Dutch mini-Luke ("NL-") extraction method followed by LC and GC-MS/MS for multi-residue analysis of pesticides in fruits and vegetables

Method developed by NVWA, Netherlands Food and Consumer Product Safety Authority, NRL for Pesticide Residues in Food and Feed in collaboration with EURL-FV

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1. Aim and scope

This report describes a validation data of 175 pesticides using a multiresidue method by LC-MS/MS and GC-MS/MS in lettuce and orange.

2. Short description

Homogenous sample is extracted with acetone and partitioned with petroleum ether and dichloromethane. 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 3 mL
- 250 ml PTFE centrifuge tubes
- 40 ml glass tubes with caps
- Vortex
- Turrax homogeniser
- Centrifuge, suitable for the centrifuge tubes employed in the procedure and capable of achieving at least 3300 rpm
- Water bath
- Injection vials, 2 ml, suitable for LC and GC auto-sampler
- Volumetric flasks

4. Chemicals

- Acetone p.a.
- Petroleum ether
- Dichloromethane
- Anhydrous sodium sulphate
- Ammonium formiate
- Ultra-pure water
- Methanol HPLC grade
- Isooctane
- Toluene
- Acetic acid
- Pesticides standards

5. Procedure

5.1. Sample preparation

Following Document No. SANCO/12571/2013, 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 toluene or methanol and were stored in screw-capped glass vials in the dark at -20 °C.

For spiking, 15 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 methanol.

The validation method was performed at three fortification levels (0.005, 0.01 and 0.02 mg/Kg). Six replicates were analysed at each level.

5.3. Extraction method

1. Weigh 15 g ± 0.1 g of sample in 250 mL PTFE centrifuge tube.
2. Add 75 µL of 10 mg/L propoxur and HCB-159 (procedure internal standards), 20 mL of acetone and 15 g Na_2SO_4.
3. Blend the sample using a Turrax homogeniser for 30 s at 1500 rpm (extraction step).
4. Add 20 ml of petroleum ether and 10 ml of dichloromethane.
5. Blend it again by Turrax for 30 s at 1500 rpm (partitioning step).
6. Centrifuge for 3 min at 3300 rpm.
7. Transfer the supernatant into 40 mL glass tube.
8. Evaporate an aliquot of the extract in a water bath programmed at 45ºC and continuing to 63ºC. The last part of the solvent was allowed to evaporate in the air.
    a. for LC analysis evaporate 0.66 mL extract and reconstitute with 1 mL of 0.025% of acetic acid in methanol containing quinalphos at 0.040 mg/kg (Injection Internal Standard) for LC analysis.

b. for GC analysis evaporate 5 mL extract and reconstitute with 1.5 mL of isooctane: toluene (9:1) containing 0.2 µg/mL of HCB-C13 and PCB-209 (Injection Internal Standards).

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.

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

5.5.1. Acquitty UPLC (Waters)

- Column: Acquity UPLC BEH C18 2.1 mm x 100 mm and 1.7 µm particle size (Waters)
- Mobile phase A: 300 mg/L ammonium formiate in milliQ water
- Mobile phase B: methanol
- Column temperature: 40°C
- Flow rate: 0.45 mL/min
- Injection volume: 1 µL

Mobile phase gradient for pesticides analyse

Time [min]	Mobile phase A	Mobile phase B
0	90%	10%
0.25	90%	10%
7.75	0%	100%
8.50	0%	100%
8.51	90%	10%

Re-equilibration with initial mobile phase: 1.5 minutes.

5.5.2. XEVO TQ-S triple quadrupole system (Waters)

- Ionisation mode: Positive mode
- ESI source gas temperature: 150 °C
- Desolvation temperature: 600 °C
- Desolvation gas flow: 1200 L/h

- Cone gas flow: 150 L/h
- Nebuliser gas: nitrogen
- Capillary voltage: 1.8 kV
- Collision gas: argon

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

5.6.1. Varian CP-3800 GC (Bruker)

- Column: Varian VF-5ms 30 m × 0.25 mm ID and 0.25 µm
- Injection mode: LVI-PTV, solvent vent
- Open liner with carbofrit
- Injection volume: 5 µl
- Injector temperature: held at 80°C (1 min) and then ramped up to 300°C at 200°C/min. This temperature was held for 19.5 min.
- Carrier gas: helium at constant flow of 1 mL/min
- Carrier gas purity: 99.999%
- Oven temperature: 80°C for 1 min, programmed to 180°C at 25°C/min, then to 280°C at 8°C/min and finally to 300°C at 30°C/min and kept at 300°C for 3.17 min.

5.6.2. Scion-TQ triple quadrupole system (Bruker)

- Ionisation mode: electron impact ionisation
- Temperature of the transfer line: 280 °C
- Temperature of ion source: 250 °C
- Temperature of manifold: 40 °C
- Collision gas: argon
- Collision gas purity: 99.999%
- Solvent delay: 3.3 minutes

6. Validation of the method

6.1. Recoveries and within-laboratory reproducibility

The results corresponding to the mean recovery (n=6) and within-laboratory reproducibility in terms of relative standard deviation (RSD_r) at three fortification levels (0.005, 0.01 and 0.02 mg/kg) are summarized in Appendix II, Table 3.

Almost all the recoveries results are within the range 70-120% except biphenyl, nitempyram, propamocarb in lettuce and aminopyralid, bifenazate, biphenyl, methamidophos, nitempyram and propamocarb in

orange. It could be explained because the high water solubility of methamidophos, nitempyram and propamocarb; high vapour pressure of biphenyl; bifenazate is a strong base and aminopiralid had a poor chromatographic behaviour.

6.2. Limits of quantitation

Document N° SANCO/12571/2013 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 97% of the pesticides is 0.005 mg/kg in lettuce and 96% in orange.

6.3. Linearity

Linearity of the tq-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 0.0005 to 0.100 mg/kg. In almost all cases, coefficient of determination (r^2) was higher than 0.99 for most of the analytes. 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.

7. References

- **Analytical quality control and method validation procedures for pesticide residues analysis in food and feed.** Document N° SANCO/12571/2013.
- **http://www.eurl-pesticides.eu**

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)
1	Acephate	1.25	20	183.9	142.8	94.6	10	25
2	Acetamiprid	3.13	35	223.1	125.9	90.0	22	35
3	Ametoctradin	6.77	20	276.3	176.1	149.0	38	36
4	Aminopyralid	0.58	25	207.1	189.0	161.0	14	18
5	Amisulbrom	6.89	25	468.1	228.9	148.0	26	50
6	Azoxystrobin	5.51	15	404.1	372.0	328.9	16	30
7	Benthiavalicarb-Isopropyl (R)	5.77	20	382.0	116.0	197.0	20	20
8	Benthiavalicarb-Isoprpoyl (S)	5.89	20	382	116.0	197	20	20
9	Bixafen	6.29	30	414.3	394.0	265.9	16	22
10	Bupirimate	6.22	35	317.2	107.9	166.0	25	25
11	Buprofezin	7.08	20	306.1	201.0	115.9	12	16
12	Carbaryl	4.56	14	202.1	144.9	126.9	12	24
13	Carbendazim	3.37	25	192.0	159.9	132.0	16	30
14	Carbofuran, 3 Hydroxy	3.20	28	238.1	163.0	181.0	16	10
15	Chlorfenvinphos	6.46+6.62	25	359.0	98.9	126.9	30	24
16	Clofentezine	6.58	20	303.0	137.9	101.9	14	35
17	Clothianidin	2.80	20	250.0	168.9	131.8	14	14
18	Cyflufenamid	6.56	25	413.3	295.0	240.9	16	22
19	Cyflumetofen	6.89	25	465.5	172.9	249.0	26	14
20	Cyproconazole	5.80+5.95	25	292.1	70.1	124.9	18	30
21	Cyprodinil	6.38	45	226.1	92.9	107.9	35	25
22	Demeton-S-methyl sulphone	2.24	30	263.0	168.9	108.9	16	30
23	Diazinon	6.43	25	305.1	169.0	96.9	22	35
24	Diethofencarb	5.48	20	268.1	123.9	152.0	30	22
25	Difenoconazole	6.70+6.73	35	406.1	250.9	187.8	25	40
26	Dimethoate	3.04	20	230.0	198.8	124.8	10	22
27	Dimethomorph	5.62+5.82	35	388.1	300.9	165.0	20	30
28	Dinotefuran	1.62	20	203.1	128.8	113.3	12	12
29	Dodine	6.60	45	228.2	56.9	59.8	23	23
30	EPN	6.73	30	324.1	156.9	295.9	23	15
31	Epoxiconazole	6.06	35	330.1	120.9	122.9	25	20
32	Ethion	7.11	20	385.0	198.9	96.9	11	45
33	Ethoprofos	6.05	30	243.0	131.0	173.0	20	15
34	Etoxazole	7.32	15	360.0	141.0	177.0	25	20
35	Fenamidone	5.62	25	312.1	92.0	236.1	25	14
36	Fenarimol	6.04	40	331.0	268.0	81.0	30	25
37	Fenazaquin	7.59	30	307.2	57.2	161.0	25	19
38	Fenbuconazole	6.16	35	337.1	70.1	124.9	18	30
39	Fenoxycarb	6.24	20	302.1	88.0	115.9	18	12
40	Fenpyroximate	7.41	30	422.3	366.1	137.9	17	31
41	Fenthion	6.37	25	279	168.9	104.9	18	25
42	Fenthion sulfoxide	4.55	40	295.0	108.9	78.9	30	24
43	Fludioxonil	5.67	15	266.0	228.9	157.9	10	35
44	Flufenoxuron	7.34	30	489.0	157.9	141.0	20	40
45	Fluopyram	5.94	35	397.1	172.8	207.9	29	23
46	Flutolanil	5.73	25	324.1	242.0	262.0	25	18

