

Determination of Residues of 446 Pesticides in Fruits and Vegetables by Three-Cartridge Solid-Phase Extraction–Gas Chromatography–Mass Spectrometry and Liquid Chromatography–Tandem Mass Spectrometry

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A method was developed for determination of residues of 446 pesticides in fruits and vegetables through the use of cleanup by a 3-cartridge solid-phase extraction–gas chromatography/ mass spectrometry (GC/MS) and liquid chromatography/tandem mass spectrometry (LC/MS/MS). Fruit and vegetable samples (20 g) were extracted with 40 mL acetonitrile, salted out, and centrifuged. Half of the supernatant was passed into an Envi-18 cartridge, eluted with acetonitrile, and cleaned up with Envi-Carb and aminopropyl Sep-Pak cartridges in series after concentration of the eluates. Pesticides were eluted with acetonitrile–toluene (3 + 1, v/v), and eluates were concentrated to 0.5 mL and then added into internal standards after solvent exchange with 2 mL hexane and used for determination of 383 pesticides by GC/MS. The other half of the supernatant was concentrated to 1 mL and cleaned up with Envi-Carb and aminopropyl Sep-Pak cartridges in series. Pesticides were eluted with acetonitrile–toluene (3 + 1, v/v), and the eluates were concentrated to 0.5 mL, dried with nitrogen gas, diluted to 1.0 mL with acetonitrile–water (3 + 2, v/v), and used for determination of 63 pesticides by LC/MS/MS. The limit of detection for the method was 0.2–600 ng/g depending on the individual pesticide. In the method, fortification recovery tests at high, medium, and low levels were conducted on 6 varieties of fruits and vegetables, i.e., apples, oranges, grapes, cabbage, tomatoes, and celery, with average recoveries falling within the range of 55.0–133.8% for 446 pesticides, among which average recoveries between 60.0–120.0% accounted for 99% of the results. The relative standard deviation was between 2.1–39.1%, of

which a relative standard deviation of 2.1–25.0% made up 96% of the results. Experiments proved that the method was applicable for determination of residues of 446 pesticides in fruit and vegetables.

Food safety and hygiene, which is closely related to the health of human beings and their survival and development, is an important issue causing great concern by governments of different countries and the relevant international organizations. The World Health Organization (WHO) puts food safety in the top agenda of global public hygiene, among which pesticide and veterinary drug residues in foodstuffs pose potential hazards to food safety. For the purpose of ensuring food safety, the Food and Agriculture Organization (FAO)/WHO/Codex Alimentarius Commission (CAC) prescribes the maximum residue limit (MRL) for more than 170 pesticide and veterinary drug residues in over 300 varieties of agricultural products and foods. The United States, Canada, Germany, and other European Union (EU) nations, as well as regional international organizations promulgate their own MRLs of pesticides and veterinary drugs for various kinds of agricultural products and foods based on the actual conditions of their individual countries or localities. Currently, CAC lists 2572 pesticide residue limits, EU 22 289, U.S. 8669, and Japan 9052. Therefore, researchers from different countries have established methods for determination of multipesticide residues. In the last 20 years in particular, multiresidue analytical methods have been increasingly studied by researchers. A comparative study was conducted on more than 20 representative multiresidue methods applied to agricultural products, such as fruits and vegetables, and the extraction systems for the contemporary multiresidue methods were categorized by the solvents acetone, ethyl acetate, and acetonitrile.

One of the most widespread acetone extraction procedures was proposed by Luke et al. (1, 2). For this method, acetone was used for extraction, liquid–liquid partitioning was done with dichloromethane–petroleum ether, and cleanup was with Florisil. Gas chromatography with an electron capture detector (GC–ECD) was adopted for detection of

Table 1. Monitoring program of selected ions for A, B, C, and D groups of pesticide by GC/MS

Segment	Start time, min	Monitored ions, <i>m/z</i>	Dwell time, ms
SIM ^a program for A group of pesticides			
1	8.30	138, 158, 173	200
2	9.60	124, 140, 166, 172, 183, 211	90
3	10.50	121, 154, 234	200
4	10.75	120, 137, 179	200
5	11.70	154, 186, 215	200
6	14.40	167, 168, 169	200
7	14.90	121, 142, 143, 153, 183, 195, 196, 198, 230, 231, 260, 276, 292, 316	30
8	16.20	88, 125, 246	200
9	16.70	137, 138, 145, 172, 174, 179, 187, 202, 204, 205, 237, 246, 249, 295, 304	30
10	17.80	138, 173, 175, 181, 186, 194, 196, 201, 210, 225, 236, 255, 277, 292	230
11	18.80	150, 165, 173, 175, 222, 223, 251, 255, 279	50
12	19.20	125, 143, 229, 261, 263, 265, 293, 305, 307, 329	50
13	19.80	125, 261, 263, 265, 285, 287, 293, 305, 307, 329	50
14	20.10	170, 181, 184, 198, 200, 206, 212, 217, 219, 226, 227, 233, 234, 241, 246, 249, 254, 258, 263, 264, 266, 268, 285, 286, 314	10
15	21.40	143, 152, 153, 158, 169, 173, 180, 181, 208, 217, 219, 220, 247, 254, 256, 260, 275, 277, 278, 351, 353, 355	10
16	22.30	61, 143, 160, 162, 181, 186, 208, 210, 220, 235, 248, 252, 263, 268, 270, 291, 351, 353, 355	20
17	23.00	133, 143, 146, 157, 209, 211, 246, 268, 270, 274, 298, 303, 320, 357, 359, 373, 375, 377	20
18	23.70	72, 104, 133, 145, 152, 157, 160, 162, 209, 211, 215, 253, 255, 260, 263, 267, 274, 277, 283, 285, 297, 302, 309, 345, 380	10
19	24.80	128, 145, 154, 157, 171, 175, 198, 217, 225, 240, 255, 258, 271, 283, 285, 288, 302, 303	20
20	25.50	154, 185, 217, 252, 253, 254, 288, 303, 319, 324, 334	50
21	26.00	87, 139, 143, 145, 165, 173, 199, 208, 231, 235, 237, 251, 253, 273, 316, 323, 384	20
22	26.80	145, 150, 156, 165, 173, 179, 199, 231, 235, 237, 245, 247, 280, 288, 322, 323, 384	20
23	27.90	165, 166, 173, 181, 253, 259, 261, 281, 292, 293, 308, 342	40
24	28.60	118, 160, 165, 166, 181, 203, 212, 227, 228, 231, 235, 237, 272, 274, 314, 323	30
25	29.30	135, 163, 164, 212, 227, 228, 232, 233, 250, 252, 278	40
26	30.00	102, 145, 159, 160, 161, 188, 199, 227, 303, 317, 340, 356	40
27	31.00	175, 183, 184, 220, 221, 223, 232, 250, 255, 267, 373	40
28	33.00	127, 180, 181	200
29	34.40	167, 181, 225, 419	150
30	35.70	172, 174, 181	200
SIM program for B group of pesticides			
1	7.80	128, 132, 189	200
2	8.80	146, 156, 217	200
3	9.70	128, 136, 161, 171, 173, 203	90
4	10.70	127, 164, 192, 194, 196, 198	90
5	11.70	191, 193, 206	200
6	13.40	124, 203, 215, 250, 261	100
7	14.40	158, 168, 200, 242, 282, 284, 286	80
8	14.70	116, 120, 128, 148, 153, 171, 176, 188, 202, 211, 213, 234, 236, 238, 264, 266, 282, 284, 286, 306, 322, 335	10
9	16.00	116, 148, 183, 188, 219, 221, 254	80
10	16.80	153, 186, 231, 288	150
11	17.10	153, 160, 164, 169, 172, 173, 176, 197, 206, 210, 214, 223, 225, 229, 270, 318, 330, 347	20
12	18.20	61, 126, 160, 173, 176, 206, 214, 229	60
13	18.70	126, 127, 134, 148, 164, 171, 172, 180, 192, 197, 198, 210, 213, 223, 243, 286, 288, 305, 307	20
14	19.90	134, 171, 188, 197, 198, 210, 213, 237, 269, 276, 290, 305	40
15	20.60	100, 185, 211, 226, 241, 253, 257, 259, 378	50
16	21.20	73, 139, 141, 153, 161, 162, 167, 185, 191, 207, 213, 224, 226, 237, 238, 240, 250, 251, 286, 304, 318, 329, 331, 333, 351, 353, 355, 387	10
17	22.00	161, 167, 207, 222, 224, 226, 238, 264, 280, 286, 351, 353, 355	40
18	22.70	161, 163, 170, 171, 182, 185, 205, 213, 217, 241, 255, 256, 265, 267, 269, 276, 323, 339	20

Table 1. (continued)

Segment	Start time, min	Monitored ions, m/z	Dwell time, ms
19	23.40	137, 160, 176, 188, 238, 240, 246, 248, 259, 267, 269, 316, 318, 323, 331, 373, 375, 377	20
20	23.90	61, 160, 166, 176, 188, 193, 194, 246, 248, 250, 259, 292, 294, 297, 316, 318, 329, 331, 333, 339, 374, 377, 379	20
21	24.90	61, 105, 165, 167, 172, 175, 177, 187, 199, 214, 231, 235, 236, 237, 238, 256, 263, 292, 294, 297, 302, 305, 311, 313, 317, 339, 345, 374	10
22	25.60	77, 105, 139, 141, 165, 169, 171, 199, 202, 213, 223, 235, 237, 251, 252, 253, 256, 271, 276, 283, 297, 300, 325, 360, 361	10
23	26.70	105, 157, 165, 195, 199, 235, 237, 246, 276, 297, 325, 339, 342, 360, 363	30
24	27.60	148, 157, 161, 169, 172, 173, 201, 206, 257, 303, 310, 325	40
25	28.90	89, 99, 126, 127, 157, 161, 169, 172, 181, 183, 257, 260, 265, 272, 292, 303, 339, 341, 349, 365, 387, 389	10
26	29.80	79, 181, 183, 265, 311, 349	90
27	30.00	128, 157, 169, 171, 189, 252, 310, 323, 341, 375, 377, 379	40
28	31.20	132, 139, 154, 160, 161, 182, 189, 251, 310, 330, 341, 367	40
29	32.90	180, 199, 206, 226, 266, 308, 334, 362, 364	50
30	34.00	181, 250, 252	200
SIM program for C group of pesticides			
1	7.30	109, 185, 220	200
2	8.70	152, 153, 154	200
3	9.30	58, 128, 129, 146, 188, 203	90
4	11.20	126, 161, 163	200
5	11.75	125, 126, 141, 158, 169, 170, 187, 208, 240	50
6	13.50	122, 123, 124, 151, 215, 250	90
7	14.70	107, 121, 150, 264, 276, 292	90
8	16.00	174, 202, 217	200
9	16.50	126, 141, 143, 156, 168, 176, 198, 199, 200, 210, 225, 268, 270, 277, 279	30
10	17.60	88, 173, 183, 186, 200, 215, 219, 254, 274	50
11	18.40	104, 130, 159, 161, 204, 237, 246, 257, 272, 285, 288, 313, 337	40
12	18.90	128, 129, 161, 163, 165, 175, 204, 217, 242, 246, 257, 264, 285, 288, 303, 306, 313, 326, 335	20
13	19.80	73, 89, 146, 162, 185, 212, 223, 227, 250, 265, 267	50
14	20.30	61, 144, 146, 162, 170, 185, 198, 199, 212, 213, 223, 227, 258	40
15	20.70	61, 103, 118, 144, 170, 181, 198, 199, 210, 217, 219, 222, 240, 254, 255	30
16	21.35	108, 117, 151, 160, 161, 170, 219, 221, 224, 225, 257, 267, 351, 353, 355	30
17	22.20	107, 108, 119, 123, 136, 145, 176, 219, 221, 246, 248, 263, 318, 351, 353, 355	20
18	22.70	77, 141, 165, 167, 174, 176, 206, 234, 239, 246, 248, 267, 268, 297, 299, 318	20
19	23.20	105, 123, 134, 161, 248, 250, 267, 297, 299	50
20	23.50	131, 143, 157, 161, 171, 220, 248, 250, 262, 296, 304, 329, 336, 338, 404	30
21	24.30	112, 130, 162, 168, 238, 262	90
22	25.10	112, 116, 130, 131, 162, 168, 206, 233, 234, 235, 238, 262	40
23	25.30	254, 282, 321, 323, 356, 383	90
24	26.00	131, 152, 206, 233, 234, 236, 251, 253, 315	50
25	26.90	149, 162, 176, 177, 190, 232, 268, 270, 328	50
26	27.90	105, 119, 120, 135, 140, 173, 266, 267, 269, 350, 394	50
27	28.80	105, 117, 123, 140, 145, 160, 183, 266, 267, 350, 394	50
28	29.00	117, 123, 127, 145, 154, 160, 183, 248, 350	50
29	29.60	116, 178, 186, 191, 219, 255	90
30	30.30	132, 162, 178, 184, 219, 226, 281, 293, 334	50
31	31.10	120, 136, 141, 147, 181, 183, 184, 192, 197, 247, 255, 289, 309, 364	30
32	32.00	112, 141, 147, 170, 183, 184, 255, 309, 364, 428, 447, 449	40
33	32.60	112, 141, 163, 170, 183, 376, 428, 447, 449	50
34	33.10	163, 165, 178, 181, 251, 279	90
35	33.80	157, 199, 451	200
36	34.70	181, 225, 250, 252, 419	100
37	35.40	259, 265, 287, 323, 325, 354	90
38	36.40	308, 318, 423	200

Table 1. (continued)

Segment	Start time, min	Monitored ions, <i>m/z</i>	Dwell time, ms
SIM program for D group of pesticides			
1	5.50	110, 153, 154	200
2	8.00	153, 184, 212	200
3	11.00	139, 155, 211, 215, 250, 252	90
4	13.00	142, 156, 165, 171, 196, 197, 200, 201, 202	50
5	14.00	143, 155, 158, 167, 192, 203, 211, 220, 229, 231, 246	40
6	15.00	106, 142, 190, 237, 265, 280	90
7	16.00	108, 136, 145, 158, 164, 171, 173, 182, 186, 196, 197, 201, 211, 216, 213, 288	20
8	17.20	161, 174, 177, 197, 200, 202, 214, 229, 246, 357, 359, 394	40
9	17.90	89, 114, 128, 172, 173, 174, 175, 186, 189, 198, 223, 229, 230, 231, 233, 253, 256, 258, 263, 265, 268, 277, 282, 292, 297	10
10	19.20	142, 143, 154, 157, 162, 184, 185, 199, 200, 201, 202, 203, 214, 220, 229, 230, 247, 251, 252, 255, 263, 264, 270, 278, 285, 287, 292	10
11	20.00	153, 180, 197, 199, 200, 201, 202, 230, 239, 247, 251, 252, 266, 305, 308, 311, 343, 375, 380, 412	15
12	21.00	115, 184, 193, 195, 196, 198, 215, 221, 225, 250, 252, 263, 269, 276, 285, 297, 301, 332	20
13	21.60	128, 170, 194, 195, 210, 212, 224, 225, 236, 254, 279, 294	40
14	22.10	129, 155, 182, 184, 200, 201, 210, 212, 216, 224, 225, 229, 230, 254, 262, 263, 291, 300, 314, 326, 351, 353, 355	10
15	23.00	136, 171, 199, 215, 230, 251, 253, 266, 289, 407, 409, 411	40
16	23.90	130, 148, 178, 187, 202, 211, 223, 224, 226, 240, 258, 267, 295, 299, 311, 313, 323	20
17	25.00	129, 130, 145, 148, 164, 168, 184, 185, 196, 201, 218, 219, 227, 254, 259, 290, 299, 326, 330, 340, 360	15
18	26.00	156, 159, 184, 185, 213, 218, 227, 229, 270, 272, 290, 360	40
19	27.10	143, 160, 171, 206, 222, 223, 224, 230, 238, 251, 266, 294, 312, 338, 349	30
20	28.00	136, 174, 186, 202, 215, 231, 233, 237, 254, 278, 279, 294, 310, 311, 326, 366, 379	20
21	29.00	136, 153, 192, 194, 220, 234, 276, 318, 324, 333, 359, 394	40
22	30.00	160, 161, 171, 173, 175, 214, 317, 375, 377	50
23	30.80	173, 175, 196, 213, 230, 274, 292, 300, 304, 316, 319, 320, 335, 373	30
24	32.40	147, 236, 238, 340, 341, 342	90
25	34.00	125, 129, 198	200

^a SIM = Selected ion monitoring.

organochlorine, organonitrogen, and organosulfur pesticides, and organophosphorus pesticides were determined by GC with a flame photometric detector (GC-FPD); 79 pesticide residues were determined by the method of Luke et al. Stan and Linkerhagner (3, 4) extracted with acetone before liquid–liquid partitioning with dichloromethane and cleaning up with gel permeation chromatography (GPC). GC with an atomic emission detector (GC-AED) was used for determining 385 pesticides. Then, extraction switched to acetone with liquid–liquid partitioning by ethyl acetate–cyclohexane and cleanup by GPC. Three kinds of GC detectors [ECD, nitrogen–phosphorous detector (NPD), and mass selective detector (MSD)] were used for detection of more than 400 pesticides. Gamon et al. (5) extracted with acetone, liquid–liquid partitioning was done with dichloromethane–petroleum ether, and determination was by GC with tandem mass spectrometry (GC/MS/MS) with an electron impact (EI) or chemical ionization (CI) source for detection of residues of 80 organophosphorus, organochlorine, organonitrogen, and pyrethroids pesticides. Gelsomino et al. (6) used extraction with acetone, liquid–liquid partitioning with dichloromethane, and cleaned up with GPC for determination of 77 pesticides by GC-ECD and confirmation by GC/MS.

