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Pesticide analysis in Hops and Cannabis by GC-MS-MS

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Introduction

The rising popularity of medical and recreational cannabis has dramatically increased the demand for this plant. Cultivators of the closely related hops plant and cannabis may use pesticides or other chemical residues to protect their plants from mold and insects, however few of these substances may be legally used in cannabis. The possible adverse health effects of unapproved chemicals have drawn significant public attention. Many chemical residues may be measured using LC-MS however GC-MS is also needed for some compounds. In this work we used GC-MS-MS with a modified QuEChERS extraction and cleanup to rapidly measure pesticides in hops and cannabis with high performance.

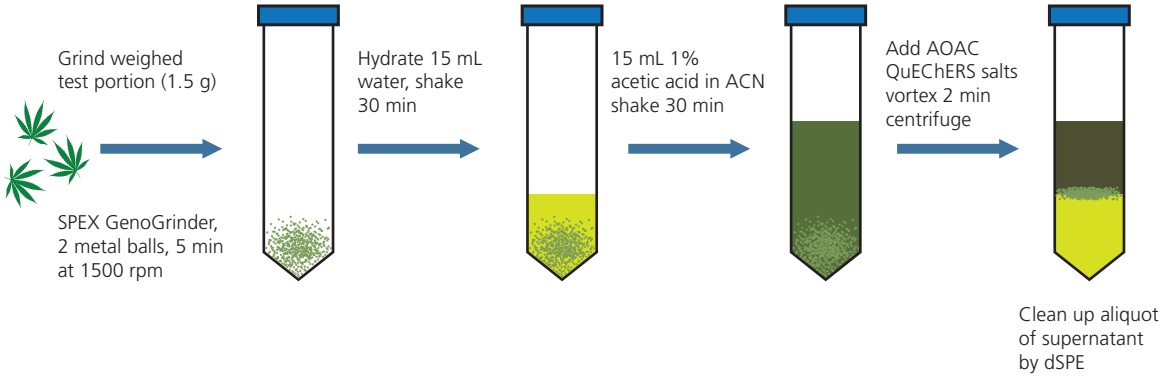

Figure 1 Modified QuEChERS Extraction

Method

Test portions of dried hops or cannabis flower were homogenized by grinding and extracted using QuEChERS extraction with SPE cleanup. Detection was carried out by GC-MS and GC-MS-MS using a GCMS-TQ8040 triple quadrupole mass spectrometer. Pesticide recovery was determined using spiking experiments and calibration curves were prepared using matrix matched standards. All cannabis analysis was carried out in state-certified testing labs with proper licenses in force.

Table 1 Method conditions

Inj. Temp	: 250 °C
Inj. Mode	: Splitless (High Press. Inj. 250 kPa, 1.5 min)
GC Column	: Rxi-5MS (30 m x 0.25 mm ID, df = 0.25µm) with Rxi-Guard (5 m x 0.25 mm ID)
GC Oven Temp	: 105 °C (3 min), 10 °C/min to 130, 4 °C/min to 200, 8 °C/min to 290 (6 min)
Flow Mode	: Constant linear velocity (44.1 cm/sec)
Interface Temp	: 280 °C
Ion Source Temp	: 230 °C

