Analysis of Cannabis for Pesticide Residues by GC/Q-TOF

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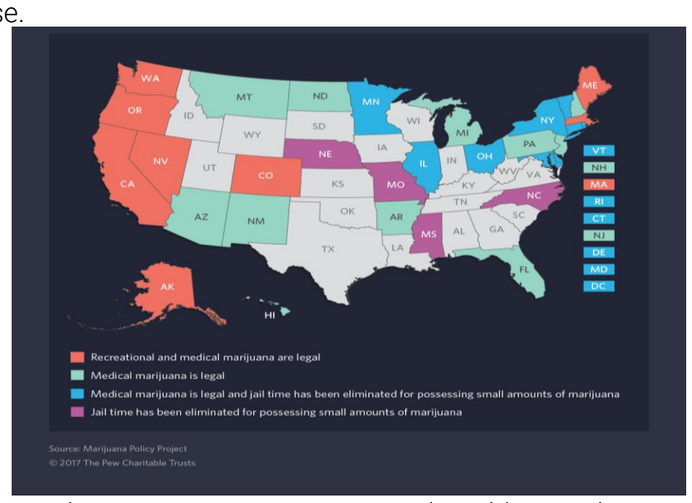
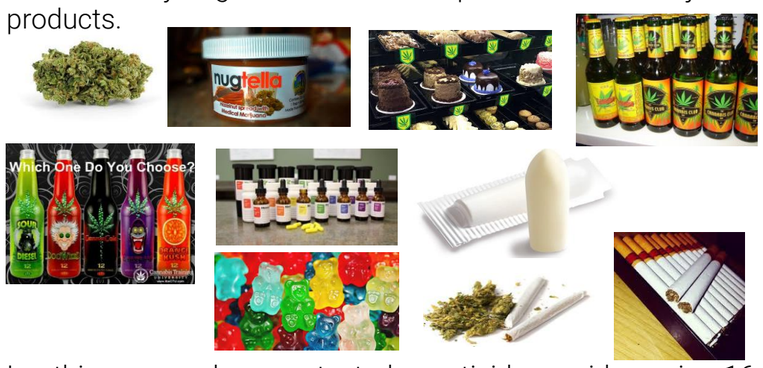
Introduction

In the United States, the use of cannabis for medical purposes has been legalized in 29 states. Eight states (CO, WA, OR, NV, CA, AK, ME, and MA) have approved recreational use.



Like other crops, marijuana is vulnerable to destructive insects and fungus. Unlike other crops, it is illegal under federal law and therefore the EPA has not approved any pesticides or fungicides for it and there are no federal guidelines for how much residual pesticide can be left on marijuana products.

In 2017, Steep Hill Labs in Berkeley, one of the nation's largest cannabis testing laboratories, tested 44 marijuana products for 16 pesticides. They found 41 out of 44 samples (93 %) tested positive for pesticides at levels high enough that those products would've been banned for sale in some other states that currently regulate the use of pesticides in marijuana products.



In this research, we tested pesticide residues in 16 confiscated marijuana samples (from medical marijuana states) as well as marijuana produced at the University of Mississippi outdoor growing facility. QuEChERS extraction was used for sample preparation followed by analysis on an Agilent 7890B/7200B GC/Q-TOF using a new pesticide PCDL and the Find by Fragments workflow in MassHunter software. This approach looks for 852 pesticides, metabolites and other contaminants in each sample.

Experimental

QuEChERS Extraction of Pesticides

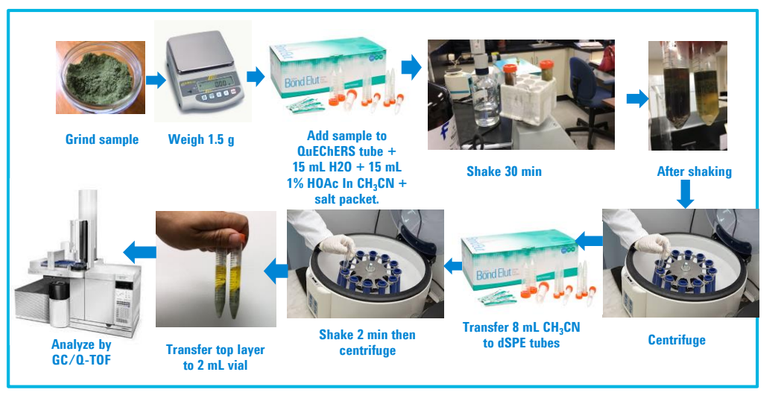


Figure 1. QuEChERS extraction procedure. Result is 0.1 g of Cannabis/mL of ACN.

