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Overview

Development of simultaneous determination of pesticide residues in food by LC-MS/MS.

Introduction

In order to protect the food safety, it is important to establish detection criteria of pesticide residues and methods to improve the accuracy for measuring the concentration of the targets. In Japan, the detection criteria of pesticide residues are established as the Positive List System by the Ministry of Health, Labor and Welfare, as well as the standard test methods.

For monitoring of pesticide by LC-MS/MS, recovery rate should be the critical issue in addition to sensitivity. Generally, standard addition method as well as

matrix-matched calibration curve are useful techniques rather than absolute calibration method in order to reduce matrix effects; however, these techniques are not always appropriate methods since each sample requires its independent calibration curve, respectively, for a wide variety of samples.

In this report, we introduce the results of investigation for basic parameters around the ESI ionization to avoid matrix effects and to maximize recovery rate of target pesticides using absolute calibration methods.

Methods and Materials

The test blank matrix solution (vegetable extract such as carrot) was prepared by a solid-phase extraction technique with QuEChERS (STQ method, performed by the Institute of Public Health in Sagamihara city, Kanagawa, Japan). Pesticides mixture solutions PL-7-2, PL-14-2 and PL-15-1 (FUJIFILM Wako Pure Chemical) were used as reference standards. Range of calibration curve for standard concentrations were set from 0.1 to 50 ng/mL by diluting with acetonitrile. The pesticides determination was performed using a triple quadrupole mass spectrometer LCMS-8050 equipped with Nexera[™] X2 UHPLC (Shimadzu).

Chromatographic separation was performed by YMC-Triart C18 reversed phase column with mobile phase as 5 mmol/L ammonium acetate and methanol containing 5 mmol/L ammonium acetate. The measurement was performed by MRM, positive and negative ion quantities simultaneously with electrospray ionization method, and the dwell time was set to 5 to 200 msec for each compounds. Analytes were loaded into the mass spectrometer at 2 to 21 minutes using a flow switching valve.

UHPLC conditions (Nexera [™] X2 system)		
Column	: Shim-pack Scepter C18-120 (100 mm x 2.0 mm, 1.9 μm)	
Mobile phase A	: 5 mmol/L Ammonium acetate-water	
Mobile phase B	: 5 mmol/L Ammonium acetate-Methanol	
Flow rate	: 0.2 mL/min (0-21 min, 27.01-32min), 0.6 mL/min (21.01-27 min)	
	or 0.4 mL/min (0-21 min, 27.01-32min), 0.6 mL/min (21.01-27 min)	
Time program	: B conc. 3% (0 min) → 10% (2 min) → 55% (6 min) → 100% (21-26 min) → 3% (26.01-32 min)	
Column temp.	: 40 °C	
Injection vol.	: 5 μL	
Rince R0	: Water	
Rince R1	: Methanol / Acetone / IPA = 1 / 1 / 1 including 0.1% Formic acid	
Rince R2	: 5 mmol/L Oxalic Acid Dihydrate-Methanol	
Needle rinse program	: inside) R1 \rightarrow R2 \rightarrow R0, 1000 μ L each, outside) R1	
MS conditions (LCMS	-8050)	
Ionization	: ESI, Positive/Negative simultaneous MRM mode	
DL temp.	: 150 °C	
Interface temp.	: 200 °C	
Heat block temp.	: 500 °C	
Nebulizer gas	: 2.0 L/min	
Heating gas	: 10 L/min	
Drying gas	: 10 L/min	
Probe position	: 2 mm or 3 mm	



High Speed Mass Spectrometer Ultra Fast Polarity Switching -5 msec Ultra Fast MRM -Max.555 transition/sec

Simultaneous determination of pesticide residues in vegetable extract by liquid chromatograph tandem mass spectrometry for high recovery rate

No.	Name	Retention Time (min)	Polarity	Transition	
1	Abamectin B1a	17.675	+	890.30→305.30	
2	Acibenzolar-S-methyl	10.270	+	210.90→136.05	
3	Aldicarb	6.637	+	208.20→115.85	
4	Aldicarb-sulfone (Aldoxycarb)	4.284	+	240.10→ 86.20	
5	Anilofos	12.568	+	368.00→125.00	
6	Azamethiphos	7.163	+	325.00→182.90	
7	Azinphos-methyl	9.566	+	318.00→132.05	
8	Azoxystrobin	10.056	+	404.00→371.95	
9	Bendiocarb	7.376	+	224.20→109.10	
10	Benzofenap	14.541	+	431.15→105.25	
11	Boscalid	10.259	+	343.00→306.95	
12	Butafenacil	11.240	+	492.10→330.85	
13	Carbaryl (NAC)	7.820	+	202.10→145.10	
14	Carbofuran	7.393	+	222.10→123.15	
15	Carpropamid	12.651	+	334.10→139.10	
16	Chloridazon	6.085	+	222.10→104.10	
17	Chloroxuron	10.986	+	291.10→ 72.15	
18	Chromafenozide	11.379	+	395.20→175.15	
19	Clofentezine	13.785	+	303.00→138.15	
20	Cloquintocet-mexyl	15.210	+	336.10→237.90	
21	Clothianidin	5.642	+	250.00→132.05	
22	Cumyluron	10.875	+	303.20→185.10	
23	Cyazofamid	11.655	+	325.00→108.10	
24	Cycloate	13.541	+	216.10→154.00	
25	Cycloprothrin	16.851	+	499.00→181.10	
26	Cyflufenamid	13.496	+	413.10→295.05	
27	Cyprodinil	12.797	+	226.10→108.00	
28	Daimuron (Dymron)	10.654	+	269.25→151.15	
29	Diflubenzuron	11.924	+	311.00→158.10	
30	Dimethirimol	8.199	+	210.20→ 71.00	
31	Directlean 1 (5 7)	10.113		202.12	
32	– Dimethomorph (E, Z)	10.546	+	388.10→301.00	
33	Diuron (DCMU)	8.894	+	233.00→ 72.10	
34	Epoxiconazole	11.544	+	330.00→121.10	
35	Fenamidone	10.103	+	312.10→236.00	
36	Fenoxaprop-ethyl	14.620	+	362.10→287.90	
37	Fenoxycarb	12.169	+	302.10→ 88.00	
38		15.640			
39	– Fenpyroximate (E, Z)	16.876	+	422.30→366.20	
40		10.243			
41	– Ferimzone (E, Z)	10.405	+	255.20→ 91.05	
42	Flufenacet	11.269	+	364.10→152.05	

