Validation of the MRM pesticides from the Working Document SANCO/12745/2013 of 21-22 November 2017 rev. 9(1)

CONTENTS

1. Aim and scope

This report describes a validation data of 50 pesticides using a multiresidue method by LC-MS/MS and GC-MS/MS in tomato, orange and avocado.

2. Short description

Homogenous sample is extracted with acetonitrile using citrate buffered and partitioning salts. The obtained extract is analysed by GC-MS/MS and LC-MS/MS.

3. Apparatus and consumables

- Automatic pipettes, suitable for handling volumes of 10 µL to 5000 µL and 1 mL to 5 mL
- 50 ml and 15 ml PTFE centrifuge tubes
- Vortex
- Shaker
- Centrifuge, suitable for the centrifuge tubes employed in the procedure and capable of achieving at least 3300 rpm
- Concentration workstation
- Injection vials, 2 ml, suitable for LC and GC auto-sampler

4. Chemicals

- Acetonitrile ultra-gradient
- Trisodium citrate dihydrate
- Disodium hydrogenocitrate sesquihydrate
- Sodium chloride
- Anhydrous magnesium sulphate
- Primary secondary amine (PSA)
- Supel QuE Z-Sep
- Ammonium formiate
- Ultra-pure water
- Methanol HPLC grade
- Formic acid
- Ethyl acetate
- Pesticides standards

5. Procedure

5.1. Sample preparation

Following Document No. SANTE/2017/11813, the sample was perfectly homogenised by grinding finely at its arrival to the laboratory.

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 or ethyl acetate and were stored in screw-capped glass vials in the dark at -20 °C.

For spiking, 10 g representative portions of previously homogenised sample were weighed in teflon tubes, where they were fortified homogenously with the appropriate amount of the working standard solution in acetonitrile.

The validation method was performed at two fortification levels (0.005 and 0.05 mg/Kg). Five replicates were analysed at each level.

5.3. Extraction method

1. Weigh 10 g ± 0.1 g of sample in 50 mL PTFE centrifuge tube.
2. Add 10 mL of acetonitrile and 10 µL of 10 mg/L carbendazim-d3, Malathion-d10 and TPP (procedure internal standards).
3. Shake the sample using an automatic axial shaker for 4 min.
4. Add 4 g of magnesium sulphate, 1 g of sodium chloride, 1 g of trisodium citrate dihydrate and 0.5 g of disodium hydrogenocitrate sesquihydrate.
5. Shake the samples again in the automatic shaker for 4 min.
6. Centrifuge the tubes at 3700 rpm for 5 min.
7. Transfer 5 mL of the supernatant to a 15 mL PTFE tube containing:
    a. 750 mg magnesium sulphate and 125 mg PSA for matrices with high water content.
    b. 750 mg magnesium sulphate and 125 mg Z-Sep for matrices with high fat content.
8. Vortex the tube for 30 sec.
9. Centrifuge the tubes at 3700 rpm for 5 min.
10. Add 40 µL of formic acid 5% in acetonitrile to option a in step 7.
11. Analysis:

a. for LC analysis, dilute 100 mL extract with 400 mL of water containing dimethoate-d6 at 0.050 mg/L (Injection Internal Standard).
b. for GC analysis, evaporate 50 µL extract and reconstitute with 50 µL of ethyl acetate containing lindane-d6 at 0.050 µg/mL (Injection Internal Standard).

With this treatment, 1 mL of sample extract represents 0.2 g of sample in LC and in GC the final matrix concentration is 1 g/mL.

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 (Table 1 for LC-MS/MS and Table 2 for GC-MS/MS parameters).

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

5.5.1. 1290 UHPLC (Agilent)

- Column: Zorbax Eclipse Plus C8 2.1x100 mm and 1.8 µm particle size (Agilent)
- Mobile phase A: Water (0.1% formic acid, 5mM ammonium formate, 2% MeOH)
- Mobile phase B: Methanol (0.1% formic acid, 5mM ammonium formate, 2% H_2O)
- Column temperature: 35°C
- Flow rate: 0.3 mL/min
- Injection volume: 5 µL

Mobile phase gradient for pesticides analyse

Time [min]	Mobile phase A	Mobile phase B
0	80%	20%
2	80%	20%
15	0%	100%
18	0%	100%

Re-equilibration with initial mobile phase: 2.5 minutes.

