6 (12)	39.5 (11)	30.1 (10)	<LOD	30.5 (2)	28.7 (4)	19.0 (13)	48.6 (17)	58.7 (3)	47.8 (12)	45.9 (16)
Oxadixyl <sup>b</sup>	<LOD	<LOD	71.3 (12)	77.2 (9)	<LOD	68.8 (3)	82.7 (2)	80.1 (3)	<LOD	72.4 (3)	83.6 (3)	81.6 (3)	<LOD	70.0 (7)	87.2 (8)	85.1 (6)
Parathion Ethyl <sup>b</sup>	<LOD	94.1 (5)	87.9 (13)	80.8 (8)	<LOD	76.2 (7)	83.5 (5)	88.7 (4)	82.8 (17)	82.6 (9)	79.7 (6)	80.0 (2)	<LOD	77.9 (4)	76.2 (11)	82.8 (10)
Parathion Methyl <sup>b</sup>	<LOD	96.1 (3)	90.3 (8)	80.3 (7)	<LOD	76.2 (9)	84.9 (9)	87.5 (5)	<LOD	72.4 (2)	76.1 (2)	77.2 (2)	<LOD	76.6 (5)	74.2 (7)	81.2 (12)
Penconazole <sup>b</sup>	82.6 (5)	87.0 (2)	88.3 (9)	86.2 (8)	65.9 (7)	69.3 (2)	72.9 (5)	79.5 (3)	<LOD	71.3 (2)	73.4 (3)	79.8 (1)	71.7 (5)	76.1 (1)	77.7 (4)	89.7 (6)
Permethrin <sup>b</sup>	<LOD	78.6 (9)	80.5 (8)	81.5 (9)	<LOD	71.4 (7)	81.9 (4)	79.1 (3)	<LOD	70.0 (10)	79.8 (7)	80.1 (3)	<LOD	77.6 (3)	75.3 (5)	84.5 (4)
Phorate <sup>b</sup>	<LOD	94.0 (4)	77.1 (11)	72.6 (9)	64.5 (8)	67.6 (4)	69.2 (6)	75.3 (4)	74.2 (9)	70.5 (3)	79.2 (5)	83.9 (2)	<LOD	66.5 (3)	79.2 (4)	77.2 (8)
Phosmet <sup>b</sup>	86.7 (16)	100.5 (10)	75.8 (13)	71.5 (15)	71.6 (7)	74.8 (6)	76.9 (9)	55.0 (5)	77.4 (12)	70.6 (3)	71.1 (3)	69.5 (1)	70.3 (13)	63.3 (8)	66.6 (7)	66.3 (13)
Pirimicarb <sup>a</sup>	<LOD	101.8 (14)	90.6 (6)	86.8 (4)	88.0 (10)	89.3 (7)	87.2 (7)	91.2 (6)	84.3 (18)	74.5 (13)	87.9 (6)	86.9 (4)	108.9 (11)	116.2 (2)	112.6 (9)	107.7 (8)
Pirimiphos Methyl <sup>a</sup>	88.6 (9)	94.9 (2)	89.8 (8)	91.0 (7)	112.6 (6)	117.1 (2)	103.8 (13)	110.8 (10)	118.9 (18)	118.6 (4)	107.0 (11)	82.0 (10)	<LOD	71.0 (10)	82.3 (8)	91.1 (10)
Profenofos <sup>a</sup>	<LOD	<LOD	<LOD	39.3 (8)	<LOD	<LOD	<LOD	40.7 (4)	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Propargite <sup>b</sup>	<LOD	<LOD	<LOD	<LOD	63.4 (10)	67.3 (4)	72.7 (8)	78.3 (3)	77.8 (10)	72.6 (4)	73.4 (3)	84.9 (1)	66.9 (7)	65.1 (1)	70.9 (5)	86.1 (4)
Propyzamide <sup>b</sup>	96.4 (11)	100.1 (13)	86.2 (9)	85.5 (8)	72.8 (9)	74.8 (7)	88.3 (7)	84.6 (3)	78.1 (10)	73.4 (3)	79.1 (3)	83.8 (2)	73.8 (15)	67.7 (6)	75.5 (9)	82.0 (9)
Pyridaben <sup>b</sup>	78.6 (7)	89.0 (2)	79.5 (4)	81.3 (7)	68.7 (13)	70.7 (9)	72.8 (9)	76.7 (7)	77.0 (8)	73.2 (3)	75.3 (4)	79.2 (3)	99.2 (19)	108.3 (14)	103.3 (18)	99.7 (23)
Pyrimethanil <sup>b</sup>	86.7 (9)	91.7 (7)	87.3 (10)	84.3 (7)	65.3 (6)	66.1 (8)	87.2 (5)	81.9 (2)	<LOD	62.2 (5)	80.2 (2)	79.5 (1)	84.0 (16)	74.9 (2)	93.2 (3)	93.9 (4)
Pyriproxyfen <sup>b</sup>	83.2 (8)	87.2 (2)	89.4 (10)	82.8 (7)	71.4 (6)	74.6 (6)	80.3 (7)	81.8 (5)	67.2 (13)	71.4 (4)	80.9 (2)	82.3 (2)	81.2 (12)	72.7 (5)	85.8 (7)	81.4 (7)
