Validation of MRM pesticides from the Working Document SANCO/12745/2013 using three Multiresidue methods (QuEChERS, ethyl acetate and Dutch mini-Luke)

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1. Aim and scope

This document describes the validation data for 47 pesticides included in the Working document SANCO/12745/2013 using three multiresidue extraction methods by LC-MS/MS and GC-MS/MS in tomato, orange and avocado.

2. Short description

Homogenous samples were extracted using three different methods (QuEChERS, ethyl acetate and Dutch mini-Luke) which were adapted in the case of avocado extractions. The obtained extracts were then analyzed 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
- Homogeinizer, e.g. Polytron PT 10-35.
- 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.
- Acetone residue of analysis grade.
- Petroleum ether residue of analysis grade.
- Dichloromethane and ethyl acetate residue of analysis grade
- Trisodium citrate dihydrate
- Disodium hydrogenocitratesesquihydrate
- Sodium chloride
- Anhydrous magnesium sulphate
- Primary secondary amine (PSA)
- Supel QuE Z-Sep
- C18

- Ammonium formate
- Ultra-pure water
- Methanol HPLC grade
- Formic acid
- Ethyl acetate
- Pesticides analytical standards

5. Procedure

5.1. Sample preparation

Following Document No. SANTE/2019/12682, the sample was perfectly homogenised by cryogenic milling at its arrival to the laboratory.

5.2. Recovery experiments for method validation

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, the 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 0.050 mg/kg). Five replicates were analysed at each level.

5.3. Extraction procedures

5.3.1. QuEChERS

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 1 g of sample in GC.

5.3.2. Ethyl acetate method

1. Weigh 10 g ± 0.1 g of sample in a 50 mL PTFE centrifuge tube.
2. Add 10 mL of ethyl acetate and 10 µL of 10 mg/L carbendazim-d3, malathion-d10 and TPP (procedure internal standards).
3. Shake with the automatic axial extractor during 15 min.
4. Add 1.5 g of sodium chloride and 8 g of magnesium sulphate.
5. Shake with the automatic axial extractor during 15 min.
6. Centrifuge for 5 min at 3500 rpm.
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, evaporate 100 µL of the extract and reconstitute with 100 of acetonitrile and 400 mL of water containing dimethoate-d6 at 0.050 mg/L (Injection Internal Standard).

    b. for GC analysis 2 µL of lindane-d6 (Injection Internal Standard) at 1.5 mg/L were added to 50 µL of ethyl acetate.

With this treatment, 1 mL of sample extract represents 0.2 g of sample in LC and 1 g of sample in GC.

5.3.3. Dutch mini-Luke method

1. Weigh 7.5 g ± 0.1 g of subsample in a 50 mL PTFE centrifuge tube.
2. Add 10 mL of acetone and 3 g of sodium chloride.
3. Add10 µL of 10 mg/L carbendazim-d3, malathion-d10 and TPP (procedure internal standards).
4. Blend the sample with Polytron homogeneizer at 1500 rpm for 30 sec.
5. Add 10 mL of petroleum ether and 5 mL of dichlorometane.
6. Blend again the sample with Polytron homogeneizer at 1500 rpm for 30 sec.
7. Centrifuge for 5 min at 3500 rpm.
8. Transfer the supernatant:

    a. Transfer 4 mL of extract to a 4 ml vial for matrices with high water content.

    b. Transfer 5 mL of extract to a 15 mL PTFE tube containing 750 mg magnesium sulphate and 125 mg of Z-Sep for matrices with high fat content.

9. Vortex the tube for 30 sec.

10. Centrifuge the tubes at 3700 rpm for 5 min.
11. Analysis:
    a. for LC analysis, evaporate 167 µL extract and reconstitute with 50 µL of acetonitrile and 200 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; 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 optimized 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 analysed

Time (min)	Mobile phase A (%)	Mobile phase B (%)
0	100	0
2	80	20
15	0	100
18	0	100

Re-equilibration with initial 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: 120°C
- Sheath gas flow: 10 L/min
- Sheath gas temperature: 375°C
- 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

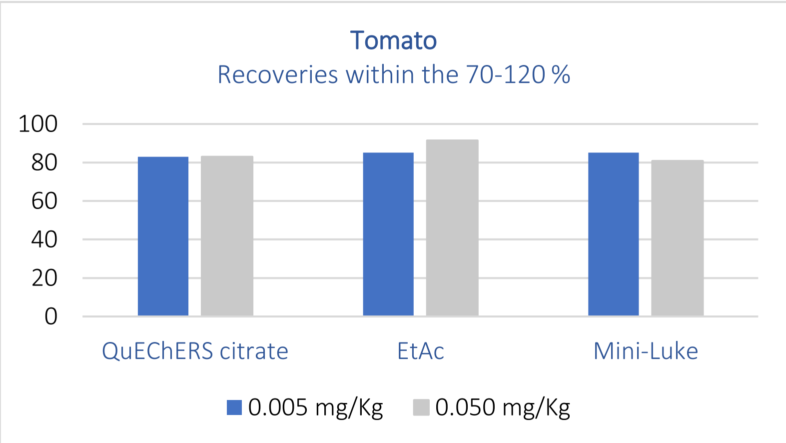
The results corresponding to the mean recovery (n=5) and within-laboratory reproducibility in terms of relative standard deviation (RSDr) at two fortification levels (0.005 and 0.050 mg/kg) are summarized in appendix II:

