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Multiresidue pesticide analysis from dried chili powder using LC/MS/MS

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Introduction

Pesticide residues in foodstuffs can cause serious health problems when consumed. LC/MS/MS methods have been increasingly employed in sensitive quantification of pesticide residues in foods and agriculture products. However, matrix effect is a phenomenon seen in Electro Spray Ionization (ESI) LC/MS/MS analysis that impacts the data quality of the pesticide analysis, especially for complex matrix like spice/herb.
Chili powder is one such complex matrix that can exhibit matrix effect (either ion suppression or enhancement). A calibration curve based on matrix matched standards can demonstrate true sensitivity of analyte in presence of matrix. Therefore, this approach was used to obtain more reliable and accurate data as compared to quantitation against neat (solvent) standards[1].
Multiresidue, trace level analysis in complex matrices is challenging and tedious. Feature of automatic MRM optimization in LCMS-8040 makes method development process less tedious. In addition, the lowest dwell time and pause time along with ultra fast polarity switching (UFswitching) enables accurate, reliable and high sensitive quantitation. UFsweeper™ II technology in the system ensures least crosstalk, which is very crucial for multiresidue pesticide analysis.

Method of Analysis

Sample Preparation

Commercially available red chili was powdered using mixer grinder. To 1 g of this chili powder, 20 mL water:methanol (1:1 v/v) was added and the mixture was sonicated for 10 mins. The mixture was centrifuged and supernatant was collected. This supernatant was used as diluent to prepare pesticide matrix matched standards at concentration levels of 0.01 ppb, 0.02 ppb, 0.05 ppb, 0.1 ppb, 0.2 ppb, 0.5 ppb, 1 ppb, 2 ppb, 5 ppb, 10 ppb and 20 ppb. Each concentration level was then filtered through 0.2 µ nylon filter and used for the analysis.

LC/MS/MS Analytical Conditions

Pesticides were analyzed using Ultra High Performance Liquid Chromatography (UHPLC) Nexera coupled with LCMS-8040 triple quadrupole system (Shimadzu Corporation, Japan), shown in Figure 1. The details of analytical conditions are given in Table 1.

Table 1. LC/MS/MS analytical conditions

• Column	: Shim-pack XR-ODS (75 mm L x 3 mm I.D.; 2.2 µm)
• Guard column	: Phenomenex SecurityGuard ULTRA Cartridge
• Mobile phase	: A: 5 mM ammonium formate in water:methanol (80:20 v/v) B: 5 mM ammonium formate in water:methanol (10:90 v/v)
• Flow rate	: 0.2 mL/min
• Oven temperature	: 40 °C
• Gradient program (B%)	: 0.0–1.0 min → 45 (%); 1.0–13.0 min → 45-100 (%); 13.0–18.0 min → 100 (%); 18.0–19.0 min → 100-45 (%); 19.0–23.0 min → 45 (%)
• Injection volume	: 15 µL
• MS interface	: ESI
• Polarity	: Positive and negative
• Nitrogen gas flow	: Nebulizing gas 2 L/min; Drying gas 15 L/min
• MS temperature	: Desolvation line 250 °C; Heat block 400 °C
• MS analysis mode	: Staggered MRM

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Figure 1. Nexera with LCMS-8040 triple quadrupole system by Shimadzu

Results

LC/MS/MS method was developed for analysis of 80 pesticides belonging to different classes like carbamate, organophosphate, urea, triazines etc. in a single run[2]. LOQ was determined for each pesticide based on the following criteria – **(1)** % RSD for area < 16 % (n=3), **(2)** % Accuracy between 80-120 % and **(3)** Signal to noise ratio (S/N) > 10.

LOQ achieved for 80 pesticides have been summarized in Table 2 and results for LOQ and linearity for each pesticide have been given in Table 3. Representative MRM chromatogram of pesticide mixture at 1 ppb level is shown in Figure 2. Representative MRM chromatograms at LOQ level for different classes of pesticides are shown in Figure 3.