Podhorniak et al. (7), Koinecke et al. (8), and Specht et al. (9) extracted with the same system, or changed either the partitioning solvent or cleanup modes, and established multiresidue methods using GC with multiple detectors.

Ethyl acetate is also a popular multiresidue extraction solvent. Kriegermann et al. (10) extracted pesticides with ethyl acetate, separated them on a glass capillary GC column, and determined 59 organophosphorus pesticides with FPD. Later on, Stan and Goebel (11) also adopted this extraction and cleanup system and determined 83 organophosphorus and organochlorine pesticides using the NPD and ECD. Holstege et al. (12) extract with ethyl acetate, cleaned up via GPC or solid-phase extraction (SPE), and used GC and liquid chromatography (LC) for determination of 43 organophosphorus, 17 organochlorine, and 11 *N*-methyl carbamate pesticides. This method is applicable to fruits, vegetables, and animal tissues. Obana et al. (13, 14) used GPC with an activated carbon cartridge for cleanup and determined 110 pesticide residues in fruits and vegetables using GC-MSD and GC-FPD as well as LC with a fluorescence detector. Aguera et al. (15) used the same method without cleanup and determined residues of 55 organophosphorus, organochlorine,

Table 2. Parameters for simultaneous determination of 446 pesticide residues in fruits and vegetables by GC/MS and LC/MS/MS

No.	Group	Pesticide	Retention time, min	Quantification ion ^a	Qualification ion 1 ^a	Qualification ion 2 ^a	Qualification ion 3 ^a	Linear range, ng	Linear equation	Correlation coefficient (r)	LOD, mg/kg	LOQ, mg/kg
1	A	Heptachlor-epoxide	22.10	353(100)	355(52)	173(15)	0.1250~5.000	$Y = 4.83 \times 10^5 X - 5.48 \times 10^4$	0.9986	0.0125	0.0250	0.0125
2	A	Alliodochlor	8.78	138(100)	158(10)	124(79)	0.0063~2.500	$Y = 3.26 \times 10^7 X + 1.03 \times 10^6$	0.9981	0.0063	0.0125	0.0125
3	A	Dichlormid	9.74	172(100)	166(41)	140(19)	0.1875~7.500	$Y = 8.12 \times 10^5 X - 2.65 \times 10^5$	0.9945	0.0188	0.0375	
4	A	Etridiazol	10.42	211(100)	183(73)	154(70)	0.1250~5.000	$Y = 1.19 \times 10^6 X + 1.14 \times 10^5$	0.9928	0.0125	0.0250	0.0125
5	A	Chlormephos	10.53	121(100)	234(70)	137(66)	0.0625~2.500	$Y = 1.01 \times 10^6 X - 5.76 \times 10^4$	0.9975	0.0063	0.0125	0.0125
6	A	Propham	11.36	179(100)	137(66)	120(51)	0.0625~2.500	$Y = 2.26 \times 10^6 X - 1.16 \times 10^5$	0.9986	0.0063	0.0125	
7	A	Cycloate	13.56	154(100)	186(5)	215(12)	0.0625~2.500	$Y = 5.81 \times 10^6 X - 3.97 \times 10^5$	0.9975	0.0063	0.0125	
8	A	Diphenylamine	14.55	169(100)	168(58)	167(29)	0.0625~2.500	$Y = 3.39 \times 10^5 X - 4.28 \times 10^4$	0.9966	0.0125	0.0250	
9	A	Chlordimeform	14.93	196(100)	198(30)	195(18)	0.1250~2.500	$Y = 5.28 \times 10^5 X - 2.60 \times 10^5$	0.9926	0.0250	0.0500	
10	A	Ethalflurialin	15.00	276(100)	316(81)	292(42)	0.2500~10.00	$Y = 5.32 \times 10^5 X - 4.50 \times 10^4$	0.9969	0.0063	0.0125	
11	A	Phorate	15.46	260(100)	121(160)	231(56)	0.0625~2.500	$Y = 3.00 \times 10^6 X - 2.40 \times 10^5$	0.9967	0.0063	0.0125	
12	A	Thiometon	16.20	88(100)	125(55)	246(9)	0.0625~2.500	$Y = 2.98 \times 10^5 X - 5.32 \times 10^4$	0.9958	0.0125	0.0250	
13	A	Quintozene	16.75	295(100)	237(159)	249(114)	0.1250~5.000	$Y = 2.26 \times 10^6 X - 1.93 \times 10^5$	0.9956	0.0063	0.0125	
14	A	Atrazine-desethyl	16.76	172(100)	187(32)	145(17)	0.0625~2.500	$Y = 3.04 \times 10^6 X - 2.30 \times 10^5$	0.9976	0.0063	0.0125	
15	A	Clonazone	17.00	204(100)	138(4)	205(13)	0.0625~2.500	$Y = 6.86 \times 10^5 X - 4.99 \times 10^4$	0.9980	0.0063	0.0125	
16	A	Diazinon	17.14	304(100)	179(192)	137(172)	0.0625~2.500	$Y = 1.43 \times 10^6 X - 1.10 \times 10^5$	0.9975	0.0063	0.0125	
17	A	Fonofos	17.31	246(100)	137(141)	174(15)	202(6)	$Y = 8.55 \times 10^5 X - 6.25 \times 10^4$	0.9976	0.0063	0.0125	
18	A	Etrimfos	17.92	292(100)	181(40)	277(31)	0.0625~2.500	$Y = 1.19 \times 10^6 X - 9.71 \times 10^4$	0.9965	0.0063	0.0125	
19	A	Simazine	17.85	201(100)	186(62)	173(42)	0.0625~2.500	$Y = 2.44 \times 10^6 X - 2.24 \times 10^5$	0.9968	0.0063	0.0125	
20	A	Propetamphos	17.97	138(100)	194(49)	236(30)	0.0625~2.500	$Y = 3.16 \times 10^6 X - 3.21 \times 10^5$	0.9952	0.0063	0.0125	
21	A	Secbumeton	18.36	196(100)	210(38)	225(39)	0.0625~2.500	$Y = 1.45 \times 10^6 X - 8.71 \times 10^4$	0.9986	0.0063	0.0125	
22	A	Dichlofenthion	18.80	279(100)	223(78)	251(38)	0.0625~2.500	$Y = 2.33 \times 10^6 X - 2.70 \times 10^5$	0.9905	0.0063	0.0125	
23	A	Pronamide	18.72	173(100)	175(62)	256(22)	0.0625~2.500	$Y = 2.74 \times 10^6 X - 9.75 \times 10^5$	0.9924	0.0188	0.0375	
24	A	Mexacarbate	18.83	165(100)	150(66)	222(27)	0.1875~7.500	$Y = 6.16 \times 10^5 X - 6.01 \times 10^4$	0.9990	0.0125	0.0250	
25	A	Aldrin	19.67	263(100)	265(65)	298(40)	0.1250~5.000	$Y = 8.42 \times 10^5 X - 3.98 \times 10^5$	0.9956	0.0250	0.0500	
26	A	Dinitramine	19.35	305(100)	307(38)	261(29)	0.2500~10.00	$Y = 2.37 \times 10^6 X - 3.41 \times 10^5$	0.9978	0.0125	0.0250	
27	A	Ronnel	19.80	285(100)	287(67)	125(32)	0.1250~5.000	$Y = 1.97 \times 10^6 X - 1.82 \times 10^5$	0.9961	0.0063	0.0125	
28	A	Prometryne	20.13	241(100)	184(78)	226(60)	0.0625~2.500	$Y = 1.81 \times 10^6 X - 1.38 \times 10^5$	0.9978	0.0063	0.0125	
29	A	Cyprazine	20.18	212(100)	227(58)	170(29)	0.0625~2.500	$Y = 4.84 \times 10^5 X - 3.88 \times 10^4$	0.9973	0.0063	0.0125	
30	A	Vindozolin	20.29	285(100)	212(109)	198(96)	0.0625~2.500	$Y = 6.87 \times 10^5 X - 3.02 \times 10^4$	0.9992	0.0063	0.0125	
31	A	beta-HCH	20.31	219(100)	217(78)	181(94)	0.0625~2.500	$Y = 1.23 \times 10^6 X - 2.59 \times 10^5$	0.9982	0.0188	0.0375	
32	A	Metalaxy	20.67	206(100)	249(53)	234(38)	0.1875~7.500	$Y = 6.21 \times 10^5 X - 7.51 \times 10^4$	0.9986	0.0125	0.0250	
33	A	Chloryrifos-ethyl	20.96	314(100)	258(57)	286(42)	0.0625~2.500	$Y = 2.91 \times 10^5 X - 2.33 \times 10^5$	0.9973	0.0063	0.0125	
34	A	Methyl-parathion	20.82	263(100)	233(66)	246(8)	0.2500~10.00	$Y = 1.06 \times 10^6 X - 6.40 \times 10^5$	0.9992	0.0250	0.0500	
35	A	Anthraquinone	21.49	208(100)	180(84)	152(69)	0.0625~2.500	$Y = 2.27 \times 10^6 X - 3.41 \times 10^5$	0.9962	0.0063	0.0125	
36	A	delta-HCH	21.16	219(100)	217(80)	181(99)	0.1250~5.000	$Y = 6.84 \times 10^5 X - 4.74 \times 10^4$	0.9985	0.0063	0.0125	
37	A	Fenthion	21.53	278(100)	169(16)	153(9)	0.0625~2.500	$Y = 1.06 \times 10^6 X - 6.40 \times 10^5$	0.9974	0.0250	0.0500	
38	A	Malathion	21.54	173(100)	158(36)	143(15)	0.2500~10.00	$Y = 1.43 \times 10^6 X - 5.23 \times 10^5$	0.9957	0.0125	0.0250	
39	A	Fenitrothion	21.62	277(100)	260(52)	247(60)	0.2500~10.00	$Y = 1.13 \times 10^6 X - 2.61 \times 10^5$	0.9892	0.0250	0.0500	
	A	Paraxoxon-ethyl	21.57	275(100)	220(60)	247(58)						

Table 2. (continued)

