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MOHWP0055.05

Method of Test for Pesticide Residues in Foods - Multiresidue Analysis (5)

1. Scope

This method is applicable for the determination of 410 pesticide residues (abamectin etc. listed in the attached tables) in fruits and vegetables, crops, dried beans, tea, spice plants and other herbs.

2. Method

After preparation of the sample solution by the QuEChERS method (Quick, Easy, Cheap, Effective, Rugged, Safe), pesticides are determined by liquid chromatography/tandem mass spectrometry (LC-MS/MS) and gas chromatography/tandem mass spectrometry (GC-MS/MS).

2.1. Equipment

2.1.1. Liquid chromatograph/tandem mass spectrometer.

2.1.1.1. Ion source: electrospray ionization, ESI.

2.1.1.2. Column: CORTECS UPLC C18, 1.6 μm, 2.1 mm i.d. × 10 cm, or an equivalent product.

2.1.1.3. Guard column: CORTECS UPLC C18, 1.6 μm, 2.1 mm i.d. × 5 mm, or an equivalent product.

2.1.2. Gas chromatograph/tandem mass spectrometer.

2.1.2.1. Ion source: electron ionization, EI.

2.1.2.2. Column: DB-5MS UI capillary column, 0.25 μm, 0.25 mm × 30 m, or an equivalent product.

2.1.3. Blender.

2.1.4. Grinder.

2.1.5. High speed dispersing device: SPEX SamplePrep 2010 GenoGrinder®, >1000 rpm, or an other mechanical shaker.

2.1.6. Centrifuge: centrifugal force > 3000 ×g, temperature control <15℃.

2.1.7. Nitrogen evaporator.

2.2. Chemicals

Glacial acetic acid, GR grade;
Formic acid, GR grade;
Ammonium acetate, GR grade;
n-Hexane, Residue grade;
Acetone, Residue grade;
Acetonitrile, HPLC grade;

Methanol, HPLC grade;
Sodium acetate anhydrous, AR grade;
Magnesium sulfate anhydrous, AR grade;
Primary secondary amine (PSA), AR grade;
Octadecysilane, end-capped (C18 EC), AR grade;
Graphitized carbon black (GCB), AR grade;
Deionized water, resistivity ≥ 18 MΩ·cm (at 25℃);
Abamectin and other pesticides listed in the attached tables, reference standards;
Triphenylphosphate, internal standard.

2.3. Apparatus

2.3.1. Centrifuge tube: 15 mL and 50 mL, PP.

2.3.2. Membrane filter: 0.22-μm, PTFE.

2.3.3. Volumetric flask: 15 mL and 50 mL.

2.3.4. Ceramic homogenizer(note 1): Bond Elut QuEChERS P/N 5982-9313, or an equivalent product.

2.3.5. Extraction powder(note 2): Containing 4 g of magnesium sulfate anhydrous and 1 g of sodium acetate anhydrous.

2.3.6. Clean-up centrifuge tube I(note 2): containing 300 mg of PSA and 900 mg of magnesium sulfate anhydrous, 6 mL, used for type I samples (fresh fruits, vegetables, spice plants and other herbs with high water content).

2.3.7. Clean-up centrifuge tube II(note 2): containing 300 mg of PSA, 300 mg of C18 EC and 900 mg of magnesium sulfate anhydrous, 6 mL, used for type II samples (crops and dried beans with high wax, fat and sugar content).

2.3.8. Clean-up centrifuge tube III(note 2): containing 450 mg of PSA, 900 mg of magnesium sulfate anhydrous, 300 mg of C18 EC and 50 mg of GCB, 6 mL, used for type III samples (dried tea, fruits, vegetables, spice plants and other herbs with high pigment content).

Note 1: Ceramic homogenizer can be used depending on the viscosity of the sample.

Note 2: Commercial extraction/clean-up kit can be used as needed.

2.4. Reagents

2.4.1. 1% Acetic acid in acetonitrile

Mix 10 mL of glacial acetic acid and 990 mL of acetonitrile.

2.4.2. 5% Formic acid in acetonitrile

Mix 5 mL of formic acid and 95 mL of acetonitrile.

2.4.3. Acetone: *n*-hexane (1:1, v/v)

Mix acetone and *n*-hexane at the ratio of 1:1 (v/v).

2.5. Mobile phase

2.5.1. Solvent A

Dissolve0.39 g of ammonium acetate with deionized water to 1000 mL, add 1 mL of formic acid, mix well, and filter with a membrane filter.

2.5.2. Solvent B

Dissolve0.39 g of ammonium acetate with methanol to 1000 mL, and filter with a membrane filter.

2.6. Internal standard solution preparation

Transfer about 50 mg of triphenylphosphate internal standard accurately weighed into a 50-mL volumetric flask, dissolve and dilute to volume with methanol as the internal standard stock solution. Store at -18℃ in the dark.

2.6.1. Dilute appropriate volume of the internal standard stock solution with methanol to 50 μg/mL as the internal standard solution for sample solution preparation in section 2.8.

2.6.2. Dilute appropriate volume of the internal standard stock solution with methanol to 5 μg/mL as the internal standard solution for analysis of LC-MS/MS in section 2.9.1.

2.6.3. Dilute appropriate volume of the internal standard stock solution with acetone to 5 μg/mL as the internal standard solution for analysis of GC-MS/MS in section 2.9.2.

2.7. Standard solution preparation

2.7.1. Transfer about 25 mg of pesticide reference standards accurately weighed to each 25-mL volumetric flask, dissolve and dilute to volume with acetonitrile as the standard stock solutions. Store at -18℃ in the dark. Mix appropriate volume of each standard stock solution, and dilute with methanol to 1 μg/mL as the standard solution for analysis of LC-MS/MS in section 2.9.1.

2.7.2. Transfer about 25 mg of pesticide reference standards accurately weighed to each 25-mL volumetric flask, dissolve and dilute to volume

with acetone or *n*-hexane as standard stock solutions. Store at -18℃ in the dark. Mix appropriate volume of each standard stock solution, and dilute with acetone: *n*-hexane (1:1, v/v) to 1 μg/mL as the standard solution for analysis of GC-MS/MS in section 2.9.2.

2.8. Sample solution preparation

2.8.1. Type I samples (fresh fruits, vegetables, spice plants and other herbs with high water content)

Transfer about 10 g of the homogenized sample accurately weighed into a 50-mL centrifuge tube, and add 10 mL of 1% acetic acid in acetonitrile and 10 μL of 50 μg/mL internal standard solution after freezing. Add 1 granule of a ceramic homogenizer and the extraction powder, cap the centrifuge tube, shake vigorously several times by hands to prevent coagulation of salt, and then shake at 1000 rpm by the high speed dispersing device or shake vigorously by hands for 1 min. Centrifuge at 3000 ×g for 1 min at 15℃, and transfer 6 mL of the supernatant to a clean-up centrifuge tube I. Shake at 1000 rpm by the high speed dispersing device or shake vigorously by hands for 1 min, and centrifuge at 3000 ×g for 2 min at 15℃. Take 1 mL of the supernatant, and evaporate to near dryness by gently flushing with a stream of nitrogen. Dissolve the residue with 1 mL of methanol, mix well, and filter with a membrane filter. Take the filtrate as the sample solution I used for analysis by LC-MS/MS. Take another 1 mL of the supernatant, and evaporate to near dryness by gently flushing with a stream of nitrogen. Dissolve the residue with 1 mL of acetone: *n*-hexane (1:1, v/v), mix well, and filter with a membrane filter. Take the filtrate as the sample solution II used for analysis by GC-MS/MS.

2.8.2. Type II samples (crops and dried beans with high wax, fat and sugar content)

Transfer about 5 g of the powdered sample accurately weighed into a 50-mL centrifuge tube, add 10 mL of pre-cooled deionized water, stand for 20 min, and add 10 mL of 1% acetic acid in acetonitrile and 10 μL of 50 μg/mL internal standard solution. Add 1 granule of a ceramic homogenizer and the extraction powder, cap the centrifuge tube, shake vigorously several times by hands to prevent coagulation of salt, and then shake at 1000 rpm by the high speed dispersing

device or shake vigorously by hands for 1 min. Centrifuge at 3000 ×g for 1 min at 15℃, and transfer 6 mL of the supernatant to a clean-up centrifuge tube II. Shake at 1000 rpm by the high speed dispersing device or shake vigorously by hands for 1 min, and centrifuge at 3000 ×g for 2 min at 15℃. Take 1 mL of the supernatant, and evaporate to near dryness by gently flushing with a stream of nitrogen. Dissolve the residue with 1 mL of methanol, mix well, and filter with a membrane filter. Take the filtrate as the sample solution I used for analysis by LC-MS/MS. Take another 1 mL of the supernatant, and evaporate to near dryness by gently flushing with a stream of nitrogen. Dissolve the residue with 1 mL of acetone: *n*-hexane (1:1, v/v), mix well, and filter with a membrane filter. Take the filtrate as the sample solution II used for analysis by GC-MS/MS.