5.5.2. 6490 triple quadrupole system (Agilent)

- Ionisation mode: Positive mode and negative mode
- Capillary (positive and negative): 3000 V
- Nebulizer: 45 psi
- Nozzle: 400 V
- Drying gas flow: 13 L/min
- Drying gas temperature: 120ºC
- Sheath gas flow: 10 L/min
- Sheath gas temperature: 375ºC
- High Pressure RF (positive): 150 V
- High Pressure RF (negative): 110 V
- Low Pressure RF (positive): 60 V
- Low Pressure RF (negative): 60 V

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

5.6.1. Intuvo 9000 GC system (Agilent)

- Column: 2 Planar columns HP-5MS UI (15 m long × 0.25 mm i.d. × 0.25 µm film thickness)
- Injection mode: Splitless
- Ultra-inert inlet liner with a glass wool frit from Agilent
- Injection volume: 1 µl
- Injector temperature: 80 °C hold for 0.1 min, then up to 300 °C at 600 °C/min and up to 250 at 100 °C/min.
- Carrier gas: Helium at constant flow = 1.611 mL/min column 1, 1811 mL/min column 2.
- Carrier gas purity: 99.999%
- Oven temperature: 60 °C for 0.5 min, up to 170 °C at 40 °C/min, and up to 310 °C at 10 °C/min.

5.6.2. 7410 triple quadrupole system (Agilent)

- Ionisation mode: electron impact ionisation
- Temperature of the transfer line: 280 °C
- Temperature of ion source: 280 °C
- Collision gas: nitrogen
- Collision gas purity: 99.999%
- Solvent delay: 2.6 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_r) at two fortification levels (0.005 and 0.05 mg/kg) are summarized in Appendix II, Table 3.

Almost all the recoveries results are within the range 70-120% except ioxynil in tomato; cyflufenamid, etoxazole, lufenuron, metrafenone, propaquizafop, proquinazid, pyrethrin I, pyrethrin II, sulfoxaflor and tricyclazole in orange; and bifenazate and pyrethrin II in avocado.

6.2. Limits of quantitation

Document N° SANTE/2017/11813 defines limit of quantitation as the lowest validated spike level meeting the method performance acceptability criteria. LOQs are summarized in Appendix II, Table 4. The LOQ for 98% of the pesticides is 0.005 mg/kg in tomato, 76% in orange and 82% in avocado.

6.3. Linearity

Linearity of the MS/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 0.002 to 0.500 mg/L. In all cases, coefficient of determination (R^2) was higher than 0.99. Linearity ranges for all pesticides are summarized in Appendix II, Table 4.

6.4. 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, Table 4.

This report aims to provide information to laboratories that analyse pesticide residues in fruits and vegetables or are interested in it.

References

- **Analytical quality control and method validation procedures for pesticide residues analysis in food and feed.** Document N° SANTE/2017/11813.

- http://www.eurl-pesticides.eu

- **Working document on pesticides to be considered for inclusion in the national control programmes to ensure compliance with maximum residue levels of pesticides residues in and on food of plant and animal origin.** SANCO/12745/2013 of 21-22 November 2017 rev. 9(1).