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)
47	Flutriafol	5.01	25	302.1	70.1	122.9	16	30
48	Fluxapyroxad	5.77	25	382.1	362.1	342.1	14	20
49	Furathiocarb	6.97	25	383.2	194.9	252.0	18	12
50	Halofenozide	5.69	34	275.0	104.8	138.8	8	16
51	Haloxyfop	5.63	25	362.0	91.0	316.0	20	30
52	Hexaconazole	6.56	30	314.1	70.1	158.8	20	40
53	Hexythiazox	7.22	20	353.1	167.9	228.0	27	17
54	Imazalil	6.35	35	297.1	69.1	158.9	18	24
55	Imazapic	1.85	30	276.2	231.1	86.1	20	24
56	Imidacloprid	2.79	25	256.1	174.9	209.0	20	12
57	Indoxacarb	6.75	30	528.1	202.9	217.9	40	25
58	Iprovalicarb	5.89+5.94	20	321.2	118.9	203.0	18	10
59	Linuron	5.51	20	249.0	159.9	181.9	20	16
60	Lufenuron	7.11	25	512.0	141.0	158.0	15	40
61	Malathion	5.82	20	331.0	126.9	285.0	12	10
62	Methamidophos	1.00	30	141.9	93.9	124.8	12	14
63	Methiocarb	5.59	20	226.1	121.0	168.9	20	10
64	Methiocarb sulfone	3.29	15	275.1	121.9	200.9	24	14
65	Methiocarb sulfoxide	3.00	25	242.1	121.9	184.9	14	30
66	Monocrotophos	2.42	20	224.0	126.8	97.9	16	14
67	Myclobutanil	5.87	30	289.1	70.1	124.9	18	30
68	Nitenpyram	2.02	25	271.1	125.9	224.9	25	12
69	Omethoate	1.47	25	214.0	124.8	182.8	22	10
70	Oxamyl-oxime	1.50	20	162.9	72.0	89.9	12	16
71	Oxydemeton-methyl	2.15	20	247.0	168.8	108.9	14	25
72	Penconazole	6.38	30	284.1	70.1	158.9	16	30
73	Pencycuron	6.66	30	329.1	124.9	218.0	30	16
74	Phosalone	6.57	25	368.0	182.0	111.0	15	40
75	Picolinafen	7.03	35	377.3	237.9	359.0	28	20
76	Pirimiphos-methyl	6.58	30	306.1	107.9	67.1	30	40
77	Prochloraz	6.59	20	376.0	307.9	70.1	12	25
78	Profenofos	6.95	30	372.9	302.6	127.9	20	40
79	Propamocarb	1.70	20	189.0	102.0	74.0	25	25
80	Propargite	7.32	20	368.3	231.1	175.0	11	15
81	Propiconazole	6.45+6.49	35	342.1	158.9	69.1	20	30
82	Propoxur (P.I.S)	4.36	20	210.1	110.9	92.9	14	24
83	Propyzamide	5.74	20	256.0	189.8	172.8	14	25
84	Proquinazid	7.50	25	373.2	330.9	288.9	16	24
85	Pymetrozine	2.25	30	218.1	104.9	78.3	18	35
86	Pyraclostrobin	6.52	25	388.1	163.0	193.9	25	12
87	Pyrimidafen	7.09	45	378.2	183.9	149.8	25	37
88	Quinalphos (I.I.S.)	6.25	20	299.0	243.0	271.0	15	15
89	Rotenone	6.20	40	395.2	213.0	191.9	25	25
90	Spinetoram I	7.63	45	748.9	141.9	114.9	30	46
91	Spinetoram II	7.82	45	761.0	141.9	114.9	30	48
92	Spinosyn A	7.44	50	732.6	142.0	98.1	31	59
93	Spinosyn D	7.64	45	746.5	142.0	98.1	31	53
94	Spirotetramat	5.97	30	374.4	330.1	302.1	16	16
95	Spiroxamine	6.27	30	298.3	144.0	100.0	20	30
96	Tebuconazole	6.39	30	308.2	70.1	124.9	24	40
97	Tebufenozide	6.22	16	353.3	132.7	297.0	16	8

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)
98	Teflubenzuron	7.12	25	381.0	141.0	158.0	15	30
99	Tembotrione	3.66	42	441.1	380.8	261.7	8	28
100	Thiabendazole	6.06	35	372.0	158.9	70.1	35	22
101	Thiacloprid	3.48	35	253.0	125.8	90.0	20	40
102	Thiamethoxam	2.27	20	292.1	210.9	180.9	12	22
103	Tolclophos-Methyl	6.58	35	301.1	125.0	174.9	17	29
104	Tolylfluanid	6.36	20	347.0	136.8	237.8	26	10
105	Triazophos	5.89	25	314.1	161.9	118.9	18	35
106	Triazoxide	4.94	40	248.2	68.1	95.0	24	24
107	Trifloxystrobin	6.77	25	409.2	185.9	145.0	14	40
108	Triflumizole	6.87	15	346.1	278.0	73.1	10	18
109	Zoxamide	6.46	30	336.0	186.9	158.9	25	40