2.8.3. Type III samples (dried tea, fruits, vegetables, spice plants and other herbs with high pigment content)

Transfer about 2 g of the powdered sample accurately weighed into a 50-mL centrifuge tube, add 10 mL of pre-cooled deionized water, stand for 20 min, and add 10 mL of 1% acetic acid in acetonitrile and 10 μL of 50 μg/mL internal standard solution. Add 1 granule of a ceramic homogenizer and the extraction powder, cap the centrifuge tube, shake vigorously several times by hands to prevent coagulation of salt, and then shake at 1000 rpm by the high speed dispersing device or shake vigorously by hands for 1 min. Centrifuge at 3000 ×g for 1 min at 15℃, and transfer 6 mL of the supernatant to a clean-up centrifuge tube III. Shake at 1000 rpm by the high speed dispersing device or shake vigorously by hands for 1 min, and centrifuge at 3000 ×g for 2 min at 15℃. Take 1 mL of the supernatant, and evaporate to near dryness by gently flushing with a stream of nitrogen. Dissolve the residue with 1 mL of methanol, mix well, and filter with a membrane filter. Take the filtrate as the sample solution I used for analysis by LC-MS/MS. Take another 1 mL of the supernatant, and evaporate to near dryness by gently flushing with a stream of nitrogen. Dissolve the residue with 1 mL of acetone: *n*-hexane (1:1, v/v), mix well, and filter with a membrane filter. Take the filtrate as the sample solution II used for analysis by GC-MS/MS.

2.9. Matrix-matched calibration curve

2.9.1. LC-MS/MS

Take a blank sample without adding the internal standard, and follow the procedure described in section 2.8 to obtain the supernatant after the clean-up procedure. Take several 1 mL of the supernatant, and evaporate to near dryness by gently flushing with a stream of nitrogen. Separately add 2 - 200 μL[(note 3)] of 1 μg/mL the standard solution, 10 μL of 5 μg/mL the internal standard solution and methanol to achieve a final volume of 1 mL, and mix well as the matrix-matched standard solutions I. Operate LC-MS/MS according to the following conditions. Establish the matrix-matched calibration curve of each pesticide by the ratios of the peak area of each pesticide to that of the internal standard vs. the added concentrations (0.002 - 0.2 μg/mL; 0.0004 - 0.04 μg/mL for fipronil and its metabolite).

LC-MS/MS operating conditions[(note 4)]:

Column: CORTECS UPLC C18, 1.6 μm, 2.1 mm i.d. × 10 cm.

Guard column: CORTECS UPLC C18, 1.6 μm, 2.1 mm i.d. × 5 mm.

Mobile phase: a gradient program of solvent A and solvent B is as follows:

Time (min)	A (%)	B (%)
0.0 → 2.0	99 → 50	1 → 50
2.0 → 8.0	50 → 30	50 → 70
8.0 → 10.0	30 → 1	70 → 99
10.0 → 13.0	1 → 1	99 → 99
13.0 → 13.5	1 → 99	99 → 1
13.5 → 15.0	99 → 99	1 → 1

Flow rate: 0.3 mL/min.

Injection volume: 5 μL.

Capillary voltage: ESI^+, 3.5 kV; ESI^-, 1.6 kV.

Ion source temperature: 150℃.

Desolvation temperature: 450℃.

Cone gas flow rate: 30 L/hr.

Desolvation flow rate: 900 L/hr.

Detection mode: multiple reaction monitoring (MRM). Detection ion

pair, cone voltage and collision energy are shown in Table 1 and Table 2.

2.9.2. GC-MS/MS

Take a blank sample without adding the internal standard, and follow the procedure described in section 2.8 to obtain the supernatant after the clean-up procedure. Take several 1 mL of the supernatant, and evaporate to near dryness by gently flushing with a stream of nitrogen. Separately add 4 - 200 μL of 1 μg/mL the standard solution, 10 μL of 5 μg/mL the internal standard solution and acetone: *n*-hexane (1:1, v/v) to achieve a final volume of 1 mL, and mix well as the matrix-matched standard solutions II. Operate GC-MS/MS according to the following conditions. Establish the matrix-matched calibration curve of each pesticide by the ratios of the peak area of each pesticide to that of the internal standard vs. the added concentrations (0.004 - 0.2 μg/mL).

GC-MS/MS operating conditions (note 4):

Column: DB-5MS UI capillary column, 0.25 μm, 0.25 mm × 30 m.

Column temperature:

Initial temperature: 60℃, 1 min;

Temperature rising rate: 40℃/min;

Middle temperature: 170℃;

Temperature rising rate: 10℃/min;

Final temperature: 310℃, 2.25 min.

Carrier gas and flow rate: helium, 1 mL/min.

Injector temperature: 280℃.

Injection mode: splitless.

Injection volume: 1 μL.

Ion source: electron ionization, 70 eV.

Ion source temperature: 300℃.

Detection mode: multiple reaction monitoring (MRM). Detection ion pair and collision energy are shown in Table 3.

Note 3: Choose an appropriate amount of fipronil and its metabolite standard solution to add for preparation of the matrix-matched calibration curve.

Note 4: All the parameters can be adjusted depending on the

instruments used if the above conditions are not applicable.

2.10. Identification and quantification

2.10.1. Matrix-matched calibration curve method

2.10.1.1. LC-MS/MS

Accurately inject 5 μL of the sample solution I and the matrix-matched standard solutions I into LC-MS/MS separately, and operate according to the conditions described in section 2.9.1. Identify each pesticide based on the retention time and the relative ion intensities(note 5). Calculate the amount of each pesticide in the sample using the following formula:

$$\text{The amount of each pesticide in the sample (ppm)} = \frac{C \times V}{M}$$

Where,

C: the concentration of each pesticide in the sample solution calculated by the matrix-matched calibration curve (ng/mL)

V: the volume of 1% acetic acid in acetonitrile for sample extraction (10 mL)

M: the weight of the sample (g)

2.10.1.2. GC-MS/MS :

Accurately inject 1 μL of the sample solution II and the matrix-matched standard solutions II into LC-MS/MS separately, and operate according to the conditions described in section 2.9.2. Identify each pesticide based on the retention time and the relative ion intensities(note 5). Calculate the amount of each pesticide in the sample using the following formula:

$$\text{The amount of each pesticide in the sample (ppm)} = \frac{C \times V}{M}$$

Where,

C: the concentration of each pesticide in the sample solution calculated by the matrix-matched calibration curve solution (ng/mL)

V: the volume of 1% acetic acid in acetonitrile for sample extraction (10 mL)

M: the weight of the sample (g)

Note 5: Relative ion intensities are calculated by peak areas of

qualitative ions divided by peak areas of quantitative ions. Maximum permitted tolerances of relative ion intensities are as follows:

Relative ion intensity (%)	Tolerance (%)
> 50	± 20
> 20～50	± 25
> 10～20	± 30
≤ 10	± 50

2.10.2. Standard addition method

2.10.2.1. LC-MS/MS

Take 1 mL of the supernatant after the clean-up procedure described in section 2.8, and evaporate to near dryness by gently flushing with a stream of nitrogen. Separately add 0 - 200 μL of 1 μg/mL the standard solution and methanol to achieve a final volume of 1 mL, mix well, and operate LC-MS/MS according to the conditions described in section 2.9.1. Establish a linear regression curve (y = mx + n) by the peak areas of each pesticide vs. the added concentrations (0 - 0.2 μg/mL) as shown in Figure 1. Calculate the amount of each pesticide in the sample by the following formula:

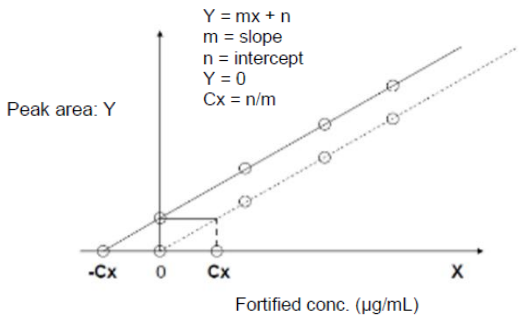

Figure 1. The linear regression curve by the standard addition method.

