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Rapid Screening and Quantitation of Pesticide Residues in *Cannabis* by Modified QuEChERS and LC-MS-MS

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Introduction

Medical and recreational use of marijuana (Cannabis spp.) is expanding in the United States at a rapid pace, and domestic production has increased more than ten-fold in the last 25 years. This extremely high value crop is vulnerable to mold and insects so growers frequently apply pesticides and antifungals to protect their plants. These chemical residues may pose a danger to consumers, so highly sensitive and selective methods for their detection in the complex cannabis matrix are required. We developed a rapid and effective LC-MS-MS method with modified QuEChERS sample preparation for detection of nearly 200 chemical residues in dried cannabis flower and used the method to test a wide selection of products offered for commercial sale.

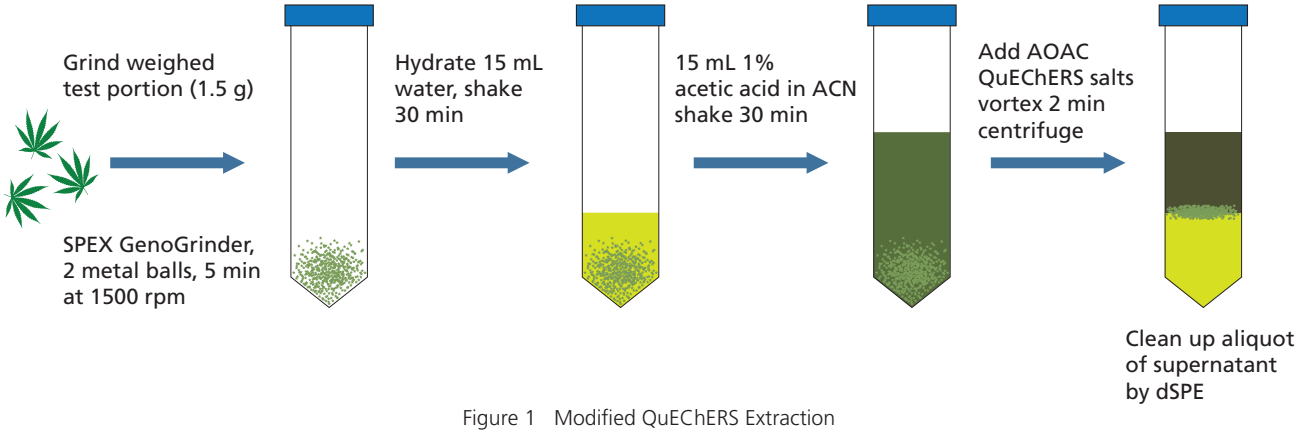

Figure 1 Modified QuEChERS Extraction

Method

Test portions of dried cannabis flower were homogenized and extracted using a modified QuEChERS extraction with dispersive SPE cleanup (Restek cat no. 26237 and 26243). Grinding was performed with a SPEX GenoGrinder. Detection was carried out by LC-MS-MS using a Shimadzu Prominence HPLC with LCMS-8050 triple quadrupole mass spectrometer. Electrospray ionization was used with continuous polarity switching to measure analytes in both modes throughout the run. Pesticide recovery was determined using spiking experiments and matrix-matched calibration curves. All analysis was carried out in a Washington state certified cannabis testing lab.

Table 1 LCMS-8050 Instrument parameters

LC Column	: Restek ARC-18 (2.1×100 mm, 3 µm)
Mobile Phase A	: 5 mM NH4OAC + 0.1% Formic Acid
Mobile Phase B	: Methanol
LC Flow Rate	: 0.5 mL/min
Heater Gas	: 10 L/min
Interface Temp	: 400 °C
Nebulizing Gas	: 3 L/min
Drying Gas	: 10 L/min
DL Temp	: 250 °C
Heat Block Temp	: 400 °C

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Figure 2 Cannabis samples for pesticide testing

