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Application News

No. C208

Liquid Chromatography Mass Spectrometry

Simultaneous Determination of Pesticide Residues in Vegetable Extract by LC/MS/MS [LCMS™-8050]

To protect food safety, it is important to establish detection criteria for pesticide residues and methods to improve accuracy when measuring the concentration of the target substances. Generally, the standard addition method and matrix-matched calibration curve are more useful techniques for reducing the matrix effect than the absolute calibration method. However, these techniques are not necessarily simple, since an independent calibration curve is required for each sample of a wide variety of samples. In this report, we introduce an LC/MS/MS analysis technique which is capable of obtaining high recovery accuracy with the absolute calibration method.

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Methods and Materials

The test matrix solution (carrot extract) was prepared by a solid-phase extraction technique with QuEChERS (STQ method). The range of the calibration curve for the standard concentrations was set from 0.1 to 50 ng/mL, and was determined by the absolute calibration method. Tables 1 and 2 below show the LC/MS analysis conditions.

Table 1 LC Conditions

[LC] Nexera™X2 system		
Column	:	Shim-pack Scepter™ C18-120 (100 mm × 2.0 mm, 1.9 µm)
Column temp.	:	40 °C
Solvent A	:	5 mmol/L ammonium acetate/water
Solvent B	:	5 mmol/L ammonium acetate/methanol
Gradient	:	B conc. 3% (0 min) → 10% (2 min) → 55% (6 min) → 100% (21-26 min) → 3% (26.01-32 min)
Flow rate	:	0.4 mL/min (0-21 min) → 0.6 mL/min (21.01-27 min) → 0.4 mL/min (27.01-32 min)
Injection vol.	:	5 µL

Table 2 MS Conditions

[MS] LCMS-8050		
Ionization	:	ESI positive and negative
DL temp.	:	150 °C
Interface temp.	:	200 °C
Block heater temp.	:	500 °C
Nebulizer gas flow	:	2 L/min
Drying gas flow	:	10 L/min
Heating gas flow	:	10 L/min
Probe position	:	3 mm
Dwell time	:	1-200 ms
Pause time	:	1 ms

Spike and Recovery Test

For analysis of the carrot extract spiked with 1 ng/mL as the final concentration of the target pesticides, the number of targets with recovery rates within 70% to 120% was 82 of a total of 89 pesticides (Fig. 1). Moreover, reproducibility under 3% (n = 10, Fig. 2) was achieved with 70 pesticides. Table 3 shows the details of the MRM transition, recovery rate, and reproducibility. Fig. 4 shows the MS chromatogram of some compounds and the calibration curves of them.

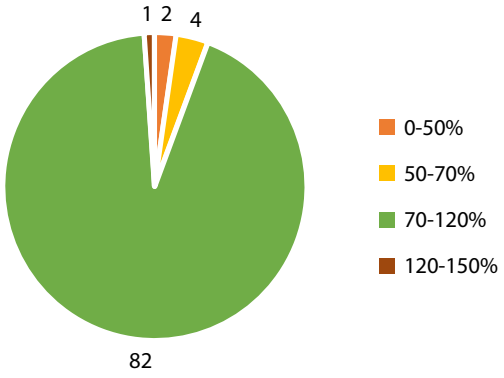

Fig. 1 Recovery Rate of Target Pesticides

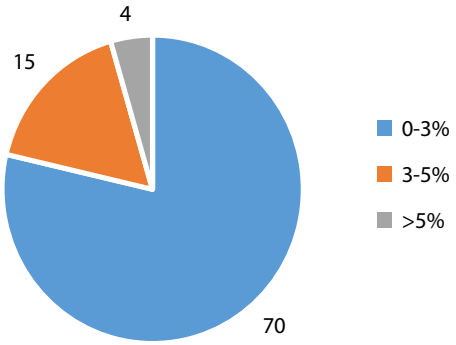

Fig. 2 Reproducibility of Target Pesticides

Table 3-1 MRM Transition, Recovery Rate, and Reproducibility of Target Pesticides (1 ng/mL)