PCDL: Personal Compound Database & Library with 852 Pesticides and Common Contaminants

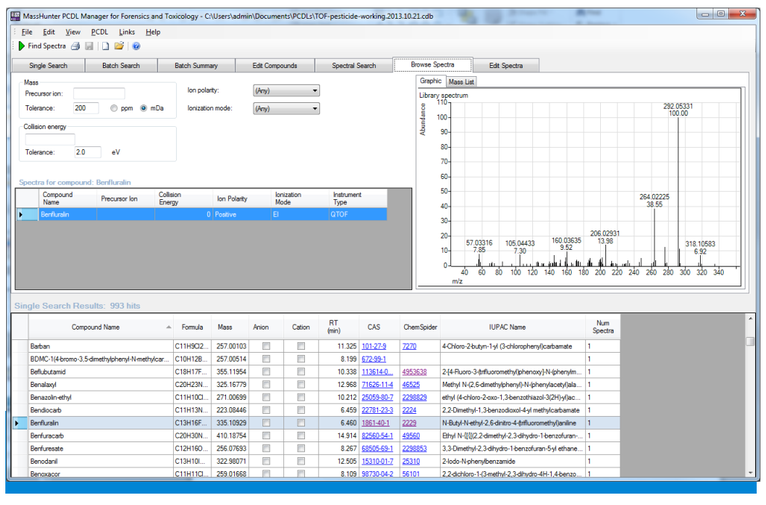


Figure 2. Personal Compound Database/Library (PCDL) containing exact mass spectrum, locked RT, CAS#, name, molecular formula, monoisotopic exact mass (and more) for 852 pesticides . The Find by Formula algorithm looks for all 852 pesticides in a sample.

Results and Discussion

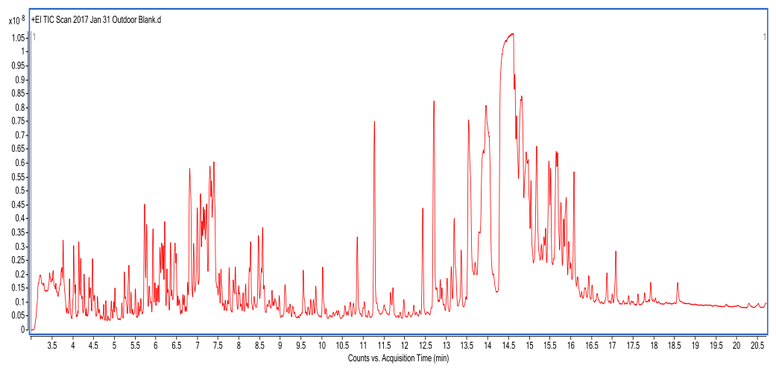


Figure 3. Typical chromatogram for a marijuana QuEChERS extract with added analyte protectants.

Pesticide PCDL Spectrum of tris(β-chloropropyl)phosphate

Extracted Ion Chromatograms for the six most significant ions

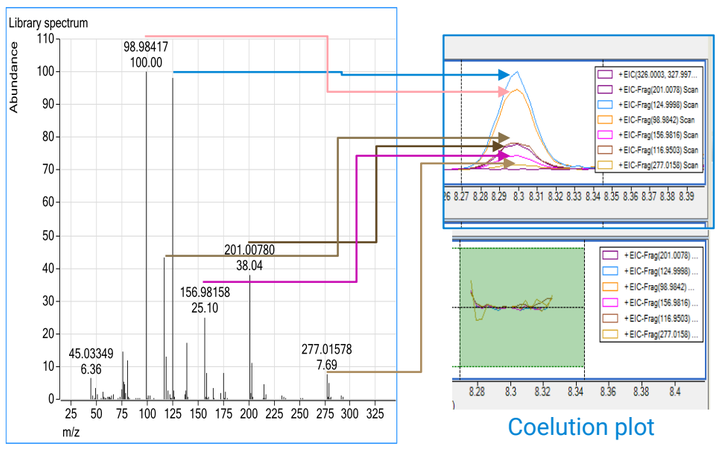


Figure 4. The Agilent Find by Fragments software extracted the six most significant ions for each pesticide in the PCDL at it's locked RT. The software looks at the peak shape and RT for each extracted ion. The coelution plot shows the normalized peak heights for each ion relative to a reference ion.