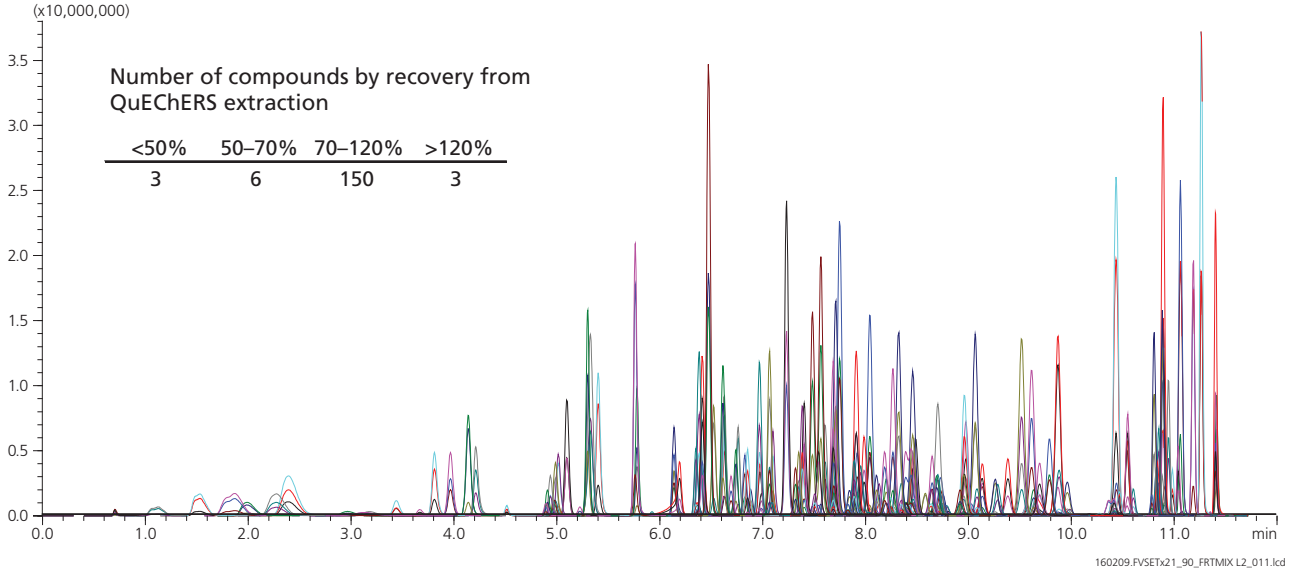

Figure 3 Representative chromatogram and number of compounds by recovery (inset)

Results and Discussion

QuEChERS extraction with dispersive SPE cleanup provided the best combination of pesticide recovery and cleanup for dried flower cannabis samples. Matrix matched calibration curves were linear within the quantitation limits established for each compound, which was compound dependent, but ranged from as low as 20 ppb or lower to greater than 500 ppb for a few substances. Detection limits and quantitation limits were required to have 3:1 and 10:1 signal to noise respectively, and quantitation limits were required to have less than 20% RSD in triplicate analyses. Recovery was compound dependent however the majority were within the range of 70-120% while outliers above and below the range were observed. The method was validated in three different cannabis strains using matrix matched calibration curves and triplicate QC spikes at three levels. In a subset of randomly tested cannabis flower samples offered for commercial sale, the three most commonly detected residues were piperonyl butoxide, myclobutanil, and boscalid. Concentrations for pesticides ranged from the detection limit up to the microgram/gram level.