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	2-Phenylphenol	6.07	170	141	20	170	115	35
2	Acrinathrin	15.95	208	181	15	208	152	30
3	Azinphos-methyl	15.68	160	104	10	160	132	5
4	Bifenazate	14.85	300	158.0	10	300.0	196.0	20
5	Bifenthrin	14.58	181	166.0	15	181.0	165.0	25
6	Biphenyl	5.20	154	153.0	15	154.0	115.0	25
7	Bitertanol	16.93	170	115.0	30	170.0	141.0	20
8	Boscalid	17.99	140	112.0	15	140	76	25
9	Bromopropylate	14.74	341	155.0	30	341.0	183.0	20
10	Carbofuran	7.64	164	122.0	10	164.0	149.0	10
11	Chlorantraniliprole	15.05	278	249.0	25	278.0	215.0	25
12	Chlorfenapyr	12.24	247	227.0	15	247.0	200.0	20
13	Chlorothalonil	4.27	266	168.0	25	266.0	231.0	15
14	Chlorpropham	7.00	213	127.0	15	213.0	171.0	10
15	Chlorpyrifos-ethyl	9.78	314	258.0	15	314.0	286.0	10
16	Chlorpyrifos-methyl	8.93	286	208.0	15	286.0	271.0	20
17	Cypermethrin	17.96	181	152.0	30	163.0	127.0	10
18	Deltamethrin	19.12	172	93.0	10	253.0	172.0	10
19	Dichlorvos	4.29	185	93.0	15	185.0	109.0	20
20	Dicloran	7.72	206	176.0	15	206.0	148.0	20
21	Diniconazole	12.77	268	171.0	20	268.0	232.0	10
22	Diphenylamine	6.84	169	167.0	30	169.0	168.0	10
23	Endosulfan-alpha	11.48	241	206.0	15	241.0	170.0	25
24	Endosulfan-beta	12.83	241	206.0	15	241.0	170.0	25
25	Endosulfan-sulfate	13.57	272	237.0	18	387.0	253.0	10
26	Etofenprox	18.11	163	107.0	15	163.0	135.0	10
27	Famoxadone	19.45	196	167.0	15	330.0	224.0	10
28	Fenhexamid	13.76	97	55.0	10	177.0	113.0	10
29	Fenitrothion	9.55	277	109.0	20	277.0	260.0	10
30	Fenpropathrin	14.86	265	210.0	15	265.0	181.0	20
31	Fenpropimorph	9.85	128	110.0	5	303.0	128.0	10
32	Fenvalerate	18.58	225	147.0	10	225.0	119.0	15
33	Fipronil	10.65	367	213.0	25	367.0	255.0	20
34	Fluopicolide	13.68	347	172.0	30	347.0	136.0	40
35	Flusilazole	12.05	233	152.0	15	233.0	165.0	15
36	HCB-C13 (I.I.S.)	7.50	290	220.0	25	290.0	255.0	15
37	Iprodione	14.59	314	271.0	10	314.0	245.0	20
38	Kresoxim-methyl	12.08	206	116.0	15	206.0	131.0	15
39	lambda-Cyhalothrin	17.96	197	141.0	15	181.0	152.0	25
40	Mepanipyrim	11.55	222	158.0	20	222.0	207.0	10
41	Metalaxyl	9.15	206	132.0	15	149.0	190.0	10
42	Methidathion	11.17	125	79.0	10	145	85	10
43	Metrafenone	16.24	393	363.0	15	393.0	299.0	20
44	Oxadixyl	12.84	163	132.0	10	233.0	146.0	10
45	Parathion methyl	9.08	247	200.0	10	247.0	230.0	10
46	PCB-153 (P.I.S.)	13.10	360	290.0	25	360.0	325.0	12
47	PCB-209 (I.I.S.)	18.21	356	286.0	30	356.0	321.0	25
48	Pendimethalin	10.47	252	162.0	15	252.0	191.0	10

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)
49	Permethrin-cis	16.79	183	153.0	20	183.0	168.0	20
50	Permethrin-trans	16.96	183	153.0	20	183.0	168.0	20
51	Phenthoate	10.82	274	121.0	10	274.0	246.0	5
52	Picoxystrobin	11.33	335	173.0	10	335.0	303.0	10
53	Piperonyl-butoxide	14.33	176	131.0	15	176.0	161.0	10
54	Pirimicarb	8.45	238	72.0	25	238.0	166.0	10
55	Pirimicarb-desmethyl	8.69	152	96.0	15	224.0	152.0	10
56	Procymidone	10.93	283	96.0	15	283.0	255.0	10
57	Prothiofos	11.69	309	239.0	15	309.0	221.0	25
58	Pyridaben	17.03	147	117.0	25	147.0	132.0	15
59	Pyrimethanil	8.20	198	158.0	15	198.0	183.0	10
60	Pyriproxyfen	15.65	136	96.0	10	226.0	186.0	15
61	Quinoxyfen	13.56	307	237.0	25	307.0	272.0	10
62	Silthiofam	8.55	252	197.0	15	252.0	210.0	15
63	Spirodiclofen	16.62	312	109.0	20	312.0	259.0	10
64	Spiromesifen	14.22	272	209.0	10	272.0	254.0	10
65	tau-Fluvalinate	18.69	250	200.0	20	250.0	208.0	25
66	Tebufenpyrad	14.99	333	171.0	20	333.0	276.0	10
67	Terbuthylazine	7.97	214	132.0	15	214.0	104.0	20
68	Tetraconazole	10.03	336	191.0	20	336.0	218.0	15
69	Tetradifon	15.40	229	166.0	20	229.0	201.0	15
70	Triadimefon	10.08	208	111.0	20	208.0	127.0	15
71	Triadimenol	10.99	168	70.0	10	168.0	112.0	5

APPENDIX II: VALIDATION RESULTS

Table 3. Accuracy data (as % recovery) and precision data (as repeatability RSD_r, n=6) at 0.005, 0.01 and 0.02 mg/kg for lettuce and orange.

No.	Pesticide	Lettuce						Orange					
		0.005 mg/kg		0.01 mg/kg		0.02 mg/kg		0.005 mg/kg		0.01 mg/kg		0.02 mg/kg	
		Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)
1	*2-Phenylphenol*	89	7.8	81	18.4	81	15.6	88	4.6	80	11.7	97	19.0
2	**Acephate**	100	11.4	94	5.5	92	3.3	79	19.5	79	10.6	70	15.2
3	**Acetamiprid**	109	4.2	109	2.2	107	1.6	110	11.2	111	7.4	108	8.0
4	*Acrinathrin*	101	13.8	87	19.3	87	19.3	105	3.4	102	5.9	119	13.7
5	**Ametoctradin**	105	3.9	107	6.9	106	5.0	102	11.4	99	5.9	104	10.1
6	**Aminopyralid**	n.d.		n.d.		n.d.		53	30.6	52	22.2	48	14.1
7	**Amisulbrom**	109	11.3	104	5.6	106	2.9	96	11.5	101	6.4	100	9.9
8	*Azinphos-methyl*	95	18.5	96	17.8	94	15.0	n.d.		n.d.		98	23.8
9	**Azoxystrobin**	106	5.3	104	4.5	103	5.5	103	12.8	112	10.2	105	7.2
10	**Benthiavalicarb-Isopropyl (R)**	109	3.6	105	5.6	105	5.1	95	11.4	100	5.4	97	4.7
11	**Benthiavalicarb-Isoprpoyl (S)**	107	3.1	100	4.5	106	4.8	98	11.6	99	13.0	95	7.2
12	*Bifenazate*	119	7.2	111	10.2	117	11.6	64	11.9	66	10.1	46	14.7
13	*Bifenthrin*	97	5.0	88	18.5	91	15.5	94	2.7	87	6.1	104	15.8
14	*Biphenyl*	66	14.4	50	27.0	50	18.3	74	3.9	64	7.8	76	19.1
15	*Bitertanol*	101	5.3	95	6.2	95	5.2	82	10.0	84	9.3	80	14.7
16	**Bixafen**	108	2.2	102	7.1	105	5.5	103	6.8	96	9.2	98	7.4
17	*Boscalid*	102	3.4	97	5.6	99	4.2	81	9.7	85	10.3	79	12.8
18	*Bromopropylate*	98	4.5	90	17.5	94	16.7	93	2.6	87	8.2	103	15.0
19	**Bupirimate**	105	4.4	105	5.0	105	6.2	104	6.4	99	7.8	97	7.0
20	**Buprofezin**	106	1.3	109	4.3	104	4.4	100	10.3	98	5.7	99	11.3
21	**Carbaryl**	111	9.5	103	8.9	104	6.9	112	15.5	116	6.2	106	6.3
22	**Carbendazim**	108	3.6	107	3.6	106	1.9	103	11.1	101	7.3	100	7.9
23	*Carbofuran*	99	19.8	83	18.0	79	18.2	86	10.9	87	9.8	84	14.8
24	**Carbofuran, 3 Hydroxy**	104	6.2	109	4.5	111	2.9	110	16.4	111	4.0	107	5.7
25	*Chlorantraniliprole*	95	11.7	91	10.0	94	10.6	86	12.7	71	11.1	71	16.3
26	*Chlorfenapyr*	92	9.8	94	12.9	94	17.1	95	9.5	89	14.0	103	16.6
27	**Chlorfenvinphos**	107	4.0	104	6.7	103	3.9	106	6.1	106	4.2	106	7.5
28	*Chlorothalonil*	100	18.9	82	19.1	73	10.3	105	11.4	88	14.7	100	25.0
29	*Chlorpropham*	97	4.5	91	10.0	92	9.6	89	6.2	87	6.3	93	16.9
30	*Chlorpyrifos-ethyl*	101	6.0	96	10.0	96	10.7	93	6.7	99	11.2	101	14.9
31	*Chlorpyrifos-methyl*	102	8.8	94	13.0	93	12.8	95	10.5	98	13.4	100	17.8
32	**Clofentezine**	73	5.5	80	9.1	70	6.5	92	8.1	90	7.2	90	10.5
33	**Clothianidin**	110	4.9	109	2.8	107	2.8	104	14.0	105	10.1	101	8.5
34	**Cyflufenamid**	109	4.5	107	4.5	105	3.9	104	7.9	96	6.4	104	8.1
35	**Cyflumetofen**	109	5.5	105	5.0	101	8.1	103	10.5	106	7.7	110	9.2
36	*Cypermethrin*	95	14.1	84	19.1	83	19.7	96	6.4	86	11.5	101	16.8
37	**Cyproconazole**	112	5.7	105	4.0	104	6.3	106	10.0	107	11.6	98	5.9
38	**Cyprodinil**	109	5.9	104	11.6	101	9.3	106	14.2	100	9.4	101	14.0
39	*Deltamethrin*	91	15.1	79	18.5	76	19.6	79	13.4	78	15.0	99	16.4
40	**Demeton-S-methyl sulphone**	109	5.1	106	3.0	103	5.1	110	14.0	112	14.9	100	13.2
41	**Diazinon**	108	3.6	107	4.9	106	4.3	108	9.1	102	7.7	103	7.8
42	*Dichlorvos*	80	10.4	71	14.3	71	16.6	75	11.7	80	6.4	76	18.8
43	*Dicloran*	96	6.6	86	19.4	87	18.2	89	4.4	80	13.0	96	18.2
44	**Diethofencarb**	101	6.4	101	8.1	104	4.9	96	11.9	100	17.7	101	7.4
45	**Difenoconazole**	105	6.5	104	6.4	104	3.7	106	9.4	97	4.6	103	6.2
46	**Dimethoate**	108	4.3	111	3.1	107	2.0	114	13.1	114	5.7	112	7.0
47	**Dimethomorph**	99	4.2	104	4.1	101	3.2	99	8.6	102	8.9	100	8.1