Quinalphos <sup>b</sup>	<LOD	<LOD	<LOD	<LOD	<LOD	67.9 (8)	82.0 (9)	84.2 (4)	<LOD	<LOD	<LOD	81.0 (5)	<LOD	<LOD	<LOD	92.0 (4)
Simazine <sup>a</sup>	85.3 (10)	98.5 (4)	83.9 (7)	80.0 (8)	90.4 (6)	92.4 (7)	94.9 (3)	91.2 (2)	66.9 (17)	78.5 (4)	85.9 (12)	86.8 (10)	116.3 (17)	118.3 (8)	95.3 (1)	93.2 (1)
Terbufos <sup>b</sup>	87.4 (8)	104.5 (6)	81.6 (11)	77.9 (9)	<LOD	77.7 (9)	88.9 (4)	85.8 (4)	78.1 (11)	76.9 (3)	83.5 (7)	91.5 (3)	72.9 (10)	70.7 (4)	80.3 (6)	79.2 (4)
Terbutylazine <sup>a</sup>	82.6 (7)	102.7 (4)	84.3 (5)	77.7 (5)	52.0 (12)	54.4 (7)	50.4 (8)	53.9 (5)	54.7 (18)	59.9 (4)	60.1 (12)	54.3 (18)	77.1 (16)	79.3 (11)	72.2 (18)	71.4 (17)
Tetrachlorvinphos <sup>b</sup>	81.0 (11)	87.6 (5)	78.4 (13)	73.0 (11)	69.9 (7)	72.0 (4)	82.1 (5)	83.8 (2)	80.1 (6)	74.5 (4)	77.3 (4)	83.6 (3)	67.2 (13)	64.9 (7)	65.2 (5)	62.1 (11)
Thiodicarb <sup>a</sup>	78.9 (7)	81.2 (3)	78.3 (8)	72.6 (5)	79.8 (3)	80.7 (1)	84.9 (3)	80.5 (1)	53.1 (15)	61.2 (9)	69.3 (7)	70.8 (9)	92.1 (15)	102.2 (10)	78.0 (11)	80.1 (13)
Triadimefon <sup>a</sup>	79.1 (4)	80.6 (1)	79.7 (3)	85.2 (3)	76.3 (7)	78.1 (6)	75.2 (6)	85.2 (2)	62.7 (19)	75.6 (14)	73.8 (13)	58.6 (13)	66.8 (9)	57.5 (4)	69.1 (7)	69.8 (5)
Triadimenol <sup>a</sup>	<LOD	83.3 (14)	88.1 (7)	87.3 (5)	<LOD	83.4 (8)	95.2 (7)	91.3 (5)	<LOD	71.4 (16)	68.9 (9)	62.2 (6)	<LOD	54.2 (10)	79.7 (5)	76.1 (3)
Triazophos <sup>b</sup>	83.2 (19)	97.0 (19)	89.0 (11)	84.3 (7)	72.4 (8)	74.2 (6)	78.4 (8)	84.6 (4)	77.3 (14)	72.8 (3)	82.3 (3)	85.2 (2)	<LOD	75.3 (1)	72.4 (5)	81.6 (8)
Trifluralin <sup>b</sup>	84.1 (8)	90.9 (1)	81.5 (9)	78.0 (7)	70.6 (6)	71.9 (5)	86.2 (9)	82.0 (5)	67.4 (7)	72.7 (1)	80.7 (3)	79.2 (3)	70.6 (6)	71.7 (1)	73.1 (4)	81.5 (6)
Vinclazolin <sup>b</sup>	<LOD	<LOD	89.5 (12)	84.0 (8)	<LOD	72.0 (6)	82.2 (4)	81.4 (3)	<LOD	<LOD	89.3 (7)	90.4 (3)	<LOD	71.5 (4)	82.1 (6)	85.0 (5)

<sup>a</sup> Analysed by LC-MS/MS

<sup>b</sup> Analysed by GC-MS/MS

Table 4. Limits of detection, limits of quantification, concentration range and matrix effects for the selected matrices studied. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement. LOD and LOQ are referred to the concentration in the sample and instrumental concentration range to the final extract which is diluted 5 times.

Compound	LOD (µg/kg)				LOQ (µg/kg)				Instrumental concentration range (µg/L)				ME(%) = ((slope matrix/slope solvent)-1) × 100			
	Green	Red	Black	Cham.	Green	Red	Black	Cham.	Green	Red	Black	Cham.	Green	Red	Black	Cham.