Table 1. MRM transitions of pesticides.

Excellence in Science

Simultaneous determination of pesticide residues in vegetable extract by liquid chromatograph tandem mass spectrometry for high recovery rate

82 Teflubenzuron 15.282 - 378.80→339.00 83 Tetrachlorvinphos (CVMP) 12.101 + 366.90→127.15	No.	Name	Retention Time (min)	Polarity	Transition
45 Furametpyr 8.531 + 334.10-+157.10 46 Furametpyr 14.816 + 333.20-+195.00 47 Hexelhururon 14.647 - 48.880-+43.00 48 Hexythiazox 15.683 + 293.10-+228.00 49 Imazali 12.430 + 297.10-+159.05 50 Indacoprid 5.068 + 226.10-174.95 51 Indacarb 11.161 + 528.110-174.95 52 Indoxarb 11.131 + 321.20-+119.15 54 Isoaflutale 8.748 + 360.10225.100 55 Linuron 9.924 + 248.80-+132.05 56 Lufenuron 15.433 - 568.90-339.00 57 Mepanipyrim 11.498 + 221.01-35.10 58 Methoazato 9.990 + 226.10-121.10 59 Methoazato 8.639 + 222.10-150.10 54 Monolinuron 8.06	43	Flufenoxuron	16.413	+	489.00→158.10
46 Fursthiocarb 14.816 + 383.20195.00 47 Heardihumuron 14.647 - 458.80-439.00 48 Hexythiazox 15.683 + 292.10-159.05 50 Imidadoprid 5.608 + 296.10-+174.95 51 Indoxfan 11.140 + 341.10-+175.15 52 Indoxfan 11.131 + 221.0-303.00 53 Iprovalicarb 11.131 + 222.10-19.15 54 Isoxaflutole 8.748 + 268.0-192.25 56 Luferuron 15.943 - 508.80-323.00 57 Mepanjøyrim 11.498 + 224.10-+77.00 58 Metholocarb 9.990 + 226.10-+121.10 59 Methocarb 9.990 + 226.10-+121.10 61 Methogrefeozide 10.828 + 369.20-+139.15 62 Monolinuron 8.060 + 215.10-+91.10 63 Naproamilde	44	Fluridone	9.828	+	330.10→309.00
47 Hexaflumuron 14.647 - 458.80439.00 48 Hexythiacox 15.663 + 353.10-228.00 49 Imazalii 12.430 + 297.10-159.05 50 ImidacOprid 5.608 + 256.10-174.95 51 Indanofan 11.640 + 341.10-175.15 52 Indoxacrab 11.131 + 321.20-203.00 53 Iprovalicarb 11.131 + 321.0-203.00 54 Ikoxaflutole 8.748 + 306.10-251.00 55 Lineron 9.924 + 248.80-1482.05 56 Luferuron 8.639 + 222.10-150.10 58 Methalexythiazoron 8.639 + 222.10-150.10 59 Methalexythiazoron 8.639 + 222.10-150.10 59 Methalexythiazoron 8.639 + 222.10-150.10 59 Methalexythiazoron 8.639 + 222.10-150.10 50 Org	45	Furametpyr	8.531	+	334.10→157.10
48 Heythiazox 15.683 + 353.10228.00 49 Imazali 12.430 + 257.10159.05 50 Inidacloprid 5.008 + 225.10173.95 51 Indanofan 11.640 + 341.10175.15 52 Indoxacrb 11.131 + 321.20119.15 54 Isoxaflutole 8.748 + 360.10251.00 55 Linron 9.924 + 248.80182.05 56 Lufenuron 15.943 - 50.80-9.330 57 Mepanipyrin 11.438 + 222.10150.10 58 Metholexthiazuron 8.639 + 222.10-150.10 59 Metholocarb 9.990 + 226.10-151.01 50 Metholocarb 9.990 + 226.10-150.10 51 Metholocarb 9.990 + 226.10-150.10 52 Monolinuron 8.669 + 221.51-9 64 Monolinuron 1	46	Furathiocarb	14.816	+	383.20→195.00
49 Imazalii 12.430 + 297.10–159.05 50 Imidacloprid 5.608 + 256.10–174.95 51 Indoxacab 11.640 + 341.10–175.15 52 Indoxacab 11.131 + 528.10–203.00 53 Iprovalicarb 11.131 + 321.20–119.15 54 Isoxaflucile 8.748 + 268.00–122.00 55 Linuron 9.924 + 248.80–182.05 56 Luferuron 15.943 - 508.90–339.00 57 Mepanipyim 11.498 + 224.10–47.00 58 Methaberzthiazuron 8.639 + 222.10–150.10 59 Methiocarb 9.990 + 226.10–121.10 60 Methonylenozide 10.828 + 369.20–149.15 61 Methoylenozide 10.828 + 292.25–171.25 64 Novaluron 14.782 + 493.00–158.00 65 Oyzaln <	47	Hexaflumuron	14.647	-	458.80→439.00
50 Imidacloprid 5.608 + 256.10–174.95 51 Indanofan 11.640 + 341.10–175.15 52 Indoxacab 14.161 + 528.10–203.00 53 Iprovalicarb 11.131 + 321.20–119.15 54 Isoxallutole 8.748 + 360.10–251.00 55 Linuron 9.924 + 248.80–182.05 56 Lufenuron 15.943 - 508.90–339.00 57 Mepanipyim 11.498 + 222.10–150.10 58 Methocarb 9.990 + 222.10–150.10 59 Methooxitb 9.990 + 226.10–121.10 60 Methonyl 4.804 + 163.00–87.90 61 Methoxyferozide 10.828 + 369.20–149.15 62 Monolinuron 8.060 + 291.25–171.25 64 Movaluron 14.782 + 493.00–158.00 65 Oryzatio 13.575 <td>48</td> <td>Hexythiazox</td> <td>15.683</td> <td>+</td> <td>353.10→228.00</td>	48	Hexythiazox	15.683	+	353.10→228.00