No.	Pesticide	Lettuce						Orange					
		0.005 mg/kg		0.01 mg/kg		0.02 mg/kg		0.005 mg/kg		0.01 mg/kg		0.02 mg/kg	
		Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)
48	*Diniconazole*	98	4.2	95	4.6	98	3.7	85	10.3	89	5.9	86	14.5
49	**Dinotefuran**	103	5.9	100	6.7	103	3.5	96	12.0	93	10.4	91	11.9
50	*Diphenylamine*	89	5.1	74	15.4	75	14.6	90	2.7	79	8.6	96	18.9
51	**Dodine**	100	7.3	98	5.1	100	2.4	80	17.5	82	5.9	78	6.1
52	*Endosulfan-alpha*	92	7.0	88	18.9	94	17.1	89	4.3	85	6.4	103	15.5
53	*Endosulfan-beta*	99	11.9	89	18.4	95	16.9	92	7.1	84	1.6	102	17.2
54	*Endosulfan-sulfate*	100	6.4	99	6.9	98	5.0	100	11.4	83	13.0	104	25.2
55	**EPN**	106	6.1	108	7.5	107	5.3	105	8.1	104	6.5	108	9.8
56	**Epoxiconazole**	110	4.0	104	7.3	106	4.3	97	4.4	105	8.6	100	5.5
57	**Ethion**	109	3.8	107	7.1	103	5.6	97	8.3	101	7.0	98	11.6
58	**Ethoprofos**	110	1.3	99	5.0	101	4.7	101	8.4	104	9.5	100	4.0
59	*Etofenprox*	101	3.4	93	5.8	95	4.8	97	13.2	96	5.7	85	14.3
60	**Etoxazole**	108	2.2	104	6.7	102	4.7	100	12.2	101	8.7	100	11.4
61	*Famoxadone*	107	19.4	87	17.8	99	17.7	89	14.4	85	10.7	74	19.6
62	**Fenamidone**	107	6.7	103	3.8	103	4.4	107	10.9	107	7.0	103	7.0
63	**Fenarimol**	114	11.4	105	10.4	111	3.0	92	19.6	112	15.1	91	16.6
64	**Fenazaquin**	105	6.6	105	9.2	103	4.5	107	12.9	107	6.1	98	6.7
65	**Fenbuconazole**	107	7.7	102	8.4	101	5.2	91	19.8	99	14.2	96	3.3
66	*Fenhexamid*	100	7.8	95	5.1	97	5.3	90	11.6	93	9.3	90	14.3
67	*Fenitrothion*	95	11.5	81	19.5	80	16.0	96	6.2	87	14.9	97	18.9
68	**Fenoxycarb**	108	3.7	110	6.2	104	4.2	103	2.9	101	8.6	94	7.7
69	*Fenpropathrin*	98	7.2	90	17.8	93	15.4	91	4.7	87	7.6	106	13.2
70	*Fenpropimorph*	99	5.8	86	12.0	98	6.4	85	11.8	87	8.3	87	19.6
71	**Fenpyroximate**	104	3.4	105	4.5	104	9.2	100	9.5	101	6.1	100	8.1
72	**Fenthion**	106	2.8	105	5.9	102	4.4	101	7.3	101	5.9	101	7.7
73	**Fenthion sulfoxide**	112	8.1	110	7.4	112	7.3	114	12.8	116	6.0	113	5.3
74	*Fenvalerate*	97	14.4	75	10.8	84	16.6	91	2.5	82	6.7	98	17.4
75	*Fipronil*	104	10.8	89	17.0	96	17.6	88	6.0	81	6.9	94	18.7
76	**Fludioxonil**	119	15.3	114	13.1	108	11.4	102	13.1	103	7.3	102	5.9
77	**Flufenoxuron**	102	3.3	104	5.0	102	4.4	106	8.6	102	6.4	96	7.8
78	*Fluopicolide*	99	4.7	92	18.3	97	15.2	86	5.8	79	13.2	95	18.2
79	**Fluopyram**	104	5.2	102	5.2	101	4.6	100	9.0	100	9.5	95	6.1
80	*Flusilazole*	103	4.3	98	5.6	100	4.3	82	10.5	84	8.6	82	16.3
81	**Flutolanil**	106	6.2	102	5.3	103	3.0	101	5.9	99	8.7	94	6.5
82	**Flutriafol**	120	13.7	115	15.6	107	16.2	109	13.6	114	8.1	105	7.0
83	**Fluxapyroxad**	107	4.1	101	4.4	101	4.5	101	11.2	101	9.1	93	6.2
84	**Furathiocarb**	107	4.5	104	3.7	103	3.4	103	8.6	100	5.3	98	9.0
85	**Halofenozide**	97	13.6	98	6.6	100	3.9	107	7.7	105	10.0	97	8.0
86	**Haloxyfop**	118	12.5	110	6.3	103	5.9	108	17.1	106	9.3	93	5.8
87	**Hexaconazole**	107	4.0	110	3.9	106	7.1	100	14.8	99	8.7	103	6.6
88	**Hexythiazox**	104	3.6	104	6.2	104	6.5	103	8.3	101	4.2	94	10.8
89	**Imazalil**	102	8.3	101	8.0	89	5.6	91	15.9	101	8.8	90	12.8
90	**Imazapic**	98	8.2	98	7.3	94	7.5	108	16.0	104	11.7	98	12.4
91	**Imidacloprid**	110	5.5	108	3.1	108	2.4	101	11.7	106	8.9	102	8.5
92	**Indoxacarb**	110	6.4	99	7.3	101	5.0	103	5.9	101	6.4	102	7.3
93	*Iprodione*	98	19.5	78	15.1	77	13.8	87	10.7	78	9.8	85	17.5
94	**Iprovalicarb**	106	9.0	104	6.0	104	5.4	101	8.8	101	10.4	93	7.8
95	*Kresoxim-methyl*	103	6.1	98	5.4	100	5.4	88	11.7	88	7.9	90	13.7
96	*lambda-Cyhalothrin*	96	9.1	76	8.2	83	17.9	90	2.3	83	6.3	99	17.5
97	**Linuron**	106	5.8	106	5.8	106	6.8	103	8.2	103	12.3	102	7.8
98	**Lufenuron**	111	26.8	98	18.4	115	12.9	87	19.2	92	18.6	94	16.6
99	**Malathion**	98	11.1	105	3.5	106	8.1	95	19.1	104	10.8	96	6.3
100	*Mepanipyrim*	100	3.4	98	4.8	99	3.4	90	8.6	88	7.6	87	13.0

