The Use of Dispersive Solid Phase Extraction in the Detection of Pesticides in Cannabis Flower by GC-MS/MS

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INTRODUCTION

As recreational and medical cannabis use becomes legalized in more jurisdictions, more pesticides are being used in the cultivation of *Cannabis*. Because certain pesticide residues can pose significant health risks to consumers, pesticide analysis of *Cannabis* in California is highly regulated by the Bureau of Cannabis Control (BCC). All legal *Cannabis* products sold in California must undergo analysis for sixty-six regulated pesticides. The action limits of these pesticides vary depending on their classification and perceived danger to human health. Extracted *Cannabis* matrix is notoriously difficult to work with as there are significant interferences present which hinder the low-level detection of pesticides.

This study presents a comprehensive method for the analysis of gas chromatograph (GC)-amendable pesticides in *Cannabis* flower. Furthermore, this method uses dispersive solid phase extraction (dSPE) to help mitigate matrix effects that are common in the flower extract. Three selected reaction monitoring (SRM) transitions were used for each target pesticide. This study was focused on developing a robust and sensitive method for GC amendable pesticides in *Cannabis* flower for use in the state of California. However, LC-MS/MS would also be required to analyze the complete California pesticide list.

EXPERIMENTAL

Sample Preparation:
Cannabis flower was ground and extracted using a mixture of acetonitrile and dimethylacetamide (DMA). The sample was spiked with a 20 ppb pesticide standard mixture consisting of the 12 compounds listed in Table 3. The extraction and dSPE workflow are outlined in Figure 1. The use of dSPE is critical for reducing matrix effects and allowing for low detection limits as shown in Figure 2.

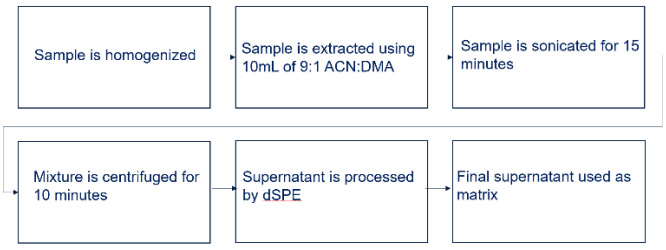

Fig 1. Sample preparation of *Cannabis* flower.

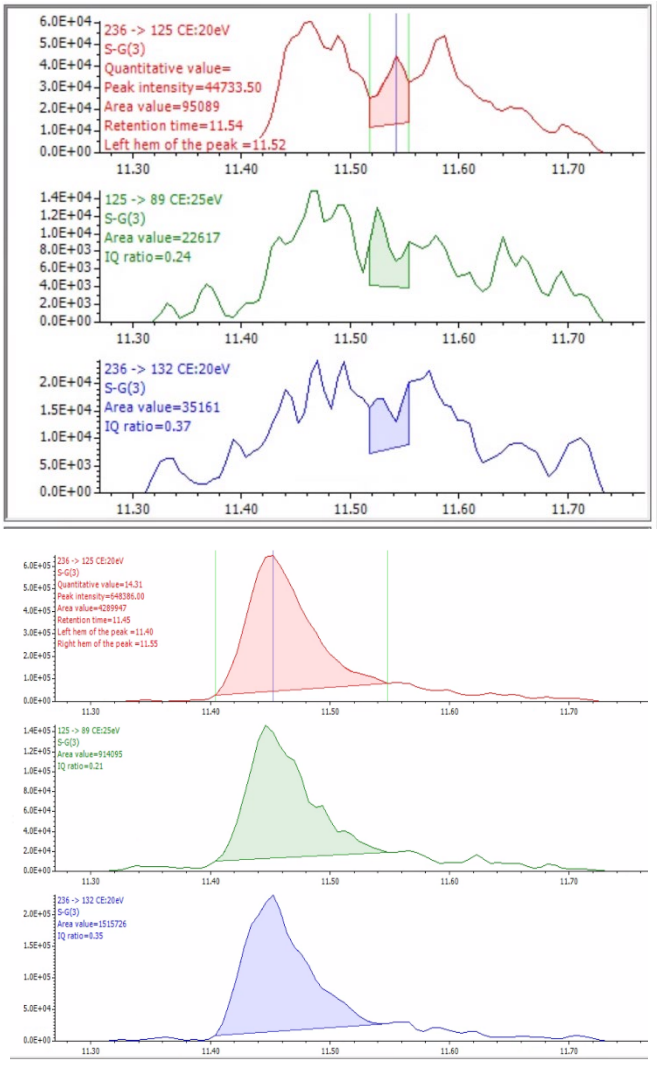

Fig 2. Cannabis matrix effects before (top) and after (bottom) using dSPE.