2,4-D <sup>a</sup>	1	3	2	3	>100	>100	>100	>100	0.5-200	2-200	2-200	2-200	-3.2	-12.6	0.1	-14.1
2,4-DP <sup>a</sup>	3	4	4	4	100	>100	>100	>100	2-200	2-200	2-200	2-200	-0.1	1.8	16.3	17.2
Acetamiprid <sup>a</sup>	1	1	3	2	10	10	10	10	0.5-200	0.5-200	2-200	2-200	-25.8	-14.6	-33.8	-24.7
Alachlor <sup>b</sup>	23	6	7	9	50	25	25	25	10-200	5-200	5-200	5-200	114.5	99.0	80.0	160.0
Atrazine <sup>a</sup>	1	1	1	2	10	10	10	10	0.5-200	0.5-200	0.5-200	2-200	-16.2	-25.8	-19.5	-51.4
Azoxystrobin <sup>a</sup>	1	1	1	1	10	10	10	10	0.5-200	0.5-200	0.5-200	0.5-200	13.5	12.9	6.0	-4.9
Benalaxyl <sup>b</sup>	8	50	50	100	25	100	100	>100	5-200	20-200	20-200	100-200	102.2	107.4	98.3	112.1
Bifenthrin <sup>b</sup>	5	6	3	7	10	10	10	10	5-200	5-200	2-200	5-200	186.1	193.5	181.0	201.1
Biphenyl <sup>b</sup>	1	4	5	1	25	25	10	25	2-200	2-200	2-200	0.5-200	36.9	38.5	31.3	43.7
Boscalid <sup>b</sup>	50	2	3	1	100	10	10	10	20-200	2-200	2-200	0.5-200	-31.9	366.8	232.0	422.8
Buprofezin <sup>a</sup>	1	2	1	1	10	10	10	>100	0.5-200	2-200	0.5-200	0.5-200	-2.0	-11.7	-6.1	-41.6
Carbaryl <sup>a</sup>	2	4	3	4	10	10	10	10	2-200	2-200	2-200	2-200	-39.4	-36.0	-38.9	-42.5
Carbendazim <sup>a</sup>	1	3	3	1	>100	25	>100	10	0.5-200	2-200	2-200	0.5-200	-35.7	-20.7	-10.0	-33.1
Carbofuran <sup>a</sup>	1	2	2	2	10	10	10	10	0.5-200	2-200	2-200	2-200	-17.8	-20.7	-23.2	-34.2
Chinomethionat <sup>b</sup>	7	6	8	6	25	25	50	10	5-200	5-200	5-200	2-200	352.9	354.3	347.4	380.1
Chlorpyrifos <sup>b</sup>	2	1	1	1	10	10	10	10	2-200	0.5-200	0.5-200	2-200	207.7	226.5	210.2	215.9
Chlorpyrifos Methyl <sup>b</sup>	11	7	8	4	25	25	25	10	5-200	5-200	5-200	2-200	86.8	86.6	80.6	110.1
Cypermethrin <sup>b</sup>	35	35	35	100	100	100	100	100	20-200	20-200	20-200	20-200	319.7	321.5	325.2	331.4
Cyproconazole <sup>b</sup>	21	13	17	12	50	25	50	25	10-200	10-200	10-200	5-200	279.9	297.3	274.5	304.8
Cyprodinil <sup>b</sup>	3	3	1	1	10	10	10	10	2-200	2-200	0.5-200	0.5-200	173.2	207.0	199.9	200.2
Diazinon <sup>b</sup>	15	7	2	1	25	25	10	10	5-200	5-200	2-200	0.5-200	-9.7	135.6	126.6	145.8
Dichlofluanid <sup>b</sup>	48	28	10	50	>100	50	25	100	20-200	10-200	5-200	20-200	171.5	179.8	171.3	207.8
Dichlorvos <sup>b</sup>	4	1	1	1	10	10	10	10	2-200	0.5-200	0.5-200	0.5-200	75.9	87.1	75.5	85.5
Dicloran <sup>b</sup>	27	24	22	25	50	50	50	50	10-200	10-200	10-200	10-200	302.7	247.7	240.7	330.2
Dimethoate <sup>a</sup>	1	3	2	2	10	10	10	10	0.5-200	2-200	2-200	2-200	-14.4	-14.6	-36.7	-20.8
Endosulfan I <sup>b</sup>	1	1	2	1	10	10	10	10	2-200	0.5-200	2-200	0.5-200	49.8	53.7	48.7	49.9
Endosulfan II <sup>b</sup>	9	9	8	7	25	25	25	25	5-200	5-200	5-200	5-200	23.8	32.8	27.7	35.0
Endosulfan Sulfate <sup>b</sup>	4	1	1	2	10	10	10	10	2-200	0.5-200	0.5-200	2-200	35.4	35.6	32.5	41.7
Ethion <sup>b</sup>	2	2	2	7	10	10	10	25	2-200	2-200	2-200	5-200	338.6	347.9	330.3	382.3

Compound	LOD (µg/kg)				LOQ (µg/kg)				Instrumental concentration range (µg/L)				ME(%) = ((slope matrix/slope solvent)-1) × 100			
	Green	Red	Black	Cham.	Green	Red	Black	Cham.	Green	Red	Black	Cham.	Green	Red	Black	Cham.