No.	Pesticide	Lettuce						Orange					
		0.005 mg/kg		0.01 mg/kg		0.02 mg/kg		0.005 mg/kg		0.01 mg/kg		0.02 mg/kg	
		Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)
101	*Metalaxyl*	100	3.1	97	5.6	101	4.1	85	9.9	86	8.3	83	13.4
102	**Methamidophos**	88	7.4	81	4.5	81	2.3	64	26.4	64	18.2	59	23.4
103	*Methidathion*	100	13.5	97	6.4	98	10.5	91	13.2	95	13.0	92	22.8
104	**Methiocarb**	107	2.8	102	7.0	101	3.9	107	11.2	110	9.6	101	5.7
105	**Methiocarb sulfone**	107	3.5	107	5.5	109	3.8	110	12.6	111	7.5	108	6.4
106	**Methiocarb sulfoxide**	107	6.6	109	2.6	108	2.3	106	10.6	107	8.2	105	8.0
107	*Metrafenone*	98	3.3	91	18.5	94	15.4	88	2.6	82	8.8	98	15.8
108	**Monocrotophos**	108	4.5	105	2.6	103	6.2	98	13.0	105	14.3	93	11.7
109	**Myclobutanil**	100	10.4	105	7.4	104	9.1	97	10.9	96	13.2	93	2.9
110	**Nitenpyram**	66	6.6	71	5.6	66	2.5	44	15.8	45	16.7	37	16.8
111	**Omethoate**	105	5.7	99	4.6	98	2.8	90	12.4	86	14.1	77	14.9
112	*Oxadixyl*	99	3.8	96	5.0	97	7.5	75	11.8	76	13.1	73	15.4
113	**Oxamyl-oxime**	108	7.2	103	8.5	102	4.9	97	14.3	97	15.2	89	11.1
114	**Oxydemeton-methyl**	106	5.9	104	3.7	103	3.6	93	13.7	96	17.5	82	16.3
115	*Parathion methyl*	94	12.8	80	16.8	79	18.2	97	10.4	84	12.0	99	21.9
116	**Penconazole**	107	8.3	110	4.4	106	6.0	101	9.4	97	11.8	101	8.4
117	**Pencycuron**	103	2.6	104	5.2	103	4.2	76	6.7	72	5.4	75	8.5
118	*Pendimethalin*	96	9.1	81	18.9	82	19.7	90	6.4	80	6.7	98	18.3
119	*Permethrin-cis*	97	7.7	88	17.7	93	15.2	92	2.8	85	8.7	99	14.8
120	*Permethrin-trans*	98	4.1	90	17.8	90	14.6	91	5.0	80	4.6	99	15.6
121	*Phenthoate*	103	10.0	97	7.5	99	7.6	93	8.6	95	9.1	89	17.5
122	**Phosalone**	110	2.4	105	8.3	104	4.1	104	7.4	99	3.6	104	8.1
123	**Picolinafen**	106	4.4	107	8.0	104	5.1	108	10.0	101	5.4	101	12.0
124	*Picoxystrobin*	102	4.7	99	4.6	100	4.1	84	10.2	93	7.8	91	13.7
125	*Piperonyl-butoxide*	101	4.8	97	5.3	98	4.3	90	8.3	93	6.7	90	13.8
126	*Pirimicarb*	99	4.7	95	5.3	97	4.4	78	8.8	77	10.6	72	16.7
127	*Pirimicarb-desmethyl*	106	5.3	99	4.4	98	10.2	88	17.2	76	16.5	66	15.4
128	**Pirimiphos-methyl**	107	4.1	102	5.3	102	5.2	104	11.5	98	7.0	100	4.9
129	**Prochloraz**	109	5.3	108	6.0	106	6.0	99	6.3	94	5.9	96	7.2
130	*Procymidone*	98	6.8	90	18.2	94	16.3	86	9.6	79	11.9	99	19.1
131	**Profenofos**	108	3.1	106	5.9	103	3.9	105	7.9	103	4.5	104	9.0
132	**Propamocarb**	57	17.1	61	6.5	62	2.7	6	78.2	6	14.8	3	30.5
133	**Propargite**	112	12.2	101	6.4	102	8.2	110	9.4	111	8.5	109	7.2
134	**Propiconazole**	105	8.1	101	10.4	106	4.5	104	7.9	103	5.0	102	8.6
135	**Propyzamide**	107	4.3	104	7.9	101	5.1	99	6.3	93	8.1	93	5.8
136	**Proquinazid**	107	2.8	107	4.5	102	5.1	105	14.7	102	6.4	97	10.5
137	*Prothiofos*	101	4.7	93	18.8	95	16.3	96	2.9	89	7.4	107	17.3
138	**Pymetrozine**	97	3.6	93	3.5	88	4.3	37	31.2	37	23.7	31	14.3
139	**Pyraclostrobin**	106	4.6	105	4.9	105	4.9	105	7.4	97	7.4	103	6.9
140	*Pyridaben*	102	5.6	95	5.5	96	4.7	91	11.0	93	5.5	89	11.6
141	*Pyrimethanil*	96	5.6	88	4.9	92	5.1	82	8.8	82	8.3	78	16.0
142	**Pyrimidafen**	106	3.5	105	6.6	102	5.3	100	10.0	100	6.8	97	8.4
143	*Pyriproxyfen*	101	4.2	96	5.9	98	4.3	91	8.6	95	6.7	91	16.4
144	*Quinoxyfen*	101	4.4	97	5.1	100	3.4	85	8.5	90	4.7	85	13.0
145	**Rotenone**	107	7.8	98	9.3	101	7.5	96	12.1	99	7.9	100	7.6
146	*Silthiofam*	97	5.1	92	5.8	93	5.4	86	8.8	90	5.4	87	14.1
147	**Spinetoram I**	100	3.2	101	4.8	99	2.5	100	10.6	100	9.4	91	5.8
148	**Spinetoram II**	101	3.7	101	4.5	96	6.9	98	13.0	98	10.7	92	12.1
149	**Spinosyn A**	104	3.6	105	5.7	102	2.1	100	14.5	95	7.0	91	7.8
150	**Spinosyn D**	100	4.4	100	4.0	99	2.5	97	14.7	97	6.2	92	5.8
151	*Spirodiclofen*	119	7.1	111	10.6	115	15.7	112	11.0	120	1.4	117	13.6
152	*Spiromesifen*	104	5.9	98	5.4	100	8.2	98	12.0	98	5.5	92	16.4
153	**Spirotetramat**	99	9.7	93	4.9	98	3.2	99	11.3	108	12.7	100	5.6

No.	Pesticide	Lettuce						Orange					
		0.005 mg/kg		0.01 mg/kg		0.02 mg/kg		0.005 mg/kg		0.01 mg/kg		0.02 mg/kg	
		Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)	Rec. (%)	RSD_r (%)
154	**Spiroxamine**	90	5.6	90	7.6	92	4.0	98	7.8	96	8.9	93	12.0
155	*tau-Fluvalinat*	97	12.4	79	19.9	78	19.7	94	3.3	85	9.9	102	17.6
156	**Tebuconazole**	109	5.7	109	4.8	104	2.3	101	10.6	101	3.4	99	9.1
157	**Tebufenozide**	99	13.4	97	12.5	103	8.3	106	13.6	99	19.1	102	8.8
158	*Tebufenpyrad*	103	3.9	100	5.6	100	3.8	87	10.2	93	5.0	90	14.1
159	**Teflubenzuron**	102	5.3	103	6.5	104	3.1	106	11.9	97	6.2	91	6.5
160	**Tembotrione**	106	6.7	103	5.6	106	4.2	116	12.6	113	5.8	119	7.3
161	*Terbuthylazine*	96	5.4	77	10.1	91	15.5	86	4.3	79	8.3	97	17.2
162	*Tetraconazole*	104	4.6	99	5.2	101	4.2	81	10.2	84	8.1	82	14.5
163	*Tetradifon*	97	5.9	90	19.7	94	17.2	91	5.7	85	8.1	102	16.5
164	**Thiabendazole**	112	5.1	107	5.7	103	4.4	96	19.1	109	7.3	111	6.2
165	**Thiacloprid**	107	3.9	107	3.5	106	2.5	114	15.7	111	6.1	113	7.5
166	**Thiamethoxam**	108	2.9	104	5.9	101	5.5	104	11.8	108	15.0	94	12.8
167	**Tolclophos-Methyl**	111	11.5	104	6.9	107	4.7	100	13.3	96	6.6	101	4.2
168	**Tolylfluanid**	109	3.8	103	5.4	102	4.8	103	9.0	100	7.7	100	8.6
169	*Triadimefon*	105	5.9	100	4.9	102	4.7	85	9.2	88	8.3	87	14.6
170	*Triadimenol*	104	7.4	97	6.3	103	5.4	84	7.6	83	9.6	79	18.9
171	**Triazophos**	104	3.3	102	5.2	102	5.9	98	7.7	105	8.3	99	4.5
172	**Triazoxide**	96	4.9	94	5.7	94	10.9	103	14.7	109	10.6	97	10.2
173	**Trifloxystrobin**	108	2.9	107	5.4	104	4.3	108	8.6	100	5.6	104	7.6
174	**Triflumizole**	111	9.5	116	2.5	109	6.8	112	13.9	104	4.7	101	8.9
175	**Zoxamide**	110	5.8	107	5.3	105	7.1	104	11.3	99	8.4	99	11.2