APPENDIX I: MASS TRANSITIONS

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

No.	Name	t_R (min)	Cone voltage (V)	Precursor ion (m/z)	Product ion 1 (m/z)	Product ion 2 (m/z)	CE 1 (eV)	CE 2 (eV)	Polarity
1	Ametoctradin	12,92	380	276,2	176,1	149	35	35	Positive
2	BAC10	11,34	380	276,2	184,3	90,8	20	25	Positive
3	BAC8	9,68	380	248,3	156,2	91,2	15	35	Positive
4	Bifenazate	11,4	380	301,1	198,2	169,9	10	20	Positive
5	Clomazone	10,4	380	240,1	127,8	124,9	10	20	Positive
6	Cyazofamid	11,84	380	325	261,2	108,1	10	15	Positive
7	Cyflufenamid	12,79	380	413	294,9	240,8	15	15	Positive
8	Emamectin benzoate B1a	13,3	380	886,5	302,2	158,1	35	40	Positive
9	Emamectin benzoate B1b	13,09	380	872,5	157,9	82	30	35	Positive
10	Etoxazole	14,02	380	360	304	140,9	20	30	Positive
11	Fenpyrazamine	11,4	380	332,2	272,1	230,2	10	20	Positive
12	Flufenacet	11,82	380	364,1	194,1	152	15	15	Positive
13	Fluxapyrosad	11,3	380	381,9	362	342	10	15	Positive
14	Ioxynil	9,98	380	369,8	214,8	126,8	30	30	Negative
15	Isoxaflutole	10	380	360	250,9	219,7	15	50	Positive
16	Lufenuron	13,6	380	508,9	339	325,9	10	10	Negative
17	Metrafenone	12,72	380	409,1	226,9	209,1	16	8	Positive
18	Penflufen	12,28	380	318,1	234	141	10	20	Positive
19	Propaquizafop	13,3	380	444,1	371	99,9	15	20	Positive
20	Proquinazid	14	380	373	331	289,1	20	20	Positive
21	Prothioconazole	12,51	380	341,9	306,1	99,8	15	20	Negative
22	Prothioconazole-desthio	11,7	380	312,1	125	70	40	20	Positive
23	Pyrethrin I	14,24	380	329,21	143	161	20	5	Positive
24	Pyrethrin II	13,14	380	373,1	161	133	10	15	Positive
25	Pyridalil	15,2	380	490	203,9	108,8	20	20	Positive
26	Quinoclamine	7,6	380	208	105,1	77	25	40	Positive
27	Rotenone	11,8	380	395	213,1	192,1	20	20	Positive
28	Spinetoram	12,97	380	748,3	142	98,1	40	40	Positive
29	Spirotetramat	11,6	380	374,2	330,3	270,1	15	20	Positive
30	Sulfoxaflor	6,15	380	278	153,9	105,1	20	10	Positive
31	Tricyclazole	6,82	380	190,1	163	136,1	25	35	Positive
32	Triticonazole	11,68	380	318,1	125,2	70,2	41	33	Positive
33	Tritosulfuron	10,48	380	446	145	110	40	48	Positive

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

No.	Name	t_R (min)	Precursor ion 1 (m/z)	Product ion 1 (m/z)	CE 1 (eV)	Precursor ion 2 (m/z)	Product ion 2 (m/z)	CE 2 (eV)
1	Anthraquinone	7,16	180	152	10	20	180	5
2	Benalaxyl	8,021	204	176	2	148	105	20
3	Ethoprophos	5,09	158	114	5	158	97	15
4	Fluopicolide	8,115	209	182	20	173	109	25
5	Heptachlor endo-epoxide	7,54	183	119	30	183	155	15
5	Heptachlor exo-epoxide	7,49	217	182	22	183	119	25
6	Isopyrazam	9,303	359	303	8	359	303	8
7	Metconazole	8,744	125	99	20	125	89	20
8	Molinate	4,492	187	126	3	126	55	12
9	Novaluron	3,83	168	140	10	335	168	20
10	Penthiopyrad	8,4	302	177	20	177	101	20
11	Phenthoate	6,887	274	246	5	274	121	10
12	Picolinafen	8,56	376	238	25	238	145	25
13	Prothiofos	7,295	309	239	15	309	221	25
14	Pyriofenone	9,08	350	320	15	365	350	5
15	Quintozene	5,558	295	265	10	295	237	15
16	Tetramethrin	8,5	164	107	15	164	77	30
17	Triallate	6,31	268	184	20	143	83	15

APPENDIX II: VALIDATION RESULTS

Table 3. Accuracy data (as % recovery) and precision data (as repeatability RSD_r, n=5) at 0.005 and 0.05 mg/kg for tomato, orange and avocado.