Table 2: Summary of LOQ achieved

LOQ (ppb)	0.01	0.02	0.05	0.1	0.2	0.5	1
Number of pesticides	1	1	3	8	17	24	26

Table 3. Results of LOQ and linearity for pesticide analysis

Sr. No.	Name of compound	MRM Transition	Polarity	LOQ (ppb)	Linearity (R^2)
1	Spinosyn D	746.20>142.10	Positive	0.01	0.9987
2	Fenpyroximate	421.90>366.10	Positive	0.02	0.9915
3	Bifenazate	301.00>198.00	Positive	0.05	0.9947
4	Spinosyn A	732.20>142.10	Positive	0.05	0.9974
5	Spiromesifen	371.00>273.10	Positive	0.05	0.9957
6	Acetamiprid	222.90>126.00	Positive	0.1	0.9910
7	Carbofuran	221.70>123.00	Positive	0.1	0.9971
8	Dimethoate	229.80>198.90	Positive	0.1	0.9970
9	Dimethomorph I	387.90>301.00	Positive	0.1	0.9991
10	Dimethomorph II	387.90>301.00	Positive	0.1	0.9992
11	Isoproturon	207.00>72.10	Positive	0.1	0.9984
12	Pirimiphos methyl	305.70>108.00	Positive	0.1	0.9997
13	Trifloxystrobin	408.90>186.00	Positive	0.1	0.9989

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Sr. No.	Name of compound	MRM Transition	Polarity	LOQ (ppb)	Linearity (R^2)
14	Anilophos	367.70>198.85	Positive	0.2	0.9974
15	Atrazine	215.90>174.00	Positive	0.2	0.9985
16	Carboxin	235.90>143.00	Positive	0.2	0.9952
17	Cyazofamid	324.85>108.10	Positive	0.2	0.9971
18	Edifenphos	310.60>111.00	Positive	0.2	0.9997
19	Ethion	384.70>198.80	Positive	0.2	0.9957
20	Fipronil	434.70>330.00	Negative	0.2	0.9973
21	Linuron	248.80>159.90	Positive	0.2	0.9945
22	Metolachlor	283.90>252.00	Positive	0.2	0.9966
23	Oxycarboxin	267.90>174.90	Positive	0.2	0.9995
24	Phosalone	367.80>181.90	Positive	0.2	0.9987
25	Phosphamidon	299.90>173.90	Positive	0.2	0.9997
26	Thiacloprid	252.90>126.00	Positive	0.2	0.9976
27	Thiobencarb	257.90>125.10	Positive	0.2	0.9977
28	Thiodicarb	354.90>88.00	Positive	0.2	0.9906
29	Triadimefon	293.90>196.90	Positive	0.2	0.9994
30	Tricyclazole	189.90>162.90	Positive	0.2	0.9977
31	Aldicarb	208.10>116.05	Positive	0.5	0.9962
32	Benfuracarb	411.10>190.10	Positive	0.5	0.9981
33	Bitertanol	338.00>99.10	Positive	0.5	0.9935
34	Buprofezin	305.70>201.00	Positive	0.5	0.9933
35	Clodinafop propargyl	349.90>266.00	Positive	0.5	0.9978
36	Chlorantraniliprole	483.75>452.90	Positive	0.5	0.9994
37	Diclofop methyl	357.90>280.80	Positive	0.5	0.9976
38	Flufenacet	363.70>193.90	Positive	0.5	0.9997
39	Flusilazole	315.90>247.00	Positive	0.5	0.9983
40	Hexaconazole	313.90>70.10	Positive	0.5	0.9996
41	Hexythiazox	352.90>227.90	Positive	0.5	0.9909
42	Iodosulfuron methyl	507.70>167.00	Positive	0.5	0.9971
43	Iprobenfos	288.70>205.00	Positive	0.5	0.9981
44	Malaoxon	314.90>99.00	Positive	0.5	0.9996
45	Malathion	330.90>284.90	Positive	0.5	0.9997
46	Mandipropamid	411.90>356.20	Positive	0.5	0.9952
47	Metalaxyl	280.00>220.10	Positive	0.5	0.9996
48	Methabenzthiazuron	221.70>150.00	Positive	0.5	0.9957
49	Methomyl	162.90>88.00	Positive	0.5	0.9988
50	Oxadiazon	362.15>303.00	Positive	0.5	0.9963
51	Penconazole	283.90>70.10	Positive	0.5	0.9992
52	Phorate	260.80>75.00	Positive	0.5	0.9987
53	Phorate sulfoxide	276.80>96.90	Positive	0.5	0.9991
54	Thiophanate methyl	342.90>151.00	Positive	0.5	0.9996
55	Avermectin B1a	890.30>305.10	Positive	1	0.9990
56	Carpropamid	333.70>139.00	Positive	1	0.9985