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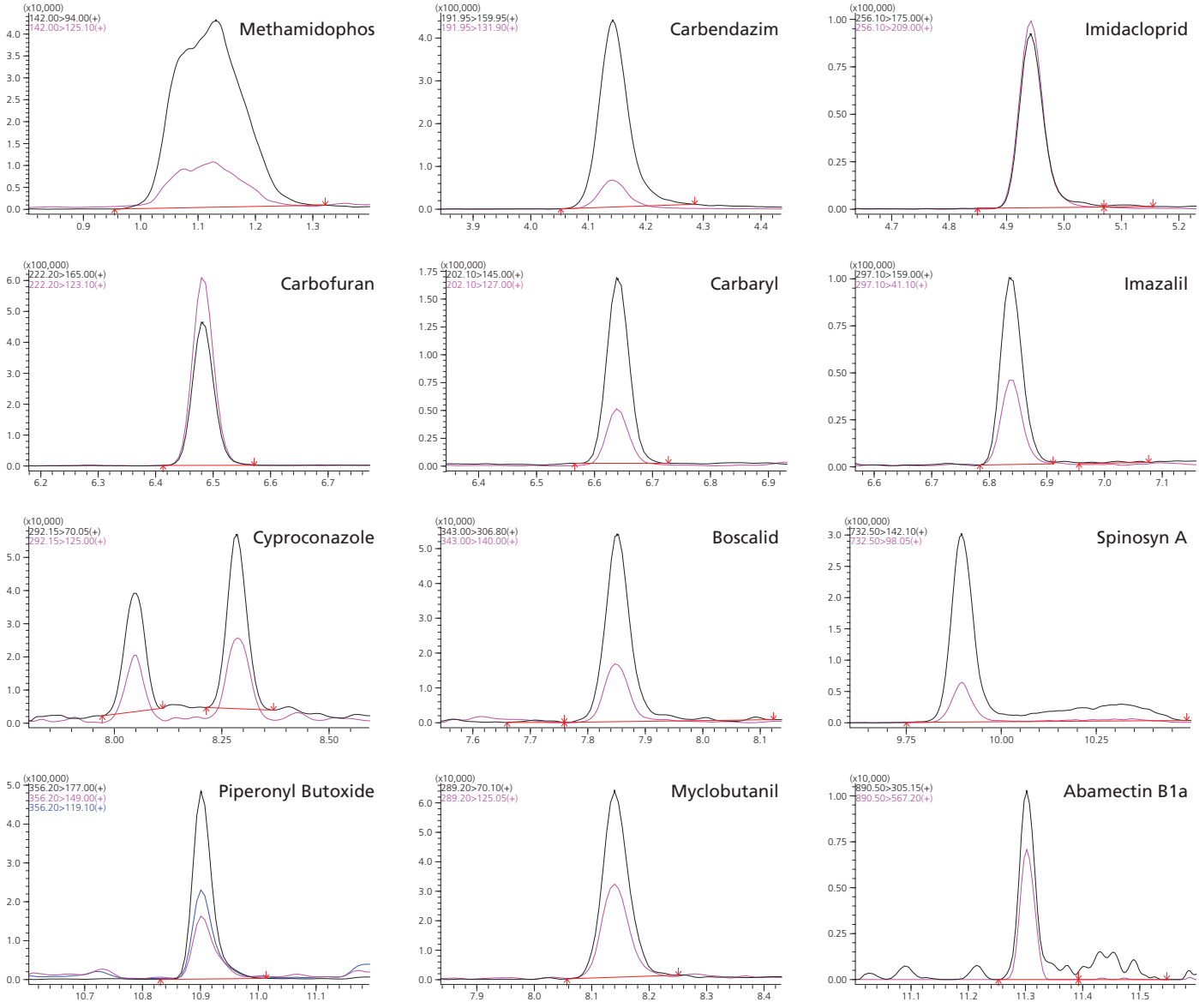

Figure 4 Representative individual chromatograms at the 100 ng/g dried cannabis spiking level (Abamectin chromatogram from 1 mcg/g level)

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Table 2 Detection of pesticides in 39 dried flower samples offered for retail sale

Survey of pesticides in dried *cannabis* flower offered for retail sale					
Sample	Residue detected	mcg/g	Sample	Residue detected	mcg/g
A			P	Piperonyl butoxide	0.32
B			Q	Imidacloprid	0.49
C			R		
D			S	Piperonyl butoxide	0.69
E			T		
F			U	Myclobutanil	0.02
G	Piperonyl butoxide	0.53	V		
H	Piperonyl butoxide	0.05	W	Piperonyl butoxide	12.46
I			X	Piperonyl butoxide	0.16
J	Spinosyn A	0.02		Fipronil	0.04
	Spinosyn D	0.02	Y		
K	Myclobutanil	0.01	Z		
L	Myclobutanil	0.02	AA		
M	Dinotefuran	13.44	AB		
	Boscalid	81.79	AC	Piperonyl butoxide	14.99
	Pyraclostrobin	0.40	AD	Permethrin	0.35
	Trifloxystrobin	0.08	AE		
	Fludioxonil	0.42	AF	Piperonyl butoxide	0.08
	Myclobutanil	1.21	AG		
N	Dinotefuran	1.20	AH		
	Boscalid	5.79	AI		
	Fludioxonil	0.01	AJ	Diuron	0.06
	Myclobutanil	0.08	AK	Piperonyl butoxide	0.13
O	Boscalid	0.15	AL		
	Myclobutanil	0.05	AM		