$$\text{The amount of each pesticide in the sample (ppm)} = \frac{C \times V}{M}$$

Where,

C: the concentration of each pesticide in the sample solution calculated from n/m (ng/mL)

V: the volume of 1% acetic acid in acetonitrile for sample extraction (10 mL)

M: the weight of the sample (g)

2.10.2.2. GC-MS/MS

Take 1 ml of the supernatant after the clean-up procedure described in section 2.8, and evaporate to near dryness by gently flushing with a stream of nitrogen. Separately add 0-200 μL of 1 μg/mL the standard solution and acetone: *n*-hexane (1:1, v/v) to achieve a final volume of 1 mL, mix well, and operate GC-MS/MS according to the conditions described in section 2.9.2. Establish a linear regression curve (y = mx + n) by the peak areas of each pesticide vs. the added concentrations (0 - 0.2 μg/mL) as shown in Figure 1. Calculate the amount (ppm) of each pesticide in the sample by the following formula:

$$\text{The amount of each pesticide in the sample (ppm)} = \frac{C \times V}{M}$$

Where,

C: the concentration of each pesticide in the sample solution calculated from n/m (ng/mL)

V: the volume of 1% acetic acid in acetonitrile for sample extraction (10 mL)

M: the weight of the sample (g)

Remark

1. Limit of quantification (LOQ) for each pesticide is listed in the attached table.
2. Whether pesticide items should be analyzed by LC-MS/MS or GC-MS/MS can be reviewed as needed.
3. Since the internal standard, triphenylphosphate (TPP), used in the procedure cannot represent the physicochemical properties of all items of pesticides, it is not necessary to use it in the formula to calculate the amount of pesticides in the sample. It can serve as quality control to confirm the procedure.
4. To ensure the correct determination of pesticides such as chlorothalonil which sensitivity is easily affected by GC-MS/MS, it needs to add 10 μL of 5% formic acid in acetonitrile to the sample solution.

5. This method is not applicable to the determination of benfuracarb, nitenpyram and pymetrozine in type III samples.
6. Because emamectin benzoate, pyrethrins, spinetoram and spinosad reference standards contain several compounds, the lowest concentration of the matrix-matched calibration curve for each compound should be calculated by its LOQ multiplied by the proportion of each compound in the reference standard.
7. Chlorobenzilate and chloropropylate have the same retention time. If a signal in the sample solution is detected as the same retention time as that of chlorobenzilate or chloropropylate in the standard solution, a Select-PAH column (0.15 μm, 0.25 mm × 30 m) or an equivalent product should be used to separate the two compounds for further quantitation.
8. Further validation should be performed when interfering compounds are found in the samples.

Reference

European Committee for Standardization. 2018. Foods of plant origin– Multimethod for the determination of pesticide residues using GC and LC-based analysis following acetonitrile extraction/partitioning and clean-up by dispersive SPE-Modular QuEChERS-method. NF EN 15662:2018 (English version).

Table 1. MRM parameters and LOQs of 216 pesticides including abamectin etc. and the internal standard (LC-MS/MS positive ion mode)

No.	Analyte	Ion pair			LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Cone voltage (V)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
1	Abamectin	890.5 > 567* 890.5 > 305	17 17	16 17	0.01	0.01	0.05
2	Acephate	184 > 143* 184 > 125	18 18	8 18	0.01	0.02	0.05
3	Acetamiprid	223 > 56* 223 > 126	20 20	15 15	0.01	0.02	0.05
4	Acibenzolar-S-methyl	211 > 136* 211 > 91	34 34	32 18	0.01	0.02	0.05
5	Alanycarb	400 > 238* 400 > 91	30 30	11 36	0.01	0.02	0.05
6	Aldicarb	208 > 116* 208 > 89	10 10	8 8	0.01	0.02	0.02
7	Aldicarb sulfone	223 > 86* 223 > 166	20 20	5 5	0.01	0.02	0.02
8	Aldicarb sulfoxide	207 > 89* 207 > 132	16 16	10 10	0.01	0.02	0.02
9	Alloxydim (sodium)	324 > 234* 324 > 266	25 25	15 11	0.01	0.02	0.05
10	Ametoctradin	276 > 149* 276 > 176	35 35	30 30	0.01	0.02	0.05
11	Ametryn	228 > 186* 228 > 96	32 32	19 25	0.01	0.02	0.05
12	Amisulbrom	468 > 229* 468 > 148	20 20	16 50	0.01	0.01	0.05
13	Atrazine	216 > 174* 216 > 96	39 39	18 23	0.01	0.02	0.05
14	Azafenidin	338 > 264* 338 > 112	55 55	30 50	0.01	0.02	0.05
15	Aziprotryne	226 > 125* 226 > 156	38 38	19 19	0.01	0.02	0.05
16	Azoxystrobin	404 > 372* 404 > 344	25 25	15 25	0.01	0.01	0.05
17	Benalaxyl	326 > 148* 326 > 91	26 26	20 34	0.01	0.02	0.05
18	Bendiocarb	224 > 109* 224 > 81	20 20	20 20	0.01	0.02	0.05
19	Benfuracarb	411 > 190* 411 > 252	10 10	10 10	0.01	0.02	—
20	Bensulfuron-methyl	411 > 149* 411 > 182	26 26	21 20	0.01	0.02	0.05

Table 1. MRM parameters and LOQs of 216 pesticides including abamectin etc. and the internal standard (LC-MS/MS positive ion mode) (continued)

No.	Analyte	Ion pair			LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Cone voltage (V)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
21	Benthiazole	239 > 180* 239 > 136	15 15	12 30	0.01	0.02	0.05
22	Benzovindiflupyr	398 > 342* 398 > 378	30 10	15 15	0.01	0.02	0.05
23	Benzoximate	364 > 199* 364 > 105	38 38	12 12	0.01	0.02	0.05
24	Bifenazate	301 > 198* 301 > 170	16 16	10 22	0.01	0.02	0.05
25	Boscalid	343 > 307* 343 > 140	36 36	18 18	0.01	0.02	0.05
26	Bufencarb	222 > 95* 222 > 71	23 23	22 20	0.01	0.01	0.03
27	Buprofezin	306 > 201* 306 > 116	20 20	13 15	0.01	0.02	0.05
28	Butafenacil	492 > 180* 492 > 331	20 20	36 40	0.01	0.02	0.05
29	Butocarboxim	213 > 75* 213 > 116	35 35	15 15	0.01	0.02	0.05
30	Carbaryl	202 > 145* 202 > 127	20 20	20 20	0.01	0.02	0.05
31	Carbendazim	192 > 160* 192 > 132	30 30	30 35	0.01	0.02	0.05
32	Carbofuran	222 > 165* 222 > 123	20 20	10 10	0.01	0.02	0.05
33	3-keto Carbofuran	236 > 208* 236 > 151	25 25	10 10	0.01	0.02	0.05
34	3-OH Carbofuran	238 > 181* 238 > 163	20 20	10 10	0.01	0.02	0.05
35	Carbosulfan	381 > 160* 381 > 118	20 20	15 15	0.01	0.02	0.05
36	Carfentrazone-ethyl	412 > 346* 412 > 366	34 34	26 20	0.01	0.02	0.05
37	Carpropamid	334 > 139* 334 > 196	20 20	20 14	0.01	0.02	0.05
38	Chlorantraniliprole	484 > 453* 484 > 286	24 24	18 18	0.01	0.02	0.03
39	Chlorbenzuron	309 > 139* 309 > 156	22 22	26 18	0.01	0.02	0.05
40	Chlorfluazuron	540.0 > 383* 540.0 > 158	32 32	20 20	0.01	0.02	0.05

Table 1. MRM parameters and LOQs of 216 pesticides including abamectin etc. and the internal standard (LC-MS/MS positive ion mode) (continued)