51 Indanofan 11.640 + 341.10175.15 52 Indoxacarb 14.161 + 528.10203.00 53 Iprovalicarb 11.131 + 321.20119.15 54 Isoxaflutole 8.748 + 360.10251.00 55 Linuron 9.924 + 248.80182.05 56 Lufenuron 15.943 - 508.90339.00 57 Mepanipyrim 11.498 + 222.10150.10 58 Methabenzthiazuron 8.639 + 222.10150.10 59 Methodyfenozide 10.828 + 369.20-149.15 61 Methoxyfenozide 10.828 + 369.22-149.15 62 Monolinuron 8.060 + 215.10-9.91.0 63 Naproanlide 12.093 + 292.25-171.25 64 Novaluron 14.782 + 493.00-158.00 65 Oryzali 13.575 + 329.1028.00 66 Oxanichom	49	Imazalil	12.430	+	297.10→159.05
52 Indoxacarb 14.161 + 528.10-203.00 53 Iprovalicarb 11.131 + 321.20-119.15 54 Isovaflutole 8.748 + 360.10-251.00 55 Linuron 9.924 + 248.80-182.05 56 Lufenuron 15.943 - 508.90-339.00 57 Mepanipyrim 11.498 + 224.10-77.00 58 Methabenzthiazuron 8.639 + 222.10-150.10 59 Methoryf 4.804 + 163.00-87.90 61 Methoryfenzide 10.828 + 292.25-112.10 62 Monolinuron 8.660 + 215.10-99.10 63 Naproaniide 12.093 + 292.25-112.55 64 Novaluron 14.782 + 493.00-158.00 65 Oryzalin 11.329 + 327.10-72.10 67 Oxazicomefone 14.670 + 376.20-190.15 68 Oxycarboxin	50	Imidacloprid	5.608	+	256.10→174.95
53 Iprovalicarb 11.131 + 321.20119.15 54 Isoxaflutole 8.748 + 360.10251.00 55 Linuron 9.924 + 248.80182.05 56 Lufenuron 15.943 - 508.90339.00 57 Megnaipyrim 11.498 + 224.10-+77.00 58 Methaberzthiazuron 8.639 + 222.10-+150.10 59 Methosytenozide 10.828 + 369.20-+149.15 61 Methoxytenozide 10.828 + 369.20-+149.15 62 Monolinuron 8.060 + 22.15-171.25 64 Novaluon 14.782 + 493.00-+158.00 65 Oryzalin 11.329 + 327.1072.10 66 Oxamyl 4.519 237.10-72.10 67 Oxazicomefone 14.670 + 362.0-190.15 68 Oxycarboxin 6.226 + 228.10-175.00 70 Pencycuron 13.57	51	Indanofan	11.640	+	341.10→175.15
54 Isoxaflutole 8.748 + 360.10251.00 55 Linuron 9.924 + 248.80182.05 56 Lufenuron 15.943 - 508.90339.00 57 Mepanipyrim 11.498 + 22.10175.00 58 Methabenzthiazuron 8.639 + 222.10-1150.10 59 Methosytenozide 10.828 + 369.20-149.15 60 Methoxylenozide 10.828 + 369.20-149.15 61 Methoxylenozide 10.828 + 369.20-149.15 62 Monolinuron 8.060 + 215.10-4.99.10 63 Naproanilide 12.093 + 292.25-171.25 64 Novaluron 14.782 + 493.00-158.00 65 Oryzalin 11.329 + 37.10-72.80 66 Oxanyl 4.519 + 237.10-72.00 67 OxaziComefone 14.670 + 366.0-175.00 68 Oxycarboxin<	52	Indoxacarb	14.161	+	528.10→203.00
55 Linuron 9.924 + 248.80-182.05 56 Lufenuron 15.943 - 508.90-339.00 57 Mepanipyrim 11.498 + 224.10-77.00 58 Methabenzthiazuron 8.639 + 222.10-150.10 59 Methocarb 9.990 + 226.10-121.10 60 Methoryl 4.804 + 163.00-87.90 61 Methoxyfenozide 10.828 + 369.20-149.15 62 Monolinuron 8.060 + 215.10-9.91.0 63 Naproanilide 12.093 + 292.25-171.25 64 Novaluron 14.782 + 493.00-158.00 65 Oryzalin 11.329 + 327.10-72.10 66 Oxamyl 4.519 + 237.10-72.10 67 Oryzaliomerone 14.670 + 362.0-191.50 68 Orycarboxin 6.226 + 268.10-175.00 70 Pencycuron 13.57	53	Iprovalicarb	11.131	+	321.20→119.15
56 Lufenuron 15.943 - 508.90-339.00 57 Mepanipyrim 11.498 + 224.10 77.00 58 Methabenzthiazuron 8.639 + 222.10150.10 59 Methiocarb 9.990 + 226.10121.10 60 Methoryl 4.804 + 163.00-87.90 61 Methoxyfenozide 10.828 + 369.20-419.15 62 Monolinuron 8.060 + 215.10-99.10 63 Naproanilide 12.093 + 292.5-171.25 64 Novaluron 14.782 + 493.00-158.00 65 Oryzalin 11.329 + 347.10-288.00 66 Oxamyl 4.519 + 237.10-72.10 67 Oxaziclomefone 14.670 + 378.20-190.15 68 Oxycarboxin 6.226 + 288.10-175.00 70 Pencycuron 13.575 + 329.10-125.00 71 Prinoar	54	Isoxaflutole	8.748	+	360.10→251.00
57 Mepanipyrim 11.498 + 224.10→ 77.00 58 Methabenzthiazuron 8.639 + 222.10→150.10 59 Methiocarb 9.990 + 226.10→121.10 60 Methoryl 4.804 + 163.00→ 87.90 61 Methoxylenozide 10.828 + 369.20→149.15 62 Monolinuron 8.060 + 215.10→ 99.10 63 Naproanilide 12.093 + 292.25→171.25 64 Novaluron 14.782 + 493.00→158.00 65 Oryzalin 11.329 + 237.10→ 72.10 66 Oxamyl 4.519 + 237.10→ 72.10 67 Oxaziclomefone 14.670 + 362.0→190.15 68 Oxycarboxin 6.226 + 268.10→175.00 70 Pentoxazone 14.788 + 371.10→286.00 71 Pirimicarb 8.351 + 239.20→ 72.00 72 Propaquizafop	55	Linuron	9.924	+	248.80→182.05