No.	Group	Pesticide	Retention time, min	Quantification ion ^a	Qualification ion 1 ^a	Qualification ion 2 ^a	Qualification ion 3 ^a	Linear range, ng	Linear equation	Correlation coefficient (r)	LOD, mg/kg	LOQ, mg/kg
40	A	Triadimenfon	22.22	208(100)	210(50)	181(74)	0.1250 ~ 5.000	$Y = 1.20 \times 10^6 X - 2.03 \times 10^5$	0.9976	0.0125	0.0250	
41	A	Parathion	22.32	291(100)	186(23)	236(35)	263(11)	$Y = 1.08 \times 10^6 X - 5.62 \times 10^5$	0.9935	0.0250	0.0500	
42	A	Pendimethalin	22.59	252(100)	220(22)	162(12)	0.2500 ~ 10.00	$Y = 2.46 \times 10^6 X - 1.12 \times 10^6$	0.9960	0.0250	0.0500	
43	A	Linuron	22.44	61(100)	248(30)	160(12)	0.2500 ~ 10.00	$Y = 4.30 \times 10^5 X - 3.08 \times 10^5$	0.9730	0.0250	0.0500	
44	A	Chlorbenside	22.96	268(100)	270(41)	143(11)	0.1250 ~ 5.00	$Y = 6.55 \times 10^5 X - 1.37 \times 10^5$	0.9946	0.0125	0.0250	
45	A	Bromophos-ethyl	23.06	359(100)	303(77)	357(74)	0.0625 ~ 2.500	$Y = 8.39 \times 10^5 X - 6.63 \times 10^4$	0.9973	0.0063	0.0125	
46	A	Quinalphos	23.10	146(100)	298(28)	157(66)	0.0625 ~ 2.500	$Y = 1.93 \times 10^6 X - 1.91 \times 10^5$	0.9959	0.0063	0.0125	
47	A	trans-Chlordane	23.29	373(100)	375(96)	377(51)	0.0625 ~ 2.500	$Y = 1.09 \times 10^6 X - 5.33 \times 10^4$	0.9989	0.0063	0.0125	
48	A	Phenthate	23.30	274(100)	246(24)	320(5)	0.1250 ~ 5.000	$Y = 1.37 \times 10^6 X - 2.52 \times 10^5$	0.9970	0.0125	0.0250	
49	A	Metazachlor	23.32	209(100)	133(120)	211(32)	0.1875 ~ 7.500	$Y = 1.18 \times 10^6 X - 2.26 \times 10^5$	0.9984	0.0188	0.0375	
50	A	Fenothiocarb	23.79	72(100)	160(37)	253(15)	1.0000 ~ 5.000	$Y = 2.27 \times 10^4 X - 1.21 \times 10^4$	0.9955	0.1000	0.2000	
51	A	Prothiophos	24.04	309(100)	267(88)	162(55)	0.0625 ~ 2.500	$Y = 9.17 \times 10^5 X - 9.14 \times 10^4$	0.9957	0.0063	0.0125	
52	A	Chlofurenol	24.15	215(100)	152(40)	274(11)	0.1875 ~ 7.500	$Y = 4.48 \times 10^6 X - 1.29 \times 10^6$	0.9960	0.0188	0.0375	
53	A	Dieklin	24.43	263(100)	277(82)	380(30)	0.1250 ~ 5.000	$Y = 3.00 \times 10^5 X - 2.58 \times 10^4$	0.9994	0.0125	0.0250	
54	A	Procyridone	24.36	283(100)	285(70)	255(15)	0.0625 ~ 2.500	$Y = 1.18 \times 10^6 X - 6.98 \times 10^4$	0.9979	0.0063	0.0125	
55	A	Methidathion	24.49	145(100)	157(2)	302(4)	0.1250 ~ 5.000	$Y = 2.58 \times 10^6 X - 5.55 \times 10^5$	0.9948	0.0125	0.0250	
56	A	Cyanazine	24.94	225(100)	240(56)	198(61)	0.1875 ~ 7.500	$Y = 1.26 \times 10^6 X - 4.10 \times 10^5$	0.9952	0.0188	0.0375	
57	A	Napropamide	24.84	271(100)	128(111)	171(34)	0.1875 ~ 7.500	$Y = 9.05 \times 10^5 X - 2.34 \times 10^5$	0.9963	0.0188	0.0375	
58	A	Oxadiazone	25.06	175(100)	258(62)	302(37)	0.0625 ~ 2.500	$Y = 1.56 \times 10^6 X - 1.01 \times 10^5$	0.9980	0.0063	0.0125	
59	A	Fenamiphos	25.29	303(100)	154(56)	288(31)	0.1875 ~ 7.500	$Y = 1.80 \times 10^6 X - 8.73 \times 10^5$	0.9864	0.0188	0.0375	
60	A	Tefrasulf	25.85	252(100)	324(64)	254(68)	0.0625 ~ 2.500	$Y = 1.60 \times 10^6 X - 1.21 \times 10^5$	0.9958	0.0063	0.0125	
61	A	Aramite	25.60	185(100)	319(37)	334(32)	0.0625 ~ 2.500	$Y = 3.89 \times 10^5 X - 3.66 \times 10^4$	0.9927	0.0063	0.0125	
62	A	Buprimate	26.00	273(100)	316(41)	208(83)	0.0625 ~ 2.500	$Y = 1.73 \times 10^6 X - 1.57 \times 10^5$	0.9954	0.0063	0.0125	
63	A	Carboxin	26.25	235(100)	143(168)	87(52)	0.1875 ~ 7.500	$Y = 1.49 \times 10^6 X - 5.15 \times 10^5$	0.9930	0.0188	0.0375	
64	A	Flutolanil	26.23	173(100)	145(25)	323(14)	0.0625 ~ 2.500	$Y = 6.85 \times 10^5 X - 7.11 \times 10^5$	0.9951	0.0063	0.0125	
65	A	4,4'-DDD	26.59	235(100)	237(64)	199(12)	165(46)	$Y = 4.46 \times 10^6 X - 5.15 \times 10^5$	0.9930	0.0063	0.0125	
66	A	Ethion	26.69	231(100)	384(13)	199(9)	0.1250 ~ 5.000	$Y = 1.91 \times 10^6 X - 4.27 \times 10^5$	0.9944	0.0125	0.0250	
67	A	Sulprofos	26.87	322(100)	156(62)	280(11)	0.1250 ~ 5.000	$Y = 1.45 \times 10^6 X - 2.67 \times 10^5$	0.9959	0.0125	0.0250	
68	A	Etaconazole-1	26.81	245(100)	173(85)	247(65)	0.1875 ~ 7.500	$Y = 5.57 \times 10^5 X - 1.69 \times 10^5$	0.9948	0.0188	0.0375	
69	A	Etaconazole-2	26.89	245(100)	173(85)	247(65)	0.1875 ~ 7.500	$Y = 8.08 \times 10^5 X - 1.78 \times 10^5$	0.9976	0.0188	0.0375	
70	A	Myclobutanil	27.19	179(100)	288(14)	150(45)	0.0625 ~ 2.500	$Y = 1.90 \times 10^6 X - 1.74 \times 10^5$	0.9958	0.0063	0.0125	
71	A	Diclofop-methyl	28.08	253(100)	281(50)	342(82)	0.0625 ~ 2.500	$Y = 1.23 \times 10^6 X - 4.28 \times 10^4$	0.9958	0.0063	0.0125	
72	A	Propiconazole	28.15	259(100)	173(97)	261(65)	0.1875 ~ 7.500	$Y = 6.40 \times 10^5 X - 1.94 \times 10^5$	0.9942	0.0188	0.0375	
73	A	Fensulfothin	27.94	292(100)	308(22)	293(73)	0.1250 ~ 5.000	$Y = 3.84 \times 10^5 X - 5.31 \times 10^4$	0.9900	0.0125	0.0250	
74	A	Bifenithrin	28.57	181(100)	166(25)	165(23)	0.0625 ~ 2.500	$Y = 7.25 \times 10^6 X - 7.29 \times 10^5$	0.9936	0.0063	0.0125	
75	A	Mirex	28.72	272(100)	237(49)	274(80)	0.0625 ~ 2.500	$Y = 1.29 \times 10^6 X - 6.90 \times 10^4$	0.9974	0.0063	0.0125	
76	A	Benodanil	29.14	231(100)	323(38)	203(22)	0.1875 ~ 7.500	$Y = 5.34 \times 10^5 X - 2.7 \times 10^5$	0.9899	0.0188	0.0375	
77	A	Nuarmol	28.90	314(100)	235(155)	203(108)	0.1250 ~ 5.000	$Y = 6.42 \times 10^5 X - 1.13 \times 10^5$	0.9962	0.0125	0.0250	
78	A	Methoxychlor	29.38	227(100)	228(16)	212(4)	0.0625 ~ 2.500	$Y = 5.40 \times 10^6 X - 6.40 \times 10^5$	0.9921	0.0063	0.0125	
79	A	Oxadixyl	29.50	163(100)	233(18)	278(11)	0.0625 ~ 2.500	$Y = 7.29 \times 10^5 X - 6.65 \times 10^4$	0.9897	0.0063	0.0125	
80	A	Tetramethrin	29.59	164(100)	135(3)	232(1)	0.1250 ~ 5.000	$Y = 4.35 \times 10^6 X - 9.91 \times 10^5$	0.9928	0.0125	0.0250	

Table 2. (continued)

No.	Group	Pesticide	Retention time, min	Quantification ion ^a	Qualification ion 1 ^a	Qualification ion 2 ^a	Qualification ion 3 ^a	Qualification ion range, ng	Linear equation	Correlation coefficient (r)	LOD, mg/kg	LOQ, mg/kg	
81	A	Tebuconazole	29.51	250(100)	163(55)	252(36)	0.1875 ~ 7.500	$Y = 1.39 \times 10^6 X - 4.05 \times 10^5$	0.9841	0.0188	0.0375		
82	A	Norfurazuron	29.99	303(100)	145(101)	102(47)	0.0625 ~ 2.500	$Y = 1.16 \times 10^6 X - 1.33 \times 10^5$	0.9879	0.0063	0.0125		
83	A	Pyridaphenthion	30.17	340(100)	199(48)	188(51)	0.0625 ~ 2.500	$Y = 1.04 \times 10^6 X - 1.47 \times 10^5$	0.9841	0.0063	0.0125		
84	A	Phosmet	30.46	160(100)	161(11)	317(4)	0.1250 ~ 5.000	$Y = 2.04 \times 10^6 X - 6.08 \times 10^5$	0.9861	0.0125	0.0250		
85	A	Tetradifon	30.70	227(100)	356(70)	159(196)	0.0625 ~ 2.500	$Y = 4.97 \times 10^5 X - 2.54 \times 10^4$	0.9866	0.0063	0.0125		
86	A	Oxycarboxin	31.00	175(100)	267(52)	250(3)	0.3750 ~ 15.00	$Y = 1.34 \times 10^6 X - 1.23 \times 10^6$	0.9850	0.0375	0.0750		
87	A	cis-Permethrin	31.42	183(100)	184(15)	255(2)	0.0625 ~ 2.500	$Y = 4.92 \times 10^6 X - 4.33 \times 10^5$	0.9835	0.0063	0.0125		
88	A	trans-Permethrin	31.68	183(100)	184(15)	255(2)	0.0625 ~ 2.500	$Y = 4.19 \times 10^6 X - 4.17 \times 10^5$	0.9911	0.0063	0.0125		
89	A	Pyrazophos	31.60	221(100)	232(35)	373(19)	0.1250 ~ 5.000	$Y = 2.23 \times 10^6 X - 5.32 \times 10^5$	0.9804	0.0125	0.0250		
90	A	Cypermethrin	33.19	181(100)	152(23)	180(16)	0.1875 ~ 7.500	$Y = 6.63 \times 10^5 X - 1.77 \times 10^5$	0.9919	0.0188	0.0375		
			33.38										
			33.46										
91	A	Fenvalerate	34.45	167(100)	225(53)	419(37)	181(41)	0.2500 ~ 10.00	$Y = 1.54 \times 10^6 X - 4.39 \times 10^5$	0.9928	0.0250	0.0500	
			34.79										
92	A	Deltamethrin	35.77	181(100)	172(25)	174(25)	0.3750 ~ 15.00	$Y = 9.80 \times 10^5 X - 6.51 \times 10^5$	0.9921	0.0375	0.0750		
93	B	EPTC	8.54	128(100)	189(30)	132(32)	0.1875 ~ 7.500	$Y = 1.57 \times 10^6 X - 1.31 \times 10^5$	0.9993	0.0188	0.0375		
94	B	Butylate	9.49	156(100)	146(115)	217(27)	0.1875 ~ 7.500	$Y = 1.10 \times 10^6 X - 1.13 \times 10^5$	0.9894	0.0188	0.0375		
95	B	Dichlobenil	9.75	171(100)	173(68)	136(15)	0.0250 ~ 0.500	$Y = 2.99 \times 10^6 X - 1.58 \times 10^4$	0.9898	0.0025	0.0050		
96	B	Rebulate	10.18	128(100)	161(21)	203(20)	0.1875 ~ 7.500	$Y = 2.11 \times 10^6 X - 2.26 \times 10^5$	0.9994	0.0188	0.0375		
97	B	Nitrapyrin	10.89	194(100)	196(97)	198(23)	0.1875 ~ 7.500	$Y = 1.41 \times 10^6 X - 4.43 \times 10^5$	0.9957	0.0188	0.0375		
98	B	Mevinphos	11.23	127(100)	192(39)	164(29)	0.1250 ~ 5.000	$Y = 1.77 \times 10^6 X - 3.53 \times 10^5$	0.9957	0.0125	0.0250		
99	B	Chloroneb	11.85	191(100)	193(67)	206(66)	0.0625 ~ 2.500	$Y = 2.04 \times 10^6 X - 9.36 \times 10^4$	0.9890	0.0063	0.0125		
100	B	Tecnazene	13.54	261(100)	203(135)	215(113)	0.2500 ~ 5.000	$Y = 3.92 \times 10^5 X - 6.99 \times 10^4$	0.9985	0.0250	0.0500		
101	B	Heptenophos	13.78	214(100)	215(117)	250(14)	0.1875 ~ 7.500	$Y = 1.71 \times 10^6 X - 4.01 \times 10^5$	0.9979	0.0188	0.0375		
102	B	Hexachlorobenzene	14.69	284(100)	286(81)	282(51)	0.0625 ~ 2.500	$Y = 1.80 \times 10^6 X - 5.09 \times 10^4$	0.9996	0.0063	0.0125		
103	B	Ethoprophos	14.40	158(100)	200(40)	242(23)	0.1875 ~ 7.500	$Y = 1.04 \times 10^6 X - 2.32 \times 10^5$	0.9982	0.0188	0.0375		
104	B	o/s-Diallate	14.75	234(100)	236(37)	128(38)	0.1250 ~ 5.000	$Y = 2.70 \times 10^5 X - 1.65 \times 10^4$	0.9898	0.0125	0.0250		
105	B	Propachlor	14.73	120(100)	176(45)	211(11)	0.1875 ~ 7.500	$Y = 2.89 \times 10^6 X - 3.00 \times 10^5$	0.9898	0.0188	0.0375		
106	B	trans-Diallate	15.29	234(100)	236(37)	128(38)	0.1250 ~ 5.000	$Y = 1.02 \times 10^6 X - 9.85 \times 10^4$	0.9994	0.0125	0.0250		
107	B	Trifluralin	15.23	306(100)	264(72)	335(7)	0.1250 ~ 5.000	$Y = 1.83 \times 10^6 X - 4.47 \times 10^5$	0.9930	0.0125	0.0250		
108	B	Chlorpropham	15.49	213(100)	171(59)	153(24)	0.1250 ~ 5.000	$Y = 7.24 \times 10^5 X - 1.22 \times 10^5$	0.9971	0.0125	0.0250		
109	B	Sulfotep	15.55	322(100)	202(43)	238(27)	0.0625 ~ 2.500	$Y = 1.61 \times 10^6 X - 8.57 \times 10^4$	0.9991	0.0063	0.0125		
110	B	Sulfatale	15.75	188(100)	116(7)	148(4)	0.1250 ~ 5.000	$Y = 2.84 \times 10^6 X - 6.05 \times 10^5$	0.9958	0.0125	0.0250		
111	B	alpha-HCH	16.06	219(100)	183(98)	221(47)	0.0625 ~ 2.500	$Y = 6.51 \times 10^5 X - 2.25 \times 10^4$	0.9994	0.0063	0.0125		
112	B	Terbufos	16.83	231(100)	153(25)	288(10)	0.1250 ~ 5.000	$Y = 1.77 \times 10^6 X - 2.82 \times 10^5$	0.9977	0.0125	0.0250		
113	B	Terbuteton	17.20	210(100)	169(66)	225(32)	0.1875 ~ 7.500	$Y = 2.47 \times 10^6 X - 5.48 \times 10^5$	0.9983	0.0188	0.0375		
114	B	Profuralin	17.36	318(100)	304(47)	347(13)	0.2500 ~ 10.00	$Y = 9.72 \times 10^5 X - 4.42 \times 10^5$	0.9855	0.0250	0.0500		
115	B	Dicofolathion	17.51	270(100)	197(43)	169(19)	0.2500 ~ 10.00	$Y = 1.58 \times 10^5 X - 2.19 \times 10^4$	0.9993	0.0250	0.0500		
116	B	Propazine	17.67	214(100)	229(67)	172(51)	0.0625 ~ 2.500	$Y = 1.63 \times 10^6 X - 9.61 \times 10^4$	0.9988	0.0063	0.0125		
117	B	Chlorbufam	17.85	223(100)	153(53)	164(64)	0.2500 ~ 10.00	$Y = 5.75 \times 10^5 X - 2.01 \times 10^5$	0.9921	0.0250	0.0500		

Table 2. (continued)