Ethoprophos <sup>b</sup>	1	10	1	2	10	25	10	10	2-200	5-200	0.5-200	2-200	263.4	364.0	337.2	388.5
Etofenprox <sup>b</sup>	7	5	11	11	10	10	25	25	2-200	2-200	5-200	5-200	293.1	310.4	293.4	331.5
Fenarimol <sup>b</sup>	4	2	4	4	10	10	10	10	2-200	2-200	2-200	2-200	169.9	230.3	198.9	213.3
Fenitrothion <sup>b</sup>	3	2	1	3	10	10	10	10	2-200	2-200	2-200	2-200	294.7	244.0	297.6	382.5
Fenpropathrin <sup>b</sup>	1	2	1	2	10	25	10	10	0.5-200	2-200	0.5-200	2-200	207.6	209.2	193.2	230.1
Fenvalerate/Esfenvalerate RR/SS <sup>b</sup>	8	8	10	10	25	25	25	25	5-200	5-200	5-200	5-200	573.6	570.7	569.6	578.0
Fenvalerate/Esfenvalerate SR/RS <sup>b</sup>	8	15	8	8	25	25	25	25	5-200	5-200	5-200	5-200	540.2	543.2	548.1	552.4
Flucythrinate <sup>b</sup>	1	1	1	1	10	10	10	10	0.5-200	2-200	2-200	0.5-200	472.9	470.1	468.1	477.4
Fludioxonil <sup>b</sup>	2	1	2	6	10	10	10	25	2-200	0.5-200	2-200	5-200	378.1	389.9	356.9	382.8
Fonofos <sup>b</sup>	50	50	78	100	100	100	>100	100	20-200	20-200	100-200	100-200	128.0	123.9	115.9	153.1
Imazalil <sup>a</sup>	2	2	2	3	10	10	25	10	2-200	2-200	2-200	2-200	-16.9	-15.8	-18.3	-28.8
Imidacloprid <sup>a</sup>	1	5	5	15	10	10	50	25	0.5-200	2-200	2-200	5-200	-33.5	-17.6	-28.8	-23.3
Iprodione <sup>b</sup>	1	1	1	1	10	10	10	10	0.5-200	0.5-200	0.5-200	0.5-200	291.1	292.9	286.3	291.7
Isocarbophos <sup>b</sup>	15	28	35	14	25	50	50	25	5-200	10-200	10-200	5-200	305.8	366.3	377.3	380.6
Isofenphos Methyl <sup>b</sup>	3	4	4	50	10	10	10	100	2-200	2-200	2-200	20-200	193.2	204.1	191.8	208.2
Kresoxim Methyl <sup>b</sup>	10	2	1	7	25	10	10	25	5-200	2-200	2-200	5-200	165.4	156.0	147.2	165.3
Lindane <sup>b</sup>	1	3	3	9	10	10	10	25	0.5-200	2-200	2-200	5-200	57.8	63.5	58.0	68.2
Malathion <sup>b</sup>	1	1	1	19	10	10	10	50	0.5-200	0.5-200	0.5-200	5-200	236.5	251.6	239.3	261.1
MCPP <sup>a</sup>	8	10	5	7	25	>100	>100	25	5-200	5-200	2-200	5-200	-8.0	-7.5	5.7	-0.1
Metalaxyl <sup>a</sup>	1	1	1	3	10	10	10	10	0.5-200	0.5-200	0.5-200	2-200	22.7	25.4	19.3	-13.6
Methidathion <sup>b</sup>	6	1	3	3	25	10	10	10	5-200	0.5-200	2-200	2-200	265.4	364.9	336.3	377.9
Methiocarb Sulfone <sup>a</sup>	4	7	3	4	10	25	10	10	2-200	5-200	2-200	2-200	22.5	33.6	12.8	26.8
Methiocarb Sulfoxide <sup>a</sup>	2	2	2	2	10	10	10	10	2-200	2-200	2-200	2-200	-40.1	-19.6	-44.8	9.0
Methiocarb <sup>a</sup>	6	5	6	8	25	10	25	25	5-200	2-200	5-200	5-200	-21.3	-20.3	-25.3	-40.5
Methomyl <sup>a</sup>	1	2	1	1	10	10	10	10	0.5-200	2-200	0.5-200	0.5-200	-28.6	-25.5	-39.2	-19.1
Metolachlor <sup>a</sup>	1	1	1	1	10	10	10	10	0.5-200	0.5-200	0.5-200	0.5-200	-10.3	-7.8	-9.8	-20.0
Metribuzin <sup>a</sup>	2	4	4	7	10	10	10	25	2-200	2-200	2-200	5-200	3.0	7.6	3.4	-15.9
Mevinphos <sup>b</sup>	210	10	100	3	>100	25	>100	10	100-200	2-200	100-200	2-200	36.2	340.5	299.8	327.9
Monocrotophos <sup>a</sup>	1	1	1	1	>100	>100	>100	10	0.5-200	0.5-200	0.5-200	0.5-200	-66.9	-21.3	-16.2	-1.5
Myclobutanil <sup>a</sup>	1	1	1	2	10	10	10	10	0.5-200	0.5-200	0.5-200	2-200	-5.6	-14.0	-12.5	11.8
Omethoate <sup>a</sup>	4	4	4	2	>100	>100	>100	10	2-200	2-200	2-200	2-200	-50.5	-24.4	-4.1	6.6
Oxadixyl <sup>b</sup>	22	14	11	16	50	25	25	25	10-200	5-200	5-200	5-200	81.1	96.1	84.8	99.2
Parathion Ethyl <sup>b</sup>	11	9	7	11	25	25	10	25	5-200	5-200	5-200	2-200	402.4	354.4	377.9	453.2



Compound	LOD (µg/kg)				LOQ (µg/kg)				Instrumental concentration range (µg/L)				ME(%) = ((slope matrix/slope solvent)-1) × 100			
	Green	Red	Black	Cham.	Green	Red	Black	Cham.	Green	Red	Black	Cham.	Green	Red	Black	Cham.