Table 1: Gas Chromatograph Parameters

GC	7890B (Agilent)
Column	ZB-5MSPlus, 30.0 m, 0.25 mm i.d., 0.25 µm (Phenomenex, Cat#:7HG-G030-11)
Inlet liner	Zebron Plus 4 mm Single Taper w/Wool on bottom (Phenomenex Cat#: AG2-0A11-05)
Inlet Temp.	260 ˚C
Carrier Gas Type, Flow	He, 1.000 mL/min constant flow
Mode	Pulsed Splitless
Pulsed Pressure, Time	206.84 kPa, 0.550 min
Purge Flow	30 mL/min, 1.0 min
Septum Purge Flow	3.0 mL/min
Saver flow, Time	15 mL/min, 5.0 min
Injection Volume	1.0 µL
Oven Program	80 ˚C (0.75 min) → 35 ˚C/min → 190 ˚C → 5 ˚C/min → 240 ˚C → 20 ˚C/min → 300 ˚C (6 min)

Table 2: Mass Spectrometer Parameters

JMS-TQ4000GC	
Ion Source Temp.	250 ˚C
Interface Temp.	300 ˚C
Ionization Mode	EI+, 70 eV, 100 µA
Measurement Mode	SRM, High Sensitivity
Target Cycle Time	Approx. 330 ms
Acquisition Rate	2.778 Hz
Channel Time	20 – 100 ms
Relative EM Voltage	900 V
Collision Gas	N_2, 10%

Instrumentation:
An Agilent 7890B GC combined with a JEOL JMS-TQ4000GC triple quadrupole mass spectrometer was used in this study. All injections were done using pulsed splitless liquid injection. Analysis parameters and SRM channels are detailed in Tables 1–3.

RESULTS

The SRM chromatograms for the three transitions of every pesticide tested are shown in Figures 3 – 14. Strong signals were observed for all pesticide transitions at 20 ppb with very little interference effects. These results clearly show that this extraction/dSPE method combined with GC-MS/MS can readily handle the action limits for GC amenable pesticides as set forth by California regulations.

CONCLUSIONS

This study showcases a rapid, sensitive, and effective method for testing GC amenable pesticides in *Cannabis* matrix. The use of a dSPE sample cleanup step coupled with GC-MS/MS allows for the rapid, selective screening of *Cannabis* products. Furthermore, low detection limits were achieved using this scenario, which in turn allows for larger dilution factors to further mitigate matrix effects. Using dSPE also allows for greater sensitivity and better chromatographic peak shapes by removing interference compounds. These results show that each pesticide can be measured at 20 ppb in cannabis matrix and that the action limits put forth by the State of California are readily achievable using this method. Furthermore, a combination of GC-MS/MS and LC-MS/MS will provide the best all-around capabilities for analyzing the entire California pesticide list.

Table 3: SRM Transitions

Analyte	Precursor	Collision Energy	Product
Boscalid	140	10	112
	140	25	76
	342	20	140
Cis-Chlordane	375	20	266
	373	25	266
	373	25	264
Trans-Chlordane	373	25	266
	373	20	264
	375	20	266
Chlorfenapyr	59	5	31
	247	15	227
	59	5	41
Fipronil	213	25	143
	367	30	213
	213	20	178
Kresoxim-methyl	116	20	89
	206	10	116
	206	10	131
Methiocarb	168	10	153
	168	15	109
	153	10	109
Propoxur	110	25	63
	152	10	110
	110	20	64
Chlorpyifos	197	15	169
	199	15	171
	197	25	134
Diazinone	137	15	84
	199	10	135
	199	15	93
Dimethoate	93	10	63
	87	10	42
	87	20	46
PCNB	295	15	237
	249	15	214
	237	20	119