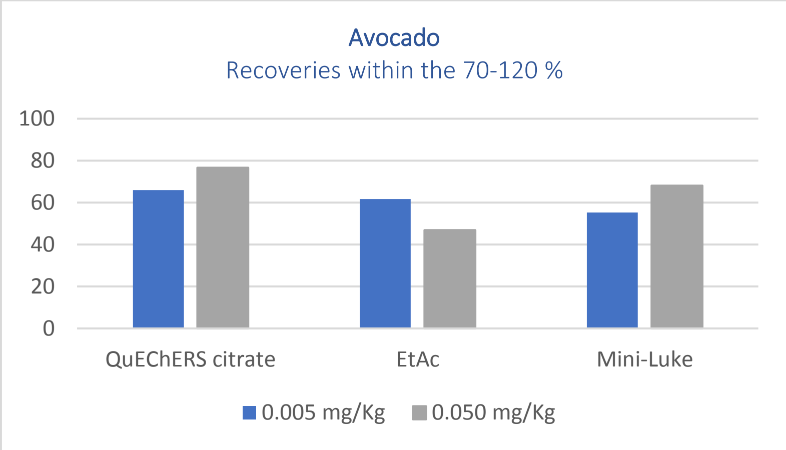
A) Table 3, for QuEChERS citrate buffered method

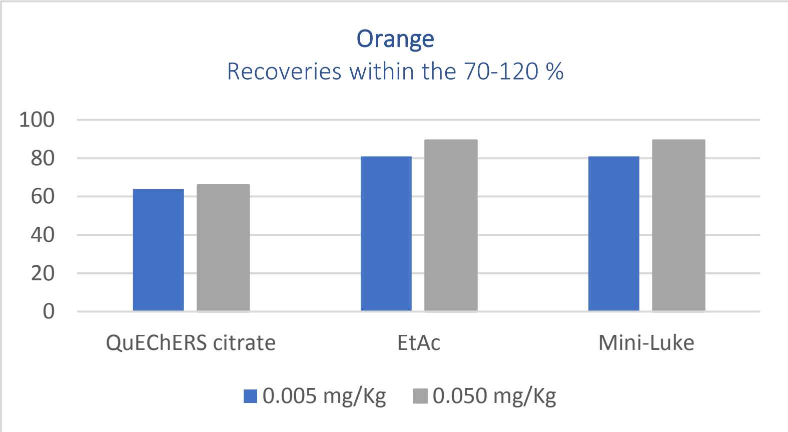
B) Table 4, for ethyl acetate method

C) Table 5, for Dutch mini-Luke method

Most recovery results are within the range 70-120% (RSD≤20%). The following graphs summarize the results obtained:







6.2. Linearity

Linearity of the MS/MS system was evaluated by assessing the signal responses of the target analytes from matrix-matched calibration solutions prepared by spiking blank extracts at six concentration levels, from 0.002 to 0.100 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:

A) Table 6, for QuEChERS citrate buffered method

B) Table 7, for ethyl acetate method

C) Table 8, for Dutch mini-Luke method

6.3. Matrix effects

Matrix effects were assessed by comparison of the slopes of six-point matrix-matched calibration curves with the slopes of the calibration curves in solvent (LC) or in tomato (GC). For values (in absolute terms) between 0 and 20 %, matrix effect was considered low; a moderate matrix effect would have values between 20 % and 50 %, and for compounds with a value above 50 %, matrix effect was considered strong. Values of matrix effects are summarized in appendix II:

A) Table 6, for QuEChERS citrate buffered method

B) Table 7, for ethyl acetate method

C) Table 8, for Dutch mini-Luke method

7. References

Analytical quality control and method validation procedures for pesticide residues analysis in food and feed. Document N° SANTE/2019/12682.

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

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 (m/z)	Product ion 1 (m/z)	Product ion 2 (m/z)	CE 1 (eV)	CE 2 (eV)	Polarity
1	2.4-D	9.46	380	219	161	163	15	15	Positive
2	Benalaxyl	12.46	380	326	148	208	15	15	Positive
3	Chlorfluazuron	14.17	380	540	382.9	158.1	20	15	Positive
4	Clomazone	10.4	380	240.1	127.8	124.9	10	20	Positive
5	Cinerin I	14.19	380	317	149	107.1	5	10	Positive
6	Cinerin II	12.11	380	361.1	301	107	15	20	Positive
7	Dazomet	36.65	380	163	119.9	90	10	5	Positive
8	Fenobucarb	10.75	380	208.2	95.1	151.9	5	20	Positive
9	Flufenacet	11.82	380	364.1	194.1	152	15	15	Positive
10	Fluxapyrosad	11.3	380	381.9	362	342	10	15	Positive
11	Ioxynil	9.98	380	369.8	214.8	126.8	30	30	Positive
12	Isoxaflutole	10	380	360	250.9	219.7	15	50	Positive
13	Jasmolin I	14.56	380	331	163.2	107	15	20	Positive
14	Jasmolin II	13.53	380	375	163	121	5	20	Positive
15	MCPA	9.85	380	199	140.7	143	10	15	Positive
16	MCPB	11.53	380	227.1	141	143	5	5	Positive
17	Meptyldinocap	14.37	380	295.1	193.8	248.1	5	4	Positive
18	Metaflumizone (E)	13.55	380	505	302	328	10	10	Positive
19	Metconazole	12.60	380	320.1	70.1	125	24	48	Positive
20	Novaluron	13.17	380	490.8	470.7	305.1	5	15	Positive
21	Oxadiargyl	12.63	380	341.1	222.9	150.9	13	33	Positive
22	Oxasulfuron	8.05	380	407.1	150.1	209.7	16	24	Positive
23	Oxyfluorfen	13.41	380	362	237.1	252	30	25	Positive
24	Penflufen	12.28	380	318.1	234	141	10	20	Positive
24	Penthiopyrad	12.40	380	357.9	149	207.6	25	20	Positive
26	Propaquizafop	13.3	380	444.1	371	99.9	15	20	Positive
27	Prothiofos	14.49	380	345	241	161	20	40	Positive