Parathion Methyl <sup>b</sup>	9	10	15	9	25	25	50	25	5-200	5-200	10-200	5-200	305.8	289.9	296.5	430.8
Penconazole <sup>b</sup>	8	3	3	1	25	10	25	10	5-200	2-200	2-200	0.5-200	149.1	168.0	149.7	164.5
Permethrin <sup>b</sup>	17	7	12	13	50	25	25	50	10-200	5-200	5-200	10-200	184.7	189.7	172.1	201.2
Phorate <sup>b</sup>	12	2	2	18	25	10	10	50	5-200	2-200	2-200	10-200	197.4	248.6	207.2	273.4
Phosmet <sup>b</sup>	2	1	1	3	10	10	10	10	2-200	0.5-200	0.5-200	2-200	525.4	877.3	843.9	915.1
Pirimicarb <sup>a</sup>	9	1	1	7	25	10	10	25	5-200	0.5-200	0.5-200	5-200	-29.6	-23.7	-26.9	-21.2
Pirimiphos Methyl <sup>a</sup>	5	5	1	15	10	10	10	50	2-200	2-200	0.5-200	10-200	-34.0	-40.4	-27.7	-65.7
Profenofos <sup>a</sup>	25	28	35	60	>100	>100	>100	>100	10-200	20-200	20-200	100-200	-75.8	-67.6	-52.6	-95.8
Propargite <sup>b</sup>	100	3	3	1	>100	10	10	10	100-200	2-200	2-200	0.5-200	217.5	271.8	248.5	208.0
Propyzamide <sup>b</sup>	1	3	2	5	10	10	10	25	0.5-200	2-200	2-200	5-200	93.3	127.0	122.2	136.1
Pyridaben <sup>b</sup>	3	2	2	3	10	10	10	10	2-200	2-200	2-200	2-200	425.4	458.7	419.7	458.7
Pyrimethanil <sup>b</sup>	1	4	8	2	10	10	25	10	0.5-200	2-200	5-200	2-200	134.7	190.3	173.5	196.1
Pyriproxyfen <sup>b</sup>	1	1	1	1	10	10	10	10	0.5-200	0.5-200	0.5-200	0.5-200	529.7	566.0	525.0	573.0
Quinalphos <sup>b</sup>	100	13	50	75	>100	50	100	100	100-200	10-200	20-200	20-200	208.7	275.3	256.4	289.2
Simazine <sup>a</sup>	1	1	1	4	10	10	10	10	0.5-200	0.5-200	0.5-200	2-200	-15.3	-26.6	-24.1	-34.8
Terbufos <sup>b</sup>	5	7	5	4	10	25	10	10	2-200	5-200	2-200	2-200	135.0	184.6	166.1	202.3
Terbutylazine <sup>a</sup>	1	2	2	2	10	>100	>100	10	0.5-200	2-200	2-200	2-200	-25.1	-35.9	-31.6	-44.3
Tetrachlorvinphos <sup>b</sup>	1	1	1	1	10	10	10	10	0.5-200	0.5-200	0.5-200	0.5-200	277.9	334.8	307.8	316.5
Thiodicarb <sup>a</sup>	1	1	1	1	10	10	25	10	0.5-200	0.5-200	0.5-200	0.5-200	-6.8	-28.3	-15.2	-4.9
Triadimefon <sup>a</sup>	1	4	1	2	10	10	10	10	0.5-200	2-200	0.5-200	2-200	-26.3	-35.8	-31.9	-65.5
Triadimenol <sup>a</sup>	10	16	10	15	25	50	25	50	5-200	10-200	5-200	10-200	-1.3	16.3	-14.5	-49.3
Triazophos <sup>b</sup>	1	3	2	7	10	10	10	25	2-200	2-200	2-200	5-200	413.3	454.4	422.6	458.1
Trifluralin <sup>b</sup>	1	1	1	1	10	10	10	10	0.5-200	0.5-200	0.5-200	0.5-200	456.5	408.5	408.8	407.6
Vinclozolin <sup>b</sup>	23	12	24	12	50	25	50	25	10-200	5-200	10-200	5-200	65.3	66.5	59.3	100.0

<sup>a</sup> Analysed by LC-MS/MS

<sup>b</sup> Analysed by GC-MS/MS



Table 5. Precision of the chromatographic methods in the different matrices (n=5). Concentration referred to the vial.

Compound	Intra-day precision (RSD, %)								Inter-day precision (RSD, %)							
	5 µg/L				20 µg/L				5 µg/L				20 µg/L			
	Green	Red	Black	Cham.	Green	Red	Black	Cham.	Green	Red	Black	Cham.	Green	Red	Black	Cham.