No.	Name	Retention time (min)	+/-	MRM transition	Recovery rate (%)	Repro-ducibility (%)	Determination range (ng/mL)
1	Abamectin B1a	17.70	+	890.30 > 305.30	52.3	3.7	0.1-50
2	Acibenzolar-S-methyl	10.30	+	210.90 > 136.05	97.9	5.2	0.1-50
3	Aldicarb	6.65	+	208.20 > 115.85	95.8	2.5	0.1-50
4	Aldicarb-sulfone (Aldoxycarb)	4.31	+	240.10 > 86.20	98.3	0.5	0.1-50
5	Anilofos	12.60	+	368.00 > 125.00	97.6	3.1	0.1-50
6	Azamethiphos	7.17	+	325.00 > 182.90	98.1	1.1	0.1-20
7	Azinphos-methyl	9.60	+	318.00 > 132.05	100.0	3.1	0.1-50
8	Azoxystrobin	10.08	+	404.00 > 371.95	103.1	2.8	0.1-50
9	Bendiocarb	7.39	+	224.20 > 109.10	86.0	2.1	0.1-50
10	Benzofenap	14.57	+	431.15 > 105.25	95.2	1.2	0.1-50
11	Boscalid	10.29	+	343.00 > 306.95	80.1	1.1	0.1-50
12	Butafenacil	11.26	+	492.10 > 330.85	103.0	2.2	0.1-50
13	Carbaryl (NAC)	7.84	+	202.10 > 145.10	79.2	4.1	0.1-50
14	Carbofuran	7.41	+	222.10 > 123.15	87.2	1.3	0.1-50
15	Carpropamid	12.68	+	334.10 > 139.10	129.1	4.7	0.1-50
16	Chloridazon	6.10	+	222.10 > 104.10	94.2	1.1	0.1-50
17	Chloroxuron	11.02	+	291.10 > 72.15	101.8	1.5	0.1-50
18	Chromafenozide	11.41	+	395.20 > 175.15	95.0	1.2	0.1-50
19	Clofentezine	13.82	+	303.00 > 138.15	77.8	1.9	0.1-50
20	Cloquintocet-mexyl	15.24	+	336.10 > 237.90	102.6	2.7	0.1-50
21	Clothianidin	5.66	+	250.00 > 132.05	96.5	1.4	0.1-20
22	Cumyluron	10.91	+	303.20 > 185.10	106.1	2.7	0.1-50
23	Cyazofamid	11.69	+	325.00 > 108.10	95.4	3.1	0.1-50
24	Cycloate	13.57	+	216.10 > 154.00	104.9	8.6	0.5-50
25	Cycloprothrin	16.87	+	499.00 > 181.10	90.4	2.0	0.1-20
26	Cyflufenamid	13.52	+	413.10 > 295.05	96.8	2.0	0.1-50
27	Cyprodinil	12.83	+	226.10 > 108.00	98.6	4.7	0.1-50
28	Daimuron (Dymron)	10.69	+	269.25 > 151.15	104.8	2.1	0.1-50
29	Diflubenzuron	11.96	+	311.00 > 158.10	46.2	2.4	0.1-50
30	Dimethirimol	8.22	+	210.20 > 71.00	97.6	1.1	0.1-50
31	Dimethomorph (*E,Z*)	10.11	+	388.10 > 301.00	93.4	2.9	0.1-20
32		10.58			97.7	3.3	0.1-50
33	Diuron (DCMU)	8.92	+	233.00 > 72.10	99.5	1.2	0.1-50
34	Epoxiconazole	11.57	+	330.00 > 121.10	98.2	2.6	0.1-50
35	Fenamidone	10.13	+	312.10 > 236.00	99.2	1.4	0.1-50
36	Fenoxaprop-ethyl	14.65	+	362.10 > 287.90	99.1	1.2	0.1-50
37	Fenoxycarb	12.20	+	302.10 > 88.00	94.1	1.5	0.1-50
38	Fenpyroximate (*E,Z*)	15.66	+	422.30 > 366.20	96.9	1.2	0.1-50
39		16.90			98.2	1.4	0.1-50
40	Ferimzone (*E,Z*)	10.27	+	255.20 > 91.05	98.7	3.6	0.1-50
41		10.43			103.7	1.8	0.1-50
42	Flufenacet	11.29	+	364.10 > 152.05	90.0	2.0	0.1-50
43	Flufenoxuron	16.44	+	489.00 > 158.10	91.9	1.2	0.1-50
44	Fluridone	9.85	+	330.10 > 309.00	106.9	1.9	0.1-50
45	Furametpyr	8.55	+	334.10 > 157.10	94.8	1.5	0.1-50
46	Furathiocarb	14.84	+	383.20 > 195.00	97.9	1.9	0.1-50
47	Hexaflumuron	14.68	-	458.80 > 439.00	115.5	1.3	0.1-50
48	Hexythiazox	15.71	+	353.10 > 228.00	85.1	1.1	0.1-50
49	Imazalil	12.46	+	297.10 > 159.05	94.6	3.3	0.1-50
50	Imidacloprid	5.62	+	256.10 > 174.95	98.3	1.2	0.1-20