No.	Name	t_R (min)	Cone voltage (V)	Precursor (m/z)	Product ion 1 (m/z)	Product ion 2 (m/z)	CE 1 (eV)	CE 2 (eV)	Polarity
28	Pyrethrin I	14.24	380	329.21	143	161	20	5	Positive
29	Pyrethrin II	13.14	380	373.1	161	133	10	15	Positive
30	Pyridate	14.66	380	379.1	206.8	351.1	5	10	Positive
31	Quinalphos	12.02	380	299.1	270.8	242.8	10	10	Positive
32	Quinoclamine	7.6	380	208	105.1	77	25	40	Positive
33	Quizalofop-ethyl	13.15	380	373.1	255.1	271.2	20	35	Positive
34	Rotenone	11.8	380	395	213.1	192.1	20	20	Positive
35	Sulfoxaflor	6.15	380	278	153.9	105.1	20	10	Positive
36	Tolfenpyrad	13.42	380	384.1	197	170.9	25	20	Positive
37	Triflumizole	13.18	380	346.1	277.8	72.9	5	15	Positive
38	Triticonazole	11.68	380	318.1	125.2	70.2	41	33	Positive
39	Tritosulfuron	10.48	380	446	145	110	40	48	Positive

Table 2. Detection 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	Cyhalothrin Lambda	9.27	197	141	10	197	161	5
2	Heptachlor	6.31	272	237	10	272	143	40
3	Isopyrazam	9.30	359	303	8	359	303	8
4	Molinate	4.49	187	126	3	126	55	12
5	Phenthoate	6.88	274	246	5	274	121	10
6	Picolinafen	8.56	376	238	25	238	145	25
7	Quintozene	5.55	295	265	10	295	237	15
8	Tetramethrin	8.5	164	107	15	164	77	30

APPENDIX II: VALIDATION RESULTS.

Table 3. Accuracy data (as % recovery) and precision data (as repeatibility RSDr, n=5) at 0.005 and 0.050 mg/ kg for tomato, orange, avocado by using QuEChERS citrate.

		Tomato				Orange				Avocado			
No.	Compund	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	**2.4-D**	13	15	15	15	27	29	29	17	80	6	92	7
2	**Benalaxyl**	84	9	96	4	81	11	74	4	115	2	120	7
3	**Cinerin I**	83	4	113	6	ND	ND	35	38	ND	ND	103	12
4	**Cinerin II**	ND	ND	ND	ND	ND	ND	98	14	ND	ND	ND	ND
5	**Chlorfluazuron**	96	2	103	8	13	9	29	28	120	22	100	20
6	**Clomazone**	86	11	95	5	104	6	90	2	96	3	99	4
7	*Cyhalothrin Lambda*	91	5	78	4	143	8	108	7	ND	ND	72	4
8	**Dazomet**	38	9	44	18	70	20	41	11	ND	ND	ND	ND
9	**Fenobucarb**	91	7	94	5	97	10	102	3	97	9	98	2
10	**Flufenacet**	81	9	94	4	92	6	94	2	107	8	100	3
11	**Fluxapyrosad**	120	13	113	10	95	7	102	6	105	8	105	4
12	*Heptachlor*	102	4	84	5	100	7	87	6	96	4	57	9
13	**Ioxynil**	71	7	73	6	72	2	70	2	94	11	91	4
14	*Isopyrazam*	85	4	75	7	120	6	94	8	132	17	104	16

No.	Compund	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 (%)
15	**Isoxaflutole**	93	9	103	11	99	5	92	5	103	4	103	2
16	**Jasmolin I**	98	13	112	12	8	37	31	16	ND	ND	ND	ND
17	**Jasmolin II**	ND	ND	102	4	26	23	35	32	ND	ND	ND	ND
18	**MCPA**	17	52	16	6	ND	ND	29	19	96	14	97	4
19	**MCPB**	ND	ND	ND	ND	ND	ND	63	19	ND	ND	ND	ND
20	**Meptyldinocap**	ND	ND	ND	ND	14	26	74	12	75	19	79	4
21	**Metaflumizone (E)**	90	4	106	11	10	19	25	32	99	11	86	3
22	**Metconazole**	92	8	95	1	85	1	89	3	111	6	100	4
23	*Molinate*	101	6	67	9	76	7	74	10	109	7	76	7
24	**Novaluron**	94	8	106	15	112	7	84	1	106	6	104	7
25	**Oxadiargyl**	103	20	104	4	64	14	56	13	115	4	105	8
26	**Oxasulfuron**	47	12	49	9	78	6	74	2	101	7	97	3
27	**Oxyfluorfen**	95	20	120	13	ND	ND	ND	ND	ND	ND	ND	ND
28	**Penflufen**	88	7	88	2	86	8	83	6	106	10	105	9
29	**Penthiopyrad**	86	8	103	3	80	7	93	12	100	13	112	5
30	*Phenthoate*	90	10	81	8	119	8	93	8	126	6	84	7
31	*Picolinafen*	94	10	88	8	118	9	94	9	117	13	87	8