2,4-D <sup>a</sup>	1.9	4.6	3.7	2.2	11.9	2.5	15.9	0.5	5.6	7.4	9.0	8.6	4.5	3.8	5.8	8.8
2,4-DP <sup>a</sup>	2.8	2.9	2.4	1.1	13.7	1.4	8.1	0.9	4.9	4.1	8.8	11.4	4.5	2.0	2.7	10.2
Acetamiprid <sup>a</sup>	8.9	1.4	2.4	2.1	10.8	2.5	2.7	0.8	7.8	3.0	11.1	6.1	6.6	1.2	9.0	4.3
Alachlor <sup>b</sup>	5.7	3.3	5.7	4.2	3.9	2.0	5.2	1.5	10.8	13.4	7.8	17.0	4.8	11.0	8.5	9.5
Atrazine <sup>a</sup>	1.4	1.9	1.6	0.8	2.6	1.5	2.4	1.7	9.1	7.5	9.0	13.6	6.0	5.6	11.0	7.9
Azoxystrobin <sup>a</sup>	2.5	3.4	1.2	4.7	2.9	4.7	6.3	2.3	4.6	7.5	12.7	19.7	6.6	12.0	8.5	16.9
Benalaxyl <sup>b</sup>	2.9	-	-	-	1.2	0.8	1.5	3.8	16.6	-	-	-	6.5	10.4	16.8	16.0
Bifenthrin <sup>b</sup>	1.5	13.2	11.8	3.8	6.8	10.7	16.4	2.5	6.1	11.2	9.1	15.7	6.3	11.6	10.5	10.7
Biphenyl <sup>b</sup>	2.7	7.4	12.5	2.0	7.2	14.1	17.2	2.2	7.0	12.4	9.9	9.1	7.3	9.9	11.1	13.0
Boscalid <sup>b</sup>	-	0.2	3.1	0.7	9.4	0.4	1.6	1.2	-	19.3	16.6	23.0	10.4	18.5	13.9	19.9
Buprofezin <sup>a</sup>	3.6	2.1	1.9	4.1	3.1	1.8	1.1	3.1	4.9	3.5	2.1	5.3	4.3	2.9	2.3	4.9
Carbaryl <sup>a</sup>	1.7	3.5	3.5	3.2	1.1	1.5	6.5	3.1	3.6	11.0	3.7	8.8	5.9	5.7	3.8	8.2
Carbendazim <sup>a</sup>	8.1	4.0	2.3	1.8	4.0	2.0	1.3	1.1	17.2	9.6	17.1	7.8	18.0	11.5	18.5	9.3
Carbofuran <sup>a</sup>	3.3	3.3	2.4	4.2	5.6	3.6	1.9	4.0	7.2	5.1	7.0	5.4	3.0	5.5	7.8	5.9
Chinomethionat <sup>b</sup>	2.9	1.5	7.2	1.6	1.9	3.3	1.9	3.2	11.4	13.8	13.2	13.3	4.8	11.3	9.1	13.7
Chlorpyrifos <sup>b</sup>	2.3	1.2	2.0	1.9	1.4	0.8	2.7	0.6	5.6	10.9	9.1	8.7	7.0	7.6	8.8	9.5
Chlorpyrifos Methyl <sup>b</sup>	1.8	1.6	1.9	1.8	1.5	2.7	2.3	1.2	3.7	11.4	8.6	7.7	5.5	6.2	9.4	7.5
Cypermethrin <sup>b</sup>	-	-	-	-	7.8	5.7	6.1	8.4	-	-	-	-	6.1	8.3	8.6	12.8
Cyproconazole <sup>b</sup>	8.0	3.7	4.4	3.1	1.4	1.8	2.0	2.3	18.6	3.6	4.5	11.5	5.6	10.5	9.8	8.7
Cyprodinil <sup>b</sup>	7.3	0.9	5.1	1.5	4.2	0.7	2.0	1.6	8.5	2.9	7.3	3.7	6.8	3.5	6.0	2.9
Diazinon <sup>b</sup>	6.6	3.2	4.3	1.8	2.1	3.1	2.6	1.8	10.3	13.5	6.5	8.8	4.1	8.0	10.8	9.4
Dichlofluanid <sup>b</sup>	-	-	5.8	-	3.4	2.6	3.2	3.3	-	-	17.5	-	2.0	8.5	10.7	11.6
Dichlorvos <sup>b</sup>	1.8	1.1	0.7	1.4	2.1	0.8	1.0	0.9	16.3	12.1	4.4	13.4	17.7	11.6	10.8	10.5
Dicloran <sup>b</sup>	-	2.8	4.0	-	2.4	1.9	5.9	2.9	-	6.4	10.3	-	8.6	15.3	14.7	18.3
Dimethoate <sup>a</sup>	2.3	2.3	2.7	4.8	2.6	1.9	3.6	0.8	3.1	5.4	4.9	7.8	2.8	2.8	7.2	4.2
Endosulfan I <sup>b</sup>	2.7	4.0	3.0	2.4	1.6	1.8	4.9	1.9	1.8	15.1	7.5	8.3	5.0	9.0	9.8	13.7
Endosulfan II <sup>b</sup>	3.7	2.4	4.8	6.0	1.1	3.7	1.9	3.0	6.3	8.1	10.5	12.4	3.6	10.9	11.0	9.8
Endosulfan Sulfate <sup>b</sup>	2.4	7.8	3.3	7.3	6.6	11.4	7.9	5.5	6.4	5.2	12.9	8.5	5.9	9.4	6.7	13.2
Ethion <sup>b</sup>	0.9	2.1	1.0	1.9	1.3	1.3	1.2	0.3	7.2	12.5	12.7	13.5	8.1	12.1	11.7	9.9
Ethoprophos <sup>b</sup>	3.1	1.0	1.7	1.9	1.2	1.2	1.3	0.6	9.0	5.1	12.7	12.4	9.2	13.3	15.1	11.3
Etofenprox <sup>b</sup>	9.6	0.8	3.1	2.1	3.2	0.8	2.0	2.0	5.6	14.3	13.7	10.4	5.6	9.2	8.3	9.1

Compound	Intra-day precision (RSD, %)								Inter-day precision (RSD, %)							
	5 µg/L				20 µg/L				5 µg/L				20 µg/L			
	Green	Red	Black	Cham.	Green	Red	Black	Cham.	Green	Red	Black	Cham.	Green	Red	Black	Cham.