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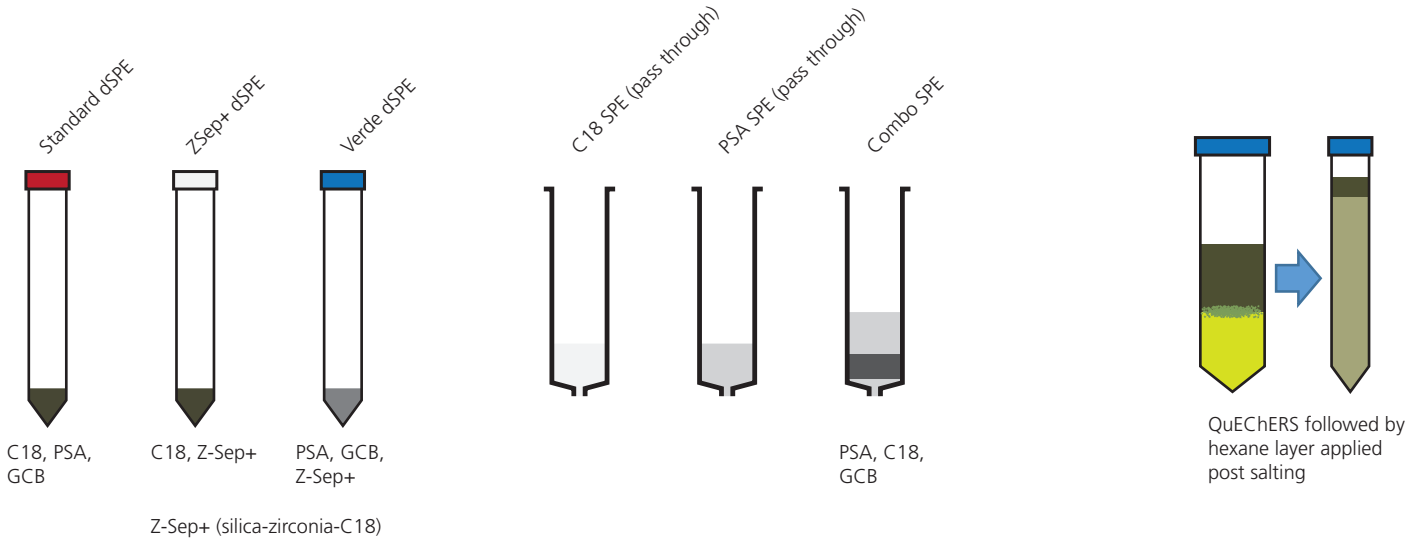

Figure 2 Various sample cleanup techniques investigated. Z-Sep+ is silica-zirconia-C18 material.