58 Methabenzthiazuron 8.639 + 222.10-150.10 59 Methiocarb 9.990 + 226.10-121.10 60 Methonyl 4.804 + 163.00-87.90 61 Methoxyfenozide 10.828 + 369.20-149.15 62 Monolinuron 8.060 + 22.5-171.25 64 Novaluron 14.782 + 493.00-158.00 65 Oryzalin 11.329 + 347.10-288.00 66 Oxamyl 4.519 + 372.10-72.10 67 Oxaziclomefone 14.670 + 376.20-190.15 68 Oxycarboxin 6.226 + 28.10-175.00 69 Pencycuron 13.575 + 329.10-125.00 70 Pentoxazone 14.788 + 371.10-286.00 71 Pirimicarb 8.351 + 239.20-72.00 72 Propaquizafop 15.067 + 444.10-100.15 73 Pyrazolynate <t< td=""><td>56</td><td>Lufenuron</td><td>15.943</td><td>-</td><td>508.90→339.00</td></t<>	56	Lufenuron	15.943	-	508.90→339.00
59 Methiocarb 9.990 + 226.10-+121.10 60 Methomyl 4.804 + 163.00->87.90 61 Methoxyfenozide 10.828 + 369.20->149.15 62 Monolinuron 8.060 + 215.10->99.10 63 Naproanilide 12.093 + 292.25->171.25 64 Novaluron 14.782 + 493.00->158.00 65 Oryzalin 11.329 + 347.10->288.00 66 Oxamyl 4.519 + 237.10->72.10 67 Oxaziclomefone 14.670 + 376.20->190.15 68 Oxycarboxin 6.226 + 268.10->175.00 70 Pentoxazone 14.788 + 371.10->286.00 71 Pirimicarb 8.351 + 239.20->72.00 72 Propaquizafop 15.067 + 449.10->101.15 73 Pyrazolynate 13.657 + 439.10-> 91.15 74 Pyriftalid	57	Mepanipyrim	11.498	+	224.10→ 77.00
60 Methomyl 4.804 + 163.0087.90 61 Methoxyfenozide 10.828 + 369.20149.15 62 Monolinuron 8.060 + 215.1099.10 63 Naproanilide 12.093 + 292.25171.25 64 Novaluron 14.782 + 493.00158.00 65 Oryzalin 11.329 + 347.10288.00 66 Oxamyl 4.519 + 237.1072.10 67 Oxaziclomefone 14.670 + 376.20190.15 68 Oxycarboxin 6.226 + 268.10175.00 69 Pencycuron 13.575 + 329.10125.00 70 Pentoxazone 14.788 + 371.10286.00 71 Pirimicarb 8.351 + 239.2072.00 72 Propaquizafop 15.067 + 439.1091.15 73 Pyrazolynate 13.657 + 439.1091.15 74 Pyriftalid	58	Methabenzthiazuron	8.639	+	222.10→150.10
61 Methoxyfenozide 10.828 + 369.20->149.15 62 Monolinuron 8.060 + 215.10->99.10 63 Naproanilide 12.093 + 292.25->171.25 64 Novaluron 14.782 + 493.00->158.00 65 Oryzalin 11.329 + 347.10->288.00 66 Oxamyl 4.519 + 237.10->72.10 67 Oxaziclomefone 14.670 + 376.20->190.15 68 Oxycarboxin 6.226 + 268.10->175.00 69 Pencycuron 13.575 + 329.10->125.00 70 Pentoxazone 14.788 + 371.10->286.00 71 Pirimicarb 8.351 + 239.20->72.00 72 Propaquizafop 15.067 + 444.10-=100.15 73 Pyrazolynate 13.657 + 439.10->91.15 74 Pyriftaid 9.746 + 319.10->139.10 75 Quizalofop-et	59	Methiocarb	9.990	+	226.10→121.10
62 Monolinuron 8.060 + 215.10-+ 99.10 63 Naproanilide 12.093 + 292.25-171.25 64 Novaluron 14.782 + 493.00-158.00 65 Oryzalin 11.329 + 347.10-288.00 66 Oxamyl 4.519 + 237.10-72.10 67 Oxaziclomefone 14.670 + 376.20-190.15 68 Oxycarboxin 6.226 + 268.10-175.00 69 Pencycuron 13.575 + 329.10-125.00 70 Pentoxazone 14.788 + 371.10-286.00 71 Pirimicarb 8.351 + 239.20-72.00 72 Propaquizafop 15.067 + 444.10-100.15 73 Pyrazolynate 13.657 + 319.10-313.10 74 Pyrifalid 9.746 + 319.10-328.90 75 Quizalofop-ethyl 14.641 + 373.10-298.90 76 Silafluofen	60	Methomyl	4.804	+	163.00→ 87.90
63 Naproanilide 12.093 + 292.25→171.25 64 Novaluron 14.782 + 493.00→158.00 65 Oryzalin 11.329 + 347.10→288.00 66 Oxamyl 4.519 + 237.10→72.10 67 Oxaziclomefone 14.670 + 376.20→190.15 68 Oxycarboxin 6.226 + 268.10→175.00 69 Pencycuron 13.575 + 329.10→125.00 70 Pentoxazone 14.788 + 371.10→286.00 71 Pirimicarb 8.351 + 239.20→72.00 72 Propaquizafop 15.067 + 444.10→100.15 73 Pyrazolynate 13.657 + 439.10→ 91.15 74 Pyriftalid 9.746 + 319.10→139.10 75 Quizalofop-ethyl 14.641 + 373.10→298.90 76 Silafluofen 19.913 + 426.30→287.15 77 Simeconazole	61	Methoxyfenozide	10.828	+	369.20→149.15
64 Novaluron 14.782 + 493.00→158.00 65 Oryzalin 11.329 + 347.10→288.00 66 Oxamyl 4.519 + 237.10→72.10 67 Oxaziclomefone 14.670 + 376.20→190.15 68 Oxycarboxin 6.226 + 268.10→175.00 69 Pencycuron 13.575 + 329.10→125.00 70 Pentoxazone 14.788 + 371.10→286.00 71 Pirimicarb 8.351 + 239.20→72.00 72 Propaquizafop 15.067 + 444.10→100.15 73 Pyrazolynate 13.657 + 439.10→91.15 74 Pyrifalid 9.746 + 319.10→139.10 75 Quizalofop-ethyl 14.641 + 373.10→298.90 76 Silafluofen 19.913 + 426.30→287.15 77 Simeconazole 11.078 + 294.10→ 69.95 78 Spinosyn A	62	Monolinuron	8.060	+	215.10→ 99.10