Fenarimol <sup>b</sup>	8.3	4.8	3.3	2.4	2.2	2.6	1.5	1.7	16.7	21.5	18.0	12.2	9.1	13.3	13.3	11.4
Fenitrothion <sup>b</sup>	0.5	3.4	2.6	4.3	1.5	10.7	2.0	1.9	6.3	14.3	13.7	16.0	6.9	14.5	14.7	11.6
Fenpropathrin <sup>b</sup>	5.4	1.7	3.3	1.2	1.3	3.6	1.3	0.7	9.6	14.9	6.3	14.0	7.9	10.0	11.6	14.6
Fenvalerate/Esfenvalerate RR/SS <sup>b</sup>	7.5	10.7	12.4	8.3	5.8	8.1	7.2	5.2	10.3	12.6	15.6	13.1	9.7	5.4	8.6	7.5
Fenvalerate/Esfenvalerate SR/RS <sup>b</sup>	6.2	13.4	9.3	7.6	3.9	9.7	4.0	1.8	8.5	15.0	11.7	8.7	6.6	12.5	6.5	4.9
Flucythrinate <sup>b</sup>	4.7	0.6	3.2	2.6	1.6	1.7	2.5	2.4	10.2	11.5	10.8	13.5	7.6	11.5	12.2	12.7
Fludioxonil <sup>b</sup>	3.7	2.2	3.1	1.2	1.6	1.5	2.7	0.9	8.0	6.5	10.3	15.5	5.5	5.9	9.6	10.7
Fonofos <sup>b</sup>	-	-	-	-	2.0	0.9	6.7	4.3	-	-	-	-	8.1	17.4	14.8	14.5
Imazalil <sup>a</sup>	2.4	1.6	1.8	1.5	2.3	3.0	4.1	2.3	8.2	5.9	2.8	18.9	8.5	4.2	5.1	8.1
Imidacloprid <sup>a</sup>	12.0	2.0	3.6	10.2	8.8	2.5	4.6	4.1	8.2	10.2	18.1	18.0	6.6	4.6	18.9	7.1
Iprodione <sup>b</sup>	1.7	3.1	1.7	0.8	1.9	1.3	2.2	0.4	5.3	8.5	10.3	10.2	7.0	10.8	10.9	11.2
Isocarbophos <sup>b</sup>	3.7	-	-	3.3	2.8	1.3	4.0	1.4	8.6	-	-	14.0	8.2	10.4	10.5	10.7
Isofenphos Methyl <sup>b</sup>	2.1	0.7	2.2	-	1.0	1.1	1.1	0.2	6.4	11.7	8.1	-	6.0	8.5	9.2	8.4
Kresoxim Methyl <sup>b</sup>	3.7	0.5	1.7	2.1	2.1	2.0	1.2	0.4	8.3	9.1	14.8	11.8	7.2	11.0	11.0	9.4
Lindane <sup>b</sup>	3.4	1.6	2.3	2.3	1.3	1.1	2.6	1.5	4.7	7.0	7.9	14.4	4.7	5.8	10.1	10.1
Malathion <sup>b</sup>	0.6	1.5	2.9	2.9	1.0	1.1	0.9	0.5	12.2	16.0	8.2	10.8	19.2	8.5	9.0	9.6
MCPP <sup>a</sup>	1.8	1.5	2.4	1.3	2.5	1.1	7.3	0.9	3.6	3.7	8.1	12.7	4.4	1.8	3.9	8.0
Metalaxyl <sup>a</sup>	2.1	4.1	1.1	1.6	2.2	1.2	1.5	1.0	4.5	4.0	5.7	10.4	3.5	2.4	5.4	10.2
Methidathion <sup>b</sup>	1.8	1.0	3.1	2.4	2.5	0.9	1.4	0.5	4.0	10.1	10.6	10.7	5.2	10.7	7.9	8.4
Methiocarb Sulfone <sup>a</sup>	7.9	5.1	9.2	9.7	8.2	2.8	4.0	4.9	7.2	9.0	7.6	17.8	3.7	4.3	3.8	12.9
Methiocarb Sulfoxide <sup>a</sup>	10.1	8.4	15.3	13.5	9.3	7.5	12.7	11.2	11.2	1.3	9.5	14.3	5.1	3.6	8.1	8.5
Methiocarb <sup>a</sup>	12.5	12.4	7.7	12.1	5.1	9.2	9.5	8.5	9.1	8.8	13.0	17.5	8.8	4.0	14.1	10.1
Methomyl <sup>a</sup>	0.3	2.6	1.8	1.6	1.5	0.9	0.2	1.2	2.7	6.1	4.9	5.0	1.5	1.9	3.6	1.6
Metolachlor <sup>a</sup>	0.8	5.5	1.8	3.3	2.7	2.5	6.6	9.9	4.0	6.5	10.7	18.1	6.2	7.4	3.6	8.8
Metribuzin <sup>a</sup>	2.1	5.8	5.9	8.5	1.5	2.7	1.6	1.8	13.2	8.3	15.5	9.2	8.9	5.5	12.6	12.8
Mevinphos <sup>b</sup>	-	2.5	-	2.7	-	0.9	1.2	1.6	-	13.1	-	9.6	-	9.3	7.3	14.7
Monocrotophos <sup>a</sup>	1.6	2.5	4.1	1.4	2.9	1.3	3.3	1.2	17.6	5.4	4.8	5.9	12.4	4.3	4.2	2.9
Myclobutanil <sup>a</sup>	1.2	1.9	2.4	2.7	3.3	4.7	5.7	2.9	6.7	5.4	16.6	26.7	4.0	12.4	9.7	27.5
Omethoate <sup>a</sup>	11.1	8.1	1.9	9.3	2.3	4.0	4.8	4.4	16.6	10.8	9.9	13.8	17.2	16.0	11.8	14.4
Oxadixyl <sup>b</sup>	1.3	3.5	1.1	6.4	2.7	0.7	0.9	1.2	7.0	13.6	14.0	8.0	10.2	10.5	9.4	10.6
Parathion Ethyl <sup>b</sup>	3.2	5.6	3.8	5.3	1.5	1.8	2.6	1.6	10.5	16.9	14.6	15.3	9.5	14.8	17.4	13.7
Parathion Methyl <sup>b</sup>	1.7	2.0	2.8	3.2	1.0	1.6	1.1	2.0	4.0	10.4	8.3	4.8	10.6	3.5	10.1	7.1
Penconazole <sup>b</sup>	3.4	1.9	1.2	2.8	1.5	0.7	1.5	1.1	2.1	11.7	13.2	11.2	6.6	8.7	11.6	12.0
Permethrin <sup>b</sup>	12.2	5.4	5.3	6.0	6.5	1.0	3.9	0.9	13.8	13.3	8.7	13.7	6.4	9.4	12.2	10.7
Phorate <sup>b</sup>	6.1	2.2	3.9	0.8	3.3	1.9	1.5	1.3	7.8	13.9	10.9	8.7	3.5	10.1	11.9	6.1

Compound	Intra-day precision (RSD, %)								Inter-day precision (RSD, %)							
	5 µg/L				20 µg/L				5 µg/L				20 µg/L			
	Green	Red	Black	Cham.	Green	Red	Black	Cham.	Green	Red	Black	Cham.	Green	Red	Black	Cham.