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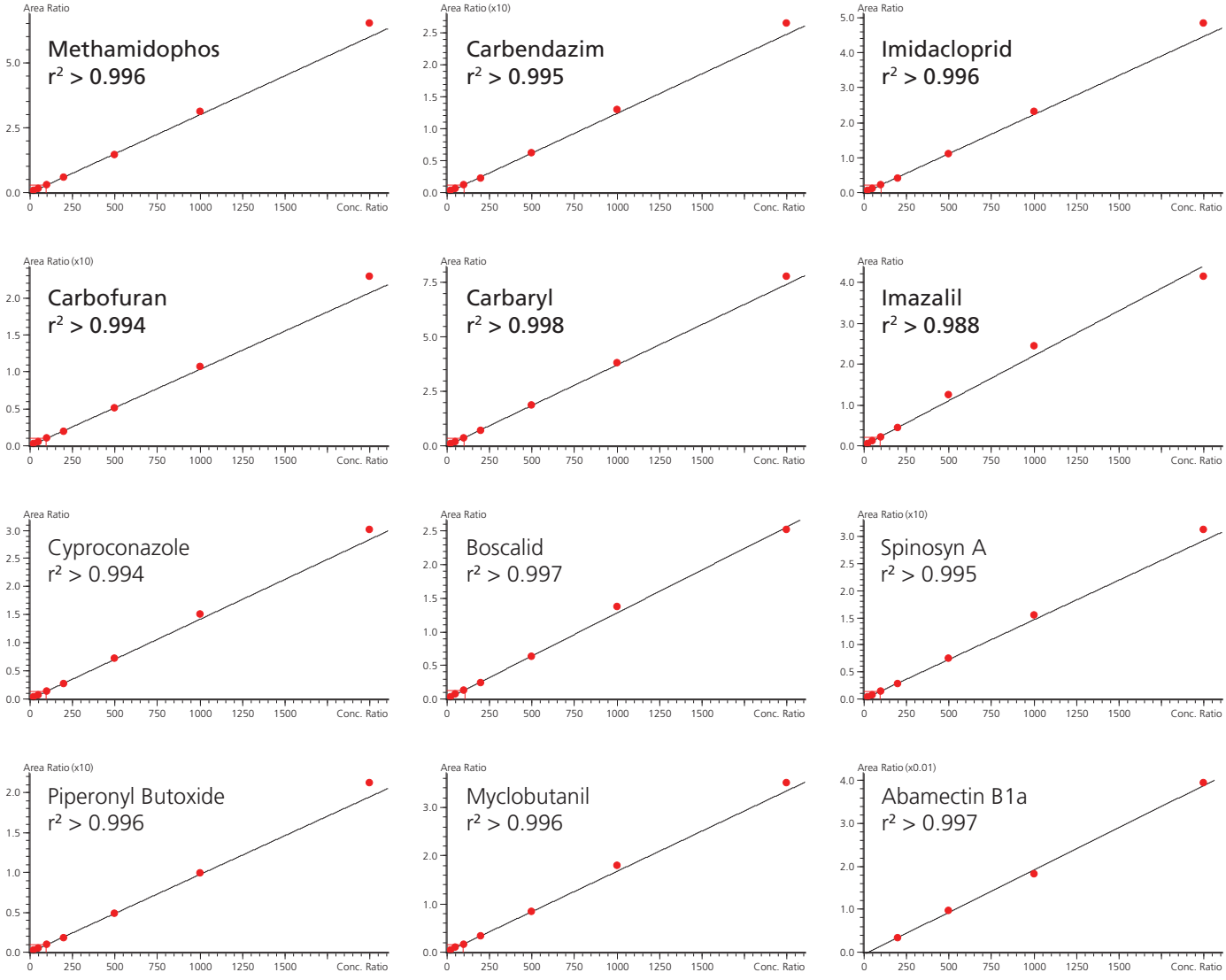