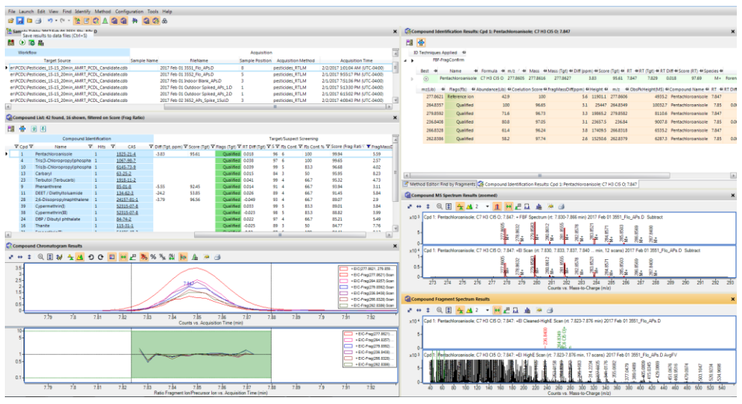


Figure 5. Find by Formula results screen for pesticides tentatively identified in a confiscated marijuana sample. The specific results are for Pentachloroanisole

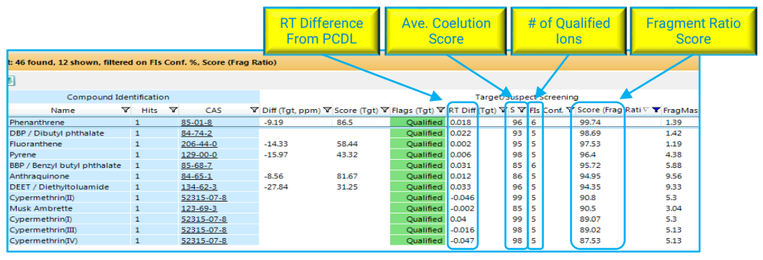


Figure 6. Find by Formula Compound Identification Results showing some of the information available to help identify a "hit."

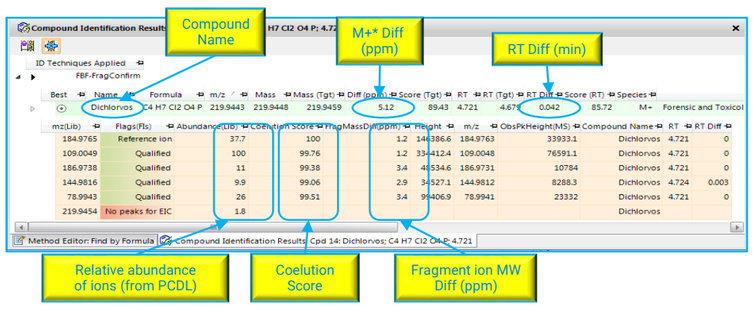


Figure 7. Compound Identification results for Dichlorvos showing 5 of the 6 ions with excellent coelution scores, good mass accuracy and a close RT match to the PCDL value.

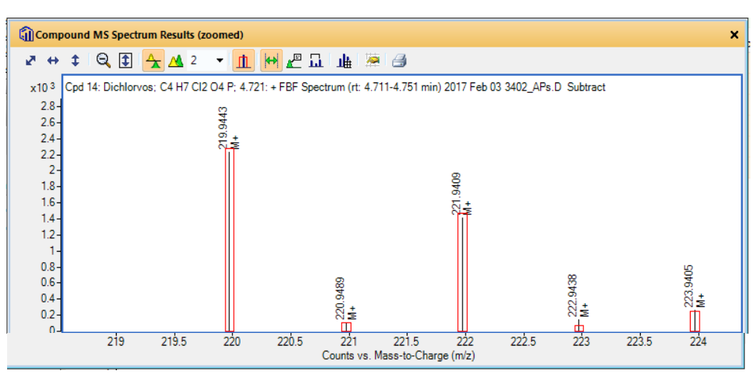
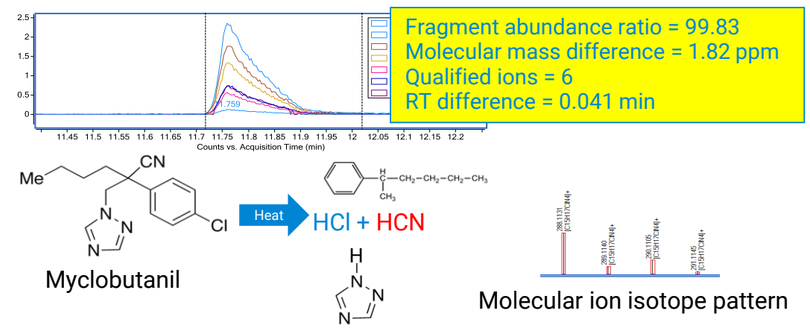


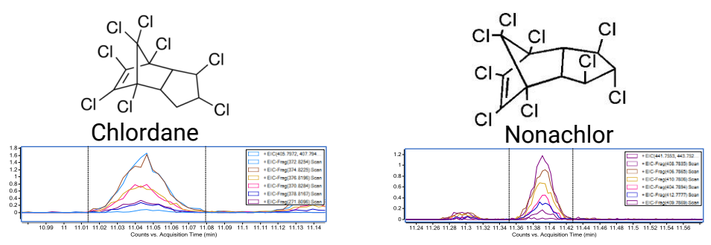
Figure 8. Molecular ion isotope pattern for Dichlorvos. Note: M+* is only 1.8% of the base peak. The red rectangles show the theoretical spacing and abundance of the isotopes.