No.	Group	Pesticide	Retention time, min	Quantification ion ^a	Qualification ion 1 ^a	Qualification ion 2 ^a	Qualification ion 3 ^a	Linear range, ng	Linear equation	Correlation coefficient (r)	LOD, mg/kg	LOQ, mg/kg
118	B	Dicloran	17.89	206(100)	176(128)	160(52)		0.2500 ~ 10.00	$Y = 6.59 \times 10^5 X - 1.86 \times 10^5$	0.9963	0.0250	0.0500
119	B	Terbutylazine	18.07	214(100)	229(33)	173(35)		0.0625 ~ 2.500	$Y = 9.62 \times 10^5 X - 1.21 \times 10^5$	0.9886	0.0063	0.0125
120	B	Monolinuron	18.15	61(100)	126(45)	214(51)		0.2500 ~ 10.00	$Y = 1.78 \times 10^6 X - 9.80 \times 10^5$	0.9888	0.0250	0.0500
121	B	Flufenoxuron	18.83	305(100)	126(67)	307(32)		0.1875 ~ 7.500	$Y = 1.40 \times 10^5 X + 5.53 \times 10^4$	0.9929	0.0188	0.0375
122	B	Cyanophos	18.73	243(100)	180(8)	148(3)		0.1250 ~ 5.000	$Y = 2.01 \times 10^6 X - 2.99 \times 10^5$	0.9980	0.0125	0.0250
123	B	Chlorpyrifos-methyl	19.38	286(100)	288(70)	197(5)		0.0625 ~ 2.500	$Y = 1.55 \times 10^6 X - 1.25 \times 10^5$	0.9972	0.0063	0.0125
124	B	Desmetryn	19.64	213(100)	198(60)	171(30)		0.0625 ~ 2.500	$Y = 1.92 \times 10^6 X - 1.86 \times 10^5$	0.9864	0.0063	0.0125
125	B	Dimethachlor	19.80	134(100)	197(47)	210(16)		0.1875 ~ 7.500	$Y = 3.98 \times 10^6 X - 7.53 \times 10^5$	0.9889	0.0188	0.0375
126	B	Alachlor	20.03	188(100)	237(35)	269(15)		0.1875 ~ 7.500	$Y = 1.27 \times 10^6 X - 2.26 \times 10^5$	0.9990	0.0188	0.0375
127	B	Pririmiphos-methyl	20.30	290(100)	276(86)	305(74)		0.0625 ~ 2.500	$Y = 1.36 \times 10^6 X - 1.07 \times 10^5$	0.9977	0.0063	0.0125
128	B	Terbutryn	20.61	226(100)	241(64)	185(73)		0.1250 ~ 5.000	$Y = 1.95 \times 10^6 X - 3.07 \times 10^5$	0.9980	0.0125	0.0250
129	B	Thiobencarb	20.63	100(100)	257(25)	259(9)		0.1250 ~ 5.000	$Y = 4.00 \times 10^6 X - 5.32 \times 10^5$	0.9987	0.0125	0.0250
130	B	Aspon	20.62	211(100)	253(52)	378(14)		0.1250 ~ 5.000	$Y = 3.58 \times 10^6 X - 1.49 \times 10^5$	0.9994	0.0125	0.0250
131	B	Dicofol	21.33	139(100)	141(72)	250(23)	251(4)	0.1250 ~ 5.000	$Y = 1.00 \times 10^6 X - 1.25 \times 10^5$	0.9980	0.0125	0.0250
132	B	Metolachlor	21.34	238(100)	162(159)	240(33)		0.0625 ~ 2.500	$Y = 2.13 \times 10^6 X - 1.69 \times 10^5$	0.9977	0.0063	0.0125
133	B	Oxy-chlordane	21.63	387(100)	237(50)	185(68)		0.2500 ~ 2.500	$Y = 1.97 \times 10^5 X - 1.23 \times 10^4$	0.9997	0.0250	0.0500
134	B	Primiphos-ethyl	21.59	333(100)	318(93)	304(69)		0.1250 ~ 5.000	$Y = 1.16 \times 10^6 X - 1.83 \times 10^5$	0.9980	0.0125	0.0250
135	B	Methoprene	21.71	73(100)	191(29)	153(29)		0.2500 ~ 10.00	$Y = 3.30 \times 10^6 X - 1.31 \times 10^6$	0.9975	0.0250	0.0500
136	B	Bromofos	21.75	331(100)	329(75)	213(7)		0.1250 ~ 5.000	$Y = 1.50 \times 10^6 X - 1.98 \times 10^5$	0.9987	0.0125	0.0250
137	B	Dichlofluanid	21.68	224(100)	226(74)	167(120)		0.3750 ~ 15.00	$Y = 5.53 \times 10^5 X - 3.40 \times 10^5$	0.9977	0.0375	0.0750
138	B	Ethofumesate	21.84	207(100)	161(54)	286(27)		0.1250 ~ 5.000	$Y = 2.00 \times 10^6 X - 2.03 \times 10^5$	0.9992	0.0125	0.0250
139	B	Isopropalin	22.10	280(100)	238(40)	222(4)		0.1250 ~ 5.000	$Y = 1.54 \times 10^6 X - 2.40 \times 10^5$	0.9982	0.0125	0.0250
140	B	Endosulfan-1	23.10	241(100)	265(66)	339(46)		0.3750 ~ 15.00	$Y = 1.47 \times 10^5 X - 3.22 \times 10^4$	0.9991	0.0375	0.0750
141	B	Propanil	22.68	161(100)	217(21)	163(62)		0.1250 ~ 5.000	$Y = 1.99 \times 10^6 X - 4.75 \times 10^5$	0.9930	0.0125	0.0250
142	B	Isofenphos	22.99	213(100)	255(44)	185(45)		0.1250 ~ 5.000	$Y = 1.54 \times 10^6 X - 2.40 \times 10^5$	0.9982	0.0125	0.0250
143	B	Crufomate	22.93	256(100)	182(154)	276(58)		0.3750 ~ 15.00	$Y = 1.85 \times 10^6 X - 1.63 \times 10^6$	0.9914	0.0375	0.0750
144	B	Chlorenvinphos	23.19	323(100)	267(139)	269(92)		0.1875 ~ 7.500	$Y = 8.38 \times 10^5 X - 2.30 \times 10^5$	0.9876	0.0188	0.0375
145	B	cis-Chlordane	23.55	373(100)	375(96)	377(51)		0.1250 ~ 5.000	$Y = 9.13 \times 10^5 X - 7.13 \times 10^4$	0.9994	0.0125	0.0250
146	B	Tolylfluanide	23.45	238(100)	240(71)	137(210)		0.1875 ~ 7.500	$Y = 5.19 \times 10^5 X - 1.68 \times 10^5$	0.9981	0.0188	0.0375
147	B	4,4'-DDE	23.92	318(100)	316(80)	246(139)	248(70)	0.0625 ~ 2.500	$Y = 1.41 \times 10^6 X - 5.29 \times 10^4$	0.9994	0.0063	0.0125
148	B	Butachlor	23.82	176(100)	160(75)	188(46)		0.1250 ~ 5.000	$Y = 1.84 \times 10^6 X - 3.26 \times 10^5$	0.9970	0.0125	0.0250
149	B	Chlozinate	23.83	259(100)	188(83)	331(91)		0.1250 ~ 5.000	$Y = 6.77 \times 10^5 X - 6.41 \times 10^4$	0.9994	0.0125	0.0250
150	B	Crotoxyphos	23.94	193(100)	194(16)	166(51)		0.3750 ~ 15.00	$Y = 4.98 \times 10^5 X - 4.39 \times 10^5$	0.9904	0.0375	0.0750
151	B	Iodofenphos	24.33	377(100)	379(37)	250(6)		0.1250 ~ 5.000	$Y = 1.32 \times 10^6 X - 3.31 \times 10^5$	0.9940	0.0125	0.0250
152	B	Tetrachlorvinphos	24.36	329(100)	331(96)	333(31)		0.1875 ~ 7.500	$Y = 1.61 \times 10^6 X - 4.88 \times 10^5$	0.9975	0.0188	0.0375
153	B	Chlorbromuron	24.37	61(100)	294(17)	292(13)		1.5000 ~ 60.00	$Y = 1.63 \times 10^5 X - 6.33 \times 10^5$	0.9843	0.1500	0.3000
154	B	Profenofos	24.65	339(100)	374(39)	297(37)		0.3750 ~ 15.00	$Y = 4.53 \times 10^5 X - 2.76 \times 10^5$	0.9969	0.0375	0.0750
155	B	Fluorochloridone	25.14	311(100)	313(64)	187(85)		0.5000 ~ 5.000	$Y = 1.14 \times 10^5 X - 1.75 \times 10^4$	0.9994	0.0500	0.1000
156	B	Buprofezin	24.87	105(100)	172(54)	305(24)		0.1250 ~ 5.000	$Y = 7.95 \times 10^6 X - 8.95 \times 10^5$	0.9987	0.0125	0.0250
157	B	2,4'-DDD	24.94	235(100)	237(65)	165(39)	199(15)	0.1250 ~ 2.500	$Y = 1.16 \times 10^5 X + 2.92 \times 10^4$	0.9997	0.0125	0.0250
158	B	Endrin	25.15	263(100)	317(30)	345(26)		0.7500 ~ 30.00	$Y = 3.08 \times 10^5 X - 2.37 \times 10^5$	0.9982	0.0750	

Table 2. (continued)

No.	Group	Pesticide	Retention time, min	Quantification ion ^a	Qualification ion 1 ^a	Qualification ion 2 ^a	Qualification ion 3 ^a	Linear range, ng	Correlation coefficient (r)	LOD, mg/kg	LOQ, mg/kg
159	B	Hexaconazole	24.92	214(100)	231(62)	256(26)	0.7500 ~ 15.00	$Y = 5.28 \times 10^4 X - 2.04 \times 10^4$	0.9989	0.0750	0.1500
160	B	Chlortenson	25.05	302(100)	175(222)	177(103)	0.1250 ~ 5.000	$Y = 5.95 \times 10^5 X - 8.13 \times 10^4$	0.9980	0.0125	0.0250
161	B	2,4'-DDT	25.56	235(100)	237(63)	165(37)	0.1250 ~ 5.000	$Y = 2.71 \times 10^6 X - 4.24 \times 10^5$	0.9978	0.0125	0.0250
162	B	Pacllobutrazol	25.21	236(100)	238(37)	167(39)	0.1875 ~ 7.500	$Y = 1.76 \times 10^6 X - 6.51 \times 10^5$	0.9941	0.0188	0.0375
163	B	Methoprotynone	25.63	256(100)	213(24)	271(17)	0.1875 ~ 7.500	$Y = 1.80 \times 10^6 X - 5.13 \times 10^5$	0.9973	0.0188	0.0375
164	B	Ergon	25.68	169(100)	171(35)	223(30)	0.1250 ~ 2.500	$Y = 4.86 \times 10^5 X - 4.10 \times 10^4$	0.9994	0.0125	0.0250
165	B	Chlorpropionate	25.85	251(100)	253(64)	141(18)	0.0625 ~ 2.500	$Y = 2.99 \times 10^6 X - 2.62 \times 10^5$	0.9970	0.0063	0.0125
166	B	Flamprop-methyl	25.90	105(100)	77(26)	276(11)	0.0625 ~ 2.500	$Y = 6.68 \times 10^6 X - 4.53 \times 10^5$	0.9983	0.0063	0.0125
167	B	Nitrofen	26.12	283(100)	253(90)	202(48)	0.3750 ~ 15.00	$Y = 1.20 \times 10^6 X - 1.04 \times 10^6$	0.9905	0.0375	0.0750
168	B	Oxyfluorfen	26.13	252(100)	361(35)	300(35)	0.2500 ~ 10.00	$Y = 1.54 \times 10^6 X - 7.81 \times 10^5$	0.9945	0.0250	0.0500
169	B	Chlorthiophos	26.52	325(100)	360(52)	297(54)	0.1875 ~ 7.500	$Y = 6.89 \times 10^5 X - 1.58 \times 10^5$	0.9978	0.0188	0.0375
170	B	Endosulfan-II	26.72	241(100)	265(66)	339(46)	1.5000 ~ 15.00	$Y = 2.45 \times 10^4 X - 1.10 \times 10^4$	0.9994	0.1500	0.3000
171	B	Flamprop-isopropyl	26.70	105(100)	276(19)	363(3)	0.0625 ~ 2.500	$Y = 7.37 \times 10^6 X - 5.64 \times 10^5$	0.9974	0.0063	0.0125
172	B	4,4'-DDT	27.22	235(100)	237(65)	246(7)	0.1250 ~ 5.000	$Y = 2.76 \times 10^6 X - 5.05 \times 10^5$	0.9971	0.0125	0.0250
173	B	Carbofenthion	27.19	157(100)	342(49)	199(28)	0.1250 ~ 5.000	$Y = 1.32 \times 10^6 X - 2.79 \times 10^5$	0.9955	0.0125	0.0250
174	B	Benzyl	27.54	148(100)	206(32)	325(8)	0.0625 ~ 2.500	$Y = 3.38 \times 10^6 X - 2.55 \times 10^5$	0.9972	0.0063	0.0125
175	B	Edifenphos	27.94	173(100)	310(76)	201(37)	0.1250 ~ 5.000	$Y = 1.25 \times 10^6 X - 3.66 \times 10^5$	0.9912	0.0125	0.0250
176	B	Triazophos	28.23	161(100)	172(47)	257(38)	0.1875 ~ 7.500	$Y = 1.05 \times 10^6 X - 3.63 \times 10^5$	0.9944	0.0188	0.0375
177	B	Cyanoéphosphos	28.43	157(100)	169(56)	303(20)	0.0625 ~ 2.500	$Y = 2.34 \times 10^6 X - 1.98 \times 10^5$	0.9967	0.0063	0.0125
178	B	Chlorbenside sulfone	28.88	127(100)	99(14)	89(33)	0.1250 ~ 5.000	$Y = 1.89 \times 10^6 X - 2.89 \times 10^5$	0.9966	0.0125	0.0250
179	B	Endosulfan-sulfate	29.05	387(100)	272(165)	389(64)	0.1875 ~ 7.500	$Y = 2.46 \times 10^5 X - 3.43 \times 10^4$	0.9985	0.0188	0.0375
180	B	Bromopropionate	29.30	341(100)	183(34)	339(49)	0.1250 ~ 5.000	$Y = 3.62 \times 10^6 X - 6.59 \times 10^5$	0.9963	0.0125	0.0250
181	B	Benzylprop-ethyl	29.40	292(100)	365(36)	260(37)	0.1875 ~ 7.500	$Y = 5.20 \times 10^5 X - 1.00 \times 10^5$	0.9983	0.0188	0.0375
182	B	Fenpropathrin	29.56	265(100)	181(237)	349(25)	0.1250 ~ 5.000	$Y = 4.35 \times 10^5 X - 7.38 \times 10^4$	0.9966	0.0125	0.0250
183	B	Leptophos	30.19	377(100)	375(73)	379(28)	0.2500 ~ 10.00	$Y = 2.08 \times 10^6 X - 1.17 \times 10^6$	0.9913	0.0250	0.0500
184	B	EPN	30.06	157(100)	169(53)	323(14)	0.1875 ~ 7.500	$Y = 5.21 \times 10^6 X - 1.27 \times 10^6$	0.9970	0.0188	0.0375
185	B	Hexazinone	30.14	171(100)	252(3)	128(12)	0.1250 ~ 5.000	$Y = 1.19 \times 10^6 X - 2.42 \times 10^5$	0.9955	0.0125	0.0250
186	B	Phosalone	31.22	182(100)	367(30)	154(20)	0.7500 ~ 15.00	$Y = 1.82 \times 10^5 X - 1.18 \times 10^5$	0.9971	0.0750	0.1500
187	B	Azinphos-methyl	31.41	160(100)	132(71)	77(58)	0.1250 ~ 5.000	$Y = 1.19 \times 10^6 X - 1.33 \times 10^5$	0.9993	0.0125	0.0250
188	B	Fenainmol	31.65	139(100)	219(70)	330(42)	0.1250 ~ 5.000	$Y = 1.15 \times 10^6 X - 2.82 \times 10^5$	0.9930	0.0125	0.0250
189	B	Azinphos-ethyl	32.01	160(100)	132(103)	77(51)	0.3750 ~ 15.00	$Y = 5.01 \times 10^5 X - 5.72 \times 10^4$	0.9919	0.0375	0.0750
190	B	Prochloraz	33.07	180(100)	308(59)	266(18)	0.3750 ~ 15.00	$Y = 7.20 \times 10^5 X - 4.57 \times 10^5$	0.9955	0.0375	0.0750
191	B	Coumaphos	33.22	362(100)	364(39)	334(15)	0.7500 ~ 30.00	$Y = 2.38 \times 10^5 X - 1.95 \times 10^5$	0.9966	0.0750	0.1500
192	B	Cyfluthrin	32.94	206(100)	199(63)	226(72)	0.7500 ~ 30.00	$Y = 3.44 \times 10^6 X - 3.89 \times 10^6$	0.9954	0.0750	0.1500
193	B	Fluvalinate	34.94	250(100)	252(38)	181(18)	0.7500 ~ 30.00	$Y = 3.44 \times 10^6 X - 3.89 \times 10^6$	0.9954	0.0750	0.1500
194	C	Dichlorvos	7.80	109(100)	185(34)	220(7)	0.3750 ~ 15.00	$Y = 2.58 \times 10^6 X - 9.22 \times 10^5$	0.9990	0.0375	0.0750
195	C	Biphenyl	9.00	154(100)	153(40)	152(27)	0.0625 ~ 2.500	$Y = 6.61 \times 10^6 X - 1.66 \times 10^5$	0.9998	0.0063	0.0125
196	C	Vernolate	9.82	128(100)	146(17)	203(9)	0.0625 ~ 2.500	$Y = 2.12 \times 10^6 X - 6.55 \times 10^4$	0.9997	0.0063	0.0125
197	C	3,5-Dichloraniline	11.20	161(100)	163(62)	126(10)	0.0625 ~ 2.500	$Y = 9.29 \times 10^5 X + 1.10 \times 10^5$	0.9905	0.0063	0.0125