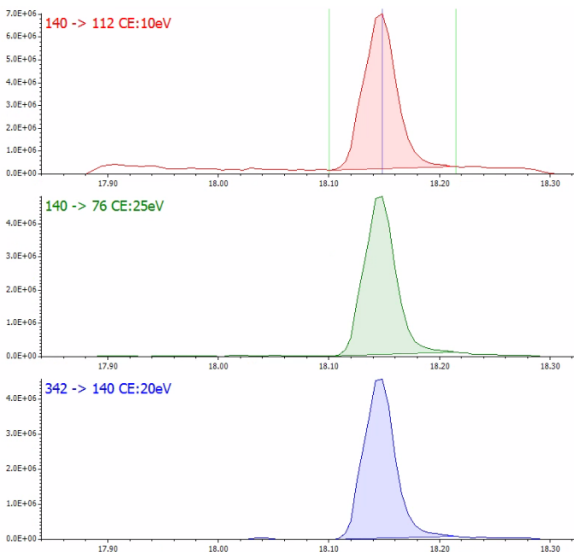

Fig 3. SRM chromatograms for boscalid.

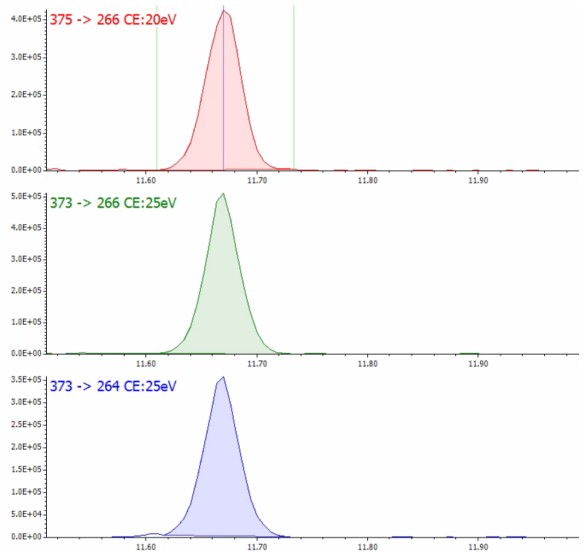

Fig 4. SRM chromatograms for *cis*-chlordane

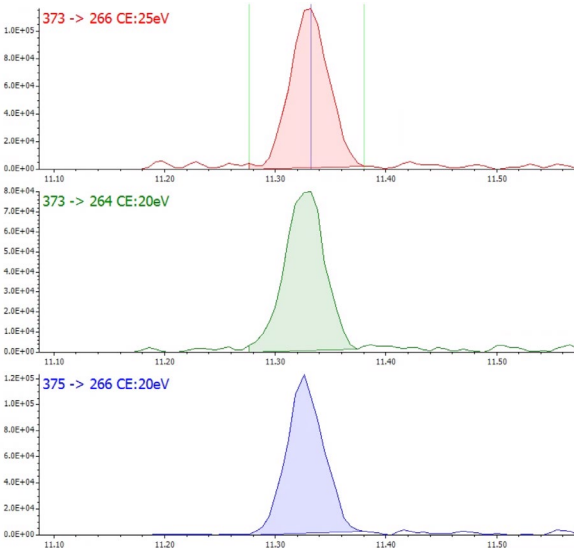

Fig 5. SRM chromatograms for *trans*-chlordane.

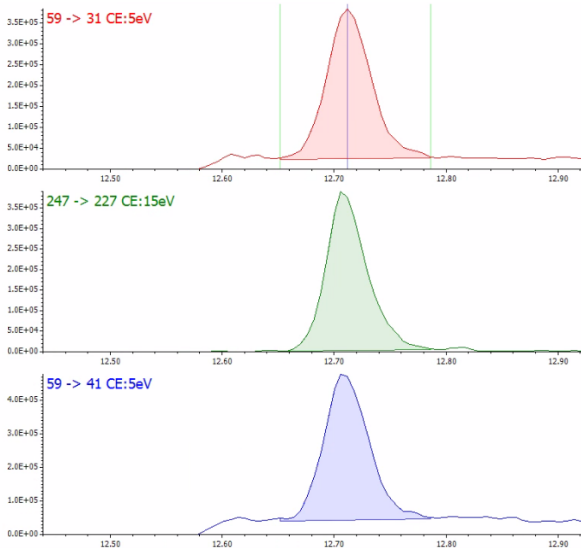

Fig 6. SRM chromatograms for chlorfenapyr.