In bold, pesticides analysed by LC-MS/MS
In italic, pesticides analysed by GC-MS/MS
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.	Pesticide	Lettuce				Orange			
		LOQ (mg/kg)	Linearity range (mg/kg)	R^2 matrix	ME (%)	LOQ (mg/kg)	Linearity range (mg/kg)	R^2 matrix	ME (%)
1	*2-Phenylphenol*	0.005	0.0005-0.100	0.9971	10	0.005	0.0005-0.100	0.9995	6
2	**Acephate**	0.005	0.002-0.100	0.9963	3	0.005	0.001-0.100	0.9963	-1
3	**Acetamiprid**	0.005	0.0005-0.100	0.9999	-1	0.005	0.0005-0.100	0.9875	-2
4	*Acrinathrin*	0.005	0.0005-0.100	0.9982	37	0.005	0.0005-0.100	0.9969	52
5	**Ametoctradin**	0.005	0.0005-0.100	0.9998	-7	0.005	0.0005-0.100	0.9968	-10
6	**Aminopyralid**	n.d.	0.01-0.100	0.9785	-22	n.f.r.	0.002-0.100	0.9988	-31
7	**Amisulbrom**	0.005	0.0005-0.100	0.9999	4	0.005	0.0005-0.100	0.9997	-2
8	*Azinphos-methyl*	0.005	0.005-0.100	0.9929	302	n.d.	0.01-0.100	0.9907	561
9	**Azoxystrobin**	0.005	0.0005-0.100	0.9999	-1	0.005	0.0005-0.100	0.9997	-29
10	**Benthiavalicarb-Isopropyl (R)**	0.005	0.0005-0.100	0.9999	-6	0.005	0.0005-0.100	0.9996	-62
11	**Benthiavalicarb-Isoprpoyl (S)**	0.005	0.0005-0.100	0.9995	-3	0.005	0.0005-0.100	0.9996	-51
12	*Bifenazate*	0.005	0.0005-0.100	0.9906	-71	n.f.r.	0.0005-0.100	0.9967	-2
13	*Bifenthrin*	0.005	0.0005-0.100	0.9971	14	0.005	0.0005-0.100	0.9999	16
14	*Biphenyl*	0.005*	0.0005-0.100	0.9864	8	0.005	0.0005-0.100	0.9966	-15
15	*Bitertanol*	0.005	0.0005-0.100	0.9981	42	0.005	0.0005-0.100	0.9987	74
16	**Bixafen**	0.005	0.0005-0.100	0.9996	3	0.005	0.0005-0.100	0.9999	-7
17	*Boscalid*	0.005	0.0005-0.100	0.9966	5	0.005	0.0005-0.100	0.9997	17
18	*Bromopropylate*	0.005	0.0005-0.100	0.9985	28	0.005	0.0005-0.100	0.9998	49
19	**Bupirimate**	0.005	0.0005-0.100	0.9987	-5	0.005	0.0005-0.100	0.9994	-11
20	**Buprofezin**	0.005	0.0005-0.100	0.9999	2	0.005	0.0005-0.100	0.9983	-3
21	**Carbaryl**	0.005	0.002-0.100	0.9995	1	0.005	0.002-0.100	0.9901	-6
22	**Carbendazim**	0.005	0.0005-0.100	1.0000	1	0.005	0.0005-0.100	0.9616	-10
23	*Carbofuran*	0.005	0.0005-0.100	0.9963	17	0.005	0.001-0.100	0.9998	37
24	**Carbofuran, 3 Hydroxy**	0.005	0.0005-0.100	0.9998	1	0.005	0.001-0.100	0.9882	-5
25	*Chlorantraniliprole*	0.005	0.001-0.100	0.9963	-14	0.005	0.0005-0.100	0.9887	-8
26	*Chlorfenapyr*	0.005	0.001-0.100	0.9972	29	0.005	0.0005-0.100	0.9998	27
27	**Chlorfenvinphos**	0.005	0.0005-0.100	0.9997	1	0.005	0.0005-0.100	0.9998	-5
28	*Chlorothalonil*	0.005	0.001-0.100	0.9942	79	0.005	0.005-0.100	0.9939	140
29	*Chlorpropham*	0.005	0.0005-0.100	0.9985	8	0.005	0.0005-0.100	0.9999	4
30	*Chlorpyrifos-ethyl*	0.005	0.0005-0.100	0.9990	12	0.005	0.0005-0.100	0.9999	17
31	*Chlorpyrifos-methyl*	0.005	0.0005-0.100	0.9982	24	0.005	0.0005-0.100	0.9993	70
32	**Clofentezine**	0.005	0.0005-0.100	0.9994	-1	0.005	0.0005-0.100	0.9994	-10
33	**Clothianidin**	0.005	0.0005-0.100	0.9999	3	0.005	0.0005-0.100	0.9881	13
34	**Cyflufenamid**	0.005	0.0005-0.100	0.9991	4	0.005	0.0005-0.100	0.9999	-8
35	**Cyflumetofen**	0.005	0.0005-0.100	0.9996	8	0.005	0.0005-0.100	0.9994	-4
36	*Cypermethrin*	0.005	0.0005-0.100	0.9981	20	0.005	0.0005-0.100	0.9990	41
37	**Cyproconazole**	0.005	0.002-0.100	0.9988	-1	0.005	0.002-0.100	0.9992	-16
38	**Cyprodinil**	0.005	0.0005-0.100	0.9987	-1	0.005	0.0005-0.100	0.9971	-8
39	*Deltamethrin*	0.005	0.0005-0.100	0.9981	19	0.005	0.0005-0.100	0.9982	45
40	**Demeton-S-methyl sulphone**	0.005	0.0005-0.100	0.9999	0	0.005	0.0005-0.100	0.9997	-7
41	**Diazinon**	0.005	0.0005-0.100	0.9997	3	0.005	0.0005-0.100	1.0000	-7
42	*Dichlorvos*	0.005	0.0005-0.100	0.9792	10	0.005	0.0005-0.100	0.9944	-6
43	*Dicloran*	0.005	0.0005-0.100	0.9974	9	0.005	0.0005-0.100	0.9993	11
44	**Diethofencarb**	0.005	0.0005-0.100	0.9995	3	0.005	0.001-0.100	0.9989	-30
45	**Difenoconazole**	0.005	0.0005-0.100	0.9992	5	0.005	0.001-0.100	0.9993	-7
46	**Dimethoate**	0.005	0.0005-0.100	0.9998	2	0.005	0.0005-0.100	0.9865	-9
47	**Dimethomorph**	0.005	0.0005-0.100	0.9986	3	0.005	0.001-0.100	0.9998	-13
48	*Diniconazole*	0.005	0.0005-0.100	0.9984	31	0.005	0.0005-0.100	0.9998	52