No.	Compounds	Tomato				Orange				Avocado			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
1	**Ametoctradin**	103	5	102	3	100	4	115	3	ND	ND	108	10
2	*Anthraquinone*	88	7	101	3	104	5	107	6	91	8	91	2
3	**BAC10**	109	5	104	4	114	2	119	4	114	4	128	9
4	**BAC8**	109	5	104	5	118	8	118	8	112	5	113	5
5	*Benalaxyl*	102	7	105	3	90	6	104	4	108	4	109	4
6	**Bifenazate**	84	1	91	18	92	5	103	3	5	14	19	15
7	**Clomazone**	111	4	110	5	109	6	115	4	111	6	112	5
8	**Cyazofamid**	103	8	111	6	83	7	88	7	112	8	120	9
9	**Cyflufenamid**	102	4	110	4	33	10	28	4	112	18	120	7
10	**Emamectin benzoate B1a**	102	7	110	10	109	10	119	8	101	7	107	8
11	**Emamectin benzoate B1b**	112	12	102	6	98	6	98	6	ND	ND	102	6
12	*Ethoprophos*	92	5	100	5	102	11	107	6	101	3	101	0
13	**Etoxazole**	71	5	14	8	10	34	4	9	108	9	113	19
14	**Fenpyrazamine**	103	11	115	5	110	3	114	6	110	4	115	8
15	**Flufenacet**	113	6	111	6	94	11	89	8	110	8	119	6
16	*Fluopicolide*	97	6	96	5	102	7	109	8	108	4	104	2
17	**Fluxapyrosad**	106	6	114	8	115	8	115	4	118	4	119	4
18	*Heptachlor endo-epoxide*	109	9	106	5	ND	ND	108	1	ND	ND	100	6
18	*Heptachlor exo-epoxide*	85	17	107	5	ND	ND	107	2	ND	ND	99	3
19	**Ioxynil**	62	15	51	14	73	7	78	8	99	5	100	4
20	*Isopyrazam*	88	5	96	4	101	7	109	7	110	3	108	2

No.	Compounds	Tomato				Orange				Avocado			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
21	**Isoxaflutole**	107	2	115	6	114	9	111	3	105	5	113	5
22	**Lufenuron**	119	11	97	10	21	19	9	11	111	17	114	21
23	*Metconazole*	79	6	97	6	100	6	105	12	87	7	104	3
24	**Metrafenone**	109	3	106	3	42	9	37	7	106	16	119	12
25	*Molinate*	92	11	87	9	102	16	96	6	104	3	90	2
26	*Novaluron*	115	3	99	2	97	3	93	6	127	6	113	5
27	**Penflufen**	112	7	111	5	101	7	99	7	110	6	119	5
28	*Penthiopyrad*	83	4	97	4	102	8	110	8	112	3	107	2
29	*Phenthoate*	90	7	100	2	113	11	112	5	112	5	104	2
30	*Picolinafen*	85	1	96	2	106	8	111	5	97	3	100	3
31	**Propaquizafop**	105	3	111	6	25	13	20	5	112	19	116	13
32	**Proquinazid**	103	3	101	2	11	29	5	7	82	14	84	19
33	**Prothioconazole**	101	10	108	7	74	13	66	4	ND	ND	23	19
34	**Prothioconazole-desthio**	101	10	108	7	100	4	100	2	120	6	113	8
35	*Prothiofos*	87	4	94	2	101	9	111	5	76	4	79	3
36	**Pyrethrin I**	100	6	99	4	10	28	4	15	ND	ND	84	13
37	**Pyrethrin II**	99	8	109	6	ND	ND	28	7	ND	ND	129	11
38	**Pyridalil**	117	9	87	9	ND	ND	ND	ND	39	32	54	23
39	*Pyriofenone*	91	6	101	3	104	8	112	4	106	2	102	3
40	**Quinoclamine**	111	4	114	4	116	10	142	6	111	4	116	4
41	*Quintozene*	86	15	83	15	87	15	103	3	72	4	74	2
42	**Rotenone**	114	8	112	3	73	6	79	5	111	7	118	5
43	**Spinetoram**	115	6	110	5	108	11	120	5	105	7	117	6
44	**Spirotetramat**	98	3	93	4	ND	ND	104	5	89	4	86	10
45	**Sulfoxaflor**	110	2	109	3	132	5	154	5	109	4	115	3

No.	Compounds	Tomato				Orange				Avocado			
		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg		0.005 mg/kg		0.050 mg/kg	
		Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
46	*Tetramethrin*	90	8	98	16	98	8	114	5	114	20	104	6
47	*Triallate*	89	8	94	7	101	10	108	4	90	2	83	2
48	**Tricyclazole**	107	1	107	2	115	6	119	5	<u>63</u>	5	<u>68</u>	7
49	**Triticonazole**	104	6	120	4	ND	ND	113	6	113	6	117	10
50	**Tritosulfuron**	87	5	86	5	78	8	92	2	ND	ND	109	6

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS
ND: Not Detected
Underlined, pesticides with recovery lower than 70%.