65 Oryzalin 11.329 + 347.10→288.00 66 Oxamyl 4.519 + 237.10→ 72.10 67 Oxaziclomefone 14.670 + 376.20→190.15 68 Oxycarboxin 6.226 + 268.10→175.00 69 Pencycuron 13.575 + 329.10→125.00 70 Pentoxazone 14.788 + 371.10→286.00 71 Pirimicarb 8.351 + 239.20→72.00 72 Propaquizafop 15.067 + 444.10→100.15 73 Pyrazolynate 13.657 + 439.10→91.15 74 Pyriftalid 9.746 + 319.10→139.10 75 Quizalofop-ethyl 14.641 + 373.10→298.90 76 Silafluofen 19.913 + 426.30→287.15 77 Simeconazole 11.078 + 294.10→ 69.95 78 Spinosyn A 18.633 + 732.60→142.20 79 Spinosyn D	63	Naproanilide	12.093	+	292.25→171.25
66 Oxamyl 4.519 + 237.10→72.10 67 Oxaziclomefone 14.670 + 376.20→190.15 68 Oxycarboxin 6.226 + 268.10→175.00 69 Pencycuron 13.575 + 329.10→125.00 70 Pentoxazone 14.788 + 371.10→286.00 71 Pirimicarb 8.351 + 239.20→72.00 72 Propaquizafop 15.067 + 444.10→100.15 73 Pyrazolynate 13.657 + 439.10→ 91.15 74 Pyriftalid 9.746 + 319.10→139.10 75 Quizalofop-ethyl 14.641 + 373.10→298.90 76 Silafluofen 19.913 + 426.30→287.15 77 Simeconazole 11.078 + 294.10→69.95 78 Spinosyn A 18.633 + 746.60→142.20 79 Spinosyn D 18.633 + 353.20→133.10 81 Tebuthiuron	64	Novaluron	14.782	+	493.00→158.00
67 Oxaziclomefone 14.670 + 376.20→190.15 68 Oxycarboxin 6.226 + 268.10→175.00 69 Pencycuron 13.575 + 329.10→125.00 70 Pentoxazone 14.788 + 371.10→286.00 71 Primicarb 8.351 + 239.20→72.00 72 Propaquizafop 15.067 + 444.10→100.15 73 Pyrazolynate 13.657 + 439.10→91.15 74 Pyriftalid 9.746 + 319.10→139.10 75 Quizalofop-ethyl 14.641 + 373.10→298.90 76 Silafluofen 19.913 + 426.30→287.15 77 Simeconazole 11.078 + 294.10→ 69.95 78 Spinosyn A 18.645 + 353.20→133.10 79 Spinosyn D 18.633 + 353.20→133.10 81 Tebuthiuron 7.575 + 229.10→172.00 82 Teflubenzuron<	65	Oryzalin	11.329	+	347.10→288.00
68 Oxycarboxin 6.226 + 268.10→175.00 69 Pencycuron 13.575 + 329.10→125.00 70 Pentoxazone 14.788 + 371.10→286.00 71 Pirimicarb 8.351 + 239.20→72.00 72 Propaquizafop 15.067 + 444.10→100.15 73 Pyrazolynate 13.657 + 439.10→91.15 74 Pyriftalid 9.746 + 319.10→139.10 75 Quizalofop-ethyl 14.641 + 373.10→298.90 76 Silafluofen 19.913 + 426.30→287.15 77 Simeconazole 11.078 + 294.10→ 69.95 78 Spinosyn A 18.045 + 732.60→142.20 79 Spinosyn D 18.633 + 353.20→133.10 81 Tebuthiuron 7.575 + 229.10→172.00 82 Teflubenzuron 15.282 - 378.80→339.00 83 Tetrachlorvinp	66	Oxamyl	4.519	+	237.10→ 72.10
69 Pencycuron 13.575 + 329.10→125.00 70 Pentoxazone 14.788 + 371.10→286.00 71 Pirimicarb 8.351 + 239.20→ 72.00 72 Propaquizafop 15.067 + 444.10→100.15 73 Pyrazolynate 13.657 + 439.10→ 91.15 74 Pyriftalid 9.746 + 319.10→139.10 75 Quizalofop-ethyl 14.641 + 373.10→298.90 76 Silafluofen 19.913 + 426.30→287.15 77 Simeconazole 11.078 + 294.10→ 69.95 78 Spinosyn A 18.645 + 732.60→142.20 79 Spinosyn D 18.633 + 353.20→133.10 81 Tebuthiuron 7.575 + 229.10→172.00 82 Teflubenzuron 15.282 - 378.80→339.00 83 Tetrachlorvinphos (CVMP) 12.101 + 366.90→127.15	67	Oxaziclomefone	14.670	+	376.20→190.15
70 Pentoxazone 14.788 + 371.10→286.00 71 Pirimicarb 8.351 + 239.20→72.00 72 Propaquizafop 15.067 + 444.10→100.15 73 Pyrazolynate 13.657 + 439.10→91.15 74 Pyriftalid 9.746 + 319.10→139.10 75 Quizalofop-ethyl 14.641 + 373.10→298.90 76 Silafluofen 19.913 + 426.30→287.15 77 Simeconazole 11.078 + 294.10→ 69.95 78 Spinosyn A 18.045 + 732.60→142.20 79 Spinosyn D 18.633 + 353.20→133.10 81 Tebuthiuron 7.575 + 229.10→172.00 82 Teflubenzuron 15.282 - 378.80→339.00 83 Tetrachlorvinphos (CVMP) 12.101 + 366.90→127.15	68	Oxycarboxin	6.226	+	268.10→175.00
71 Pirimicarb 8.351 + 239.20→ 72.00 72 Propaquizafop 15.067 + 444.10→100.15 73 Pyrazolynate 13.657 + 439.10→ 91.15 74 Pyriftalid 9.746 + 319.10→139.10 75 Quizalofop-ethyl 14.641 + 373.10→298.90 76 Silafluofen 19.913 + 426.30→287.15 77 Simeconazole 11.078 + 294.10→ 69.95 78 Spinosyn A 18.045 + 732.60→142.20 79 Spinosyn D 18.633 + 746.60→142.10 80 Tebufenozide 12.083 + 353.20→133.10 81 Tebuthiuron 7.575 + 229.10→172.00 82 Teflubenzuron 15.282 - 378.80→339.00 83 Tetrachlorvinphos (CVMP) 12.101 + 366.90→127.15	69	Pencycuron	13.575	+	329.10→125.00