No.	Pesticide	Lettuce				Orange			
		LOQ (mg/kg)	Linearity range (mg/kg)	R^2 matrix	ME (%)	LOQ (mg/kg)	Linearity range (mg/kg)	R^2 matrix	ME (%)
49	**Dinotefuran**	0.005	0.002-0.100	0.9995	-1	0.005	0.001-0.100	0.9927	7
50	*Diphenylamine*	0.005	0.0005-0.100	0.9937	2	0.005	0.0005-0.100	0.9986	-5
51	**Dodine**	0.005	0.002-0.100	0.9996	-3	0.005	0.002-0.100	0.9995	0
52	*Endosulfan-alpha*	0.005	0.0005-0.100	0.9971	14	0.005	0.0005-0.100	0.9993	-20
53	*Endosulfan-beta*	0.005	0.0005-0.100	0.9972	56	0.005	0.0005-0.100	0.9998	1
54	*Endosulfan-sulfate*	0.005	0.0005-0.100	0.9985	17	0.005	0.0005-0.100	0.9989	44
55	**EPN**	0.005	0.0005-0.100	0.9998	1	0.005	0.0005-0.100	0.9975	-5
56	**Epoxiconazole**	0.005	0.0005-0.100	0.9997	-2	0.005	0.001-0.100	0.9999	-12
57	**Ethion**	0.005	0.0005-0.100	0.9993	-1	0.005	0.0005-0.100	0.9981	-2
58	**Ethoprofos**	0.005	0.0005-0.100	0.9997	-2	0.005	0.001-0.100	0.9991	-5
59	*Etofenprox*	0.005	0.0005-0.100	0.9985	4	0.005	0.0005-0.100	0.9998	15
60	**Etoxazole**	0.005	0.0005-0.100	0.9997	-1	0.005	0.0005-0.100	0.9923	-1
61	*Famoxadone*	0.005	0.005-0.100	0.9716	515	0.005	0.0005-0.100	0.9995	62
62	**Fenamidone**	0.005	0.0005-0.100	0.9999	4	0.005	0.0005-0.100	0.9992	-13
63	**Fenarimol**	0.005	0.0005-0.100	0.9992	2	0.005	0.001-0.100	0.9973	-8
64	**Fenazaquin**	0.005	0.0005-0.100	0.9994	3	0.005	0.0005-0.100	0.9914	-6
65	**Fenbuconazole**	0.005	0.0005-0.100	0.9996	-6	0.005	0.0005-0.100	0.9985	4
66	*Fenhexamid*	0.005	0.0005-0.100	0.9987	127	0.005	0.0005-0.100	0.9996	80
67	*Fenitrothion*	0.005	0.0005-0.100	0.9971	41	0.005	0.0005-0.100	0.9972	152
68	**Fenoxycarb**	0.005	0.0005-0.100	0.9998	-2	0.005	0.0005-0.100	0.9989	-9
69	*Fenpropathrin*	0.005	0.0005-0.100	0.9982	11	0.005	0.0005-0.100	0.9998	18
70	*Fenpropimorph*	0.005	0.001-0.100	0.9975	13	0.005	0.0005-0.100	0.9996	-5
71	**Fenpyroximate**	0.005	0.0005-0.100	0.9995	0	0.005	0.002-0.100	0.9880	-12
72	**Fenthion**	0.005	0.0005-0.100	0.9989	1	0.005	0.001-0.100	0.9957	-7
73	**Fenthion sulfoxide**	0.005	0.0005-0.100	0.9997	0	0.005	0.001-0.100	0.9965	-1
74	*Fenvalerate*	0.005	0.0005-0.100	0.9979	14	0.005	0.0005-0.100	0.9980	36
75	*Fipronil*	0.005	0.0005-0.100	0.9985	137	0.005	0.0005-0.100	0.9998	15
76	**Fludioxonil**	0.005	0.001-0.100	0.9989	3	0.005	0.001-0.100	0.9978	-16
77	**Flufenoxuron**	0.005	0.0005-0.100	0.9997	1	0.005	0.0005-0.100	0.9922	4
78	*Fluopicolide*	0.005	0.0005-0.100	0.9990	23	0.005	0.0005-0.100	0.9997	18
79	**Fluopyram**	0.005	0.0005-0.100	0.9998	1	0.005	0.0005-0.100	0.9999	-11
80	*Flusilazole*	0.005	0.0005-0.100	0.9988	10	0.005	0.0005-0.100	0.9996	5
81	**Flutolanil**	0.005	0.0005-0.100	0.9997	4	0.005	0.0005-0.100	0.9999	-36
82	**Flutriafol**	0.005	0.0005-0.100	1.0000	-38	0.005	0.0005-0.100	0.9950	-21
83	**Fluxapyroxad**	0.005	0.0005-0.100	0.9998	-3	0.005	0.0005-0.100	0.9999	-65
84	**Furathiocarb**	0.005	0.0005-0.100	0.9998	0	0.005	0.0005-0.100	0.9976	-3
85	**Halofenozide**	0.005	0.002-0.100	0.9993	0	0.005	0.001-0.100	0.9999	-5
86	**Haloxyfop**	0.005	0.001-0.100	0.9980	3	0.005	0.0005-0.100	0.9951	5
87	**Hexaconazole**	0.005	0.0005-0.100	0.9997	3	0.005	0.0005-0.100	0.9990	2
88	**Hexythiazox**	0.005	0.0005-0.100	0.9996	6	0.005	0.001-0.100	0.9944	2
89	**Imazalil**	0.005	0.0005-0.100	0.9998	1	0.005	0.0005-0.100	0.9993	-7
90	**Imazapic**	0.005	0.0005-0.100	0.9998	0	0.005	0.0005-0.100	0.9948	-4
91	**Imidacloprid**	0.005	0.0005-0.100	0.9997	3	0.005	0.0005-0.100	0.9902	28
92	**Indoxacarb**	0.005	0.0005-0.100	0.9994	2	0.005	0.0005-0.100	0.9989	-5
93	*Iprodione*	0.005	0.0005-0.100	0.9996	23	0.005	0.0005-0.100	0.9997	56
94	**Iprovalicarb**	0.005	0.0005-0.100	0.9999	0	0.005	0.002-0.100	0.9993	-33
95	*Kresoxim-methyl*	0.005	0.0005-0.100	0.9983	28	0.005	0.0005-0.100	0.9999	10
96	*lambda-Cyhalothrin*	0.005	0.0005-0.100	0.9972	16	0.005	0.0005-0.100	0.9987	37
97	**Linuron**	0.005	0.0005-0.100	0.9999	3	0.005	0.0005-0.100	0.9991	-12
98	**Lufenuron**	0.010	0.002-0.100	0.9971	2	0.005	0.002-0.100	0.9935	-1
99	**Malathion**	0.005	0.002-0.100	0.9992	-5	0.005	0.0005-0.100	0.9984	-38
100	*Mepanipyrim*	0.005	0.0005-0.100	0.9983	28	0.005	0.005-0.100	0.9991	10