Table 2. (continued)

No.	Group	Pesticide	Retention time, min	Quantification ion ^a	Qualification ion 1 ^a	Qualification ion 2 ^a	Qualification ion 3 ^a	Linear range, ng	Linear equation	Correlation coefficient (r)	LOD, mg/kg	LOQ, mg/kg
198	C	Molinate	11.92	126(100)	187(24)	158(2)		0.0625 ~ 2.500	$Y = 2.55 \times 10^6 X - 8.80 \times 10^4$	0.9996	0.0063	0.0125
199	C	Methacrylos	11.86	125(100)	208(74)	240(44)		0.0625 ~ 2.500	$Y = 1.10 \times 10^6 X - 5.10 \times 10^4$	0.9994	0.0063	0.0125
200	C	2-Phenylphenol	12.47	170(100)	169(72)	141(31)		0.0625 ~ 1.2500	$Y = 1.70 \times 10^6 X + 3.54 \times 10^4$	0.9946	0.0063	0.0125
201	C	cis-1,2,3,6-Tetrahydronaphthalimide	13.39	151(100)	123(16)	122(16)		0.1875 ~ 7.500	$Y = 1.06 \times 10^6 X - 2.31 \times 10^5$	0.9985	0.0188	0.0375
202	C	Fenobucarb	14.60	121(100)	150(32)	107(8)		0.1250 ~ 5.000	$Y = 5.44 \times 10^6 X - 7.85 \times 10^5$	0.9982	0.0125	0.0250
203	C	Benfluralin	15.23	292(100)	264(20)	278(13)		0.0625 ~ 2.500	$Y = 2.07 \times 10^6 X - 2.74 \times 10^5$	0.9888	0.0063	0.0125
204	C	Hexaflumuron	16.20	176(100)	279(28)	277(43)		0.1875 ~ 7.500	$Y = 1.47 \times 10^6 X - 3.19 \times 10^5$	0.9988	0.0188	0.0375
205	C	Prometon	16.86	210(100)	225(91)	168(67)		0.1250 ~ 5.000	$Y = 8.94 \times 10^5 X - 9.82 \times 10^4$	0.9893	0.0125	0.0250
206	C	Triallate	17.12	268(100)	270(73)	143(19)		0.0625 ~ 2.500	$Y = 5.84 \times 10^6 X - 4.82 \times 10^5$	0.9980	0.0063	0.0125
207	C	Pyriproxyfen	17.28	198(100)	199(45)	200(5)		0.1250 ~ 5.000	$Y = 7.39 \times 10^5 X - 3.27 \times 10^4$	0.9998	0.0125	0.0250
208	C	gamma-HCH	17.48	183(100)	219(93)	254(13)	221(40)	0.0625 ~ 2.500	$Y = 2.37 \times 10^6 X - 1.88 \times 10^5$	0.9983	0.0063	0.0125
209	C	Disulfoton	17.61	88(100)	274(15)	186(18)		0.0625 ~ 2.500	$Y = 1.60 \times 10^6 X - 1.05 \times 10^5$	0.9991	0.0063	0.0125
210	C	Atrazine	17.64	200(100)	215(62)	173(29)		0.0625 ~ 2.500	$Y = 6.01 \times 10^5 X - 1.16 \times 10^5$	0.9990	0.0188	0.0375
211	C	Heptachlor	18.49	272(100)	237(40)	337(27)		0.1875 ~ 7.500	$Y = 1.47 \times 10^6 X - 6.69 \times 10^5$	0.9895	0.0188	0.0375
212	C	Iprobenitos	18.44	204(100)	246(18)	288(17)		0.1875 ~ 7.500	$Y = 8.48 \times 10^5 X - 9.19 \times 10^4$	0.9994	0.0125	0.0250
213	C	Isazofos	18.54	161(100)	257(53)	285(39)	313(14)	0.1250 ~ 5.000	$Y = 4.07 \times 10^5 X - 7.16 \times 10^4$	0.9992	0.0250	0.0500
214	C	Flufenate	18.87	217(100)	175(96)	242(91)		0.2500 ~ 5.000	$Y = 8.00 \times 10^6 X - 5.62 \times 10^5$	0.9989	0.0063	0.0125
215	C	Propiconizole	19.22	128(100)	303(5)	129(9)		0.0625 ~ 2.500	$Y = 3.03 \times 10^6 X - 1.80 \times 10^5$	0.9991	0.0063	0.0125
216	C	Transflutim	19.04	163(100)	165(23)	335(7)		0.0625 ~ 2.500	$Y = 9.56 \times 10^5 X - 4.69 \times 10^5$	0.9952	0.0250	0.0500
217	C	Fluchloralin	18.89	306(100)	326(87)	264(54)		0.2500 ~ 10.00	$Y = 3.46 \times 10^6 X - 1.95 \times 10^5$	0.9991	0.0063	0.0125
218	C	Tolclofos-methyl	19.69	265(100)	267(36)	250(10)		0.0625 ~ 2.500	$Y = 1.96 \times 10^6 X - 4.43 \times 10^5$	0.9989	0.0188	0.0375
219	C	Propisodolor	19.89	162(100)	223(200)	146(17)		0.1875 ~ 7.500	$Y = 2.26 \times 10^6 X - 2.94 \times 10^5$	0.9990	0.0125	0.0250
220	C	Ametrym	20.11	227(100)	212(53)	185(17)		0.1250 ~ 5.000	$Y = 1.67 \times 10^5 X - 6.17 \times 10^4$	0.9986	0.0375	0.0750
221	C	Simetryn	20.18	213(100)	170(26)	198(16)		0.3750 ~ 15.00	$Y = 1.61 \times 10^6 X - 3.48 \times 10^5$	0.9986	0.0188	0.0375
222	C	Metobromuron	20.07	61(100)	258(11)	170(16)		0.1875 ~ 7.500				
223	C	Metribuzin	20.33	198(100)	199(21)	144(12)		0.2500 ~ 10.00				
224	C	Dimethipin	20.38	118(100)	210(26)	103(20)		0.0625 ~ 2.500				
225	C	epsilon-HCH	20.78	181(100)	219(76)	254(15)	217(40)	0.0625 ~ 2.500	$Y = 1.67 \times 10^6 X - 1.52 \times 10^5$	0.9976	0.0063	0.0125
226	C	Dipropyryl	20.82	255(100)	240(42)	222(20)		0.0625 ~ 2.500	$Y = 1.12 \times 10^5 X - 3.13 \times 10^4$	0.9993	0.0500	0.1000
227	C	Formothion	21.42	170(100)	224(97)	257(63)		0.5000 ~ 5.000	$Y = 1.15 \times 10^6 X - 6.62 \times 10^5$	0.9877	0.0375	0.0750
228	C	Diethofencarb	21.43	267(100)	225(98)	151(31)		0.3750 ~ 15.00	$Y = 2.12 \times 10^4 X + 4.02 \times 10^4$	1.0000	0.2500	0.5000
229	C	Dimepiperate	22.28	119(100)	145(30)	263(8)		2.5000 ~ 5.000	$Y = 5.69 \times 10^4 X - 3.15 \times 10^4$	1.0000	0.1250	0.2500
230	C	Bioallethrin-1	22.29	123(100)	136(24)	107(29)		0.2500 ~ 10.00	$Y = 1.37 \times 10^6 X - 7.09 \times 10^5$	0.9941	0.0250	0.0500
231	C	Bioallethrin-2	22.34	123(100)	136(24)	107(29)		0.2500 ~ 10.00	$Y = 1.49 \times 10^6 X - 5.77 \times 10^5$	0.9983	0.0250	0.0500
232	C	2,4'-DDE	22.64	246(100)	318(34)	176(26)	248(65)	0.0625 ~ 2.500	$Y = 2.26 \times 10^6 X - 1.16 \times 10^5$	0.9993	0.0063	0.0125
233	C	Fenson	22.54	141(100)	268(53)	77(104)		1.2500 ~ 2.500	$Y = 5.69 \times 10^4 X - 3.15 \times 10^4$	1.0000	0.1250	0.2500
234	C	Diphenamid	22.87	167(100)	239(30)	165(43)		0.0625 ~ 2.500	$Y = 4.01 \times 10^6 X - 2.59 \times 10^5$	0.9989	0.0063	0.0125
235	C	Chlorthion	22.86	297(100)	267(162)	298(45)		0.5000 ~ 5.000	$Y = 3.72 \times 10^5 X - 2.23 \times 10^5$	0.9857	0.0500	0.1000
236	C	Prallethrin	23.11	123(100)	105(17)	134(9)		0.1875 ~ 7.500	$Y = 3.52 \times 10^6 X - 1.22 \times 10^6$	0.9964	0.0188	0.0375
237	C	Penconazole	23.17	248(100)	250(33)	161(50)		0.1875 ~ 7.500	$Y = 2.32 \times 10^6 X - 4.76 \times 10^5$	0.9992	0.0188	0.0375
238	C	Mecarbam	23.46	131(100)	296(22)	329(40)		0.2500 ~ 10.00	$Y = 2.87 \times 10^5 X - 2.80 \times 10^5$	0.9986	0.0250	0.0500

Table 2. (continued)

No.	Group	Pesticide	Retention time, min	Quantification ion ^a	Qualification ion 1 ^a	Qualification ion 2 ^a	Qualification ion 3 ^a	Linear range, ng	Correlation coefficient (r)	LOD, mg/kg	LOQ, mg/kg	
239	C	Tetraconazole	23.35	336(100)	171(10)	0.1875 ~ 7.500	Y = 2.72 × 10 ⁶ X - 5.43 × 10 ⁵	0.9992	0.0188	0.0375		
240	C	Propaphos	23.92	304(100)	220(34)	0.1250 ~ 5.000	Y = 2.51 × 10 ⁶ X - 7.70 × 10 ⁵	0.9873	0.0125	0.0250		
241	C	Flumelein	24.10	143(100)	157(25)	0.04(10)	Y = 1.90 × 10 ⁶ X - 5.96 × 10 ⁵	0.9972	0.0188	0.0375		
242	C	Triadimenol	24.22	112(100)	168(81)	130(15)	0.1875 ~ 7.500	Y = 1.40 × 10 ⁶ X - 2.48 × 10 ⁵	0.9980	0.0125	0.0250	
243	C	Pretilachlor	24.67	162(100)	238(26)	262(8)	0.1250 ~ 5.000	Y = 2.45 × 10 ⁶ X - 2.13 × 10 ⁵	0.9976	0.0063	0.0125	
244	C	Kresoxim-methyl	25.04	116(100)	206(25)	131(66)	0.0625 ~ 2.500	Y = 2.18 × 10 ⁶ X - 2.27 × 10 ⁵	0.9961	0.0063	0.0125	
245	C	Fluazifop-butyl	25.21	282(100)	383(44)	254(49)	0.0625 ~ 2.500	Y = 1.55 × 10 ⁵ X - 9.15 × 10 ³	0.9980	0.0375	0.0750	
246	C	Chlorfluazuron	25.27	321(100)	323(71)	356(8)	0.3750 ~ 7.500	Y = 2.62 × 10 ⁶ X - 2.29 × 10 ⁵	0.9977	0.0063	0.0125	
247	C	Chlorbenzilate	25.90	251(100)	253(65)	152(5)	0.0625 ~ 2.500	Y = 1.23 × 10 ⁶ X - 2.13 × 10 ⁵	0.9983	0.0125	0.0250	
248	C	Uronicazole	26.15	234(100)	236(40)	131(15)	0.1250 ~ 5.000	Y = 4.23 × 10 ⁶ X - 1.07 × 10 ⁶	0.9983	0.0188	0.0375	
249	C	Flusilazole	26.19	233(100)	206(33)	315(9)	0.1875 ~ 7.500					
250	C	Fluorodifen	26.59	190(100)	328(35)	162(34)						
251	C	Diniconazole	27.03	268(100)	270(65)	232(13)	0.1875 ~ 7.500	Y = 1.62 × 10 ⁶ X - 3.37 × 10 ⁵	0.9936	0.0188	0.0375	
252	C	Piperonyl butoxide	27.46	176(100)	177(33)	149(14)	0.0625 ~ 2.500	Y = 3.50 × 10 ⁶ X - 4.69 × 10 ⁵	0.9919	0.0063	0.0125	
253	C	Propargite	27.87	135(100)	350(7)	173(16)	0.1250 ~ 5.000	Y = 1.43 × 10 ⁶ X - 1.30 × 10 ⁵	0.9995	0.0125	0.0250	
254	C	Mepronil	27.91	119(100)	269(26)	120(9)	0.0625 ~ 2.500	Y = 5.96 × 10 ⁶ X - 6.83 × 10 ⁵	0.9941	0.0063	0.0125	
255	C	Dimefuron	27.82	140(100)	105(75)	267(36)	0.2500 ~ 10.00	Y = 2.79 × 10 ⁵ X - 1.10 × 10 ⁴	0.9885	0.0250	0.0500	
256	C	Diflufenican	28.45	266(100)	394(25)	267(14)	0.0625 ~ 2.500	Y = 3.75 × 10 ⁶ X - 4.25 × 10 ⁵	0.9950	0.0063	0.0125	
257	C	Fenaziquin	28.97	145(100)	160(46)	117(10)	0.0625 ~ 2.500	Y = 5.25 × 10 ⁶ X - 5.73 × 10 ⁵	0.9950	0.0063	0.0125	
258	C	Phenothrin	29.08	123(100)	183(74)	350(6)	0.0625 ~ 2.500	Y = 2.13 × 10 ⁶ X - 2.47 × 10 ⁵	0.9950	0.0063	0.0125	
259	C	Fludioxonil	28.93	248(100)	127(24)	154(21)	0.0625 ~ 2.500	Y = 2.12 × 10 ⁶ X - 2.08 × 10 ⁵	0.9963	0.0063	0.0125	
260	C	fenoxycarb	29.57	255(100)	186(82)	116(93)	0.3750 ~ 15.00	Y = 1.81 × 10 ⁵ X + 1.11 × 10 ⁵	0.9902	0.0375	0.0750	
261	C	Sethoxydin	29.63	178(100)	281(51)	219(36)	0.5625 ~ 22.50	Y = 2.11 × 10 ⁵ X + 1.26 × 10 ⁵	0.9868	0.0563	0.1125	
262	C	Anilofos	30.68	226(100)	184(52)	334(10)	0.2500 ~ 5.000	Y = 5.65 × 10 ⁵ X - 1.83 × 10 ⁵	0.9954	0.0250	0.0500	
263	C	Acrinathrin	31.07	181(100)	289(31)	247(12)	0.1250 ~ 5.000	Y = 1.21 × 10 ⁶ X - 2.74 × 10 ⁵	0.9839	0.0125	0.0250	
264	C	lambda-Cyhalothrin	31.11	181(100)	197(100)	141(20)	0.0625 ~ 2.500	Y = 1.83 × 10 ⁶ X - 1.43 × 10 ⁵	0.9882	0.0063	0.0125	
265	C	Mefenacet	31.29	192(100)	120(35)	136(29)	0.1875 ~ 7.500	Y = 2.02 × 10 ⁶ X - 7.14 × 10 ⁵	0.9828	0.0188	0.0375	
266	C	Permethrin	31.57	183(100)	184(14)	255(1)	0.1250 ~ 5.000	Y = 2.92 × 10 ⁶ X - 5.21 × 10 ⁵	0.9967	0.0125	0.0250	
267	C	Pyridaben	31.86	147(100)	117(11)	364(7)	0.0625 ~ 2.500	Y = 5.18 × 10 ⁶ X - 4.92 × 10 ⁵	0.9958	0.0063	0.0125	
268	C	Fluoroglycofan-ethyl	32.01	447(100)	428(20)	449(35)	0.7500 ~ 30.00	Y = 4.13 × 10 ⁵ X - 8.77 × 10 ⁵	0.9826	0.0750	0.1500	
269	C	Biteranol	32.25	170(100)	112(8)	141(6)	0.1875 ~ 7.500	Y = 4.06 × 10 ⁶ X - 1.42 × 10 ⁶	0.9931	0.0188	0.0375	
270	C	Etofenprox	32.75	163(100)	376(4)	183(6)	0.0625 ~ 2.500	Y = 6.57 × 10 ⁶ X - 3.60 × 10 ⁵	0.9961	0.0063	0.0125	
271	C	Cycloxydim	33.05	178(100)	279(7)	251(4)	0.7500 ~ 30.00	Y = 7.64 × 10 ⁵ X + 8.13 × 10 ⁵	0.9907	0.0750	0.1500	
272	C	alpha-Cypermethrin	33.35	163(100)	181(84)	165(63)	0.1250 ~ 5.000	Y = 1.422 × 10 ⁶ X - 2.51 × 10 ⁵	0.9974	0.0125	0.0250	
273	C	Flucythrinate	33.58	199(100)	157(90)	451(22)	0.1250 ~ 5.000	Y = 9.93 × 10 ⁵ X - 2.33 × 10 ⁵	0.9903	0.0125	0.0250	
274	C	Esfenvalerate	34.65	419(100)	225(158)	181(189)	0.2500 ~ 10.00	Y = 3.68 × 10 ⁵ X - 7.15 × 10 ⁴	0.9983	0.0250	0.0500	
275	C	Difencozazole	35.40	323(100)	325(66)	265(33)	0.3750 ~ 15.00	Y = 1.08 × 10 ⁶ X - 3.85 × 10 ⁵	0.9860	0.0375	0.0750	
276	C	Flumioxazin	35.50	354(100)	287(24)	259(15)				0.0125	0.0250	
277	C	Flumidoborapentyl	36.34	423(100)	308(51)	318(29)	0.1250 ~ 5.000	Y = 9.93 × 10 ⁵ X - 2.33 × 10 ⁵	0.9903	0.0125	0.0250	