Table 4. Limits of quantification, linearity range, coefficient of determination and matrix effects for the selected matrices studied. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement.

No.	Compound	LOQ (mg/kg)			Linear Range (mg/kg)				R^2			Matrix effects (%)		
		Tomato	Orange	Avocado	Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
1	**Ametoctradin**	0.005	0.005	0.05	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9988	0.9978	0.9993	-7	-22	-15
2	*Anthraquinone*	0.005	0.005	0.005	0.005-0.5	0.002-0.5	0.002-0.5	0.005-0.5	0.9996	0.9999	0.9995	15	94	75
3	**BAC10**	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.005-0.5	0.9998	0.9955	0.9997	-17	-21	-14
4	**BAC8**	0.005	0.005	0.005	0.005-0.5	0.002-0.5	0.002-0.5	0.005-0.5	0.9994	0.9977	0.9991	-7	-25	-4
5	*Benalaxyl*	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9998	0.9997	0.9994	58	44	26
6	**Bifenazate**	0.005	0.005	n.f.r.	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9997	0.9988	0.9982	-10	-32	-53
7	**Clomazone**	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9997	0.9994	0.9998	-11	-28	-16
8	**Cyazofamid**	0.005	0.005	0.005	0.005-0.5	0.005-0.5	0.005-0.5	0.005-0.5	0.9962	0.9977	0.9996	-17	-25	-25
9	**Cyflufenamid**	0.005	n.f.r.	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9987	0.9970	0.9993	-3	-11	-13
10	**Emamectin benzoate B1a**	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9993	0.9992	0.9998	-8	-11	-6
11	**Emamectin benzoate B1b**	0.005	0.005	0.05	0.005-0.5	0.005-0.5	0.005-0.5	0.010-0.5	0.9994	0.9977	0.9999	-8	-18	-11
12	*Ethoprophos*	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9997	0.9997	0.9988	35	94	58
13	**Etoxazole**	0.005	n.f.r.	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9992	0.9954	0.9963	0	-24	-27
14	**Fenpyrazamine**	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9999	0.9999	0.9998	-12	-22	-15
15	**Flufenacet**	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9981	0.9995	0.9995	-12	-18	-12
16	*Fluopicolide*	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	1.0000	0.9999	0.9994	87	121	84
17	**Fluxapyrosad**	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9990	0.9997	0.9987	-4	-18	-6
18	*Heptachlor endo-epoxide*	0.005	0.05	0.05	0.005-0.5	0.005-0.5	0.010-0.5	0.010-0.5	0.9994	0.9991	0.9998	21	26	15
18	*Heptachlor exo-epoxide*	0.005	0.05	0.05	0.010-0.5	0.005-0.5	0.010-0.5	0.010-0.5	0.9998	0.9982	0.9992	24	22	15
19	**Ioxynil**	0.005*	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9995	0.9984	0.9995	-8	-13	-10
20	*Isopyrazam*	0.005	0.005	0.005	0.002-0.5	0.005-0.5	0.002-0.5	0.002-0.5	0.9980	0.9999	0.9994	37	116	80
21	**Isoxaflutole**	0.005	0.005	0.005	0.002-0.5	0.005-0.5	0.005-0.5	0.005-0.5	0.9992	0.9990	0.9981	2	-46	11
22	**Lufenuron**	0.005	n.f.r.	0.005	0.002-0.5	0.005-0.5	0.002-0.5	0.002-0.5	0.9924	0.9997	0.9979	-29	10	-15