No.	Analyte	Ion pair			LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Cone voltage (V)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
41	Chromafenozide	395 > 175* 395 > 339	15 15	17 8	0.01	0.02	0.05
42	Cinosulfuron	414 > 183* 414 > 157	25 25	23 23	0.01	0.02	0.05
43	Clethodim	360 > 164* 360 > 268	23 23	18 12	0.01	0.02	0.05
44	Clofentezine	303 > 138* 303 > 102	22 22	22 35	0.01	0.02	0.05
45	Clomazone	240 > 125* 240 > 89	29 29	20 44	0.01	0.02	0.05
46	Clomeprop	324 > 203* 324 > 120	25 25	17 15	0.01	0.02	0.05
47	Clothianidin	250 > 169* 250 > 132	20 20	20 30	0.01	0.01	0.03
48	Cyanazine	241 > 214* 241 > 104	30 30	18 34	0.01	0.02	0.05
49	Cyantraniliprole	475 > 286* 475 > 444	10 10	15 15	0.01	0.02	0.05
50	Cyazofamid	325 > 108* 325 > 261	15 15	15 9	0.01	0.02	0.05
51	Cyclaniliprole	602.0 > 284* 602.0 > 177	30 30	23 50	0.01	0.02	0.05
52	Cyclosulfamuron	422 > 261* 422 > 218	24 24	16 27	0.01	0.02	0.05
53	Cycloxydim	326 > 280* 326 > 180	23 23	16 22	0.01	0.02	0.05
54	Cyenopyrafen	394 > 310* 394 > 111	2 2	22 40	0.01	0.02	0.05
55	Cyflufenamid	413 > 295* 413 > 241	30 30	18 25	0.01	0.02	0.05
56	Cyflumetofen	448 > 173* 448 > 249	28 28	28 8	0.01	0.01	0.05
57	Cymoxanil	199 > 128* 199 > 111	17 17	8 18	0.01	0.02	0.05
58	Cyprodinil	226 > 93* 226 > 108	50 50	33 25	0.01	0.01	0.05
59	Demeton-S-methyl	231 > 89* 231 > 61	13 13	10 32	0.01	0.02	0.05
60	Dialifos	394 > 187* 394 > 208	15 15	10 10	0.01	0.02	0.05

Table 1. MRM parameters and LOQs of 216 pesticides including abamectin etc. and the internal standard (LC-MS/MS positive ion mode) (continued)

No.	Analyte	Ion pair			LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Cone voltage (V)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
61	Dicrotophos	238 > 112* 238 > 193	20 20	10 10	0.01	0.02	0.05
62	Dimethenamid	276 > 244* 276 > 168	25 25	14 23	0.01	0.01	0.05
63	Dimethoate	230 > 199* 230 > 125	17 17	9 23	0.01	0.02	0.05
64	Dimethomorph	388 > 165* 388 > 301	25 25	25 40	0.01	0.02	0.05
65	Dinotefuran	203 > 157* 203 > 129	20 20	8 14	0.01	0.02	0.05
66	Diuron	233 > 72* 233 > 160	23 23	15 27	0.01	0.02	0.05
67	Dymron	269 > 151* 269 > 91	30 30	10 40	0.01	0.02	0.05
68	Emamectin benzoate B_{1a}	886.5 > 158* 886.5 > 126	6 6	42 46	0.007	0.02	0.03
69	Emamectin benzoate B_{1b}	872.5 > 158* 872.5 > 126	44 44	38 56			
70	Ethiprole	397 > 351* 397 > 255	34 34	18 36	0.01	0.02	0.05
71	Ethirimol	210 > 140* 210 > 98	38 38	22 28	0.01	0.02	0.05
72	Etoxazole	360 > 141* 360 > 304	35 35	35 17	0.01	0.01	0.05
73	Famoxadone	392 > 331* 392 > 238	10 10	12 14	0.01	0.02	0.05
74	Fenamiphos	304 > 217* 304 > 202	26 26	22 35	0.01	0.01	0.05
75	Fenazaquin	307 > 161* 307 > 57	20 20	20 20	0.01	0.02	0.05
76	Fenbutatin-oxide	519.7 > 197* 519.7 > 351	44 44	54 32	0.01	0.02	0.05
77	Fenhexamid	302 > 97* 302 > 55	35 35	22 38	0.01	0.02	0.05
78	Fenobucarb	208 > 95* 208 > 152	20 20	10 10	0.01	0.02	0.05
79	Fenothiocarb	254 > 160* 254 > 107	17 17	11 26	0.01	0.02	0.05
80	Fenoxanil	329 > 302* 329 > 189	30 30	16 24	0.01	0.02	0.05

Table 1. MRM parameters and LOQs of 216 pesticides including abamectin etc. and the internal standard (LC-MS/MS positive ion mode) (continued)

No.	Analyte	Ion pair			LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Cone voltage (V)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
81	Fenoxycarb	302 > 116* 302 > 88	28 28	11 20	0.01	0.02	0.05
82	Fenpyrazamine	332 > 230* 332 > 216	40 40	15 15	0.01	0.02	0.05
83	Fenpyroximate	422 > 366* 422 > 135	20 20	25 25	0.01	0.02	0.05
84	Fenthion	279 > 169* 279 > 247	27 27	16 13	0.01	0.01	0.05
85	Ferimzone	255 > 132* 255 > 91	20 20	20 30	0.01	0.02	0.05
86	Flazasulfuron	408 > 182* 408 > 139	20 20	15 45	0.01	0.02	0.05
87	Flonicamid	230 > 203* 230 > 174	32 32	18 18	0.01	0.02	0.05
88	Florpyrauxifen-benzyl	439 > 91* 439 > 65	30 30	20 50	0.01	0.02	0.05
89	Fluazifop-P-butyl	384 > 282* 384 > 328	34 34	22 17	0.01	0.02	0.05
90	Fludioxonil	266 > 158* 266 > 185	13 13	33 34	0.01	0.02	0.06
91	Flufenoxuron	489 > 158* 489 > 141	25 25	30 30	0.01	0.02	0.05
92	Fluopicolide	385 > 175* 385 > 147	29 29	23 49	0.01	0.02	0.03
93	Fluopyram	397 > 173* 397 > 208	50 50	20 20	0.01	0.02	0.05
94	Flupyradifurone	289 > 126* 289 > 90	35 35	34 40	0.01	0.02	0.05
95	Flusilazole	316 > 165* 316 > 247	25 25	25 25	0.01	0.02	0.05
96	Flutriafol	302 > 70* 302 > 123	20 20	25 25	0.01	0.02	0.05
97	Formetanate	222 > 165* 222 > 46	25 25	17 24	0.01	0.02	0.05
98	Fosthiazate	284 > 228* 284 > 104	28 28	10 22	0.01	0.02	0.05
99	Furametpyr	334 > 157* 334 > 131	28 28	32 24	0.01	0.02	0.05
100	Haloxyfop-methyl	376 > 316* 376 > 91	25 25	20 20	0.01	0.02	0.05

Table 1. MRM parameters and LOQs of 216 pesticides including abamectin etc. and the internal standard (LC-MS/MS positive ion mode) (continued)

No.	Analyte	Ion pair			LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Cone voltage (V)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
101	Hexaconazole	314 > 70* 314 > 159	31 31	20 36	0.01	0.02	0.05
102	Hexaflumuron	461 > 158* 461 > 141	25 25	25 25	0.05	0.05	0.05
103	Hexythiazox	353 > 228* 353 > 168	20 20	20 20	0.01	0.02	0.05
104	Imazalil	297 > 159* 297 > 69	40 40	22 22	0.01	0.01	0.05
105	Imicyafos	305 > 201* 305 > 235	40 40	10 10	0.01	0.02	0.05
106	Imidacloprid	256 > 209* 256 > 175	25 25	20 20	0.01	0.01	0.05
107	Indoxacarb	528.1 > 150* 528.1 > 293	20 20	30 20	0.01	0.01	0.01
108	Iprovalicarb	321 > 119* 321 > 203	25 25	26 9	0.01	0.02	0.05
109	Isazofos	314 > 162* 314 > 120	20 20	20 20	0.01	0.02	0.05
110	Isofetamid	360 > 210* 360 > 125	20 20	10 10	0.01	0.02	0.05
111	Isoprocarb	194 > 95* 194 > 137	20 20	10 10	0.01	0.02	0.05
112	Isopyrazam	360 > 244* 360 > 320	45 45	20 20	0.01	0.02	0.05
113	Isouron	212 > 167* 212 > 72	30 30	15 23	0.01	0.02	0.05
114	Isoxaflutole	360 > 251* 360 > 220	30 30	31 39	0.01	0.02	0.05
115	Linuron	249 > 160* 249 > 182	21 21	21 18	0.01	0.02	0.05
116	Mandipropamid	412 > 328* 412 > 356	16 16	16 10	0.01	0.02	0.03
117	Mecarbam	330 > 227* 330 > 97	21 21	8 35	0.01	0.02	0.05
118	Mefentrifluconazole	398 > 70* 398 > 182	65 65	20 30	0.01	0.02	0.05
119	Mepanipyrim	224 > 106* 224 > 131	38 38	24 22	0.01	0.02	0.05
120	Metaflumizone	507.1 > 287* 507.1 > 267	40 40	26 32	0.01	0.02	0.05