Table 2. (continued)

No.	Group	Pesticide	Retention time, min	Quantification ion ^a	Qualification ion 1 ^a	Qualification ion 2 ^a	Qualification ion 3 ^a	Linear range, ng	Linear equation	Correlation coefficient (r)	LOD, mg/kg	LOQ, mg/kg
278	D	Dimefox	5.62	110(100)	154(75)	153(17)		0.1875 ~ 7.500	$Y = 1.34 \times 10^6 X - 1.07 \times 10^5$	0.9992	0.0188	0.0375
279	D	Disulfoton-sulfoxide	8.41	212(100)	153(61)	184(20)		0.1250 ~ 5.000	$Y = 2.77 \times 10^5 X - 2.21 \times 10^4$	0.9993	0.0125	0.0250
280	D	Pentachlorobenzene	11.11	250(100)	252(64)	215(24)		0.0625 ~ 2.500	$Y = 2.14 \times 10^6 X - 3.01 \times 10^4$	0.9998	0.0063	0.0125
281	D	Tri-isobutyl phosphate	11.65	155(100)	139(67)	211(24)				0.0063	0.0125	
282	D	Crimidine	13.13	142(100)	156(90)	171(84)		0.0625 ~ 2.500	$Y = 1.32 \times 10^6 X - 5.33 \times 10^4$	0.9987	0.0063	0.0125
283	D	BDMC-1	13.25	200(100)	202(104)	201(13)		0.2500 ~ 5.000	$Y = 2.00 \times 10^5 X + 2.44 \times 10^4$	0.9978	0.0250	0.0500
284	D	Chlorfenprop-methyl	13.57	165(100)	196(87)	197(49)		0.0625 ~ 2.500	$Y = 1.34 \times 10^6 X - 4.92 \times 10^4$	0.9989	0.0063	0.0125
285	D	Thionazin	14.04	143(100)	192(39)	220(14)		0.0625 ~ 2.500	$Y = 6.15 \times 10^5 X - 3.47 \times 10^4$	0.9869	0.0063	0.0125
286	D	2,3,5,6-Tetrachloroaniline	14.22	231(100)	229(76)	158(25)		0.0625 ~ 2.500	$Y = 1.72 \times 10^6 X - 5.14 \times 10^4$	0.9894	0.0063	0.0125
287	D	Tri-n-butyl phosphate	14.33	155(100)	211(61)	167(8)		0.1250 ~ 5.000	$Y = 1.40 \times 10^6 X - 2.15 \times 10^5$	0.9972	0.0125	
288	D	2,3,4,5-Tetrachloroanisole	14.66	246(100)	203(70)	231(51)		0.0625 ~ 2.500	$Y = 1.11 \times 10^6 X - 2.36 \times 10^4$	0.9997	0.0063	0.0125
289	D	Pentachloroanisole	15.19	280(100)	265(100)	237(85)		0.0625 ~ 2.500	$Y = 8.25 \times 10^5 X - 1.64 \times 10^4$	0.9996	0.0063	0.0125
290	D	Tebutam	15.30	190(100)	106(38)	142(24)		0.1250 ~ 5.000	$Y = 1.22 \times 10^6 X - 8.63 \times 10^4$	0.9990	0.0125	0.0250
291	D	Dioxabenzofos	16.14	216(100)	201(26)	171(5)		0.6250 ~ 25.00	$Y = 4.35 \times 10^5 X - 2.36 \times 10^5$	0.9980	0.0625	0.1250
292	D	Methabenzthiazuron	16.34	164(100)	136(81)	108(27)		0.6250 ~ 25.00	$Y = 1.30 \times 10^6 X - 1.65 \times 10^6$	0.9930	0.0625	0.1250
293	D	Simetone	16.69	197(100)	196(40)	182(38)		0.1250 ~ 5.000	$Y = 1.93 \times 10^6 X - 2.26 \times 10^5$	0.9984	0.0125	0.0250
294	D	Atralone	16.70	196(100)	211(68)	197(105)		0.0625 ~ 2.500	$Y = 2.38 \times 10^6 X - 1.24 \times 10^5$	0.9988	0.0063	0.0125
295	D	Desisopropyl-atrazine	16.89	173(100)	158(84)	145(73)		0.5000 ~ 20.00	$Y = 8.37 \times 10^5 X - 4.16 \times 10^5$	0.9875	0.0500	0.1000
296	D	Terbufos sulfone	16.79	231(100)	288(11)	186(15)		0.0625 ~ 2.500	$Y = 2.08 \times 10^6 X - 1.20 \times 10^5$	0.9980	0.0063	0.0125
297	D	Tefluthrin	17.24	177(100)	197(26)	161(5)		0.0625 ~ 2.500	$Y = 5.47 \times 10^6 X - 2.89 \times 10^5$	0.9980	0.0063	0.0125
298	D	Bromocyclen	17.43	359(100)	357(99)	394(14)		0.0625 ~ 2.500	$Y = 5.19 \times 10^5 X - 2.05 \times 10^4$	0.9990	0.0063	0.0125
299	D	Triazine	17.53	200(100)	229(51)	214(45)		0.0625 ~ 2.500	$Y = 2.17 \times 10^6 X - 9.66 \times 10^4$	0.9987	0.0063	0.0125
300	D	Etrimsfos oxon	17.83	292(100)	277(35)	263(12)		0.0625 ~ 2.500	$Y = 4.07 \times 10^6 X - 1.85 \times 10^5$	0.9990	0.0063	0.0125
301	D	Cycluron	17.95	89(100)	198(36)	114(9)		0.1875 ~ 7.500	$Y = 6.73 \times 10^5 X - 1.27 \times 10^5$	0.9982	0.0188	0.0375
302	D	2,6-Dichlorobenzamide	17.93	173(100)	189(36)	175(62)		0.1250 ~ 5.000	$Y = 1.57 \times 10^6 X - 1.74 \times 10^5$	0.9983	0.0125	0.0250
303	D	DE-PCB-28	18.15	256(100)	186(53)	258(97)		0.0625 ~ 1.250	$Y = 5.60 \times 10^6 X - 5.83 \times 10^4$	0.9997	0.0063	0.0125
304	D	DE-PCB-31	18.19	256(100)	186(53)	258(97)		0.0625 ~ 1.250	$Y = 5.45 \times 10^6 X - 5.64 \times 10^4$	0.9997	0.0063	0.0125
305	D	Desethyl-sebutylazine	18.32	172(100)	174(32)	186(11)		0.1250 ~ 5.000	$Y = 3.58 \times 10^6 X - 3.93 \times 10^5$	0.9985	0.0125	0.0250
306	D	2,3,4,5-Tetrachloroaniline	18.55	231(100)	229(76)	233(48)		0.1250 ~ 5.000	$Y = 1.61 \times 10^6 X - 1.25 \times 10^5$	0.9989	0.0125	0.0250
307	D	Musk ambrette	18.62	253(100)	268(35)	223(18)				0.0063	0.0125	
308	D	Musk xylene	18.66	282(100)	297(10)	128(20)				0.0063	0.0125	
309	D	Pentachloroaniline	18.91	265(100)	263(63)	230(8)		0.0625 ~ 2.500	$Y = 1.63 \times 10^6 X - 5.38 \times 10^4$	0.9990	0.0063	0.0125
310	D	Aziprothine	19.11	199(100)	184(83)	157(31)		0.5000 ~ 20.00	$Y = 4.43 \times 10^5 X - 1.80 \times 10^5$	0.9979	0.0500	0.1000
311	D	Sebutylazine	19.26	200(100)	214(14)	229(13)		0.0625 ~ 2.500	$Y = 3.74 \times 10^6 X - 1.70 \times 10^5$	0.9989	0.0063	0.0125
312	D	Isocarbamid	19.24	142(100)	185(2)	143(6)		0.3125 ~ 12.50	$Y = 2.55 \times 10^6 X - 9.72 \times 10^4$	0.9965	0.0313	0.0625
313	D	DE-PCB-52	19.48	292(100)	220(88)	255(32)		0.0625 ~ 2.500	$Y = 1.92 \times 10^6 X - 3.05 \times 10^4$	0.9997	0.0063	0.0125
314	D	Musk moskane	19.46	263(100)	278(12)	264(15)				0.0063	0.0125	
315	D	Prostifocarb	19.51	251(100)	252(14)	162(10)		0.0625 ~ 2.500	$Y = 1.04 \times 10^6 X - 5.13 \times 10^4$	0.9988	0.0063	0.0125
316	D	Dimethenamid	19.55	154(100)	230(43)	203(21)		0.0625 ~ 2.500	$Y = 3.66 \times 10^6 X - 1.48 \times 10^5$	0.9990	0.0063	0.0125
317	D	Fenchlorphos oxon	19.72	285(100)	287(70)	270(7)		0.1250 ~ 5.000	$Y = 2.18 \times 10^6 X - 1.77 \times 10^5$	0.9991	0.0125	0.0250
318	D	BDMC-2	19.74	200(100)	202(101)	201(12)		0.1250 ~ 5.000	$Y = 1.46 \times 10^6 X - 3.49 \times 10^5$	0.9912	0.0125	

Table 2. (continued)

