Technical Article

High-Quality Analysis of Pesticides in Cannabis

Using QuEChERS, Cartridge SPE Cleanup, and GCxGC-TOFMS

By Jack Cochran, Julie Kowalski, Sharon Lupo, Michelle Misselwitz, and Amanda Rigdon

- Quickly and effectively extract medical marijuana samples for pesticide analysis.
- Cartridge SPE cleanup of dirty extracts improves GC inlet and column lifetimes.
- Selective GC columns increase accuracy of pesticide determinations for complex samples.

Over 20 states in the U.S. have legalized the use of recreational or medical cannabis because of therapeutic benefits for ailments such as cancer, multiple sclerosis, and ALS. Dosing methods include smoking or vaporizing and baked goods. Unlike other prescribed medicines regulated by U.S. FDA, marijuana is a Schedule 1 drug and is illegal on the federal level. As a result, medical cannabis patients have no safety assurances for their medication, which could contain harmful levels of pesticide residues. Currently, medical marijuana pesticide residue analysis methods are poorly defined and challenging to develop due to matrix complexity and a long list of potential target analytes.

In order to address matrix complexity, we combined a simple QuEChERS extraction approach with cartridge SPE (cSPE) cleanup, followed by GCxGC-TOFMS. Acceptable recoveries were obtained for most pesticides, and incurred pesticide residues were detected in some of the illicit marijuana samples used for method development.

QuEChERS Extraction Saves Time and Reduces Hazardous Solvent Use

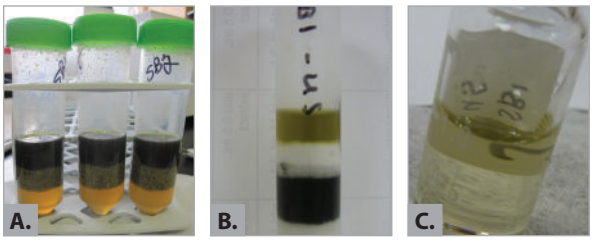
Trace residue extraction procedures from dry materials like medical cannabis typically involve large amounts of solvent, long extraction times, and tedious concentration steps similar to the Soxhlet procedure or multiresidue methods from the Pesticide Analytical Manual. QuEChERS, with its simple 10 mL acetonitrile shake extraction and extract partitioning with salts and centrifugation, offers time savings, glassware use reduction, and lower solvent consumption.

Water was added to finely ground, dry cannabis samples to increase QuEChERS extraction efficiency, especially for more polar pesticides. A vortex mixer was used to shake the solvent and sample for at least 30 minutes prior to extract partitioning. When finished, it was easy to transfer the supernatant from the QuEChERS extraction tube for subsequent cSPE cleanup prior to analysis with GC or LC (Figure 1).

Cartridge SPE Cleanup Improves GC Inlet Uptime

Injecting chlorophyll-laden extracts into a GC gives reduced recoveries for less volatile pesticides, and results in degradation of sensitive pesticides like DDT and Dicofol (Table I). SPE cleanup with a 500 mg graphitized carbon black/500 mg PSA cartridge removes chlorophyll and traps fatty acids that interfere with qualitative pesticide identification and bias quantification. cSPE has increased sorbent capacity over dispersive SPE for thorough cleanup of complex extracts.

Figure 1: A quick and easy QuEChERS extraction, combined with cSPE, effectively prepared extracts for pesticide residue analysis from highly complex marijuana samples.



Post-centrifugation QuEChERS extracts

QuEChERS extracts loaded on SPE cartridge

Final extract

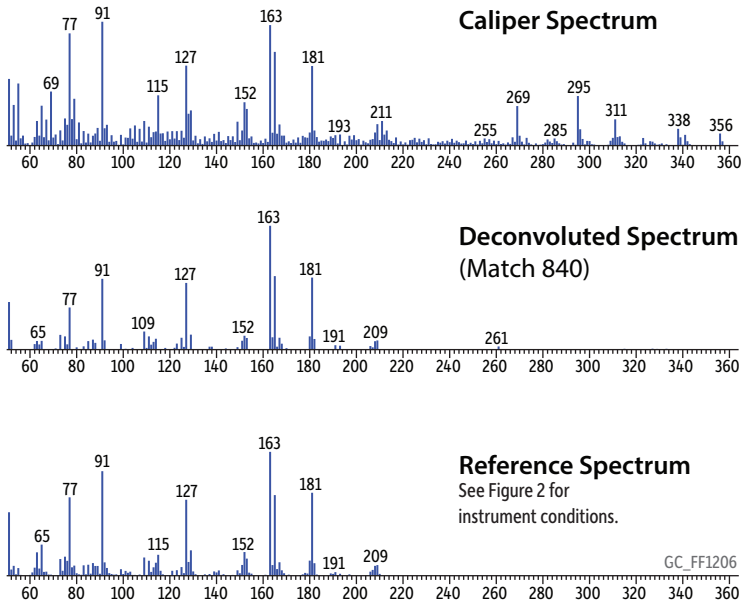
Orthogonal GC Columns Increase Separation Power for More Accurate Pesticide Results