No.	Compund	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 (%)
32	**Propaquizafop**	98	4	100	6	51	5	34	16	109	12	97	10
33	**Prothiofos**	99	19	105	11	119	6	94	5	42	45	78	11
34	**Pyrethrin I**	98	3	104	10	9	32	25	27	ND	ND	ND	ND
35	**Pyrethrin II**	92	13	105	3	30	5	36	2	ND	ND	ND	ND
36	**Pyridate**	74	4	72	16	96	12	20	20	86	20	84	13
37	**Quinalphos**	94	5	88	1	80	7	90	6	97	5	95	12
38	**Quinoclamine**	89	9	94	1	95	10	91	6	95	8	89	4
39	*Quintozene*	108	3	75	7	97	8	87	4	84	5	57	7
40	**Quizalofop-ethyl**	100	5	100	7	79	8	80	15	101	19	99	11
41	**Rotenone**	99	2	93	5	78	10	75	14	99	8	116	2
42	**Sulfoxaflor (sum)**	88	5	95	1	99	8	88	1	105	4	98	4
43	*Tetramethrin (sum)*	93	7	76	5	119	7	100	10	115	10	91	9
44	**Tolfenpyrad**	95	6	98	13	18	5	36	12	92	20	107	11
45	**Triflumizole**	81	5	82	2	71	2	79	7	102	25	95	17
46	**Triticonazole**	94	8	107	7	95	6	87	11	100	17	92	3
47	**Tritosulfuron**	70	9	77	6	78	3	78	6	ND	ND	ND	ND

In bold, pesticides analysed by LC-MS/MS

In italic, pesticides analysed by GC-MS/MS

ND: Not Detected

Underlined, pesticides with recovery out of the range 70-120% and RSD >20%.

Table 4. Accuracy data (as % recovery) and precision data (as repeatability RSDr, n=5) at 0.005 and 0.050 mg/kg for tomato, orange, avocado by using ethyl acetate method

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 (%)
2.4-D	108	8	98	6	113	8	110	4	ND	ND	<u>10</u>	2
Benalaxyl	118	6	97	7	89	6	106	6	79	20	73	1
Cinerin I	89	16	110	8	96	7	101	10	ND	ND	ND	ND
Cinerin II	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorfluazuron	106	3	114	9	103	9	120	7	105	5	<u>62</u>	14
Clomazone	106	6	91	4	107	3	99	1	97	2	82	0
Cyhalothrin Lambda	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dazomet	<u>15</u>	10	<u>22</u>	7	<u>57</u>	9	<u>59</u>	3	ND	ND	<u>17</u>	6
Fenobucarb	101	9	102	7	99	1	104	8	87	1	86	4
Flufenacet	105	5	98	7	122	2	104	4	101	7	84	2
Fluxapyrosad	99	20	104	3	84	2	98	3	89	1	84	3
Heptachlor	117	7	83	4	119	9	107	2	ND	ND	ND	ND
Ioxynil	102	5	99	2	106	4	103	5	<u>36</u>	4	<u>39</u>	6
Isopyrazam	117	3	86	5	119	5	105	3	105	9	81	2
Isoxaflutole	94	14	96	2	103	3	107	3	101	3	81	3

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 (%)
Jasmolin I	104	3	110	11	<u>124</u>	3	118	3	<u>132</u>	<u>47</u>	<u>44</u>	<u>27</u>
Jasmolin II	111	19	97	12	111	6	109	3	ND	ND	ND	ND
MCPA	104	2	113	3	116	2	111	1	<u>9</u>	4	<u>13</u>	4
MCPB	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Meptyldinocap	<u>132</u>	10	102	7	100	6	107	11	ND	ND	83	5
Metaflumizone (E)	113	6	107	10	111	7	103	4	104	6	<u>64</u>	19
Metconazole	118	6	90	7	94	6	116	2	96	6	80	4
Molinate	109	3	78	7	112	6	84	7	119	5	82	5
Novaluron	118	7	92	2	118	1	105	1	<u>146</u>	6	96	5
Oxadiargyl	<u>121</u>	2	101	6	88	2	99	7	112	1	73	20
Oxasulfuron	105	7	94	1	89	1	90	2	86	4	89	3
Oxyfluorfen	ND	ND	98	11	ND	ND	ND	ND	ND	ND	ND	ND
Penflufen	94	3	93	8	110	11	107	3	93	3	79	1
Penthiopyrad	97	2	118	3	109	5	106	2	114	4	81	5
Phenthoate	<u>123</u>	5	90	4	<u>127</u>	2	106	3	106	6	80	2
Picolinafen	116	4	86	4	119	4	105	3	112	5	77	4
Propaquizafop	104	11	111	9	98	3	118	6	114	3	<u>51</u>	<u>31</u>

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 (%)
Prothiofos	118	2	89	3	105	2	98	11	90	10	46	40
Pyrethrin I	104	2	109	10	103	4	114	5	87	19	36	45
Pyrethrin II	90	11	106	10	105	5	115	5	ND	ND	59	9
Pyridate	107	4	108	12	105	6	111	10	78	14	59	24
Quinalphos	100	2	98	2	104	7	109	3	97	5	66	12
Quinoclamine	103	5	99	2	95	5	98	0	85	9	85	2
Quintozene	116	7	86	3	119	3	102	0	109	2	74	6
Quizalofop-ethyl	110	9	93	8	110	2	112	7	95	16	46	26
Rotenone	98	3	109	3	114	8	114	3	95	20	60	9
Sulfoxaflor	100	6	92	0	93	5	92	6	101	5	85	1
Tetramethrin	119	3	87	4	113	7	104	3	126	3	77	2
Tolfenpyrad	96	7	107	12	111	4	118	2	96	10	39	48
Triflumizole	108	11	92	2	105	5	103	5	96	4	56	10
Triticonazole	107	5	83	7	103	6	95	5	68	8	64	5
Tritosulfuron	101	1	99	3	93	11	111	4	96	9	91	2

In bold, pesticides analysed by LC-MS/MS

In italic, pesticides analysed by GC-MS/MS

ND: Not Detected

Underlined, pesticides with recovery out of the range 70-120% and RSD >20%.