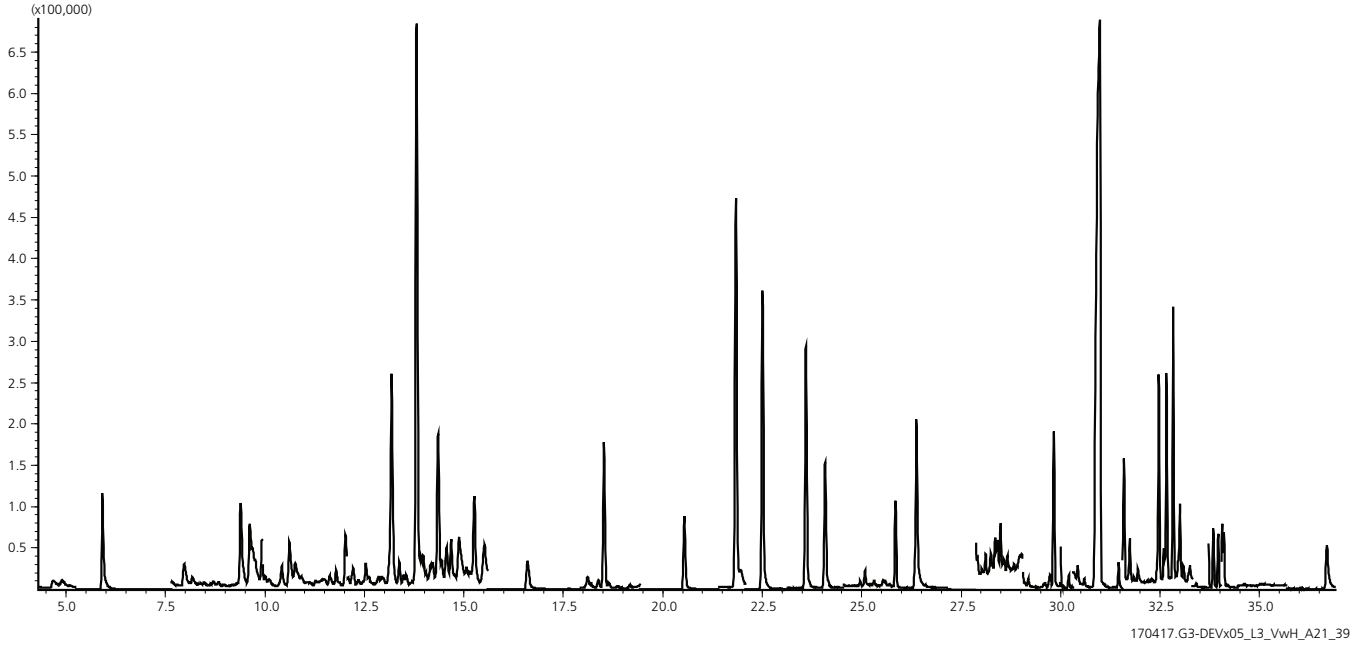

Figure 3 Representative GCMS chromatogram of pesticides spiked into cannabis matrix blank

Results and Discussion

QuEChERS extraction with dispersive SPE cleanup were tested to determine which provided the best combination of pesticide recovery and cleanup for dried flower cannabis samples. A wide variety of dSPE sorbent brands were tested and the best results were obtained with Sigma Verde dSPE, which removed a large amount cannabinoids as shown in Figure 7. Hexane treatment resulted in removal of a large portion of the early eluting background, which we determined contained low molecular weight compounds such as terpenes. The recoveries of some pesticides were slightly reduced in the hexane treatment, therefore we plan to test different volumes of hexane treatment to find an optimum amount. 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. Recovery was compound dependent however the majority were within the range of 70-120% while outliers above and below the range were observed. In a random sampling of 15 dried flower cannabis samples offered for retail sale, pesticides were detected in three samples as shown below.