72 Propaquizafop 15.067 + 444.10→100.15 73 Pyrazolynate 13.657 + 439.10→ 91.15 74 Pyriftalid 9.746 + 319.10→139.10 75 Quizalofop-ethyl 14.641 + 373.10→298.90 76 Silafluofen 19.913 + 426.30→287.15 77 Simeconazole 11.078 + 294.10→ 69.95 78 Spinosyn A 18.045 + 732.60→142.20 79 Spinosyn D 18.633 + 353.20→133.10 80 Tebufenozide 12.083 + 353.20→133.10 81 Tebuthiuron 7.575 + 229.10→172.00 82 Teflubenzuron 15.282 - 378.80→339.00 83 Tetrachlorvinphos (CVMP) 12.101 + 366.90→127.15	70	Pentoxazone	14.788	+	371.10→286.00
73Pyrazolynate13.657+ $439.10 \rightarrow 91.15$ 74Pyriftalid9.746+ $319.10 \rightarrow 139.10$ 75Quizalofop-ethyl14.641+ $373.10 \rightarrow 298.90$ 76Silafluofen19.913+ $426.30 \rightarrow 287.15$ 77Simeconazole11.078+ $294.10 \rightarrow 69.95$ 78Spinosyn A18.045+ $732.60 \rightarrow 142.20$ 79Spinosyn D18.633+ $746.60 \rightarrow 142.10$ 80Tebufenozide12.083+ $229.10 \rightarrow 172.00$ 81Tebuthiuron 7.575 + $229.10 \rightarrow 172.00$ 83Tetrachlorvinphos (CVMP)12.101+ $366.90 \rightarrow 127.15$	71	Pirimicarb	8.351	+	239.20→ 72.00
74 Pyriftalid 9.746 + 319.10→139.10 75 Quizalofop-ethyl 14.641 + 373.10→298.90 76 Silafluofen 19.913 + 426.30→287.15 77 Simeconazole 11.078 + 294.10→ 69.95 78 Spinosyn A 18.045 + 732.60→142.20 79 Spinosyn D 18.633 + 353.20→133.10 80 Tebufenozide 12.083 + 353.20→133.10 81 Tebuthiuron 7.575 + 229.10→172.00 82 Teflubenzuron 15.282 - 378.80→339.00 83 Tetrachlorvinphos (CVMP) 12.101 + 366.90→127.15	72	Propaquizafop	15.067	+	444.10→100.15
75 Quizalofop-ethyl 14.641 + 373.10→298.90 76 Silafluofen 19.913 + 426.30→287.15 77 Simeconazole 11.078 + 294.10→ 69.95 78 Spinosyn A 18.045 + 732.60→142.20 79 Spinosyn D 18.633 + 746.60→142.10 80 Tebufenozide 12.083 + 353.20→133.10 81 Tebuthiuron 7.575 + 229.10→172.00 82 Teflubenzuron 15.282 - 378.80→339.00 83 Tetrachlorvinphos (CVMP) 12.101 + 366.90→127.15	73	Pyrazolynate	13.657	+	439.10→ 91.15
76Silafluofen19.913+ $426.30 \rightarrow 287.15$ 77Simeconazole11.078+ $294.10 \rightarrow 69.95$ 78Spinosyn A18.045+ $732.60 \rightarrow 142.20$ 79Spinosyn D18.633+ $746.60 \rightarrow 142.10$ 80Tebufenozide12.083+ $353.20 \rightarrow 133.10$ 81Tebuthiuron 7.575 + $229.10 \rightarrow 172.00$ 82Teflubenzuron15.282- $378.80 \rightarrow 339.00$ 83Tetrachlorvinphos (CVMP)12.101+ $366.90 \rightarrow 127.15$	74	Pyriftalid	9.746	+	319.10→139.10
77Simeconazole11.078+ $294.10 \rightarrow 69.95$ 78Spinosyn A18.045+ $732.60 \rightarrow 142.20$ 79Spinosyn D18.633+ $746.60 \rightarrow 142.10$ 80Tebufenozide12.083+ $353.20 \rightarrow 133.10$ 81Tebuthiuron 7.575 + $229.10 \rightarrow 172.00$ 82Teflubenzuron15.282- $378.80 \rightarrow 339.00$ 83Tetrachlorvinphos (CVMP)12.101+ $366.90 \rightarrow 127.15$	75	Quizalofop-ethyl	14.641	+	373.10→298.90
78 Spinosyn A 18.045 + 732.60→142.20 79 Spinosyn D 18.633 + 746.60→142.10 80 Tebufenozide 12.083 + 353.20→133.10 81 Tebuthiuron 7.575 + 229.10→172.00 82 Teflubenzuron 15.282 - 378.80→339.00 83 Tetrachlorvinphos (CVMP) 12.101 + 366.90→127.15	76	Silafluofen	19.913	+	426.30→287.15
79 Spinosyn D 18.633 + 746.60→142.10 80 Tebufenozide 12.083 + 353.20→133.10 81 Tebuthiuron 7.575 + 229.10→172.00 82 Teflubenzuron 15.282 - 378.80→339.00 83 Tetrachlorvinphos (CVMP) 12.101 + 366.90→127.15	77	Simeconazole	11.078	+	294.10→ 69.95
80 Tebufenozide 12.083 + 353.20→133.10 81 Tebuthiuron 7.575 + 229.10→172.00 82 Teflubenzuron 15.282 - 378.80→339.00 83 Tetrachlorvinphos (CVMP) 12.101 + 366.90→127.15	78	Spinosyn A	18.045	+	732.60→142.20
81 Tebuthiuron 7.575 + 229.10→172.00 82 Teflubenzuron 15.282 - 378.80→339.00 83 Tetrachlorvinphos (CVMP) 12.101 + 366.90→127.15	79	Spinosyn D	18.633	+	746.60→142.10
82 Teflubenzuron 15.282 - 378.80→339.00 83 Tetrachlorvinphos (CVMP) 12.101 + 366.90→127.15	80	Tebufenozide	12.083	+	353.20→133.10
83 Tetrachlorvinphos (CVMP) 12.101 + 366.90→127.15	81	Tebuthiuron	7.575	+	229.10→172.00
	82	Teflubenzuron	15.282	-	378.80→339.00
	83	Tetrachlorvinphos (CVMP)	12.101	+	366.90→127.15
84 Thiabendazole 7.196 + 202.00→175.00	84	Thiabendazole	7.196	+	202.00→175.00