Table 5. Accuracy data (as % recovery) and precision data (as repeatability RSDr, n=5) at 0.005 and 0.050 mg/kg for tomato, orange, avocado by using Dutch mini-Luke method

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	**2.4-D**	78	13	101	10	76	8	127	1	ND	ND	ND	ND
2	**Benalaxyl**	93	2	94	17	96	3	88	3	90	18	76	11
3	**Cinerin I**	139	13	106	20	64	19	92	3	ND	ND	ND	ND
4	**Cinerin II**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5	**Chlorfluazuron**	103	4	89	25	86	6	81	7	99	5	106	13
6	**Clomazone**	96	3	93	11	89	3	93	5	70	5	111	1
7	*Cyhalothrin Lambda*	113	1	93	17	117	5	110	14	98	5	99	0
8	**Dazomet**	ND	ND	ND	ND	78	20	73	9	ND	ND	ND	ND
9	**Fenobucarb**	93	5	88	12	85	3	85	4	70	6	107	6
10	**Flufenacet**	110	3	99	10	102	3	90	5	101	19	74	14
11	**Fluxapyrosad**	84	18	93	7	85	3	97	3	74	5	102	7
12	*Heptachlor*	119	1	68	51	138	8	125	31	ND	ND	ND	ND
13	**Ioxynil**	97	3	97	11	98	3	102	2	10	10	24	3
14	*Isopyrazam*	113	0	87	16	144	5	103	6	86	8	91	4

		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	
No.	Compounds	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)	Recov (%)	RSD (%)
15	**Isoxaflutole**	94	3	96	14	88	3	94	1	77	12	103	2
16	**Jasmolin I**	130	8	103	19	ND	ND	83	10	ND	ND	ND	ND
17	**Jasmolin II**	79	2	123	18	ND	ND	89	10	ND	ND	ND	ND
18	**MCPA**	123	4	96	11	108	4	130	5	ND	ND	ND	ND
19	**MCPB**	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
20	**Meptyldinocap**	73	8	87	20	73	23	76	5	ND	ND	76	11
21	**Metaflumizone (E)**	114	3	96	18	101	4	77	8	120	15	73	20
22	**Metconazole**	98	6	100	12	83	7	98	7	61	19	73	10
23	*Molinate*	97	2	75	2	106	1	94	17	117	6	106	4
24	**Novaluron**	115	9	129	23	103	6	81	2	111	26	68	25
25	**Oxadiargyl**	120	6	91	16	103	10	90	10	98	37	72	13
26	**Oxasulfuron**	90	6	83	11	80	2	89	3	86	7	116	3
27	**Oxyfluorfen**	ND	ND	113	16	ND	ND	86	17	ND	ND	ND	ND
28	**Penflufen**	96	1	93	13	90	4	82	4	77	15	90	5
29	**Penthiopyrad**	95	6	95	9	91	8	90	2	96	19	90	10
30	*Phenthoate*	105	3	97	13	97	8	96	7	100	12	112	1
31	*Picolinafen*	111	0	87	14	117	6	104	10	109	2	90	6

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 (%)
32	**Propaquizafop**	102	8	104	18	88	12	86	3	84	18	81	20
33	**Prothiofos**	106	2	99	30	100	3	120	2	ND	ND	99	20
34	**Pyrethrin I**	113	2	108	20	119	7	80	4	113	15	81	12
35	**Pyrethrin II**	83	6	98	13	77	4	86	4	ND	ND	ND	ND
36	**Pyridate**	95	3	81	29	100	9	77	6	107	19	104	20
37	**Quinalphos**	100	8	92	10	82	3	82	3	112	19	70	7
38	**Quinoclamine**	93	3	98	13	86	5	96	0	63	9	125	2
39	*Quintozene*	103	5	85	19	118	3	108	8	ND	ND	ND	ND
40	**Quizalofop-ethyl**	96	2	110	16	107	10	92	2	77	19	90	17
41	**Rotenone**	107	3	94	12	112	7	89	6	88	30	90	18
42	**Sulfoxaflor**	86	17	94	12	87	4	101	1	91	6	119	2
43	*Tetramethrin*	109	2	84	13	117	5	110	11	96	13	96	2
44	**Tolfenpyrad**	120	5	117	20	99	7	83	5	104	8	82	20
45	**Triflumizole**	86	6	106	8	104	5	80	5	90	16	106	8
46	**Triticonazole**	104	10	106	10	92	2	101	6	71	6	85	5
47	**Tritosulfuron**	86	5	94	14	82	3	101	3	98	13	107	5

In bold, pesticides analysed by LC-MS/MS

In italic, pesticides analysed by GC-MS/MS

ND: Not Detected

Underlined, pesticides with recovery out of the range 70-120% and RSD >20%.