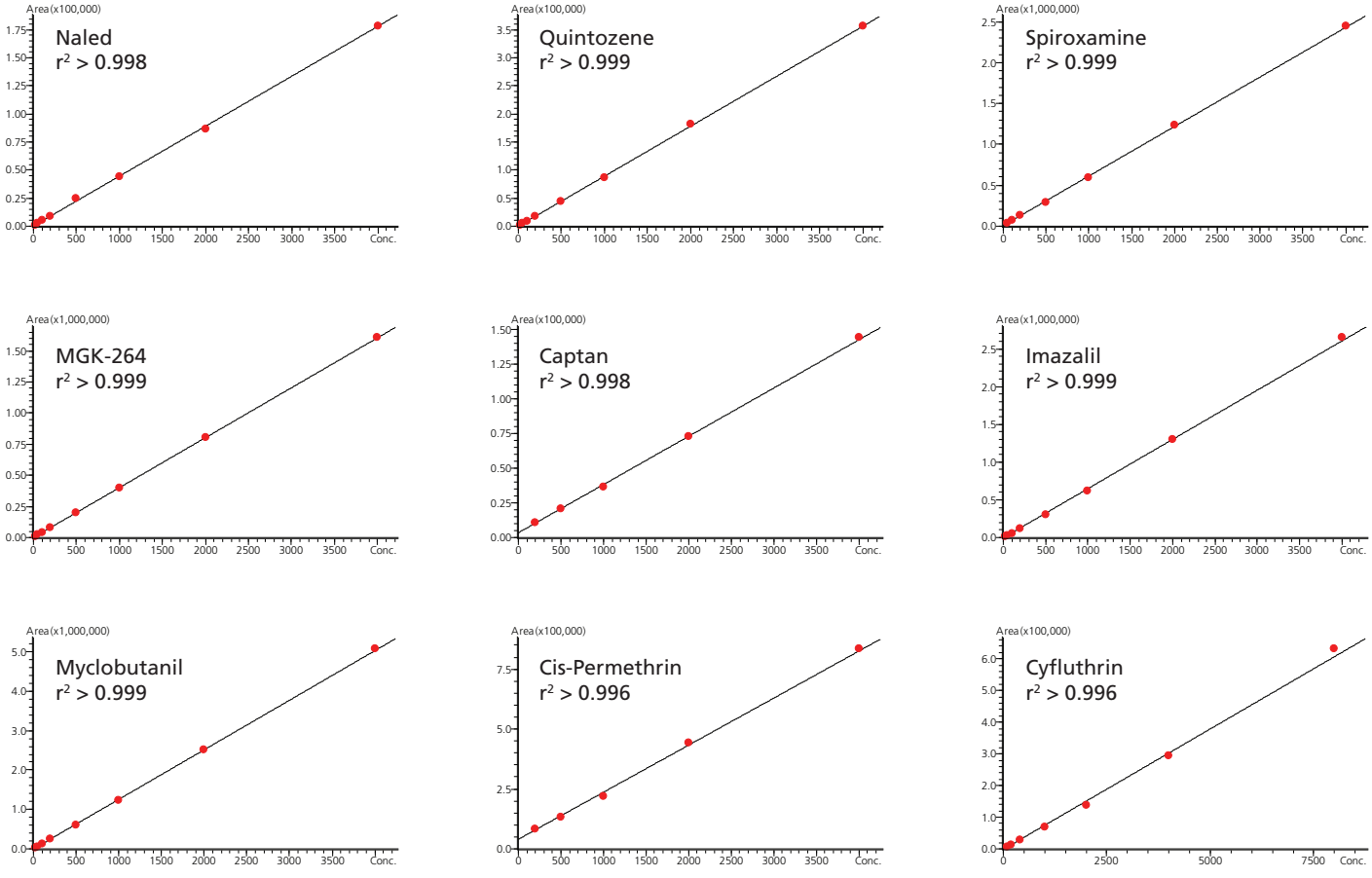

Figure 4 Representative calibration curves.

GCMS Scan (TIC) of matrix blank

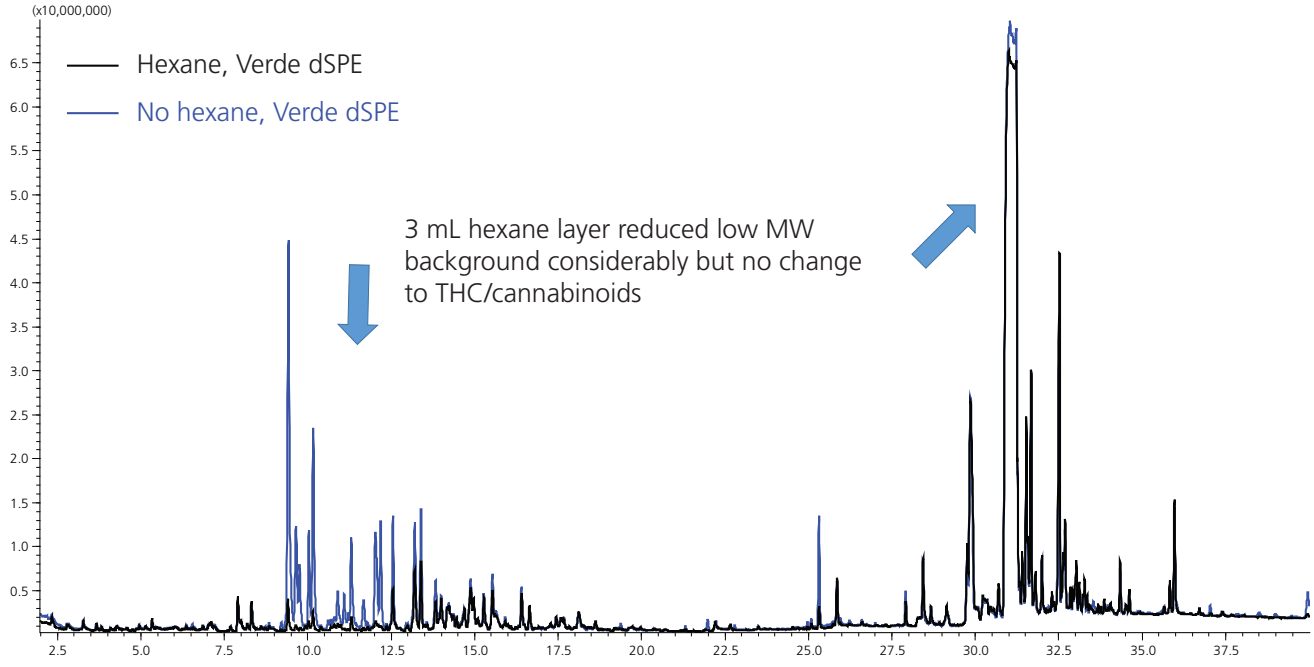

Figure 5 Chromatogram of cannabis matrix blank with hexane treatment (black) and without (blue) prepared using standard dSPE.