Table 1. MRM parameters and LOQs of 216 pesticides including abamectin etc. and the internal standard (LC-MS/MS positive ion mode) (continued)

No.	Analyte	Ion pair			LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Cone voltage (V)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
121	Metalaxyl	280 > 220* 280 > 192	26 26	13 17	0.01	0.02	0.05
122	Metconazole	320 > 70* 320 > 125	34 34	36 36	0.01	0.02	0.05
123	Methamidophos	142 > 94* 142 > 125	21 21	13 13	0.01	0.02	0.05
124	Methiocarb	226 > 121* 226 > 169	20 20	15 15	0.01	0.02	0.05
125	Methomyl	163 > 88* 163 > 106	10 10	10 10	0.01	0.02	0.05
126	Methoprene	279 > 81* 279 > 95	24 24	24 22	0.01	0.02	0.05
127	Methoxyfenozide	369 > 149* 369 > 313	34 34	18 8	0.01	0.01	0.05
128	Metobromuron	259 > 170* 259 > 148	25 25	20 15	0.01	0.02	0.05
129	Metolcarb	166 > 109* 166 > 94	15 15	25 35	0.01	0.02	0.05
130	Metrafenone	409 > 209* 409 > 227	20 20	17 29	0.01	0.02	0.05
131	Metribuzin	215 > 187* 215 > 84	25 25	20 20	0.01	0.02	0.05
132	Mevinphos	225 > 193* 225 > 127	20 20	8 16	0.01	0.02	0.05
133	Milbemectin A3	511.3 > 95** 511.3 > 493 511.3 > 147	25 25 25	15 15 15	0.01	0.02	0.05
134	Milbemectin A4	525.3 > 127* 525.3 > 161	20 20	15 11			
135	Monocrotophos	224 > 127* 224 > 98	20 20	16 13	0.01	0.01	0.05
136	MPMC (Xylylcarb)	180 > 123* 180 > 108	20 20	13 29	0.01	0.02	0.05
137	Nitenpyram	271 > 126* 271 > 237	30 30	15 15	0.01	0.02	—
138	Norflurazon	304 > 284* 304 > 160	39 39	24 33	0.01	0.02	0.05
139	Novaluron	493 > 158* 493 > 141	28 28	20 46	0.01	0.02	0.05
140	Omethoate	214 > 125* 214 > 183	19 19	22 11	0.01	0.02	0.05

Table 1. MRM parameters and LOQs of 216 pesticides including abamectin etc. and the internal standard (LC-MS/MS positive ion mode) (continued)

No.	Analyte	Ion pair			LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Cone voltage (V)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
141	Oxamyl	237 > 72* 237 > 90	11 11	13 13	0.01	0.01	0.05
142	Oxathiapiprolin	540.1 > 163* 540.1 > 500	70 70	44 18	0.01	0.02	0.05
143	Oxycarboxin	268 > 175* 268 > 147	26 26	16 25	0.01	0.02	0.05
144	Oxydemeton- methyl	247 > 169* 247 > 109	20 20	14 25	0.01	0.02	0.05
145	Pencycuron	329 > 125* 329 > 218	20 20	15 15	0.01	0.02	0.05
146	Penoxsulam	484 > 195* 484 > 164	36 36	32 34	0.01	0.01	0.05
147	Phosphamidon	300 > 174* 300 > 127	29 29	13 21	0.01	0.02	0.05
148	Phoxim	299 > 129* 299 > 153	20 20	11 7	0.01	0.02	0.05
149	Pinoxaden	401 > 317* 401 > 57	30 30	10 10	0.01	0.05	0.05
150	Piperonyl butoxide	356 > 177* 356 > 119	16 16	12 36	0.01	0.02	0.05
151	Pirimicarb	239 > 72* 239 > 182	20 20	15 15	0.01	0.02	0.05
152	Pretilachlor	312 > 252* 312 > 176	18 18	18 27	0.01	0.02	0.05
153	Probenazole	224 > 41* 224 > 166	20 20	10 20	0.01	0.02	0.05
154	Prochloraz	376 > 308* 376 > 266	17 17	11 14	0.01	0.02	0.05
155	Profenophos	373 > 128* 373 > 303	29 29	45 19	0.01	0.02	0.05
156	Promecarb	208 > 151* 208 > 109	15 15	10 10	0.01	0.02	0.02
157	Propamocarb hydrochloride	189 > 102* 189 > 144	27 27	17 13	0.01	0.02	0.05
158	Propanil	218 > 162* 218 > 127	20 20	20 20	0.01	0.02	0.05
159	Propargite	368 > 231* 368 > 175	15 15	10 20	0.01	0.02	0.05
160	Propoxur	210 > 111* 210 > 93	12 12	20 20	0.01	0.02	0.05

Table 1. MRM parameters and LOQs of 216 pesticides including abamectin etc. and the internal standard (LC-MS/MS positive ion mode) (continued)

No.	Analyte		Ion pair			LOQ (ppm)		
			Precursor ion (*m/z*) > product ion (*m/z*)	Cone voltage (V)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
161	Proquinazid		373 > 289* 373 > 272	31 31	28 35	0.01	0.02	0.05
162	Pydiflumetofen		426 > 193* 426 > 166	50 50	30 20	0.01	0.02	0.05
163	Pyflubumide		536.2 > 155* 536.2 > 111	40 40	20 50	0.01	0.02	0.05
164	Pymetrozine		218 > 105* 218 > 79	28 28	16 32	0.01	0.01	—
165	Pyracarbolid		218 > 125* 218 > 97	20 40	15 15	0.01	0.02	0.05
166	Pyraclostrobin		388 > 194* 388 > 163	20 20	12 21	0.01	0.01	0.05
167	Pyrazosulfuron-ethyl		415 > 182* 415 > 139	21 21	24 45	0.01	0.02	0.05
168	Pyrethrin I	Pyrethrins	329 > 161* 329 > 143	25 25	10 20	0.01	0.02	0.05
169	Pyrethrin II		373 > 161* 373 > 105	20 20	5 25			
170	Cinerin I		317 > 149* 317 > 107	15 15	10 20			
171	Cinerin II		361 > 107* 361 > 149	15 15	15 5			
172	Jasmolin I		331 > 163* 331 > 123	25 15	10 20			
173	Jasmolin II		375 > 163* 375 > 107	20 20	10 20			
174	Pyribencarb		362 > 207* 362 > 239	35 35	29 23	0.01	0.02	0.05
175	Pyridaben		365 > 147* 365 > 309	20 20	26 14	0.01	0.02	0.05
176	Pyrifluquinazon		465 > 92* 465 > 423	40 40	35 25	0.01	0.02	0.05
177	Pyriofenone		366 > 184* 366 > 209	20 20	10 10	0.01	0.02	0.05
178	Pyridate		379 > 207* 379 > 351	19 19	18 10	0.01	0.02	0.05
179	Pyrifenox		295 > 93* 295 > 67	31 31	22 60	0.01	0.02	0.05
180	Quinoxyfen		308 > 197* 308 > 162	43 43	31 44	0.01	0.01	0.05

Table 1. MRM parameters and LOQs of 216 pesticides including abamectin etc. and the internal standard (LC-MS/MS positive ion mode) (continued)