No.	Pesticide	Lettuce				Orange			
		LOQ (mg/kg)	Linearity range (mg/kg)	R^2 matrix	ME (%)	LOQ (mg/kg)	Linearity range (mg/kg)	R^2 matrix	ME (%)
101	*Metalaxyl*	0.005	0.0005-0.100	0.9998	6	0.005	0.0005-0.100	0.9999	2
102	**Methamidophos**	0.005	0.0005-0.100	0.9998	-2	0.010*	0.0005-0.100	0.9997	-1
103	*Methidathion*	0.005	0.0005-0.100	0.9961	81	0.005	0.0005-0.100	0.9983	170
104	**Methiocarb**	0.005	0.0005-0.100	0.9997	-5	0.005	0.0005-0.100	0.9998	-8
105	**Methiocarb sulfone**	0.005	0.0005-0.100	1.0000	-3	0.005	0.0005-0.100	0.9748	-9
106	**Methiocarb sulfoxide**	0.005	0.0005-0.100	1.0000	-2	0.005	0.0005-0.100	0.9878	-7
107	*Metrafenone*	0.005	0.0005-0.100	0.9942	9	0.005	0.0005-0.100	0.9998	11
108	**Monocrotophos**	0.005	0.0005-0.100	0.9999	0	0.005	0.0005-0.100	0.9968	-6
109	**Myclobutanil**	0.005	0.0005-0.100	0.9982	11	0.005	0.0005-0.100	0.9999	-54
110	**Nitenpyram**	0.005*	0.001-0.100	0.9998	-1	0.005*	0.001-0.100	0.9988	6
111	**Omethoate**	0.005	0.0005-0.100	0.9993	2	0.005	0.0005-0.100	0.9929	2
112	*Oxadixyl*	0.005	0.0005-0.100	0.9972	10	0.005	0.0005-0.100	0.9991	-15
113	**Oxamyl-oxime**	0.005	0.001-0.100	0.9999	-4	0.005	0.0005-0.100	0.9908	7
114	**Oxydemeton-methyl**	0.005	0.0005-0.100	0.9997	0	0.005	0.0005-0.100	0.9997	-7
115	*Parathion methyl*	0.005	0.0005-0.100	0.9985	52	0.005	0.0005-0.100	0.9967	170
116	**Penconazole**	0.005	0.0005-0.100	0.9997	-1	0.005	0.0005-0.100	0.9999	-14
117	**Pencycuron**	0.005	0.0005-0.100	0.9997	-3	0.005	0.0005-0.100	0.9999	-5
118	*Pendimethalin*	0.005	0.0005-0.100	0.9987	26	0.005	0.0005-0.100	0.9984	31
119	*Permethrin-cis*	0.005	0.0005-0.100	0.9980	16	0.005	0.0005-0.100	0.9999	14
120	*Permethrin-trans*	0.005	0.0005-0.100	0.9985	15	0.005	0.0005-0.100	0.9998	15
121	*Phenthoate*	0.005	0.0005-0.100	0.9972	68	0.005	0.0005-0.100	0.9997	60
122	**Phosalone**	0.005	0.0005-0.100	0.9996	0	0.005	0.0005-0.100	0.9995	-10
123	**Picolinafen**	0.005	0.0005-0.100	0.9994	4	0.005	0.001-0.100	0.9939	1
124	*Picoxystrobin*	0.005	0.0005-0.100	0.9987	18	0.005	0.0005-0.100	0.9999	11
125	*Piperonyl-butoxide*	0.005	0.0005-0.100	0.9977	21	0.005	0.0005-0.100	0.9995	22
126	*Pirimicarb*	0.005	0.0005-0.100	0.9984	2	0.005	0.0005-0.100	0.9995	4
127	*Pirimicarb-desmethyl*	0.005	0.0005-0.100	0.9951	6	0.005	0.0005-0.100	0.9839	-15
128	**Pirimiphos-methyl**	0.005	0.0005-0.100	0.9992	0	0.005	0.0005-0.100	0.9995	-3
129	**Prochloraz**	0.005	0.0005-0.100	0.9995	-3	0.005	0.001-0.100	0.9996	-17
130	*Procymidone*	0.005	0.0005-0.100	0.9999	9	0.005	0.0005-0.100	0.9997	1
131	**Profenofos**	0.005	0.0005-0.100	0.9999	2	0.005	0.0005-0.100	0.9994	-3
132	**Propamocarb**	0.005*	0.002-0.100	0.9996	-8	n.f.r.	0.0005-0.100	0.9951	-10
133	**Propargite**	0.005	0.0005-0.100	0.9991	-5	0.005	0.001-0.100	0.9985	0
134	**Propiconazole**	0.005	0.0005-0.100	0.9998	4	0.005	0.002-0.100	0.9979	-3
135	**Propyzamide**	0.005	0.0005-0.100	0.9999	1	0.005	0.0005-0.100	0.9997	-62
136	**Proquinazid**	0.005	0.0005-0.100	0.9999	-3	0.005	0.0005-0.100	0.9842	3
137	*Prothiofos*	0.005	0.0005-0.100	0.9985	17	0.005	0.0005-0.100	0.9998	26
138	**Pymetrozine**	0.005	0.0005-0.100	0.9998	-2	n.f.r.	0.0005-0.100	0.9993	3
139	**Pyraclostrobin**	0.005	0.0005-0.100	0.9998	1	0.005	0.0005-0.100	0.9997	-7
140	*Pyridaben*	0.005	0.0005-0.100	0.9981	23	0.005	0.0005-0.100	0.9992	21
141	*Pyrimethanil*	0.005	0.0005-0.100	0.9989	6	0.005	0.001-0.100	0.9996	3
142	**Pyrimidafen**	0.005	0.0005-0.100	0.9998	1	0.005	0.0005-0.100	0.9976	-4
143	*Pyriproxyfen*	0.005	0.0005-0.100	0.9943	8	0.005	0.0005-0.100	0.9998	19
144	*Quinoxyfen*	0.005	0.0005-0.100	0.9992	19	0.005	0.0005-0.100	0.9996	9
145	**Rotenone**	0.005	0.0005-0.100	0.9998	9	0.005	0.0005-0.100	0.9993	6
146	*Silthiofam*	0.005	0.0005-0.100	0.9996	8	0.005	0.0005-0.100	0.9999	6
147	**Spinetoram I**	0.005	0.002-0.100	0.9997	-2	0.005	0.001-0.100	0.9813	-10
148	**Spinetoram II**	0.005	0.005-0.100	0.9991	-2	0.005	0.005-0.100	0.9791	-5
149	**Spinosyn A**	0.005	0.0005-0.100	0.9999	-2	0.005	0.0005-0.100	0.9879	-4
150	**Spinosyn D**	0.005	0.001-0.100	0.9998	-1	0.005	0.001-0.100	0.9807	-6
151	*Spirodiclofen*	0.005	0.0005-0.100	0.9977	16	0.005	0.0005-0.100	0.9992	17
152	*Spiromesifen*	0.005	0.0005-0.100	0.9994	30	0.005	0.0005-0.100	0.9999	12

No.	Pesticide	Lettuce				Orange			
		LOQ (mg/kg)	Linearity range (mg/kg)	R^2 matrix	ME (%)	LOQ (mg/kg)	Linearity range (mg/kg)	R^2 matrix	ME (%)
153	**Spirotetramat**	0.005	0.0005-0.100	0.9989	5	0.005	0.001-0.100	0.9998	6
154	**Spiroxamine**	0.005	0.0005-0.100	0.9978	6	0.005	0.0005-0.100	0.9968	-4
155	*tau-Fluvalinate*	0.005	0.0005-0.100	0.9968	33	0.005	0.0005-0.100	0.9971	73
156	**Tebuconazole**	0.005	0.001-0.100	0.9997	3	0.005	0.001-0.100	0.9997	-10
157	**Tebufenozide**	0.005	0.001-0.100	0.9994	-1	0.005	0.001-0.100	0.9961	-12
158	*Tebufenpyrad*	0.005	0.0005-0.100	0.9982	8	0.005	0.0005-0.100	0.9998	11
159	**Teflubenzuron**	0.005	0.0005-0.100	0.9995	0	0.005	0.001-0.100	0.9964	-5
160	**Tembotrione**	0.005	0.0005-0.100	0.9994	2	0.005	0.0005-0.100	0.9852	-15
161	*Terbuthylazine*	0.005	0.0005-0.100	0.9995	3	0.005	0.0005-0.100	0.9996	3
162	*Tetraconazole*	0.005	0.0005-0.100	0.9995	17	0.005	0.0005-0.100	0.9998	5
163	*Tetradifon*	0.005	0.0005-0.100	0.9985	6	0.005	0.0005-0.100	0.9998	1
164	**Thiabendazole**	0.005	0.0005-0.100	0.9996	1	0.005	0.0005-0.100	0.9897	-10
165	**Thiacloprid**	0.005	0.0005-0.100	0.9999	0	0.005	0.0005-0.100	0.9636	-16
166	**Thiamethoxam**	0.005	0.0005-0.100	0.9998	4	0.005	0.002-0.100	0.9996	6
167	**Tolclophos-Methyl**	0.005	0.0005-0.100	0.9999	0	0.005	0.0005-0.100	0.9982	-7
168	**Tolylfluanid**	0.005	0.001-0.100	0.9992	3	0.005	0.0005-0.100	0.9997	-6
169	*Triadimefon*	0.005	0.0005-0.100	0.9989	15	0.005	0.0005-0.100	0.9997	6
170	*Triadimenol*	0.005	0.0005-0.100	0.9986	17	0.005	0.0005-0.100	0.9998	27
171	**Triazophos**	0.005	0.0005-0.100	0.9997	-1	0.005	0.0005-0.100	0.9998	-30
172	**Triazoxide**	0.005	0.0005-0.100	0.9987	-5	0.005	0.0005-0.100	0.9938	-14
173	**Trifloxystrobin**	0.005	0.0005-0.100	0.9997	2	0.005	0.0005-0.100	0.9976	-4
174	**Triflumizole**	0.005	0.001-0.100	0.9993	-4	0.005	0.002-0.100	0.9930	-1
175	**Zoxamide**	0.005	0.0005-0.100	0.9998	-1	0.005	0.0005-0.100	0.9991	-5

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
n.d. : Not detectable