No.	Group	Pesticide	Retention time, min	Quantification ion ^a	Qualification ion 1 ^a	Qualification ion 2 ^a	Qualification ion 3 ^a	Qualification ion 3 ^a	Linear range, ng	Correlation coefficient (r)	LOD, mg/kg	LOQ, mg/kg
319	D	Paraxon-methyl	19.83	230(100)	247(93)	200(40)	0.500 ~ 5.000	Y = 3.57 × 10 ⁵ X - 2.04 × 10 ⁵	0.9852	0.0500	0.1000	
320	D	Monalide	20.02	197(100)	199(31)	238(45)	0.1250 ~ 5.000	Y = 7.65 × 10 ⁵ X - 5.97 × 10 ⁴	0.9988	0.0125	0.0250	
321	D	Musk tibeten	20.40	251(100)	266(25)	252(14)				0.0063	0.0125	
322	D	Isobenzan	20.55	311(100)	375(31)	412(7)	0.0625 ~ 2.500	Y = 5.29 × 10 ⁵ X - 1.51 × 10 ⁴	0.9995	0.0063	0.0125	
323	D	Octachlorostyrene	20.60	380(100)	343(94)	308(120)	0.0625 ~ 2.500	Y = 6.84 × 10 ⁵ X - 1.55 × 10 ⁴	0.9997	0.0063	0.0125	
324	D	Pyrimifate	20.59	305(100)	153(116)	180(49)	0.0625 ~ 2.500	Y = 7.73 × 10 ⁵ X - 9.06 × 10 ³	0.9982	0.0063	0.0125	
325	D	Isodrin	21.01	193(100)	263(46)	195(63)	0.1250 ~ 5.000	Y = 1.60 × 10 ⁶ X - 2.21 × 10 ⁵	0.9970	0.0125	0.0250	
326	D	Isomethiazin	21.06	225(100)	198(86)	184(13)	0.0625 ~ 2.500	Y = 1.49 × 10 ⁶ X - 6.67 × 10 ⁴	0.9989	0.0063	0.0125	
327	D	Trichloromat	21.10	297(100)	269(86)	196(16)	0.0625 ~ 2.500	Y = 4.04 × 10 ⁶ X - 1.08 × 10 ⁵	0.9995	0.0063	0.0125	
328	D	Dacthal	21.25	301(100)	332(31)	221(16)	0.0625 ~ 2.500	Y = 1.13 × 10 ⁶ X - 9.71 × 10 ⁴	0.9959	0.0063	0.0125	
329	D	4,4-Dichlorobenzophenone	21.29	250(100)	252(62)	215(26)	0.0625 ~ 2.500	Y = 1.80 × 10 ⁶ X - 4.91 × 10 ⁵	0.9911	0.0125	0.0250	
330	D	Nitrohal-isopropyl	21.69	236(100)	254(54)	212(74)	0.1250 ~ 5.000	Y = 5.20 × 10 ⁶ X - 6.05 × 10 ⁵	0.9931	0.0063	0.0125	
331	D	Must ketone	21.70	279(100)	294(28)	128(16)	0.0625 ~ 2.500	Y = 5.21 × 10 ⁶ X - 3.06 × 10 ⁵	0.9977	0.0063	0.0125	
332	D	Robenazole	21.73	212(100)	170(26)	195(19)	0.0625 ~ 2.500					
333	D	Cyprodinil	21.94	224(100)	225(62)	210(9)	0.0625 ~ 2.500					
334	D	Fuberidazole	22.10	184(100)	155(21)	129(12)	0.0625 ~ 2.500					
335	D	Isofenphos oxon	22.04	229(100)	201(2)	314(12)	0.3125 ~ 12.50	Y = 1.75 × 10 ⁶ X - 1.05 × 10 ⁶	0.9946	0.0313	0.0625	
336	D	Dicaphthon	22.44	262(100)	263(10)	216(10)	0.0625 ~ 2.500	Y = 1.74 × 10 ⁶ X - 3.67 × 10 ⁴	0.9994	0.0063	0.0125	
337	D	DE-PCB 101	22.62	326(100)	254(66)	291(18)	0.0625 ~ 2.500	Y = 6.47 × 10 ⁵ X - 4.71 × 10 ⁴	0.9966	0.0063	0.0125	
338	D	MCPA-butoxethyl ester	22.61	300(100)	200(71)	182(41)	0.0625 ~ 2.500					
339	D	Isocarbophos	22.87	136(100)	230(26)	289(22)	0.0625 ~ 2.500	Y = 8.24 × 10 ⁵ X - 5.08 × 10 ⁴	0.9946	0.0063	0.0125	
340	D	Phorate sulfone	23.15	199(100)	171(30)	215(11)	0.0625 ~ 2.500	Y = 2.04 × 10 ⁶ X - 1.30 × 10 ⁵	0.9975	0.0063	0.0125	
341	D	Chlорfenothol	23.29	251(100)	253(66)	266(12)	0.0625 ~ 2.500	Y = 1.13 × 10 ⁶ X - 3.81 × 10 ⁴	0.9990	0.0063	0.0125	
342	D	trans-Nonachlor	23.62	409(100)	407(89)	411(63)	0.0625 ~ 2.500	Y = 5.32 × 10 ⁵ X - 1.34 × 10 ⁶	0.9788	0.1250	0.2500	
343	D	Dinobuton	23.88	211(100)	240(15)	223(15)	0.1250 ~ 5.000	Y = 7.30 × 10 ⁵ X - 1.05 × 10 ⁵	0.9971	0.0125	0.0250	
344	D	DEF	24.08	202(100)	226(51)	258(55)	0.1250 ~ 5.000	Y = 1.26 × 10 ⁶ X - 1.66 × 10 ⁵	0.9979	0.0125	0.0250	
345	D	Flurochloridone	24.31	311(100)	187(74)	313(66)	0.0625 ~ 2.500	Y = 1.20 × 10 ⁶ X - 1.00 × 10 ⁵	0.9937	0.0063	0.0125	
346	D	Bromfenifos	24.62	267(100)	323(56)	295(18)	0.0625 ~ 2.500	Y = 7.03 × 10 ⁶ X - 3.66 × 10 ⁵	0.9974	0.0063	0.0125	
347	D	Perthane	24.81	223(100)	224(20)	178(9)	0.0625 ~ 2.500	Y = 2.75 × 10 ⁶ X - 1.67 × 10 ⁵	0.9976	0.0063	0.0125	
348	D	Diatalinfos	24.82	130(100)	148(43)	298(34)	0.0625 ~ 2.500	Y = 9.51 × 10 ⁵ X - 2.57 × 10 ⁵	0.9890	0.0125	0.0250	
349	D	DE-PCB 118	25.08	326(100)	254(38)	184(16)	0.0625 ~ 2.500	Y = 2.10 × 10 ⁶ X - 6.14 × 10 ⁴	0.9985	0.0063	0.0125	
350	D	4,4-Dibromobenzophenone	25.30	340(100)	259(30)	185(179)	0.1250 ~ 2.500	Y = 5.97 × 10 ⁵ X - 7.56 × 10 ⁴	0.9945	0.0125	0.0250	
351	D	Flutriafol	25.31	219(100)	164(96)	201(7)	0.1250 ~ 5.000	Y = 1.40 × 10 ⁶ X - 1.75 × 10 ⁵	0.9985	0.0125	0.0250	
352	D	Mephosfolan	25.29	196(100)	227(49)	168(60)	0.1250 ~ 5.000	Y = 9.51 × 10 ⁵ X - 2.57 × 10 ⁵	0.9957	0.0250	0.0500	
353	D	Athidathion	25.63	145(100)	330(1)	129(12)	0.1250 ~ 5.000	Y = 1.88 × 10 ⁵ X - 5.69 × 10 ³	0.9995	0.0125	0.0250	
354	D	DE-PCB 153	25.64	360(100)	290(62)	218(24)	0.0625 ~ 2.500	Y = 1.60 × 10 ⁶ X - 4.19 × 10 ⁴	0.9992	0.0063	0.0125	
355	D	Diclobutazole	25.95	270(100)	272(68)	159(42)	0.2500 ~ 10.00	Y = 1.90 × 10 ⁶ X - 5.90 × 10 ⁵	0.9966	0.0125	0.0250	
356	D	Disulfoton sulfone	26.16	213(100)	229(4)	185(11)	0.1250 ~ 5.000	Y = 1.39 × 10 ⁶ X - 1.94 × 10 ⁵	0.9981	0.0500	0.1000	
357	D	Hexythiazox	26.48	227(100)	156(158)	184(93)	0.500 ~ 20.00	Y = 3.00 × 10 ⁵ X - 1.65 × 10 ⁵	0.9991	0.0063	0.0125	
358	D	DE-PCB 138	26.84	360(100)	290(68)	218(26)	0.0625 ~ 2.500	Y = 1.31 × 10 ⁶ X - 3.38 × 10 ⁴	0.9991	0.0125	0.0250	
359	D	Triamiphos	27.02	160(100)	294(28)	251(16)						

Table 2. (continued)

No.	Group	Pesticide	Retention time, min	Quantification ion 1 ^a	Qualification ion 2 ^a	Qualification ion 3 ^a	Linear range, ng	Linear equation	Correlation coefficient (r)	LOD, mg/kg	LOQ, mg/kg	
442	E	Quizalofop-ethyl	29.05	373/299; 373/271	373/299	55	15, 30	0.0030 ~ 1,600	$Y = 1.36 \times 10^4 X - 8.92 \times 10^2$	0.9994	0.0020	0.0040
443	E	Haloxifop-2-ethoxyethyl	29.58	434/316; 434/117	434/316	50	22, 12	0.0160 ~ 3,200	$Y = 6.09 \times 10^3 X - 2.14 \times 10^2$	0.9991	0.0040	0.0080
444	E	Furathiocarb	30.26	383/195; 383/252	383/195	80	12, 33	0.0040 ~ 0.800	$Y = 1.60 \times 10^4 X + 5.73 \times 10^2$	0.9990	0.0020	0.0040
445	E	Fluazifop-butyl	30.76	384/328; 384/282	384/328	80	27, 27	0.0030 ~ 0.400	$Y = 1.14 \times 10^4 X - 1.80 \times 10^3$	0.9991	0.0040	0.0080
446	E	Flufenoxuron	31.00	489/158; 489/141	489/158	80	50, 43	0.0030 ~ 0.400	$Y = 6.59 \times 10^3 X - 9.78 \times 10^2$	0.9991	0.0040	0.0080

^a The value in parentheses is the relative abundance.

Table 3. Mobile phase program and flow rate

Time, min	Flow rate, $\mu\text{L}/\text{min}$	Water, %	Acetonitrile, %
0.00	200	70.0	30.0
10.00	200	60.0	40.0
15.00	200	40.0	60.0
30.00	200	5.0	95.0
40.00	200	5.0	95.0
40.01	200	70.0	30.0
55.00	200	70.0	30.0

and pyrethroide pesticides in fruits and vegetables by GC/MS/MS.

Recently, much attention has been given to the use of acetonitrile as a pesticide residue extraction solvent. Liao et al. (16) utilized extraction of pesticide residues with acetonitrile and salting out with sodium chloride, and they determined 143 pesticides using GC/MS to split into groups after dehydration. Lehotay et al. (17–19) conducted a systematic study on establishing a QuEChERS (quick, easy, cheap, effective, rugged, and safe) method. Extraction of pesticide residues was done with acetonitrile, salting out with MgSO_4 and NaCl , dispersive SPE with PSA (primary secondary amine) sorbent for cleanup, and GC/MS and LC/MS/MS for determination of 229 pesticides in food. Fillion et al. (20–22) analyzed 251 pesticide residues by use of an SPE cartridge for cleanup and LC. Ueno et al. (23–25) also used the previous treatment system but with addition of GPC for cleanup, and the established 3 multiresidue methods for determination of 58–87 pesticides using GC with multiple detectors.

In the past, Pang and coworkers developed 5 multiresidue methods for pyrethroid pesticides that utilized, respectively acetone–petroleum ether (26, 27), methanol (28, 29), acetone and acetonitrile (30) as extraction solvents; Florisil column cleanup; and GC-ECD, GC-MSD, and LC with an ultraviolet detector (LC-UV) for determination of 8–11 pyrethrins pesticide residues in agricultural products. The fifth method underwent an interlaboratory collaborative study, participated in by 14 laboratories from 6 countries, that was successful and led to establishment of an AOAC Official Method (30).

On the basis of the study of Fillion et al. (22), we have made appropriate modifications to the extraction and cleanup procedures and at the same time conducted a detailed study of the interferences among the product ions of more than 400 pesticides, with a new analysis mode proposed having the name "Sequential Detection Based on Time Frame and Groups." The objective achieved is that as long as the target pesticide was applicable to such an extraction and cleanup system, the number of pesticide varieties for simultaneous determination can increase without limit, thus making the multiresidue analysis operate as easily as single residue analysis. Tests proved that the method has good selectivity, relatively high sensitivity, and wide application scope, and it is suitable for the simultaneous determination of residues of 446

pesticides with samples processed only once. Presently, this method has been adopted as the national standard of the P.R. China and it is widely used for residue monitoring of 446 pesticides in more than 20 fruits and vegetables, such as apples, pears, oranges, bananas, grapes, pineapples, kiwi, cabbage, tomatoes, cucumbers, green peppers, spinach, cauliflower, celery, string beans, carrots, potatoes, lettuce, etc.

Experimental

Reagents and Materials

(a) *Solvents*.—LC grade acetonitrile and methanol; pesticide grade toluene, acetone, dichloromethane, *n*-hexane, and acetic acid.

(b) *Sodium sulfate anhydrous*.—Heated to 650°C for 4 h and keep in a desiccator.

(c) *Envi-18 SPE cartridges*.—12 mL/2.0 g, Supelco No. 57114 (State College, PA).

(d) *Envi-carb SPE cartridges*.—6 mL/0.5 g, Supelco No. 57094.

(e) *Aminopropyl Sep-Pak vac cartridges*.—3 mL/0.5 g, Waters No. WAT020840 (Milford, MA).

(f) *Pesticide standard*.—Purity ≥95% (LGC Promochem, Wesel, Germany).

(g) *Stock standard solutions*.—Accurately weigh 5–10 mg of individual pesticide standards (accurate to 0.1 mg) into a 10 mL volumetric flask. Dissolve and dilute to volume with toluene, toluene + acetone combination, dichloromethane, methanol, etc., depending upon the solubility of each individual compound solubility.

(h) *Standard mixture solutions*.—Pesticides are split into 5 different mixed standard solutions, A–E, based upon their properties and retention times. The concentration of each analyte is determined by its sensitivity on the instrument used for analysis. Standard mixtures A–D are prepared in toluene for GC/MS determination, and standard mixture E is prepared in methanol for LC/MS/MS determination. All standard mixtures are stored in the dark at 4°C and can be used for 1 month.

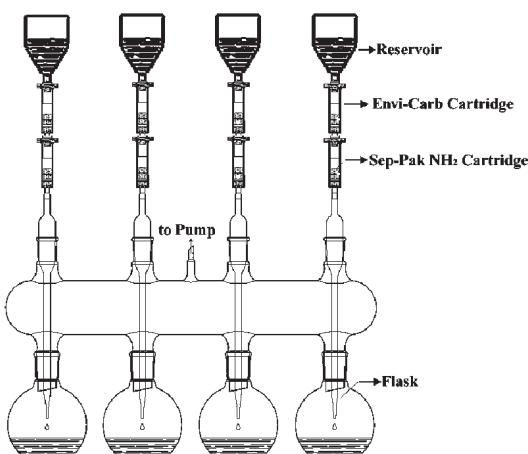


Figure 1. SPE vacuum glass assembly.

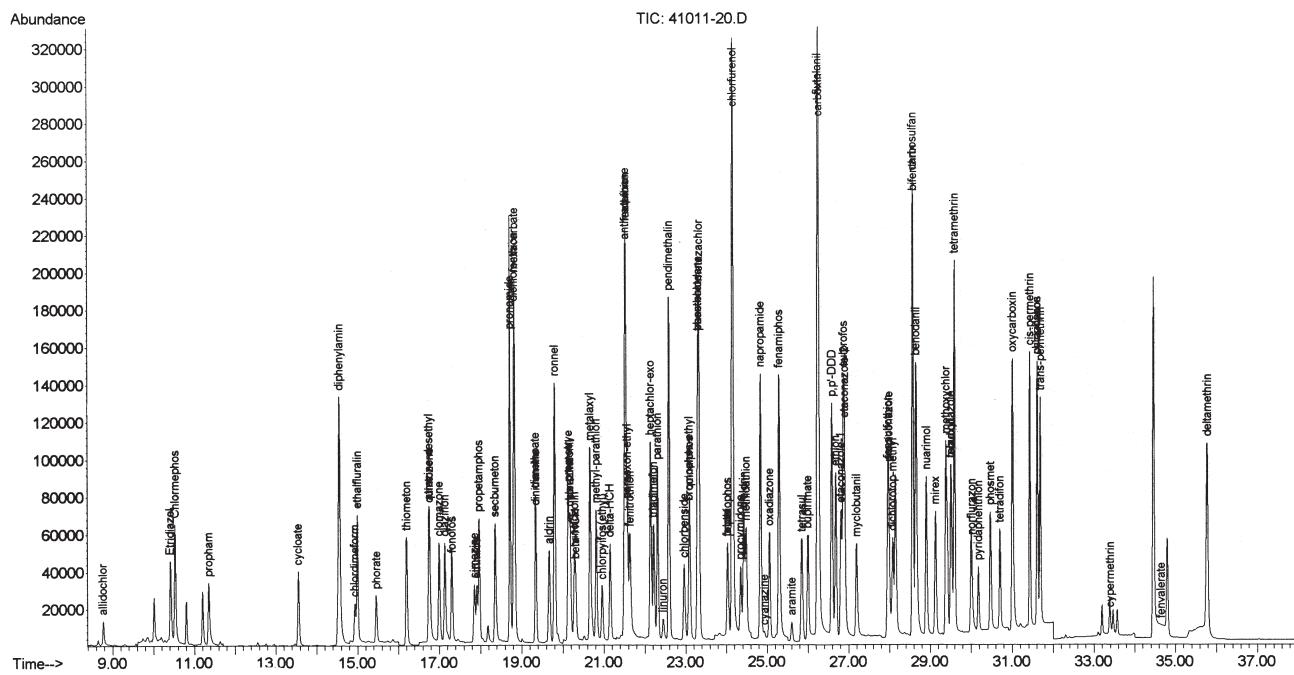


Figure 2. GC/MS chromatogram of 92 pesticides in apple samples (A group).