No.	Compound	LOQ (mg/kg)			Linear Range (mg/kg)				R^2			Matrix effects (%)		
		Tomato	Orange	Avocado	Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
23	*Metconazole*	0.005	0.005	0.005	0.005-0.5	0.005-0.5	0.005-0.5	0.005-0.5	0.9987	0.9997	0.9989	24	88	16
24	**Metrafenone**	0.005	n.f.r.	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9983	0.9998	0.9966	-9	-11	-21
25	*Molinate*	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.005-0.5	0.9998	0.9997	0.9974	25	50	43
26	*Novaluron*	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9998	0.9996	0.9992	66	38	56
27	**Penflufen**	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9959	0.9995	0.9972	-8	-14	-15
28	*Penthiopyrad*	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9992	0.9998	0.9992	27	114	96
29	*Phenthoate*	0.005	0.005	0.005	0.050-0.5	0.005-0.5	0.002-0.5	0.002-0.5	0.9980	0.9997	0.9996	53	149	130
30	*Picolinafen*	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9999	0.9998	0.9992	21	76	53
31	**Propaquizafop**	0.005	n.f.r.	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9964	0.9997	0.9995	-3	-2	-14
32	**Proquinazid**	0.005	n.f.r.	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9987	0.9984	0.9997	-18	-20	-14
33	**Prothioconazole**	0.005	0.005	0.05	0.002-0.5	0.002-0.5	0.002-0.5	0.010-0.5	0.9992	1.0000	0.9974	-2	6	-62
34	**Prothioconazole-desthio**	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9930	0.9942	0.9953	-6	-22	-26
35	*Prothiofos*	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9992	0.9997	0.9998	35	67	52
36	**Pyrethrin I**	0.005	n.f.r.	0.05	0.002-0.5	0.002-0.5	0.005-0.5	0.010-0.2	0.9988	0.9997	0.9987	-21	-26	-24
37	**Pyrethrin II**	0.005	n.f.r.	n.f.r.	0.005-0.5	0.005-0.5	0.005-0.5	0.005-0.5	0.9993	0.9996	0.9954	-12	-9	-23
38	**Pyridalil**	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9996	1.0000	0.9999	326	277	193
39	*Pyriofenone*	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9998	0.9999	0.9988	28	46	27
40	**Quinoclamine**	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9999	0.9999	0.9999	-6	-36	-20
41	*Quintozene*	0.005	0.005	0.005	0.005-0.5	0.002-0.5	0.005-0.5	0.002-0.5	0.9980	0.9988	1.0000	30	77	61
42	**Rotenone**	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9981	0.9977	0.9999	-5	-13	-17
43	**Spinetoram**	0.005	0.005	0.005	0.005-0.5	0.005-0.5	0.002-0.5	0.002-0.5	0.9997	0.9998	0.9995	-14	-24	-19
44	**Spirotetramat**	0.005	0.05	0.005	0.002-0.5	0.002-0.5	0.050-0.5	0.002-0.5	0.9979	0.9994	0.9999	-10	-21	10
45	**Sulfoxaflor**	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	1.0000	0.9989	1.0000	-8	-36	-13
46	*Tetramethrin*	0.005	0.005	0.005	0.010-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9995	0.9999	0.9997	57	137	58
47	*Triallate*	0.005	0.005	0.005	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9995	0.9998	0.9993	20	43	40
48	**Tricyclazole**	0.005	0.005	0.005*	0.002-0.5	0.002-0.5	0.002-0.5	0.002-0.5	0.9998	0.9998	0.9998	-11	-72	-15

No.	Compound	LOQ (mg/kg)			Linear Range (mg/kg)				R^2			Matrix effects (%)		
		Tomato	Orange	Avocado	Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
49	**Triticonazole**	0.005	0.05	0.005	0.005-0.5	0.005-0.5	0.010-0.5	0.005-0.5	0.9988	0.9988	0.9999	-7	-27	-12
50	**Tritosulfuron**	0.005	0.005	0.05	0.005-0.5	0.005-0.5	0.005-0.5	0.010-0.5	0.9995	0.9993	0.9997	-6	17	11

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS
* Lowest spike level detectable with good precision, but recovery <70%
n.f.r.: not fulfilling requirements for quantitative method (Recovery < 30 %)