Table 3-2 MRM Transition, Recovery Rate and Reproducibility of Target Pesticides (1 ng/mL)

No.	Name	Retention time (min)	+/-	MRM transition	Recovery rate (%)	Repro-ducibility (%)	Determination range (ng/mL)
51	Indanofan	11.67	+	341.10 > 175.15	97.8	2.6	0.1-50
52	Indoxacarb	14.19	+	528.10 > 203.00	96.1	1.5	0.1-50
53	Iprovalicarb	11.16	+	321.20 > 119.15	51.9	4.0	0.1-50
54	Isoxaflutole	8.78	+	360.10 > 251.00	81.9	5.7	0.1-50
55	Linuron	9.96	+	248.80 > 182.05	88.6	2.0	0.1-50
56	Lufenuron	15.97	-	508.90 > 339.00	115.1	2.3	0.1-50
57	Mepanipyrim	11.53	+	224.10 > 77.00	87.7	4.4	0.1-50
58	Methabenzthiazuron	8.67	+	222.10 > 150.10	95.7	2.0	0.1-50
59	Methiocarb	10.02	+	226.10 > 121.10	93.1	6.6	0.2-50
60	Methomyl	4.82	+	163.00 > 87.90	95.4	1.7	0.1-50
61	Methoxyfenozide	10.86	+	369.20 > 149.15	103.4	1.3	0.1-50
62	Monolinuron	8.08	+	215.10 > 99.10	88.7	2.1	0.1-50
63	Naproanilide	12.13	+	292.25 > 171.25	96.1	1.7	0.1-20
64	Novaluron	14.81	+	493.00 > 158.00	68.0	2.0	0.1-20
65	Oryzalin	11.36	+	347.10 > 288.00	36.1	3.5	0.1-50
66	Oxamyl	4.53	+	237.10 > 72.10	98.1	1.4	0.1-50
67	Oxaziclomefone	14.70	+	376.20 > 190.15	99.2	3.7	0.1-50
68	Oxycarboxin	6.24	+	268.10 > 175.00	90.8	2.6	0.1-50
69	Pencycuron	13.61	+	329.10 > 125.00	100.0	2.0	0.1-50
70	Pentoxazone	14.82	+	371.10 > 286.00	85.2	1.9	0.1-20
71	Pirimicarb	8.37	+	239.20 > 72.00	99.9	1.7	0.1-50
72	Propaquizafop	15.09	+	444.10 > 100.15	83.1	2.4	0.1-50
73	Pyrazolynate	13.69	+	439.10 > 91.15	102.6	3.0	0.1-50
74	Pyriftalid	9.77	+	319.10 > 139.10	100.2	1.9	0.1-50
75	Quizalofop-ethyl	14.67	+	373.10 > 298.90	79.8	2.5	0.1-50
76	Silafluofen	19.93	+	426.30 > 287.15	101.8	1.1	0.1-50
77	Simeconazole	11.11	+	294.10 > 69.95	63.0	1.9	0.1-50
78	Spinosyn A	18.07	+	732.60 > 142.20	102.9	1.5	0.1-50
79	Spinosyn D	18.65	+	746.60 > 142.10	105.0	1.7	0.1-50
80	Tebufenozide	12.11	+	353.20 > 133.10	97.1	1.1	0.1-50
81	Tebuthiuron	7.59	+	229.10 > 172.00	97.7	1.4	0.1-50
82	Teflubenzuron	15.32	-	378.80 > 339.00	99.0	2.7	0.1-50
83	Tetrachlorvinphos (CVMP)	12.13	+	366.90 > 127.15	98.1	3.2	0.1-50
84	Thiabendazole	7.21	+	202.00 > 175.00	104.3	2.8	0.1-50
85	Thiacloprid	6.44	+	253.00 > 126.05	95.5	1.3	0.1-50
86	Thiamethoxam	4.95	+	292.00 > 211.10	93.9	1.5	0.1-50
87	Thiodicarb	8.40	+	355.00 > 88.00	99.6	2.5	0.1-50
88	Triflumuron	13.35	+	359.00 > 156.05	91.6	0.9	0.1-50
89	Triticonazole	11.18	+	318.10 > 70.15	87.1	2.1	0.1-50