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Sr. No.	Name of compound	MRM Transition	Polarity	LOQ (ppb)	Linearity (R^2)
57	Clomazone	241.90>127.00	Positive	1	0.9967
58	Clorimuron ethyl	415.30>186.00	Positive	1	0.9965
59	Cymoxanil	198.90>128.10	Positive	1	0.9949
60	Diafenthiuron	385.00>329.10	Positive	1	0.9961
61	Diflubenzuron	310.80>158.00	Positive	1	0.9982
62	Dodine	228.10>60.00	Positive	1	0.9980
63	Emamectin benzoate	886.30>158.10	Positive	1	0.9983
64	Fenamidone	311.90>236.10	Positive	1	0.9997
65	Fenarimol	330.70>268.00	Positive	1	0.9900
66	Fenazaquin	306.95>57.10	Positive	1	0.9992
67	Flonicamid	229.90>202.70	Positive	1	0.9971
68	Flubendiamide	680.90>254.05	Negative	1	0.9993
69	Forchlorfenuron	247.90>129.00	Positive	1	0.9956
70	Kresoxim methyl	331.00>116.00	Positive	1	0.9996
71	Paclobutrazol	293.90>70.10	Positive	1	0.9974
72	Pencycuron	328.90>125.00	Positive	1	0.9943
73	Pendimethalin	281.90>212.10	Positive	1	0.9932
74	Profenofos	372.70>302.70	Positive	1	0.9966
75	Propargite	368.00>231.10	Positive	1	0.9950
76	Propoxur	209.90>110.90	Positive	1	0.9987
77	Pyrazosulfuron ethyl	414.90>182.00	Positive	1	0.9992
78	Pyriproxyfen	321.90>96.10	Positive	1	0.9975
79	Simazine	201.90>103.90	Positive	1	0.9992
80	Thiomethon	246.80>89.10	Positive	1	0.9989