Phosmet <sup>b</sup>	2.8	0.6	3.4	1.6	1.1	1.1	1.5	1.4	3.3	10.7	10.1	12.1	6.2	5.5	9.3	12.9
Pirimicarb <sup>a</sup>	5.6	3.5	1.4	3.3	1.0	0.3	0.9	3.2	1.8	5.7	4.7	1.3	3.7	5.0	8.0	1.1
Pirimiphos Methyl <sup>a</sup>	4.7	1.2	3.2	8.7	4.5	2.7	5.5	1.5	8.8	4.6	13.4	13.8	3.9	6.1	13.4	12.2
Profenofos <sup>a</sup>	6.2	-	-	-	4.1	5.7	3.4	3.9	7.8	-	-	-	5.9	9.3	5.0	6.2
Propargite <sup>b</sup>	-	1.3	2.2	1.3	2.9	1.7	1.9	1.1	-	13.2	9.8	4.6	5.4	12.9	12.6	6.1
Propyzamide <sup>b</sup>	1.8	2.0	3.0	4.8	2.3	1.6	1.6	2.7	12.1	10.1	10.8	9.6	8.6	5.5	9.1	16.8
Pyridaben <sup>b</sup>	1.7	1.3	1.8	2.7	1.7	1.7	2.2	1.6	8.8	5.9	13.7	11.0	8.1	9.1	10.4	12.3
Pyrimethanil <sup>b</sup>	1.7	3.3	6.5	1.7	1.7	2.6	2.7	0.8	8.1	5.9	4.7	13.5	8.6	9.1	8.0	10.8
Pyriproxyfen <sup>b</sup>	2.5	2.8	2.6	7.4	0.6	10.6	2.3	7.2	8.7	10.2	10.8	18.2	7.5	9.9	9.1	10.5
Quinalphos <sup>b</sup>	-	5.2	-	-	3.3	2.3	1.8	2.2	-	17.3	-	-	10.2	15.6	11.3	28.8
Simazine <sup>a</sup>	0.6	2.5	0.6	4.4	1.4	2.7	2.6	1.3	9.7	8.4	11.2	8.4	3.6	5.3	12.4	4.8
Terbufos <sup>b</sup>	2.5	2.1	2.4	3.3	1.5	1.4	1.1	0.9	8.6	10.3	10.5	11.4	7.5	8.3	10.4	11.2
Terbutylazine <sup>a</sup>	2.7	3.5	1.5	8.1	1.8	3.1	6.3	6.8	8.1	3.5	16.1	19.3	8.7	16.3	8.7	15.3
Tetrachlorvinphos <sup>b</sup>	0.8	0.5	1.8	2.0	1.6	1.0	0.8	1.8	3.2	5.3	7.2	9.4	3.3	5.1	8.5	7.1
Thiodicarb <sup>a</sup>	1.5	3.7	2.4	6.5	1.6	6.7	1.3	1.2	9.7	14.8	15.1	6.5	19.8	9.3	11.1	7.8
Triadimefon <sup>a</sup>	3.8	4.5	2.9	5.2	3.5	2.7	2.7	3.7	4.1	6.9	3.5	6.1	3.9	5.2	3.2	5.9
Triadimenol <sup>a</sup>	2.9	12.8	3.1	6.1	2.2	8.1	3.2	2.9	5.8	15.1	6.1	7.4	5.3	13.3	5.3	4.4
Triazophos <sup>b</sup>	1.4	1.4	3.5	1.6	1.2	1.2	1.4	0.9	7.5	8.4	11.3	12.3	8.2	10.5	10.3	11.6
Trifluralin <sup>b</sup>	2.4	1.8	2.1	1.8	1.9	2.2	1.2	0.8	6.7	10.8	15.3	13.0	9.6	12.9	13.5	14.2
Vinclozolin <sup>b</sup>	3.8	2.5	2.5	2.9	1.7	2.3	1.1	1.3	4.7	8.5	11.3	6.1	7.2	10.4	6.1	5.9

<sup>a</sup> Analysed by LC-MS/MS

<sup>b</sup> Analysed by GC-MS/MS