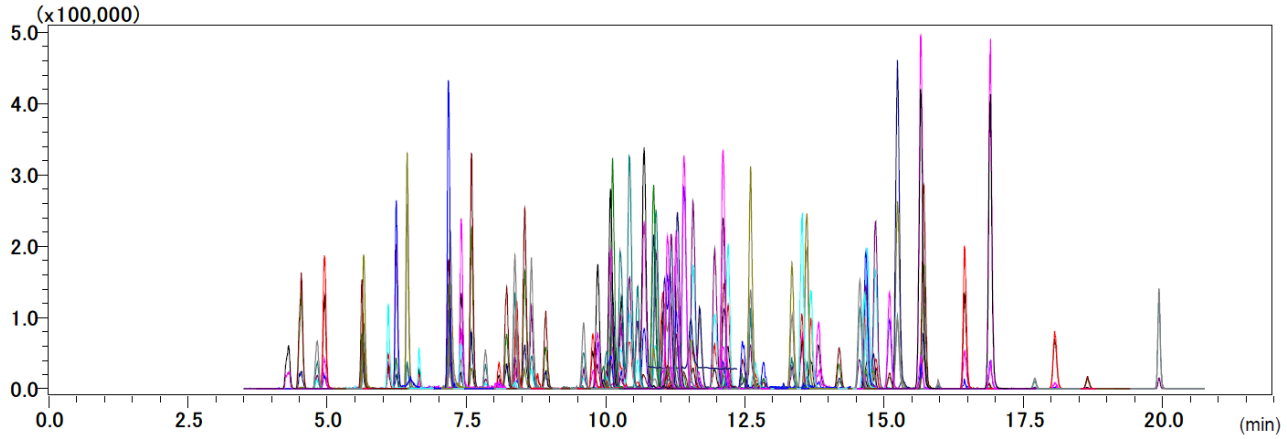

Fig. 3 MS Chromatogram of Pesticides (1 ng/mL)