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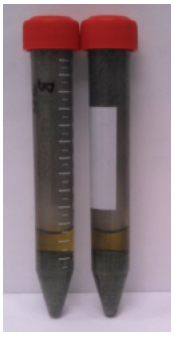
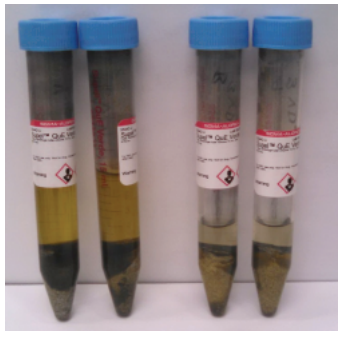
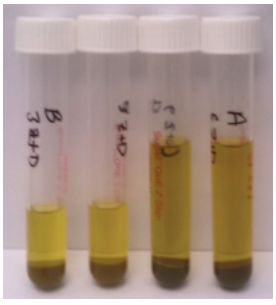
Recovery	Std SPE	Std SPE with Hexane	Verde only	Verde with Hexane	LOQ
Chlofentezine deg.	104.1%	76.6%	90.0%	44.5%	100
Dichlorvos	92.6%	91.1%	42.0%	59.8%	20
Propoxur	94.0%	103.4%	91.8%	91.5%	50
Ethoprophos	88.1%	80.8%	76.4%	76.1%	50
Naled	56.7%	85.1%	7.7%	22.7%	50
Dimethoate	89.6%	89.1%	80.1%	82.8%	20
Carbofuran	95.2%	112.1%	102.0%	93.8%	100
Quintozene	78.3%	49.4%	75.1%	44.6%	20
Diazinon	82.5%	70.1%	76.3%	69.6%	50
Parathion-methyl	84.8%	77.5%	81.1%	79.5%	20
Spiroxamine-1	57.8%	55.9%	7.3%	6.4%	50
Carbaryl	89.9%	102.4%	106.6%	73.3%	50
Metalaxyl (Mefenoxam)	85.8%	86.1%	77.2%	73.3%	50
Spiroxamine-2	57.5%	54.2%	8.2%	7.7%	20
Methiocarb	90.3%	105.0%	101.1%	76.7%	50
Malathion	89.5%	87.4%	81.5%	86.7%	20
Chlorpyrifos	79.0%	63.7%	74.6%	62.0%	20
MGK 264-1	80.4%	69.9%	77.5%	66.9%	20
Thiamethoxam deg.	84.3%	80.2%	79.2%	78.9%	50
MGK 264-2	81.1%	75.0%	77.3%	71.7%	20
Captan	107.8%	87.7%	96.6%	72.0%	200
Fipronil	87.1%	84.0%	78.1%	84.3%	20
Paclobutrazol	87.3%	89.5%	71.5%	75.5%	20
Fludioxonil	81.8%	77.2%	74.0%	77.8%	20
Myclobutanil	NA	NA	76.3%	77.5%	20
Kresoxim-methyl	85.9%	84.5%	79.8%	82.4%	20
Chlorfenapyr	83.8%	79.3%	75.6%	78.1%	20
Propiconazole-1	76.3%	76.9%	63.2%	61.0%	100
Propiconazole-2	40.8%	76.4%	70.1%	68.5%	50
Trifloxystrobin	89.9%	83.7%	83.5%	84.2%	40
Tebuconazole	83.0%	80.6%	59.0%	64.5%	20
Spiromesifen	113.1%	78.5%	76.0%	76.1%	50
Acetamiprid	87.6%	82.5%	77.1%	91.2%	500
Phosmet	NA	94.0%	82.6%	112.5%	500
Fenoxycarb	83.9%	81.8%	79.7%	87.3%	20
Bifenthrin	76.9%	47.0%	72.7%	46.2%	100
Bifenazate	NA	NA	68.4%	71.5%	40
Chlorantraniliprole	75.9%	71.2%	68.5%	71.2%	20
Etoxazole	80.6%	62.1%	70.8%	64.2%	100
cis-Permethrine	81.9%	88.6%	62.0%	70.9%	200
Pyridaben	73.2%	63.6%	67.6%	61.0%	50
trans-Permethrine	75.4%	56.3%	69.5%	54.9%	50
Cyfluthrin-1	84.8%	81.7%	79.8%	77.3%	100
Cypermethrin-1	82.5%	78.0%	76.5%	72.0%	100
Boscalid	85.6%	82.9%	77.9%	80.4%	20
Etofenprox	71.3%	54.2%	69.1%	50.9%	20
Azoxystrobin	90.8%	88.0%	81.1%	86.7%	50