Figure 5 Representative calibration curves

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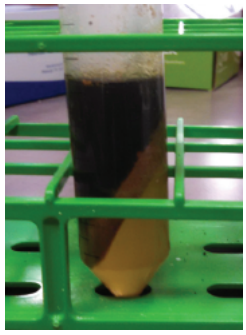
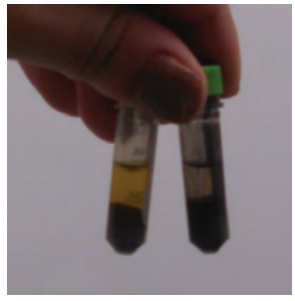
Dried flower

Coarse ground



QuEChERS extract



Dispersive SPE

Figure 6 Sample preparation

Table 3 Pesticides detected in 39 dried flower samples

Number of pesticide detections in dried *cannabis* flower		
Residue name	**Detections**	**Rate**
Boscalid	3	7.7%
Dinotefuran	2	5.1%
Diuron	1	2.6%
Fipronil	1	2.6%
Fludioxonil	2	5.1%
Imidacloprid	1	2.6%
Myclobutanil	6	15.4%
Permethrin	1	2.6%
Piperonyl butoxide	9	23.1%
Pyraclostrobin	1	2.6%
Spinosyn A	1	2.6%
Spinosyn D	1	2.6%
Trifloxystrobin	1	2.6%
One or more	**19**	**49%**

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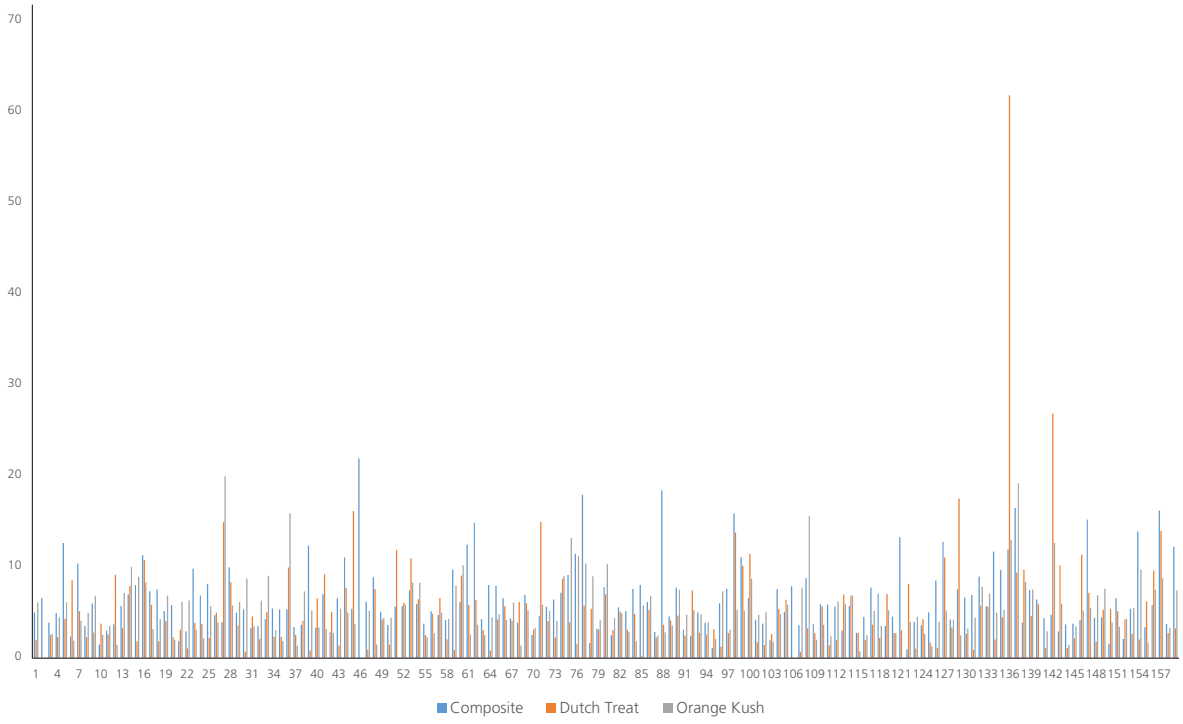

Figure 7 RSD for each compound in triplicate QC samples at the 50 ng/g spike level, in three matrices

Conclusion

A validated method for detection of chemical residues in dried cannabis flower samples was developed. Our method can detect low levels of common pesticides in samples offered for retail sale with excellent selectivity and speed. Measurements of a larger selection of commercially available cannabis samples are being carried out.

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