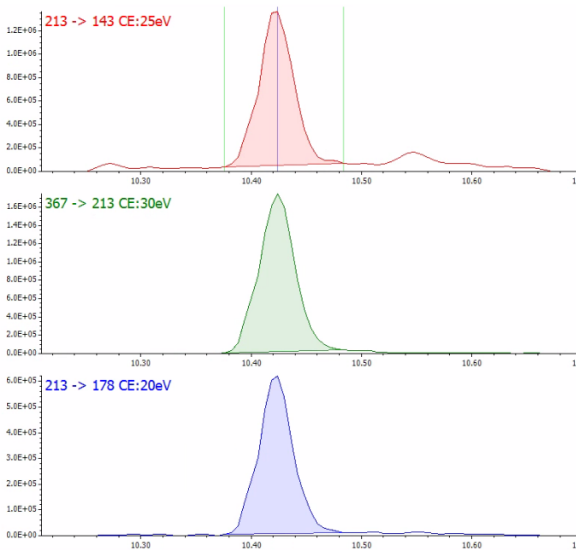

Fig 7. SRM chromatograms for fipronil.

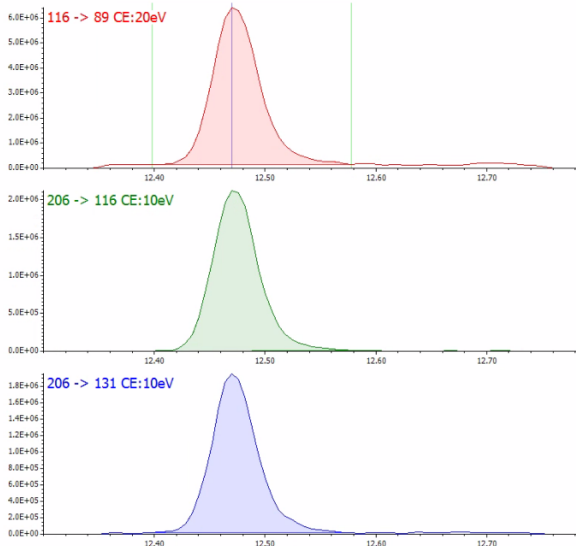

Fig 8. SRM chromatograms for kresoxim-methyl.

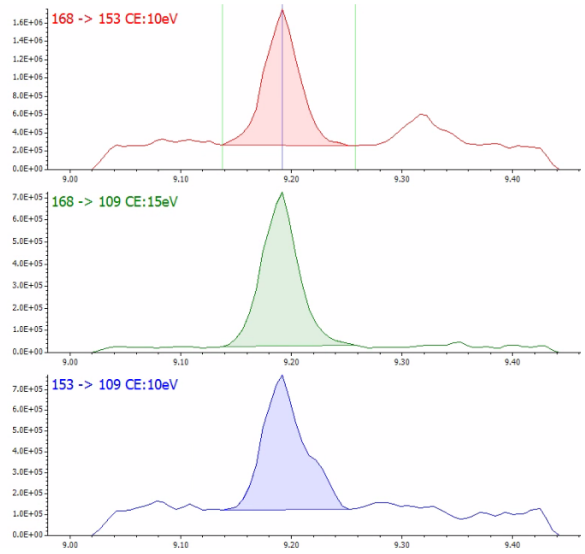

Fig 9. SRM chromatograms for methiocarb.

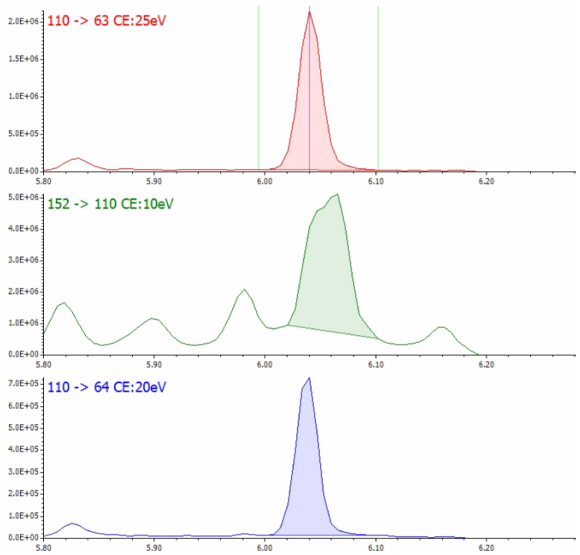

Fig 10. SRM chromatograms for propoxur.