Table 6. Linearity range, coefficient of determination and matrix effects for selected matrices studied by using QuEChERS citrate. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement.

No.	Compund	Linear Range (mg/ kg)				R^2			Matrix effects (%)		
		Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
1	**2.4-D**	0.002-0.1	0.005-0.1	0.002-0.1	0.002-0.1	0.9931	0.9981	0.9982	-3	25	24
2	**Benalaxyl**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9991	0.9950	0.9952	-8	-11	-45
3	**Cinerin I**	0.002-0.1	0.002-0.1	0.002-0.1	-	0.998	0.9949	-	-5	-38	-
4	**Cinerin II**	0.002-0.1	-	-	-	-	-	-	-	-	-
5	**Chlorfluazuron**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9985	0.9975	0.9993	-38	-69	-79
6	**Clomazone**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9995	0.9959	0.9990	0	11	-18
7	*Cyhalothrin Lambda*	0.002-0.1	0.002-0.1	0.002-0.1	0.01-0.1	0.9979	0.9935	0.9969	0	-54	57
8	**Dazomet**	0.002-0.1	0.002-0.1	0.002-0.1	-	0.9952	0.9941	-	-47	-56	-

No.	Compund	Linear Range (mg/ kg)				R^2			Matrix effects (%)		
		Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
9	**Fenobucarb**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9991	0.9967	0.9953	-6	-75	-22
10	**Flufenacet**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9994	0.9988	0.9940	6	-21	-38
11	**Fluxapyrosad**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9983	0.9976	0.9969	-2	-33	-25
12	*Heptachlor*	0.002-0.1	0.002-0.1	0.005-0.1	0.01-0.1	0.9997	0.9942	0.9945	0	40	47
13	**Ioxynil**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9994	0.9990	0.9990	1	-12	-12
14	*Isopyrazam*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9981	0.9937	0.9956	0	57	-36
15	**Isoxaflutole**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9998	0.9991	0.9970	5	-60	10
16	**Jasmolin I**	0.005-0.1	0.010-0.1	0.010-0.1	-	0.9993	0.9988	-	-23	-59	-
17	**Jasmolin II**	0.005-0.1	-	-	-	-	-	-	-	-	-
18	**MCPA**	0.002-0.1	0.01-0.1	0.002-0.1	0.002-0.1	0.997	0.9986	0.9987	-10	14	1

No.	Compund	Linear Range (mg/ kg)				R^2			Matrix effects (%)		
		Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
19	**MCPB**	0.002-0.1	-	0.002-0.1	0.002-0.1	-	0.9921	0.9955	-	1	2
20	**Meptyldinocap**	0.002-0.1	-	0.002-0.1	-	-	0.9925	-	-	-59	-
21	**Metaflumizone (E)**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9982	0.9908	0.9978	-16	-52	-67
22	**Metconazole**	0.005-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9912	0.9989	0.9975	-8	-20	-52
23	*Molinate*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9984	0.9940	0.9937	0	26	30
24	**Novaluron**	0.002-0.1	0.002-0.1	0.002-0.1	-	0.9984	0.9961	-	-13	-26	-
25	**Oxadiargyl**	0.002-0.1	0.002-0.1	0.002-0.1	-	0.9995	0.9993	-	-2	-18	-
26	**Oxasulfuron**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9992	0.9984	0.9992	3	16	18
27	**Oxyfluorfen**	0.005-0.1	-	-	-	-	-	-	-	-	-
28	**Penflufen**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9993	0.9982	0.9991	3	-14	-37

No.	Compund	Linear Range (mg/ kg)				R^2			Matrix effects (%)		
		Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
29	**Penthiopyrad**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9938	0.9976	0.9985	-12	2	-26
30	*Phenthoate*	0.002-0.1	0.002-0.1	0.002-0.1	0.005-0.1	0.9993	0.9941	0.9962	0	76	104
31	*Picolinafen*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9987	0.9939	0.9935	0	45	-5
32	**Propaquizafop**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9994	0.9981	0.9975	-8	-13	-64
33	**Prothiofos**	0.002-0.1	-	-	-	-	-	-	-	-	-
34	**Pyrethrin I**	0.002-0.1	0.002-0.1	0.002-0.1	-	0.9993	0.9938	-	-16	-51	-
35	**Pyrethrin II**	0.002-0.1	-	-	-	-	-	-	-	-	-
36	**Pyridate**	0.002-0.1	0.002-0.1	0.002-0.1	-	0.9993	0.997	-	-33	-76	-
37	**Quinalphos**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9992	0.9968	0.9985	3	-22	-43
38	**Quinoclamine**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9993	0.9975	0.9989	2	-2	-31

No.	Compund	Linear Range (mg/ kg)				R^2			Matrix effects (%)		
		Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
39	*Quintozene*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9997	0.9937	0.9929	0	64	79
40	**Quizalofop-ethyl**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9997	0.9956	0.9903	8	-5	-64
41	**Rotenone**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9996	0.9994	0.9938	4	-6	-47
42	**Sulfoxaflor (sum)**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9991	0.9987	0.9990	0	-11	-14
43	*Tetramethrin (sum)*	0.002-0.1	0.002-0.1	0.002-0.1	0.005-0.1	0.9977	0.9932	0.9957	0	58	17
44	**Tolfenpyrad**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9999	0.9958	0.9902	-9	-31	-72
45	**Triflumizole**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9994	0.9940	0.9979	-1	-20	-67
46	**Triticonazole**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.998	0.9956	0.9939	5	-31	-27
47	**Tritosulfuron**	0.002-0.1	0.002-0.1	0.002-0.1	-	0.9985	0.9988	-	-4	7	-

In bold, pesticides analysed by LC-MS/MS

In italic, pesticides analysed by GC-MS/MS

Table 7. Linearity range, coefficient of determination and matrix effects for selected matrices studied by using ethyl acetate method. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement.