No.	Analyte		Ion pair			LOQ (ppm)		
			Precursor ion (*m/z*) > product ion (*m/z*)	Cone voltage (V)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
181	Quizalofop-ethyl		373 > 299* 373 > 181	25 25	25 45	0.01	0.02	0.05
182	Rotenone		395 > 213* 395 > 192	37 37	24 24	0.01	0.02	0.05
183	Saflufenacil		501.1 > 349* 501.1 > 459	30 30	30 20	0.01	0.01	0.05
184	Sethoxydim		328 > 178* 328 > 282	25 25	21 13	0.01	0.02	0.05
185	Simazine		202 > 124* 202 > 96	40 40	16 22	0.01	0.02	0.05
186	Spinetoram J		748.5 > 142* 748.5 > 98	80 80	31 62	0.01	0.01	0.05
187	Spinetoram L		760.5 > 142* 760.5 > 98	80 80	29 40			
188	Spinosyn A	Spinosad	732.5 > 142* 732.5 > 98	56 56	31 59	0.01	0.01	0.05
189	Spinosyn D		746.5 > 142* 746.5 > 98	51 51	31 53			
190	Spirodiclofen		411 > 313* 411 > 71	25 25	11 15	0.01	0.02	0.05
191	Spiromesifen		371 > 255* 371 > 273	7 7	24 10	0.01	0.02	0.05
192	Spirotetramat		374 > 302* 374 > 216	25 25	17 35	0.01	0.02	0.05
193	Spiroxamine		298 > 144* 298 > 100	40 40	10 10	0.01	0.02	0.05
194	Sulfoxaflor		278 > 174* 278 > 154	20 20	12 21	0.01	0.02	0.05
195	Tebufenozide		353 > 297* 353 > 133	19 19	8 20	0.01	0.02	0.05
196	Tebufenpyrad		334 > 117* 334 > 145	52 52	34 28	0.01	0.02	0.05
197	Tepraloxydim		342 > 250* 342 > 166	20 20	15 23	0.01	0.02	0.05
198	Tetraniliprole		545.1 > 112* 545.1 > 376	40 40	40 20	0.01	0.02	0.05
199	Thiabendazole		202 > 175* 202 > 131	30 30	30 30	0.01	0.02	0.05
200	Thiacloprid		253 > 126* 253 > 90	41 41	20 40	0.01	0.02	0.05

Table 1. MRM parameters and LOQs of 216 pesticides including abamectin etc. and the internal standard (LC-MS/MS positive ion mode) (continued)

No.	Analyte	Ion pair			LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Cone voltage (V)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
201	Thiamethoxam	292 > 211* 292 > 181	20 20	15 25	0.01	0.01	0.05
202	Thiobencarb	258 > 125* 258 > 100	20 20	15 10	0.01	0.02	0.05
203	Thiodicarb	355 > 88* 355 > 108	25 25	15 15	0.01	0.02	0.05
204	Thiofanox	241 > 184* 219 > 57	28 10	20 20	0.01	0.02	0.05
205	Tolfenpyrad	384 > 197* 384 > 145	37 37	28 28	0.01	0.02	0.05
206	Tolylfluanid	347 > 238* 347 > 137	25 25	10 28	0.01	0.02	0.05
207	Triadimenol	296 > 70* 296 > 99	20 20	10 10	0.01	0.02	0.05
208	Trichlorfon	257 > 109* 257 > 79	25 25	17 30	0.01	0.02	0.05
209	Tricyclazole	190 > 163* 190 > 136	38 38	24 26	0.01	0.02	0.05
210	Trifloxystrobin	409 > 186* 409 > 206	15 15	15 15	0.01	0.01	0.05
211	Triflumezopyrim	399 > 121* 399 > 278	70 70	30 20	0.01	0.02	0.05
212	Triflumuron	359 > 156* 359 > 139	20 30	10 10	0.01	0.02	0.05
213	Triforine	437 > 392* 437 > 217	16 16	12 29	0.01	0.02	0.05
214	Vamidothion	288 > 146* 288 > 118	17 17	13 22	0.01	0.02	0.05
215	XMC (Macbal)	180 > 123* 180 > 95	12 12	20 20	0.01	0.02	0.05
216	Zoxamide	336 > 187* 336 > 159	32 32	25 38	0.01	0.02	0.05
I.S.	Triphenylphosphate	327 > 77*	40	35	—	—	—

[a]Applicable for fresh fruits, vegetables, spice plants and other herbs with high water content.

[b]Applicable for crops and dried beans with high wax, fat and sugar content.

[c]Applicable for dried tea, fruits, vegetables, spice plants and other herbs with high pigment content.

*The quantitative ion, and a qualitative ion can be selected based on the matrix condition.

**Due to matrix interference in analysis of Milbemectin A3, *m/z* 511.3 > 95 is selected as the quantitative ion for type I and III samples, and *m/z* 511.3 > 493 is selected as the quantitative ion for type II samples.

Table 2. MRM parameters and LOQs of 11 pesticides including acequinocyl-hydroxyl etc. (LC-MS/MS negative ion mode)

No.	Analyte	Ion pair			LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Cone voltage (V)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
1	Acequinocyl-hydroxyl	341 > 186* 341 > 313	70 70	30 28	0.01	0.02	0.05
2	Bentazone	239 > 132* 239 > 197	35 35	25 20	0.01	0.02	0.05
3	Diflubenzuron	309 > 289* 309 > 156	20 20	10 10	0.01	0.01	0.05
4	Fipronil	435 > 330* 435 > 250	25 25	20 25	0.001	0.001	0.002
5	Fipronil-sulfone	451 > 282* 451 > 415	29 28	28 16	0.001	0.001	0.002
6	Fluazinam	463 > 416* 463 > 398	30 30	20 20	0.01	0.02	0.05
7	Flubendiamide	681.0 > 254* 681.0 > 274	35 35	30 18	0.01	0.02	0.05
8	Lufenuron	509.0 > 326* 509.0 > 175	25 25	20 40	0.01	0.02	0.05
9	Penthiopyrad	358 > 149* 358 > 208	48 48	24 18	0.01	0.02	0.05
10	Sulfentrazone	385 > 307* 387 > 309	30 40	10 10	0.01	0.02	0.05
11	Teflubenzuron	379 > 339* 379 > 196	20 20	10 20	0.01	0.02	0.05

[a]Applicable for fresh fruits, vegetables, spice plants and other herbs with high water content.

[b]Applicable for crops and dried beans with high wax, fat and sugar content.

[c]Applicable for dried tea, fruits, vegetables, spice plants and other herbs with high pigment content.

*The quantitative ion.

Table 3. MRM parameters and LOQs of 183 pesticides including acetochlor etc. and the internal standard (GC-MS/MS)

No.	Analyte	Ion pair		LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
1	Acetochlor	146 > 130* 223 > 146	30 10	0.01	0.02	0.05
2	Acrinathrin	208 > 181* 181 > 152	5 30	0.01	0.02	0.05
3	Alachlor	188 > 160* 160 > 132	10 10	0.01	0.02	0.05
4	Aldrin	263 > 193* 263 > 226	40 25	0.01	0.02	0.03
5	Allethrin	123 > 81* 123 > 95	10 10	0.02	0.1	0.1
6	Azinphos-methyl	160 > 132* 160 > 77	5 20	0.01	0.02	0.1
7	Benfluralin	292 > 206* 292 > 160	10 20	0.01	0.02	0.05
8	α-BHC	181 > 145* 181 > 109	15 30	0.01	0.02	0.03
9	β-BHC	181 > 145* 181 > 109	15 30	0.01	0.02	0.05
10	γ-BHC (Lindane)	181 > 145* 181 > 109	15 30	0.01	0.02	0.05
11	δ-BHC	181 > 145* 181 > 109	15 30	0.01	0.02	0.05
12	Bifenox	341 > 310* 341 > 281	10 15	0.01	0.02	0.05
13	Bifenthrin	181 > 166* 181 > 153	10 10	0.01	0.02	0.03
14	Bitertanol	170 > 115* 170 > 141	40 25	0.01	0.02	0.05
15	Bromacil	205 > 188* 205 > 162	15 15	0.01	0.02	0.05
16	Bromophos-ethyl	359 > 303* 359 > 331	15 5	0.01	0.02	0.05
17	Bromophos	331 > 316* 331 > 286	20 30	0.01	0.02	0.05
18	Bromopropylate	183 > 155* 341 > 185	15 20	0.01	0.02	0.05
19	Bromuconazole	295 > 173* 173 > 145	15 15	0.01	0.02	0.05
20	Bupirimate	273 > 193* 208 > 165	5 15	0.01	0.02	0.05

Table 3. MRM parameters and LOQs of 183 pesticides including acetochlor etc. and the internal standard (GC-MS/MS) (continued)