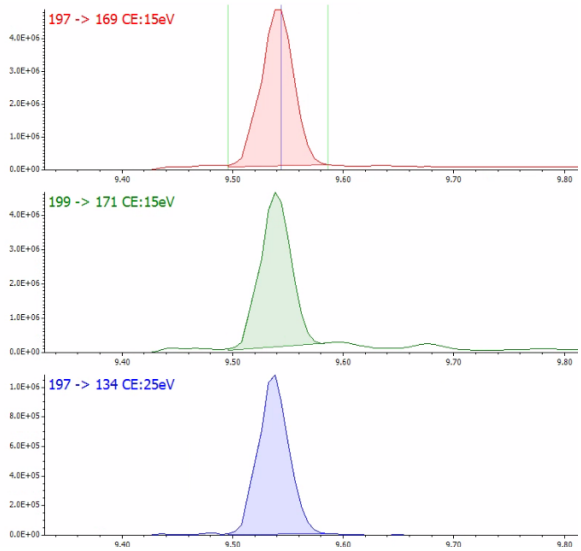

Fig 11. SRM chromatograms for chlorpyrifos.

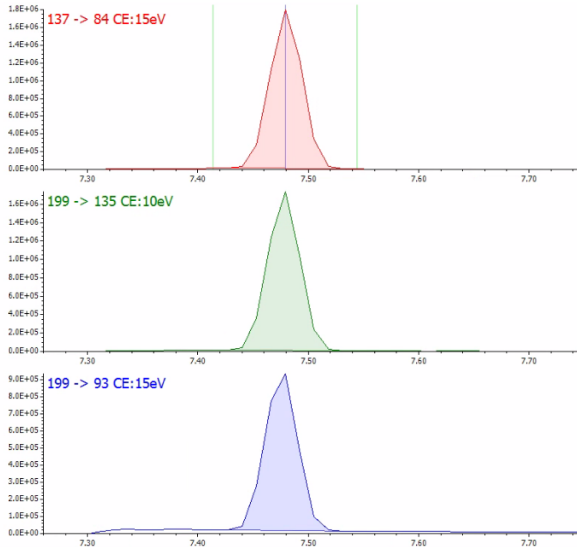

Fig 12. SRM chromatograms for diazinone.

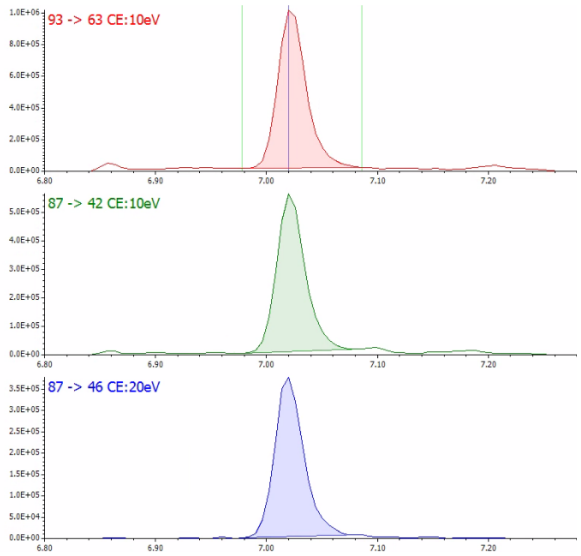

Fig 13. SRM chromatograms for dimethoate.

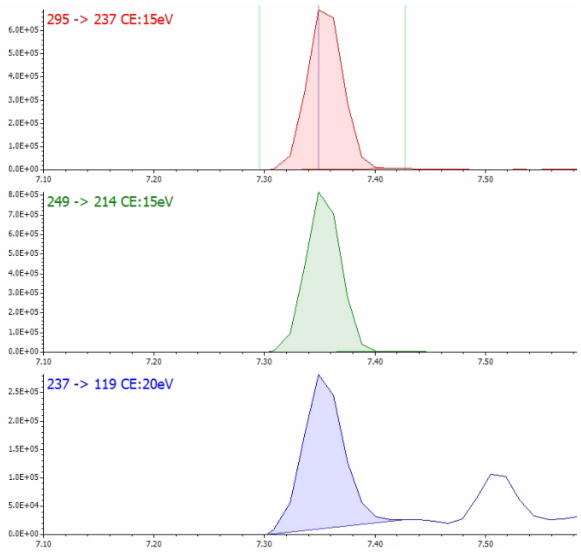

Fig 14. SRM chromatograms for pentachloro-nitrobenzene (PCNB).