No.	Compounds	Linear Range (mg/kg)				R^2			Matrix effects (%)		
		Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
1	**2,4-D**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9987	0.9993	0.9988	11	32	8
2	**Benalaxyl**	0.002-0.1	0.002-0.1	0.002-0.1	0.005-0.1	0.9965	0.9962	0.9961	-6	-12	-7
3	**Cinerin I**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9992	0.9990	ND	-31	-9	-87
4	**Cinerin II**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9959	0.9736	ND	44	33	-11
5	**Chlorfluazuron**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9990	0.9981	0.9991	164	231	195
6	**Clomazone**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9993	0.9996	0.9980	-5	-8	-13
7	*Cyhalothrin Lambda*	0.002-0.1	0.002-0.1	0.005-0.1	0.002-0.1	0.9952	0.9972	0.9971	0	19	-40
8	**Dazomet**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.05	0.9967	0.9996	0.9968	-14	64	-2
9	**Fenobucarb**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9999	0.9999	0.9995	-11	-6	-11
10	**Flufenacet**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9999	0.9998	0.9997	-7	-10	-15
11	**Fluxapyrosad**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9993	0.9932	0.9998	-2	-15	-15
12	*Heptachlor*	0.002-0.1	0.002-0.1	0.002-0.1	ND	0.9938	0.9939	ND	0	9	ND
13	**Ioxynil**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9994	0.9998	0.9999	3	-13	-8
14	*Isopyrazam*	0.002-0.1	0.005-0.05	0.005-0.05	0.002-0.1	0.9962	0.9950	0.9981	0	26	-50

No.	Compounds	Linear Range (mg/kg)				R^2			Matrix effects (%)		
		Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
15	**Isoxaflutole**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9994	0.9989	0.9997	-1	-14	-17
16	**Jasmolin I**	0.005-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9980	0.9993	0.9904	-11	23	-39
17	**Jasmolin II**	0.005-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9930	0.9986	ND	-12	-8	-92
18	**MCPA**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9999	0.9990	0.9989	12	23	0
19	**MCPB**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9976	0.9794	0.9332	22	-7	16
20	**Meptyldinocap**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9988	0.9997	0.9962	29	15	-13
21	**Metaflumizone (E)**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9999	0.9961	0.9991	165	281	220
22	**Metconazole**	0.005-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9989	0.9962	0.9978	-11	-16	-11
23	*Molinate*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9949	0.9953	0.9956	0	7	-9
24	**Novaluron**	0.002-0.1	0.002-0.1	0.002-0.1	0.005-0.1	0.9946	0.9950	0.9954	0	8	-36
25	**Oxadiargyl**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9987	0.9968	1.0000	3	-14	-89
26	**Oxasulfuron**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9987	0.9999	0.9978	17	31	3
27	**Oxyfluorfen**	0.005-0.1	0.005-0.1	0.002-0.1	0.002-0.1	0.9960	0.9541	ND	-19	-1	-84
28	**Penflufen**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9991	0.9999	0.9987	-10	-15	-17
29	**Penthiopyrad**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9928	0.9957	0.9957	2	3	-11
30	*Phenthoate*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9945	0.9953	0.9963	0	30	-12
31	*Picolinafen*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9956	0.9959	0.9971	0	23	-35
32	**Propaquizafop**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9998	0.9988	0.9999	0	-5	-80
33	**Prothiofos**	0.002-0.1	0.002-0.1	0.002-0.1	0.005-0.1	0.9949	0.9956	0.9956	78	97	23

No.	Compounds	Linear Range (mg/kg)				R^2			Matrix effects (%)		
		Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
34	**Pyrethrin I**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9985	0.9975	0.9987	-6	10	-57
35	**Pyrethrin II**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9996	0.9998	0.9090	-3	-10	-86
36	**Pyridate**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9993	0.9998	0.9941	178	323	367
37	**Quinalphos**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9989	0.9999	0.9986	-13	-7	-85
38	**Quinoclamine**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	1.0000	0.9999	0.9993	-11	-13	-22
39	*Quintozene*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9947	0.9954	0.9975	0	36	-7
40	**Quizalofop-ethyl**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.05	0.9943	0.9999	0.9996	-16	-9	-84
41	**Rotenone**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9965	0.9995	0.9981	-9	-11	-77
42	**Sulfoxaflor**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9990	0.9999	0.9996	-6	-12	2
43	*Tetramethrin*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9937	0.9943	0.9919	0	36	124
44	**Tolfenpyrad**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.05	0.9999	0.9999	0.9992	-3	-6	-66
45	**Triflumizole**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9996	0.9999	0.9993	-9	-4	-79
46	**Triticonazole**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9994	0.9987	0.9999	8	-11	-35
47	**Tritosulfuron**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9999	0.9998	0.9999	-10	-17	-4

In bold, pesticides analysed by LC-MS/MS

In italic, pesticides analysed by GC-MS/MS

Table 8. Linearity range, coefficient of determination and matrix effects for selected matrices studied by using Dutch mini-Luke method. Negative values of matrix effects mean suppression of the signal, and positives values, enhancement.