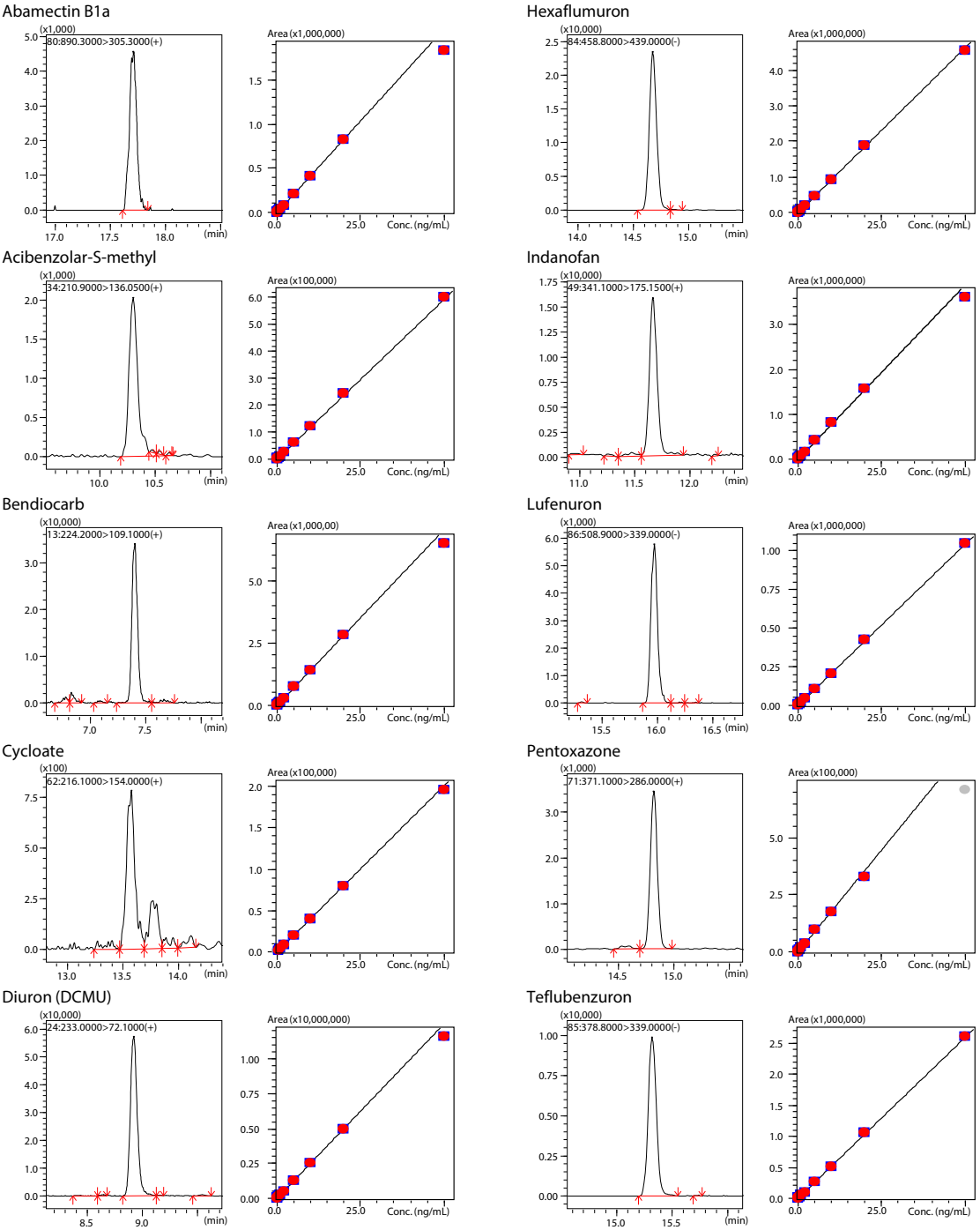

Fig. 4 MS Chromatograms of Spiked Samples (Final Concentration: 1 ng/mL) and Calibration Curves of Pesticides

Conclusion

Using an LCMS-8050 triple quadrupole mass spectrometer with Nexera X2 UHPLC, it was possible to obtain a high recovery rate and high reproducibility with the absolute calibration method.

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