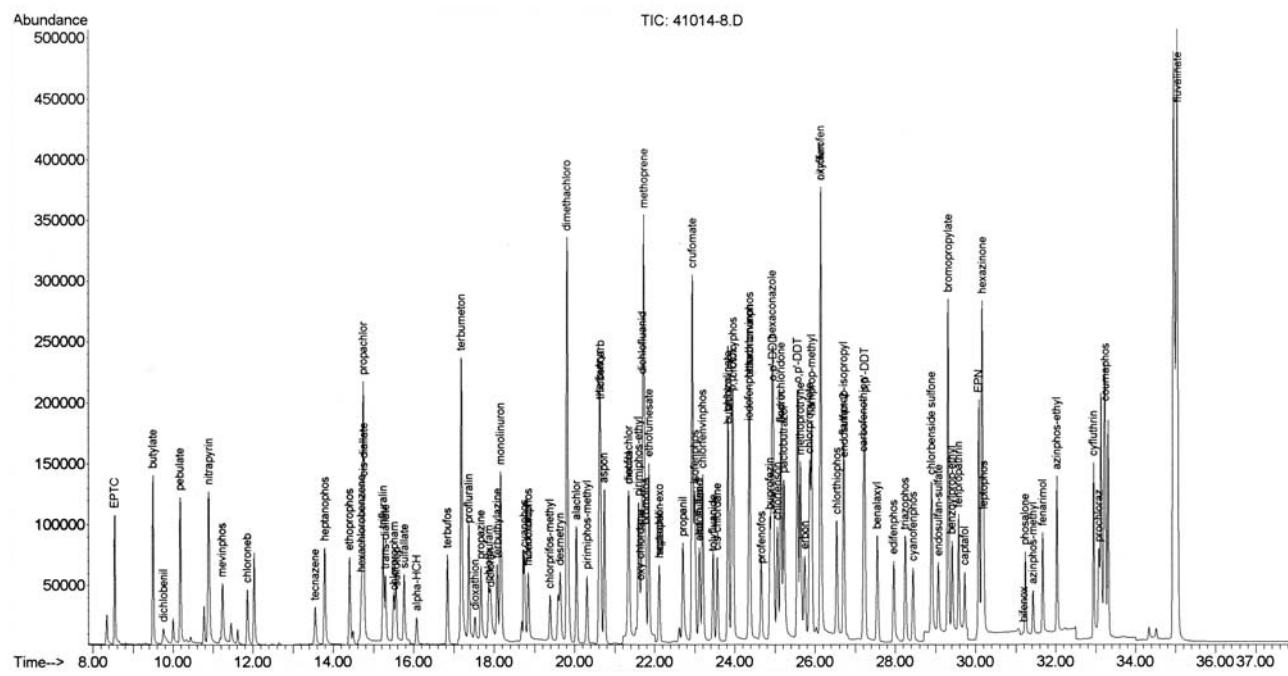


Figure 3. GC/MS chromatogram of 101 pesticides in apple samples (B group).

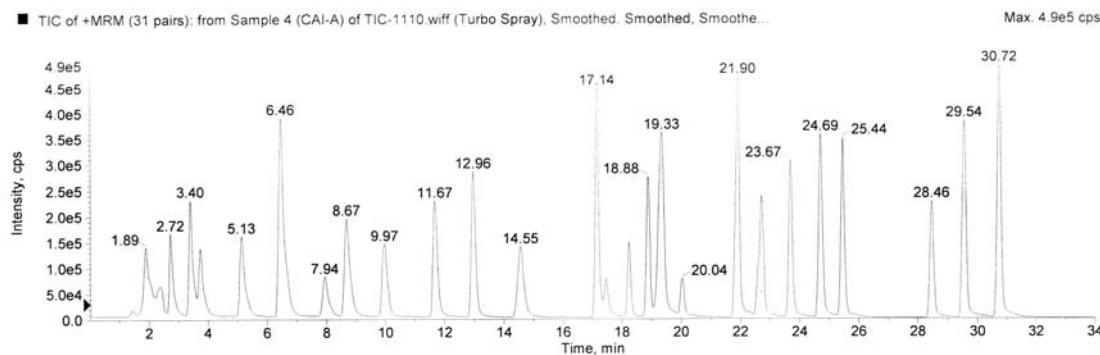


Figure 6. LC/MS/MS total ion chromatogram of standards of 30 pesticides (E group).

(i) *Internal standard solution*.—Accurately weigh 3.5 mg heptachlor epoxide into a 100 mL volumetric flask. Dissolve and dilute to volume with toluene.

(j) *Working standard mixture solution in matrix*.—Working standard mixtures A–D are prepared by diluting 40 μ L internal standard solution and adequate volume standard mixture solution to 1.0 mL with blank extract that has been taken through the method with the rest of the samples. Mix thoroughly. Working standard mixture E is prepared by diluting different volumes of standard mixture solutions with sample blank extracts. They are used for plotting the standard curve. Working standard mixture solutions in matrix must be prepared freshly.

Apparatus

(a) *GC/MS system*.—Model 6890 N gas chromatograph connected to a 5973 N MSD and equipped with a 7683 autosampler, (Agilent Technologies, Wilmington DE), and capillary column DB-1701, 30 m \times 0.25 mm \times 0.25 μ m (J&W Scientific, Folsom, CA). GC/MS operating conditions: column temperature program, 40°C hold 1 min, 30°C/min to 130°C, 5°C/min to 250°C, at 10°C/min to 300°C, hold 5 min carrier; gas, helium; purity, \geq 99.999%; flow rate, 1.2 mL/min; injection port temperature, 290°C; injection volume, 1 μ L; injection mode, splitless, purge on after 1.5 min; ionization voltage, 70 eV; ion source temperature, 230°C; GC/MS interface temperature, 280°C; selected ion monitoring (SIM)

mode. For each compound, select 1 quantifying ion and 2–3 qualifying ions. The ions selected for monitoring in each SIM segment are listed for each standard mixture in Table 1. The retention time and quantitation and qualification ions for each analyte are listed in Table 2.

(b) *LC/MS/MS system*.—Series 1100 HPLC system (Agilent Technologies) connected to an API 3000 tandem quadrupole mass spectrometer equipped with an ion sprayer interface and electrospray interface (Applied Biosystems, Foster City, CA). The column used was an Atlantis TM dC18, 3 mm, 2.1 \times 150 m (Waters). LC/MS/MS operating conditions: column temperature, 40°C; injection volume, 20 μ L; scan mode, positive ion; monitor mode, multiple reaction monitor; ion spray voltage, 5500 V; nebulizer gas, 0.076 MPa; curtain gas, 0.083 MPa; turbo ionspray gas rate, 6 L/min; ion source temperature, 350°C; monitoring ions pairs, collision energy and declustering potential as in Table 2, mobile phase progam and flow rate as in Table 3.

(c) *Homogenizer*.—T-25B (Janke & Kunkel, Staufen, Germany).

(d) *Rotary evaporator*.—Buchi EL131 (Flawil, Switzerland).

(e) *Centrifuge*.—Z 320 (B. Hermle AG, Gosheim, Germany).

(f) *Pear-shaped flask*.—200 mL.

(g) *Pipet*.—1 mL.

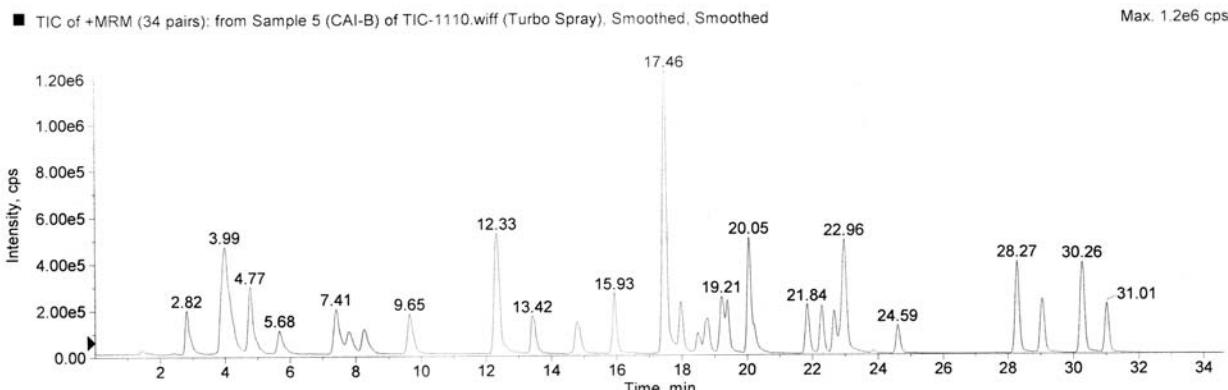


Figure 7. LC/MS/MS total ion chromatogram of standards of 33 pesticides (E group).

mixed standard prepared in blank matrix extract. The concentrations of the standard solution and the detected sample solution must be similar. Figures 2–5 are chromatograms of apples fortified with each of the 4 pesticide standard mixtures (A–D), respectively.

(c) *LC/MS/MS qualitative determination*.—In the samples determined, if the retention times of the peaks found in the sample solution chromatogram are the same as the peaks in the standard in blank matrix extract chromatogram, and the abundance ratios of multiple reaction monitoring (MRM) transitions are within the expected limits, the sample is confirmed to contain this pesticide compound.

(d) *LC/MS/MS quantitative determination*.—The external standard method is used for quantitation with standard curves for LC/MS/MS. In order to compensate for the matrix effect, quantitation is based on a series of working standard solutions prepared in blank matrix extract. The standard curves are established by injection of different concentrations of working standard mixed solutions in matrix separately. The responses of pesticides in the sample solution should be in the linear range of the instrumental detection. LC/MS/MS chromatograms of standards in apple blank matrix extracts are shown in Figures 6 and 7.

Results and Discussion

Selection of Sample Extracting Condition

Review of multiresidue pesticide methods showed that extracting solvents with higher polarities, such as acetonitrile, acetone, ethyl acetate, etc., are commonly used for extraction of pesticide residues with large differences of polarity from agricultural products of fruits and vegetables. Fillion et al. (22) determined 251 pesticides with acetonitrile extraction, Obama et al. (14) analyzed 110 pesticides with ethyl acetate extraction, and Stan et al. (4) detected over 400 pesticides with acetone extraction. Therefore, a comparative experiment was conducted to determine the extraction efficiency of these 3 solvents. Apple samples were fortified with all 446 pesticides and extracted with each solvent. Results indicated that all of the solvents were effective for the extraction of pesticides, but the acetonitrile extract was found to contain the least amount of product coextractants, such as plant pigments. Therefore, acetonitrile was selected as the extraction solvent.

Selection of Sample Cleanup Conditions

Liquid–liquid partitioning is the traditional method of cleanup, but it requires the pesticides determined to possess similar solubility features and results in relatively large consumption of the solvents. GPC is more applicable to the cleanup of lipids, waxes, and other low volatility, high molecular weight nonpolar coextractives. SPE is the cleanup method universally adopted for modern residue analysis and is used widely for residue analysis of nonfatty samples. Therefore, SPE was selected for cleanup of the acetonitrile extracts. Two SPE regimens were developed and compared: a 2-column procedure with Envi-carb + aminopropyl Sep-Pak cartridges, and a 3-column cleanup with C18 + Envi-carb + aminopropyl Sep-Pak cartridges. Results indicated the

3-column cleanup provided better removal of sample coextractives, especially plant pigments; however, some pesticides from standard mixture E for LC/MS/MS determination were lost, such as aminocarb, vamidothion, pirimicarb, imazalil, and spiroxamine. Therefore, the 3-column cleanup was used for pesticide Groups A–D and the 2-column cleanup used for pesticide Group E, with very good results.

Selection of GC/MS Conditions

For the purpose of obtaining accurate and reliable GC/MS analytical results, a scan test of each pesticide standard solution to be analyzed was conducted initially to obtain its scanning mass spectrum and retention time. One quantitative ion and 2 qualitative ions should be selected for each compound, and 3 qualitative ions should be chosen for the banned pesticides, such as HCH, DDT, nitrofen, aldrin, dieldrin, methyl-parathion, parathion, coumaphos, fenvalerate, etc. Based on the retention time of 383 pesticides, Groups A–D are formed, with about 100 pesticides included in each group. In order to ensure the sensitivity of each pesticide, all of the ions to be determined for each group should be monitored per time frame based on the peak sequence, which is what is called "Sequential Detection Based on Time Frame and Groups." Appropriate control is rendered to the number of ions within a certain time frame and dwell time, and attention should be paid to the incomplete peaking and the appearance of peaks in the first part of the time frame. The dwell time for each ion is adjustable so as to ensure that each passing chromatographic peak is of the cycling scan in the constant cycling scan time and that all of the monitored compounds possess sufficient data collection points. The change of dwell time will not affect the results of integration. Tests proved that detection procedures per group and time frame is scientifically reasonable and allows the determination of multiresidues to be as simple as single residue determination.

Selection of LC/MS/MS Conditions

Continuous infusion of each compound was carried out in positive and negative ionization modes with an ESI source. Full scan mass spectra were recorded in order to select the most abundant mass-to-charge-ratio (m/z). The relative intensity for the most abundant m/z was used to evaluate the performance of each ionization mode. The signal intensities obtained in the positive mode were high. Full scan daughter mass spectra were obtained with continuous infusion of each analyte in the product ion scan mode, keeping Q1 locked on the m/z value corresponding to the protonated molecule. The most abundant product ion for each compound was chosen for LC/MS/MS analysis in the MRM mode. The transition ions are listed in Table 2. For each analyte, the values of the voltages applied to the sampling cone, focusing lenses, collision cell, and quadrupoles were optimized in the MRM mode by continuous infusion in order to achieve the highest sensitivity possible. For LC/MS/MS analysis, optimization of the nebulizing gas, auxiliary gas, and curtain gas pressure further improved the sensitivity. Identification of the target analytes in unknown samples was

based on LC retention time compared to that of a standard and the unique combination of a precursor product ion.

Linear Range, Limit of Detection (LOD), and Limit of Quantitation (LOQ)

Under the conditions of GC/MS and LC/MS/MS selected, determination of the linear range of 446 pesticides was conducted, with the results listed in Table 2. In the linear range of each pesticide, the linear correlation coefficient (*r*) equals or is greater than 0.956, among which *r* values over 0.990 account for 94% of the fortification concentration giving a signal-to-noise ratio (S/N) ≥ 5 for a pesticide is regarded as its LOD, and the fortification concentration giving an S/N ≥ 10 is the LOQ. LOD and LOQ values of 446 pesticides are tabulated in Table 2.

Recoveries and Precision

Fortification recovery experiments were conducted at high, medium, and low levels on 3 kinds of fruits (apples, grapes, and oranges) and 3 varieties of vegetables (cabbages, tomatoes, and celeries). Samples were fortified with pesticide mixes A–E and allowed to stand for 30 min so that all of the pesticides are absorbed thoroughly by samples before making the analysis. The results of the fortification recovery studies for all 446 pesticides from the 6 selected commodities at 3 fortification levels are shown in Table 4. Dixon inspection shows that there are 177 aberrant values in the 8020 recovery data, accounting for 2.2%, with average recoveries falling between 55.0–133.8%, of which 60–120% make up 99.0%. The relative standard deviation (RSD) is between 2.1–39.1%, of which 2.1–25.0% account for 96.0%. Therefore, it can be seen that the method has good accuracy and repeatability.

Applicability of the Method

For the purpose of confirming the applicability of the method for analysis of different fruits and vegetables, fortification recovery tests were conducted on more than 20 samples, such as apples, pears, tangerines, oranges, bananas, grapes, kiwi, cabbage, tomatoes, cucumbers, green peppers, leeks, onions, cauliflower, celery, string beans, carrots, potatoes, and lettuce. All the fortification recoveries were relatively good except for leeks and onions, which gave poor results due to the relatively high interferences. This demonstrates that the method has wide applicability for samples of fruits and vegetables.

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