Table 1. MRM transitions of pesticides.

Table 1. MRM transitions of pesticides.

No.	Name	Retention Time (min)	Polarity	Transition
85	Thiacloprid	6.424	+	253.00→126.05
86	Thiamethoxam	4.936	+	292.00→211.10
87	Thiodicarb	8.387	+	355.00→ 88.00
88	Triflumuron	13.318	+	359.00→156.05
89	Triticonazole	11.153	+	318.10→ 70.15

Result

Confirmation of quantitative range

It was confirmed that 89 compounds can obtain linearity at 0.1 to 20 ng/mL by the LCMS-8050 with the basic condition. In addition, linearity was obtained at 0.1 to 50 ng/mL with 78 compounds. The MRM chromatogram of the standard at 1 ng/mL is shown in figure 1.

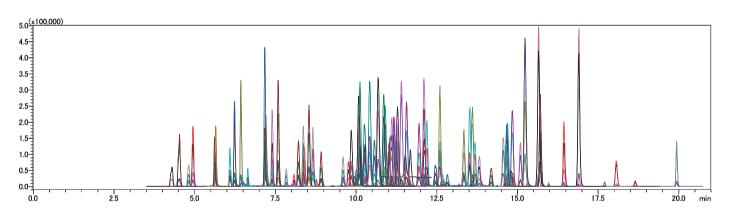


Figure 1. MRM chromatogram of reference standard (1 ng/mL) of pesticides.