No.	Compund	Linear Range (mg/ kg)				R2			Matrix effects(%)		
		Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
1	**2,4-D**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9999	0.9986	0.9988	-5	10	-4
2	**Benalaxyl**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	1.0000	0.9959	0.9994	-9	-8	-80
3	**Cinerin I**	0.002-0.1	0.005-0.1	0.002-0.1	-	0.9991	0.9979	-	-1	-7	-
4	**Cinerin II**	0.002-0.1	-	-	-	-	-	-	-	-	-
5	**Chlorfluazuron**	0.002-0.1	0.002-0.1	0.002-0.1	0.005-0.1	0.9989	0.9993	0.9961	248	152	-24
6	**Clomazone**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9991	0.9979	0.9992	-1	-7	-45
7	*Cyhalothrin Lambda*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9988	0.9984	0.9982	0	2	-61
8	**Dazomet**	0.002-0.1	-	0.002-0.1	-	-	0.9953	-	-	198	-
9	**Fenobucarb**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9998	0.9974	0.9960	-1	-75	-51
10	**Flufenacet**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9995	0.9977	0.9957	-10	-16	-81
11	**Fluxapyrosad**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9939	0.9996	0.9945	-8	-41	-52
12	*Heptachlor*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9982	0.995	0.9988	0	-2	-92
13	**Ioxynil**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9999	0.9989	0.9991	-7	-27	-3
14	*Isopyrazam*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9988	0.9984	0.9985	0	6	-67
15	**Isoxaflutole**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9999	0.9962	0.9902	21	-36	17
16	**Jasmolin I**	0.005-0.1	0.005-0.1	0.01-0.1	-	0.9974	0.9915	-	22	-10	-

No.	Compund	Linear Range (mg/ kg)				R2			Matrix effects(%)		
		Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
17	**Jasmolin II**	0.005-0.1	-	-	-	-	-	-	-	-	-
18	**MCPA**	0.002-0.1	0.005-0.1	0.005-0.1	0.002-0.1	0.9979	0.9986	0.9988	-4	-8	2
19	**MCPB**	0.002-0.1	-	-	0.010-0.1	-	-	0.9986	-	-	-5
20	**Meptyldinocap**	0.002-0.1	0.002-0.2	0.002-0.1	0.002-0.1	0.9963	0.9958	0.9949	2	-55	-54
21	**Metaflumizone (E)**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9993	0.9979	0.9957	289	225	284
22	**Metconazole**	0.005-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9998	0.9983	0.9979	-18	-17	-70
23	*Molinate*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9993	0.9987	0.9974	0	-5	-19
24	**Novaluron**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	1.0000	0.9962	0.9948	14	-4	-46
25	**Oxadiargyl**	0.002-0.1	0.002-0.1	0.002-0.1	0.005-0.1	0.9992	0.9979	0.9919	-6	-13	-74
26	**Oxasulfuron**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	1.0000	0.9989	0.9991	10	11	3
27	**Oxyfluorfen**	0.005-0.1	0.05-0.1	0.05-0.1	-	-	-	-	-	-34	-
28	**Penflufen**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	1.0000	0.9999	0.9999	-14	-18	-77
29	**Penthiopyrad**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9992	0.9992	0.9797	-7	-1	-67
30	*Phenthoate*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	1.0000	0.9977	0.9980	0	5	28
31	*Picolinafen*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9988	0.9989	0.9986	0	7	92
32	**Propaquizafop**	0.002-0.1	0.002-0.1	0.002-0.1	0.005-0.1	0.9986	0.9995	0.9965	-5	-11	-82
33	**Prothiofos**	0.002-0.1	0.002-0.1	0.002-0.1	-	0.9957	0.9693	-	50	65	-

No.	Compund	Linear Range (mg/ kg)				R2			Matrix effects(%)		
		Solvent	Tomato	Orange	Avocado	Tomato	Orange	Avocado	Tomato	Orange	Avocado
34	**Pyrethrin I**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9996	0.9998	0.9911	7	-12	-91
35	**Pyrethrin II**	0.002-0.1	0.002-0.1	0.002-0.1	-	0.9988	0.9992	-	-16	-16	-
36	**Pyridate**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9985	0.9962	0.9931	360	286	17
37	**Quinalphos**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	1.0000	0.9999	0.9989	-7	-20	-90
38	**Quinoclamine**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	1.0000	0.9993	0.9982	-10	-9	-30
39	*Quintozene*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9983	0.9964	0.9999	0	15	-44
40	**Quizalofop-ethyl**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9995	0.9983	0.9997	-5	-16	-90
41	**Rotenone**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9996	0.9997	0.9998	-9	-28	-84
42	**Sulfoxaflor (sum)**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9999	0.9993	0.9990	-6	-15	-8
43	*Tetramethrin (sum)*	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9980	0.9992	0.9968	0	11	-55
44	**Tolfenpyrad**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9999	0.9996	0.9975	-1	23	-82
45	**Triflumizole**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9999	0.9946	0.9994	-30	-22	-91
46	**Triticonazole**	0.002-0.1	0.002-0.1	0.002-0.1	0.002-0.1	0.9994	0.9991	0.9956	-16	-37	-48
47	**Tritosulfuron**	0.002-0.05	0.002-0.1	0.002-0.1	0.005-0.1	1.0000	0.9968	0.9980	4	-4	1

In bold, pesticides analysed by LC-MS/MS

In italic, pesticides analysed by GC-MS/MS