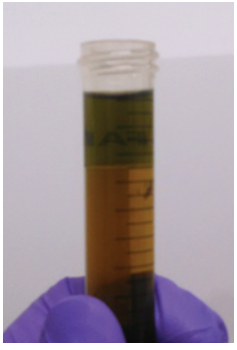
Standard dSPE
(Restek C18, PSA, GCB)



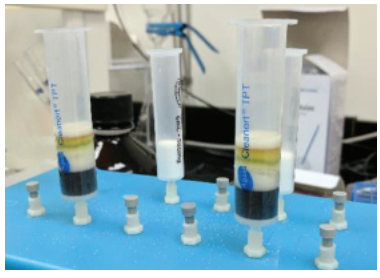
Verde dSPE
(Sigma PSA, GCB, Z-Sep+)



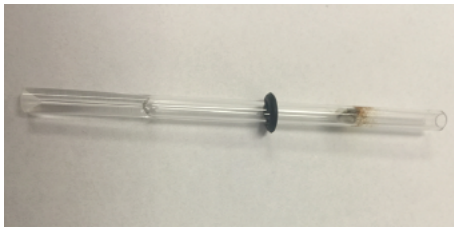
Z-Sep+
(Sigma Z-Sep+)



Hexane layer,
3 mL post-salt



Combo cartridges (Agela Cleanert TPT)



Contaminated liner

Figure 6 (Left) Table of recoveries for selected cleanup techniques.
(Right) Images of various cleanups in progress. (Below) Dirty GCMS liner.