Results and Discussion (Cont.)

Myclobutanil Residue in Cannabis. Myclobutanil decomposes when heated to produce HCN.



POPs in Pot: Two samples had cis- and trans-Chlordane and trans-Nonachlor



Banned for all uses in the US since 1988;
Banned by Stockholm POPs Convention in 2001

Pesticides found in 16 confiscated marijuana samples and marijuana grown by the U. Mississippi Marijuana Program.

Note: The fire retardants, Tris(β-chloropropyl)phosphate & Tris(3-chloropropyl)phosphate, are found widely in dust samples and may have contaminated some of these samples while in storage or elsewhere. For samples that had residues of chlordane and nonachlor, it is likely that they were grown in soil that was contaminated in the past.

Sample	Pesticide found
1055	Myclobutanil
	Cypermethrin I
	Cypermethrin III
	Tris(b-chloropropyl)phosphate
	DEET
	Terbucarb
1271	DEET
	Fenpropathrin
	2-phenylphenol
	Phenanthrene
	Terbucarb
	Fenpropathrin
2511	DEET
	Cypermethrin I
	Cypermethrin III
	Tris(b-chloropropyl)phosphate
	Terbucarb
3400	Phenanthrene
	Fluoranthene
	DEET
	Pyrene
	Cypermethrin I
	Cypermethrin III
	Terbucarb
3401	Tris(b-chloropropyl)phosphate
	trans-Chlordane
	Acrinathrin (Rufast)
	Tris(3-chloropropyl)phosphate
	Phenanthrene
	trans-Nonachlor
	2,6-diisopropylnaphthalene
	cis-chlordane

Sample	Pesticide found
3402	DEET
	Dichlorvos
	Cypermethrin I
	Tris(b-chloropropyl)phosphate
	trans-Chlordane
	Cypermethrin III
	Acrinathrin (Rufast)
	Diphenylamine
	Fenpropathrin
	2-phenylphenol
	cis-Chlordane
	Phenanthrene
	Terbucarb
3452	DEET
	Jasmone
	Phenanthrene
	Tris(b-chloropropyl)phosphate
3466	Cypermethrin I
	Cypermethrin III
	Acrinathrin
3483	Cypermethrin III
	Cypermethrin I
	TBP (Tributylphosphate)
3486	Tris(3-chloropropyl)phosphate
	DEET
	Phenanthrene
3507	Tris(3-chloropropyl)phosphate
	Tris(b-chloropropyl)phosphate
	Cypermethrin I
	Phenanthrene
	2,6-diisopropylnaphthalene
3518	Cypermethrin I
	Tris(b-chloropropyl)phosphate
	Terbucarb
	2,6-diisopropylnaphthalene

Sample	Pesticide found
3534	Benzylbenzoate
	Cypermethrin I
	Phenanthrene
	Terbucarb
	gamma-Cyhalothrin
	Acrinathrin
	2,6-diisopropylnaphthalene
3536	Tris(b-chloropropyl)phosphate
	1-Naphthol
	Phenanthrene
	DEET
	Carbaryl
	Tris(3-chloropropyl)phosphate
	Tributylphosphate
	2,6-diisopropylnaphthalene
	Cypermethrin I
	Jasmone II
3551	Pentachloroanisole
	Tris(3-chloropropyl)phosphate
	Tris(b-chloropropyl)phosphate
	Cypermethrin I
	Cypermethrin III
	Phenanthrene
	DEET
	Terbucarb
3552	Tris(b-chloropropyl)phosphate
	Cypermethrin I
	Tris(3-chloropropyl)phosphate
	2,6-diisopropylnaphthalene
U Miss Grown Outdoors	**No pesticides found**

Conclusions

- Cannabis is one of the most difficult matrices to work with.
- High concentrations of cannabinoids and terpenes get extracted along with pesticides using QuEChERS extraction.
- These heavy interferences can lead to false positives.
- But, most false positives can be eliminated by looking at the fragment ion ratios, mass and RT accuracy and the molecular ion isotope pattern (when present).
- 22 pesticides & metabolites, 2 fire retardants and 3 PAHs were found in the 16 samples.
- The fire retardants, PAHs and banned pesticides likely came from environmental contamination.
- No pesticides were found in the Marijuana grown at U Miss.

L to R: Drs. Wylie, Radwan, Gon & Wang standing in front of the Marijuana Museum

Dr. ElSohly