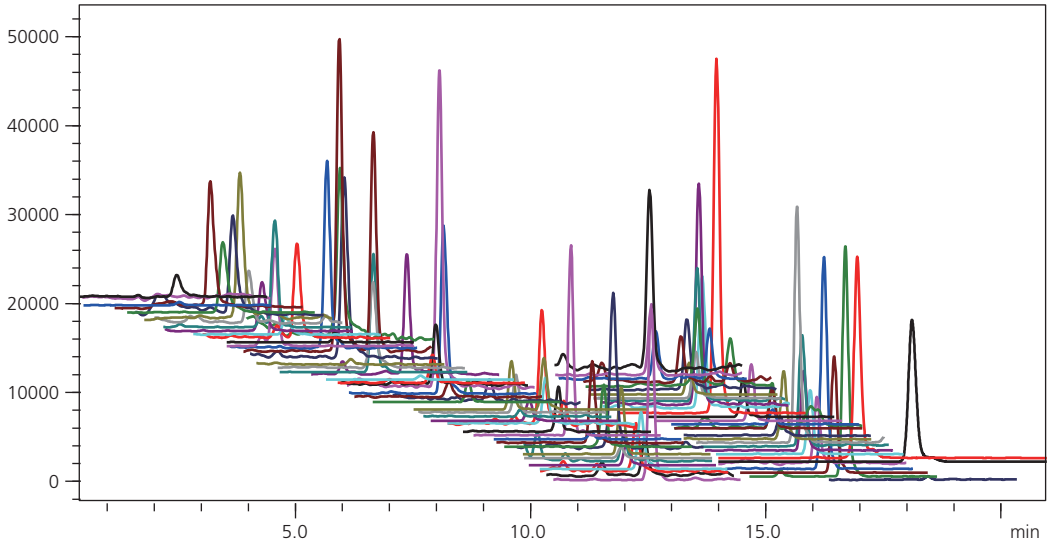

Figure 2. MRM chromatogram of pesticide mixture at 1 ppb level

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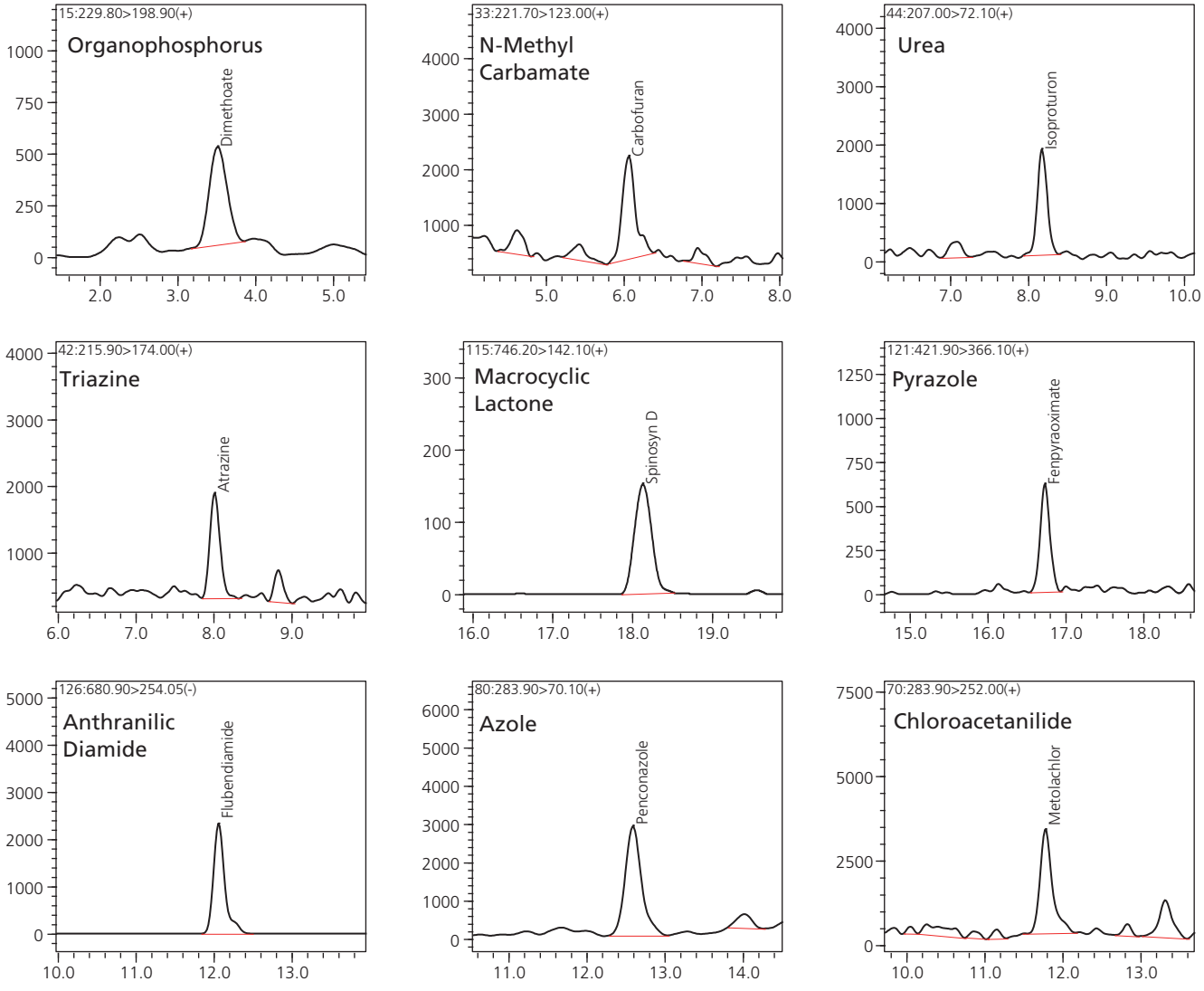

Figure 3. Representative MRM chromatograms at LOQ level from different classes of pesticides

Conclusion

- A highly sensitive method was developed for analysis of 80 pesticides belonging to different classes, from dried chili powder in a single run.
- Ultra high sensitivity, ultra fast polarity switching (UFswitching), low pause time and dwell time along with UFsweeper™ II technology enabled sensitive, selective, accurate and reproducible multiresidue pesticide analysis from complex matrix like dried chili powder.

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References

[1] Kwon H, Lehotay SJ, Geis-Asteggiante L., Journal of Chromatography A, Volume 1270, (2012), 235–245.
[2] Banerjee K, Oulkar DP et al., Journal of Chromatography A, Volume 1173, (2007), 98-109.

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