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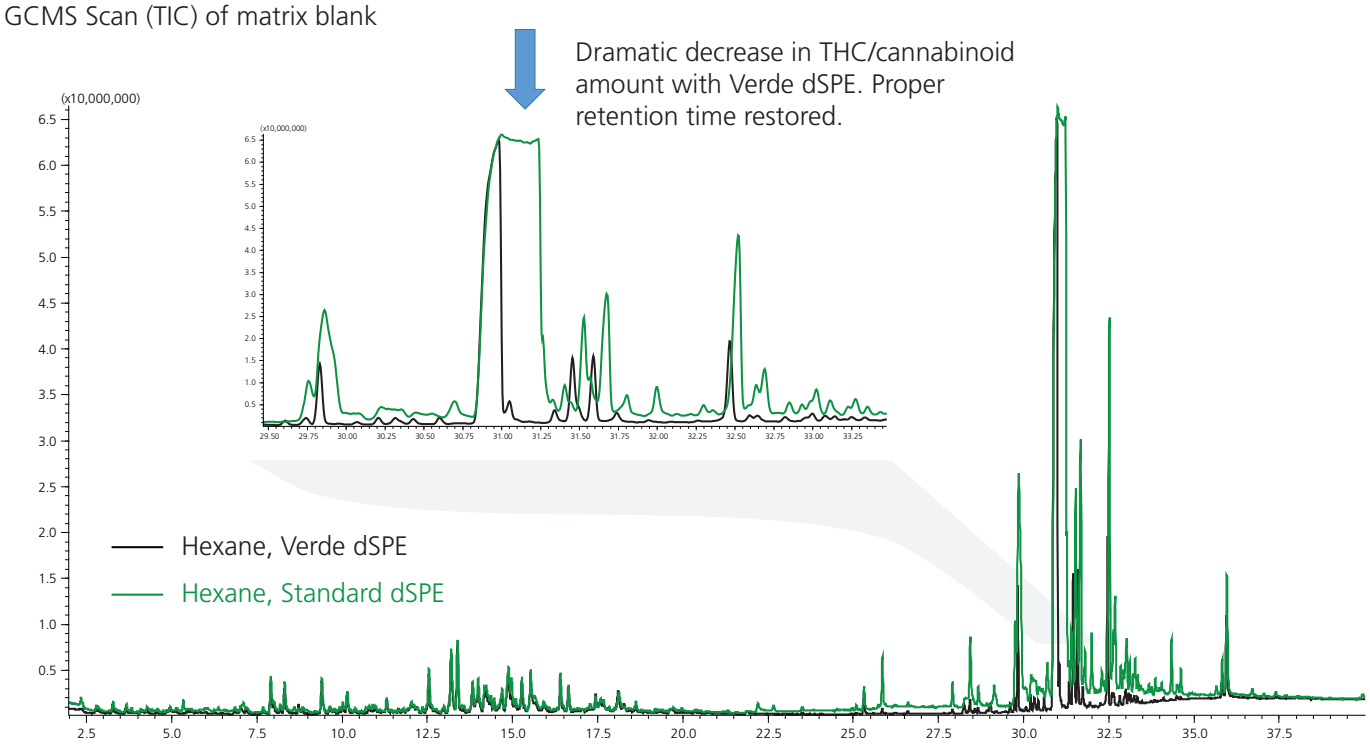
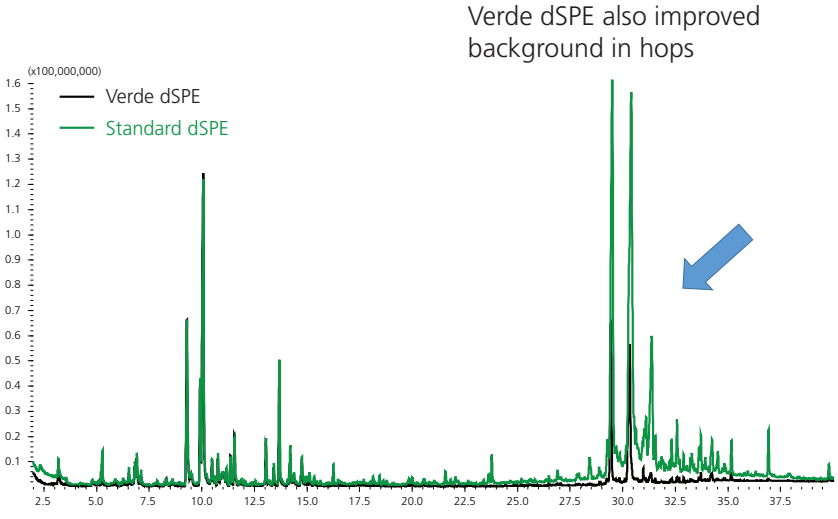


Figure 7 Chromatogram of cannabis matrix blank with standard dSPE and Verde dSPE. The Verde dSPE reduced the cannabinoid level significantly and returned proper retention times to the compounds.



Sample	Pesticides detected
BA01	
BA02	
BA03	
BA04	
BA05	
BA06	
BA07	123 ng/g cyfluthrin, 99 ng/g cypermethrin
BA08	139 ng/g chlorfenapyr
BA09	1064 ng/g chlorfenapyr
BA10	
BA11	
BA12	
BA13	
BA14	
BA15	

Figure 8 (Left) Chromatogram of hops matrix blank with standard and Verde dSPE. No hexane was used in either sample. (Right) Table of results of pesticide analysis in randomly selected cannabis samples.

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Conclusion

A method for detection of chemical residues in dried cannabis flower samples by GC-MS-MS 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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