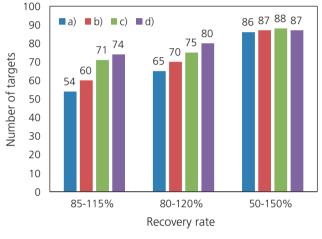
Optimization for Recovery rate and reproducibility by flow rate and/or ESI probe position

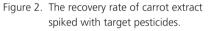
In comparison between matrix-matched calibration curve and standard addition method, absolute calibration method is strongly prone to be affected by matrix effects such as ion suppression, thus the recovery rate would be less. Yet, according to the evaluation for several measurement parameters, we obtained the result that the flow rate and ESI probe position contributed to improve the recovery ratio and reproducibility.

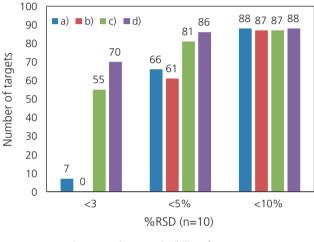
For the analyses of the carrot extract spiked with 1 ng/mL as final concentration of the target pesticides, at 0.4 mL/min flow rate with 3 mm probe position, recovery rate and reproducibility of pesticides were generally increased. Detailed results were summarized in figure 2 and figure 3.

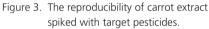
Condition	T.Flow (mL/min)	ESI probe position (mm)
a)	0.2	2
b)	0.2	3
c)	0.4	2
d)	0.4	3

Table 2. Content of conditions.



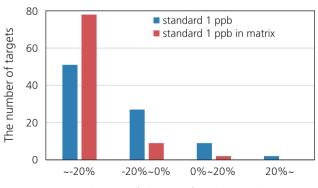




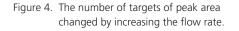


Variance of peak area in response to changes of flow rate and/or ESI probe position

The number of targets in each ratio of the area value changed by changing the flow rate from 0.2 mL/min to 0.4 mL/min is shown in figure 4. From the figure 4, when the flow rate was increased, the area values of both the standard sample and the matrix-added sample became smaller. In addition, the number of targets in each ratio of



The rate of change of peak area value



the area value fluctuated depending on the probe position from 2 mm to 3 mm is shown in figure 5. According to the figure 5, the area value increased for both the standard sample and the matrix-added sample at the long distance of the probe position.

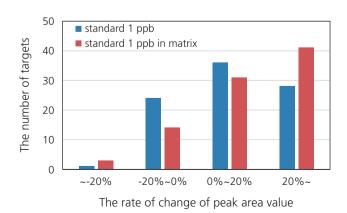


Figure 5. The number of targets of peak area changed depending on the position of the probe from 2 mm to 3 mm.

MRM chromatogram of pesticides

MRM chromatogram of negative detect compounds and low sensitivity compounds of reference standard in 1 ng/mL and carrot extract spiked with 1 ng/mL as final concentration are shown in figure 6.

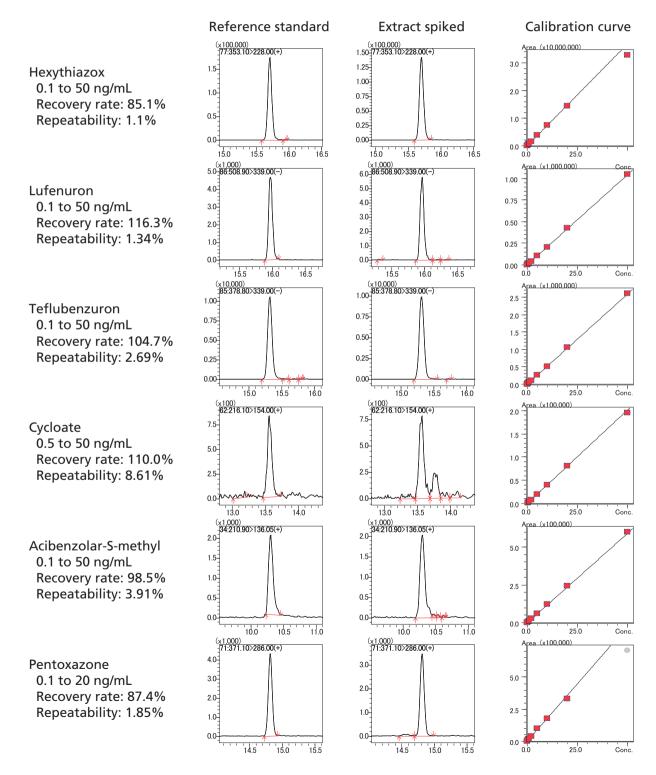


Figure 6. MRM chromatograms of reference standard 1 ng/mL, extract spiked with 1 ng/mL as final concentration with calibration curve.

Conclusions

- We established a method to obtain high recovery conditions and repeatability with the absolute calibration curve.
- 89 compounds of pesticides were detected within 32 minutes including equilibration time.
- All compounds can be quantified in the range of 0.5 to 20 ng/mL. 87 compounds can be quantified in the range of 0.1 to 20 ng/mL and 78 compounds can be quantified in the range of 0.5 to 50 ng/mL.
- For further optimization, it was found that the recovery rate was significantly improved by the optimized flow rate and probe position.
- By rising the flow rate up to 0.4 mL/min and/or the probe position at up to 3 mm, recovery rate and repeatability were most improved.

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