No.	Analyte	Ion pair		LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
21	Butachlor	237 > 160* 176 > 147	10 15	0.01	0.02	0.03
22	Butralin	266 > 174* 266 > 190	25 10	0.01	0.02	0.05
23	Butylate	156 > 57* 146 > 90	5 5	0.01	0.02	0.05
24	Cadusafos	159 > 97* 159 > 131	15 5	0.01	0.02	0.05
25	Carbophenothion	342 > 157* 342 > 296	10 5	0.01	0.02	0.05
26	Chinomethionat	206 > 148* 234 > 148	15 25	0.01	0.02	0.05
27	cis-Chlordane	373 > 266* 375 > 301	25 10	0.01	0.02	0.05
28	trans-Chlordane	373 > 266* 375 > 301	25 10	0.01	0.02	0.05
29	Chlorfenapyr	247 > 227* 247 > 200	15 30	0.01	0.02	0.05
30	Chlorfenvinphos	267 > 159* 323 > 267	15 15	0.01	0.02	0.05
31	Chlorobenzilate	251 > 139* 251 > 111	15 15	0.01	0.02	0.05
32	Chloropropylate	139 > 111* 251 > 139	15 15	0.01	0.02	0.02
33	Chlorothalonil	266 > 168* 266 > 229	30 20	0.02	0.04	0.05
34	Chlorpropham	213 > 171* 127 > 65	5 25	0.01	0.02	0.05
35	Chlorpyrifos	314 > 258* 314 > 286	15 5	0.01	0.02	0.03
36	Chlorpyrifos-methyl	286 > 93* 286 > 271	40 15	0.01	0.02	0.05
37	Chlorthal-dimethyl	301 > 223* 332 > 301	30 10	0.01	0.02	0.05
38	Chlozolinate	331 > 259* 259 > 188	5 10	0.01	0.02	0.05
39	CPMC (Etrofol)	128 > 64* 128 > 92	20 15	0.01	0.02	0.05
40	Cyanofenphos	169 > 141* 185 > 157	5 5	0.01	0.02	0.05

Table 3. MRM parameters and LOQs of 183 pesticides including acetochlor etc. and the internal standard (GC-MS/MS) (continued)

No.	Analyte	Ion pair		LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
41	Cyanophos	243 > 109* 243 > 116	14 8	0.01	0.02	0.05
42	Cyfluthrin	163 > 91* 163 > 127	15 5	0.01	0.01	0.03
43	Cyhalofop-butyl	256 > 120* 120 > 91	10 15	0.01	0.02	0.05
44	λ-Cyhalothrin	181 > 152* 197 > 141	30 15	0.01	0.01	0.03
45	Cypermethrin	163 > 91* 163 > 127	15 5	0.01	0.03	0.03
46	α-Cypermethrin	163 > 91* 163 > 127	15 8	0.01	0.03	0.03
47	Cyproconazole	222 > 125* 222 > 82	25 10	0.01	0.02	0.05
48	*o,p'*-DDD	235 > 165* 237 > 165	20 20	0.01	0.02	0.02
49	*o,p'*-DDE	248 > 176* 246 > 176	30 30	0.01	0.02	0.02
50	*o,p'*-DDT	235 > 165* 235 > 200	40 10	0.01	0.02	0.02
51	*p,p'*-DDE	246 > 176* 246 > 211	40 20	0.01	0.02	0.02
52	*p,p'*-DDT	235 > 165* 235 > 200	25 10	0.01	0.02	0.02
53	*p,p'*-DDD	235 > 165* 235 > 199	25 20	0.01	0.02	0.02
54	Deltamethrin	253 > 93* 253 > 174	20 5	0.01	0.02	0.03
55	Diazinon	304 > 179* 304 > 162	15 5	0.01	0.01	0.05
56	Dichlorvos	185 > 93* 185 > 109	10 15	0.01	0.02	0.05
57	Dicloran	206 > 175* 206 > 148	10 20	0.01	0.02	0.05
58	Dicofol	139 > 111* 251 > 139	15 15	0.01	0.02	0.05
	Dicofol (DCBP)	139 > 111* 250 > 139	15 15	0.01	0.02	0.05
59	Dieldrin	263 > 193* 263 > 228	40 25	0.01	0.02	0.05
60	Difenoconazole	323 > 265* 323 > 202	15 40	0.01	0.02	0.05

Table 3. MRM parameters and LOQs of 183 pesticides including acetochlor etc. and the internal standard (GC-MS/MS) (continued)

No.	Analyte	Ion pair		LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
61	2,6-Diisopropylnaphthalene (2,6-DIPN)	212 > 197* 197 > 155	10 10	0.1	0.2	0.5
62	Dimethipin	118 > 58* 124 > 76	5 5	0.01	0.02	0.05
63	Diniconazole	268 > 232* 268 > 135	10 40	0.01	0.02	0.05
64	Dinitramine	261 > 195* 261 > 241	20 10	0.01	0.02	0.05
65	Diphenamid	167 > 152* 239 > 167	20 5	0.01	0.02	0.05
66	Diphenylamine	169 > 66* 167 > 139	24 28	0.01	0.02	0.05
67	Disulfoton	88 > 60* 274 > 88	5 5	0.01	0.02	0.05
68	Ditalimfos	148 > 130* 130 > 102	10 15	0.01	0.02	0.03
69	Dithiopyr	354 > 306* 354 > 286	5 15	0.01	0.01	0.05
70	Edifenphos	173 > 109* 310 > 173	10 10	0.01	0.02	0.05
71	α-Endosulfan	241 > 206* 241 > 170	15 25	0.01	0.02	0.05
72	β-Endosulfan	241 > 206* 241 > 170	15 25	0.01	0.02	0.05
73	Endosulfan-sulfate	272 > 237* 272 > 235	15 15	0.01	0.02	0.05
74	Endrin	263 > 193* 263 > 228	40 25	0.01	0.02	0.05
75	EPN	157 > 77* 157 > 110	25 15	0.01	0.02	0.03
76	Epoxiconazole	192 > 138* 192 > 157	15 5	0.01	0.02	0.05
77	Esfenvalerate	225 > 119* 225 > 147	15 10	0.01	0.02	0.03
78	Ethion	231 > 175* 231 > 185	10 10	0.01	0.02	0.05
79	Ethoprophos	200 > 158* 158 > 114	5 5	0.01	0.01	0.05
80	Etofenprox	163 > 135* 163 > 107	10 20	0.01	0.01	0.05

Table 3. MRM parameters and LOQs of 183 pesticides including acetochlor etc. and the internal standard (GC-MS/MS) (continued)

No.	Analyte	Ion pair		LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
81	Etridiazole	211 > 183* 183 > 140	10 15	0.01	0.02	0.05
82	Etrimfos	292 > 181* 292 > 153	5 20	0.01	0.02	0.05
83	Fenarimol	251 > 139* 139 > 111	15 15	0.01	0.02	0.05
84	Fenbuconazole	198 > 129* 198 > 102	5 30	0.01	0.01	0.05
85	Fenchlorphos	285 > 270* 285 > 240	25 25	0.01	0.02	0.25
86	Fenitrothion	277 > 109* 277 > 260	20 5	0.01	0.02	0.05
87	Fenoxaprop-ethyl	361 > 288* 361 > 261	10 10	0.01	0.02	0.05
88	Fenpropathrin	265 > 210* 265 > 89	10 40	0.01	0.02	0.05
89	Fenpropimorph	128 > 70* 303 > 128	10 10	0.01	0.02	0.05
90	Fensulfothion	156 > 141* 292 > 109	15 15	0.01	0.02	0.05
91	Fenvalerate	225 > 119* 225 > 147	15 10	0.01	0.02	0.03
92	Flucythrinate	199 > 157* 199 > 107	5 25	0.01	0.02	0.05
93	Fluensulfone	119 > 92* 108 > 64	10 15	0.01	0.02	0.05
94	Fluroxypyr-meptyl	209 > 181* 237 > 209	10 5	0.01	0.02	0.05
95	Flutolanil	173 > 145* 281 > 173	20 10	0.01	0.02	0.05
96	Fluvalinate	250 > 200* 250 > 208	20 30	0.01	0.02	0.05
97	Fluxapyroxad	381 > 159* 159 > 139	15 10	0.01	0.01	0.03
98	Fonofos	246 > 137* 246 > 109	5 15	0.01	0.02	0.05
99	Formothion	224 > 125* 224 > 155	20 10	0.01	0.02	0.05
100	Fthalide	243 > 215* 243 > 179	20 30	0.01	0.02	0.05

Table 3. MRM parameters and LOQs of 183 pesticides including acetochlor etc. and the internal standard (GC-MS/MS) (continued)

No.	Analyte	Ion pair		LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
101	Halfenprox	263 > 235* 263 > 115	15 25	0.01	0.02	0.05
102	Heptachlor	272 > 237* 237 > 143	20 30	0.01	0.04	0.05
103	Heptachlor epoxide	353 > 263* 353 > 282	20 20	0.01	0.02	0.05
104	Heptenophos	124 > 89* 124 > 63	15 35	0.01	0.02	0.05
105	Hexazinone	171 > 71* 171 > 85	20 15	0.01	0.02	0.05
106	Imibenconazole	125 > 89* 253 > 82	20 5	0.02	0.04	0.1
107	Iprobenfos	204 > 91* 204 > 122	10 15	0.01	0.02	0.05
108	Iprodione	314 > 245* 314 > 271	10 5	0.01	0.02	0.05
109	Isofenphos	213 > 185* 213 > 121	5 15	0.01	0.02	0.05
110	Isoprothiolane	290 > 204* 290 > 118	5 10	0.01	0.02	0.05
111	Isotianil	180 > 91* 297 > 180	15 15	0.01	0.02	0.05
112	Isoxathion	105 > 77* 105 > 51	20 40	0.01	0.02	0.1
113	Kresoxim-methyl	116 > 89* 206 > 116	15 5	0.01	0.02	0.05
114	Leptophos	171 > 77* 171 > 124	20 20	0.01	0.02	0.05
115	Malathion	173 > 127* 173 > 99	5 15	0.01	0.02	0.05
116	Mefenacet	192 > 136* 192 > 109	15 35	0.01	0.02	0.05
117	Mephosfolan	196 > 168* 196 > 140	5 10	0.01	0.02	0.05
118	Mepronil	119 > 91* 269 > 119	15 15	0.01	0.02	0.05
119	Metazachlor	133 > 117* 209 > 132	30 20	0.01	0.02	0.05
120	Methacrifos	125 > 79* 125 > 62	5 5	0.01	0.02	0.05

Table 3. MRM parameters and LOQs of 183 pesticides including acetochlor etc. and the internal standard (GC-MS/MS) (continued)

No.	Analyte	Ion pair		LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
121	Methidathion	145 > 85* 145 > 58	5 15	0.01	0.02	0.05
122	Methyl pentachlorophenyl sulfide	296 > 246* 296 > 281	35 20	0.01	0.02	0.02
123	Metolachlor	238 > 162* 162 > 133	10 15	0.01	0.02	0.05
124	Mirex	272 > 237* 332 > 262	20 40	0.01	0.04	0.05
125	Molinate	126 > 55* 187 > 126	15 5	0.01	0.02	0.05
126	Myclobutanil	179 > 125* 179 > 152	15 5	0.01	0.02	0.05
127	Napropamide	271 > 128* 128 > 72	5 5	0.01	0.02	0.05
128	Nuarimol	235 > 139* 235 > 123	15 15	0.01	0.02	0.05
129	Oxadiazon	258 > 175* 258 > 112	5 30	0.01	0.02	0.05
130	Oxadixyl	163 > 132* 163 > 117	10 30	0.01	0.02	0.05
131	Oxyfluorfen	302 > 274* 252 > 146	10 40	0.01	0.02	0.05
132	Paclobutrazol	236 > 125* 236 > 167	10 10	0.01	0.02	0.05
133	Parathion	291 > 109* 291 > 137	10 5	0.01	0.02	0.05
134	Parathion-methyl	125 > 47* 125 > 79	15 5	0.01	0.02	0.05
135	Penconazole	248 > 157* 248 > 192	30 15	0.01	0.02	0.05
136	Pendimethalin	252 > 162* 252 > 191	10 5	0.01	0.02	0.05
137	Penflufen	274 > 141* 317 > 141	15 25	0.01	0.01	0.05
138	Pentachloroaniline	265 > 158* 265 > 167	20 20	0.01	0.02	0.02
139	Permethrin	183 > 153* 183 > 168	15 15	0.01	0.02	0.05
140	Phenothiol	245 > 102* 245 > 142	10 10	0.01	0.02	0.05

Table 3. MRM parameters and LOQs of 183 pesticides including acetochlor etc. and the internal standard (GC-MS/MS) (continued)

No.	Analyte	Ion pair		LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
141	Phenothrin	123 > 81* 183 > 168	5 10	0.01	0.02	0.05
142	Phenthoate	274 > 246* 274 > 121	5 10	0.01	0.02	0.05
143	2-Phenylphenol	169 > 115* 170 > 141	25 25	0.01	0.02	0.05
144	Phorate	260 > 75* 260 > 231	10 5	0.01	0.02	0.05
145	Phosalone	182 > 111* 182 > 138	15 5	0.01	0.02	0.05
146	Phosmet	160 > 77* 160 > 133	25 15	0.01	0.02	0.05
147	Pirimiphos-ethyl	318 > 166* 318 > 182	15 15	0.01	0.02	0.05
148	Pirimiphos-methyl	290 > 125* 290 > 151	25 20	0.01	0.02	0.05
149	Procymidone	283 > 95* 283 > 255	20 10	0.01	0.02	0.05
150	Prometryn	241 > 199* 184 > 69	5 15	0.01	0.02	0.05
151	Propaphos	220 > 140* 220 > 125	10 30	0.01	0.02	0.05
152	Propazine	214 > 172* 229 > 58	10 10	0.01	0.02	0.05
153	Propiconazole	173 > 145* 259 > 69	15 10	0.01	0.02	0.05
154	Prothiofos	267 > 239* 267 > 221	10 20	0.01	0.02	0.05
155	Prothoate	115 > 73* 115 > 82	5 5	0.01	0.02	0.05
156	Pyraclofos	360 > 194* 360 > 139	10 15	0.01	0.02	0.05
157	Pyraflufen-ethyl	412 > 349* 349 > 307	10 15	0.01	0.02	0.05
158	Pyrazophos	221 > 193* 232 > 204	10 10	0.01	0.02	0.05
159	Pyridaphenthion	340 > 199* 340 > 109	5 20	0.01	0.02	0.05
160	Pyrimethanil	198 > 156* 198 > 118	25 40	0.02	0.04	0.05

Table 3. MRM parameters and LOQs of 183 pesticides including acetochlor etc. and the internal standard (GC-MS/MS) (continued)

No.	Analyte	Ion pair		LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
161	Pyrimidifen	184 > 169* 161 > 135	20 15	0.01	0.02	0.05
162	Pyriproxyfen	136 > 96* 136 > 78	15 25	0.01	0.01	0.05
163	Pyroquilon	173 > 130* 173 > 144	25 25	0.01	0.02	0.05
164	Quinalphos	298 > 156* 298 > 190	10 10	0.01	0.02	0.05
165	Quintozene (PCNB)	295 > 214* 295 > 237	40 20	0.01	0.02	0.02
166	Salithion	216 > 201* 216 > 183	10 10	0.01	0.02	0.03
167	Sedaxane	172 > 130* 263 > 234	10 15	0.01	0.01	0.05
168	Silafluofen	179 > 151* 179 > 91	10 25	0.01	0.02	0.05
169	Tebuconazole	250 > 125* 250 > 153	25 10	0.01	0.02	0.05
170	Terbufos	231 > 175* 153 > 97	10 10	0.01	0.01	0.05
171	Tetraconazole	336 > 218* 336 > 204	20 35	0.01	0.02	0.05
172	Tetradifon	356 > 159* 356 > 229	10 10	0.01	0.02	0.05
173	Tetramethrin	164 > 107* 164 > 135	15 5	0.01	0.02	0.05
174	Thenylchlor	288 > 141* 127 > 59	10 10	0.01	0.02	0.05
175	Thifluzamide	194 > 166* 194 > 125	10 30	0.01	0.02	0.05
176	Thiometon	125 > 47* 125 > 79	15 10	0.01	0.02	0.05
177	Tolclofos-methyl	265 > 250* 250 > 220	15 10	0.01	0.02	0.05
178	Triadimefon	208 > 181* 208 > 111	5 25	0.01	0.02	0.05
179	Triazophos	257 > 162* 257 > 119	5 30	0.01	0.02	0.05
180	Tridiphane	187 > 159* 173 > 145	15 15	0.01	0.02	0.05

Table 3. MRM parameters and LOQs of 183 pesticides including acetochlor etc. and the internal standard (GC-MS/MS) (continued)

No.	Analyte	Ion pair		LOQ (ppm)		
		Precursor ion (*m/z*) > product ion (*m/z*)	Collision energy (eV)	Type I[a]	Type II[b]	Type III[c]
181	Triflumizole	278 > 73* 206 > 179	5 15	0.01	0.02	0.05
182	Trifluralin	306 > 264* 306 > 206	5 15	0.01	0.02	0.04
183	Vinclozolin	285 > 212* 285 > 178	10 15	0.01	0.02	0.05
I.S.	Triphenylphosphate	326 > 169*	30	—	—	—

[a]Applicable for fresh fruits, vegetables, spice plants and other herbs with high water content.

[b]Applicable for crops and dried beans with high wax, fat and sugar content.

[c]Applicable for dried tea, fruits, vegetables, spice plants and other herbs with high pigment content.

*The quantitative ion.