GCxGC is a powerful multidimensional approach that gives two independent separations in one instrumental analysis. An Rxi®-5Sil MS and Rtx®-200 column combination distributes pesticides broadly in both dimensions, providing a highly orthogonal GCxGC system. More important though is separating pesticides from potential isobaric matrix interferences, as seen in the surface plot for the insecticide cypermethrin (Figure 2). Cypermethrin gas chromatographs as four isomers, and all would have experienced qualitative interference and quantitative bias from peaks in the foreground of the surface plot had only 1-dimensional GC been used. With GCxGC-TOFMS, cypermethrin was unequivocally identified in a marijuana sample at a low ppm level (Figure 3).

Summary

QuEChERS and cSPE produced usable extracts from highly complex cannabis samples for high-quality pesticide residue analysis. The multidimensional separation power of GCxGC-TOFMS was then used to correctly identify and quantify pesticides in these complex extracts.

Figure 3: Positive mass spectral identification of incurred cypermethrin in illicit marijuana.



Acknowledgment: Randy Hoffman, a Police Evidence Technician at The Pennsylvania State University (PSU), supplied the seized marijuana samples while overseeing their handling. Frank Dorman at PSU assisted with QuEChERS extractions.

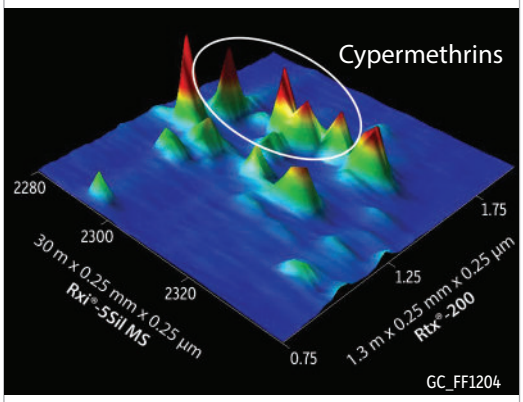
Initially published in *Restek® Advantage*.

Table I: Pesticide recoveries for a QuEChERS extract of cannabis give higher results when cSPE is used for cleanup. Dicofol and DDT are degraded in the inlet for the dirtier extract, yielding high DDD results.

Pesticide	Classification	With cSPE Cleanup (%)	Without cSPE Cleanup (%)
4,4'-DDD	Organochlorine	83	230
4,4'-DDT	Organochlorine	77	9
Bifenthrin	Pyrethroid	86	89
Dicofol	Organochlorine	84	ND
Azinphos methyl	Organophosphorus	79	53
trans-Permethrin	Organochlorine	68	17
Pyraclostrobin	Strobilurin	73	19
Fluvalinate	Pyrethroid	72	23
Difenoconazole	Triazole	67	21
Deltamethrin	Pyrethroid	68	20
Azoxystrobin	Strobilurin	72	27

ND = no peak detected

Figure 2: GCxGC-TOFMS and orthogonal Rxi®-5Sil MS and Rtx®-200 columns allow incurred cypermethrins in a marijuana extract to be separated from interferences (m/z 163 quantification ion).



Peaks	RT 1 (sec.)	RT 2 (sec.)
1. Cypermethrin 1	2292	1.50
2. Cypermethrin 2	2304	1.54
3. Cypermethrin 3	2310	1.53
4. Cypermethrin 4	2313	1.58

Column: Rxi®-5Sil MS 30 m, 0.25 mm ID, 0.25 µm (cat.# 13623), Rtx®-200 1.3 m, 0.25 mm ID, 0.25 µm (cat.# 15124); **Sample:** Diluent: Toluene; **Injection:** Inj. Vol.: 1 µL splitless (hold 1 min); Liner: Restek Premium 4mm single taper w/ wool (cat.# 23303.1); Inj. Temp.: 250 °C; Purge Flow: 40 mL/min; **Oven:** Oven Temp: Rxi®-5Sil MS: 80 °C (hold 1 min) to 310 °C at 5 °C/min, Rtx®-200: 85 °C (hold 1 min) to 315 °C at 5 °C/min; **Carrier Gas:** He, corrected constant flow (2 mL/min); **Modulation**: Modulator Temp. Offset: 20 °C; Second Dimension Separation Time: 3 sec.; Hot Pulse Time: 0.9 sec.; Cool Time between Stages: 0.6 sec.; **Instrument**: LECO Pegasus 4D GCxGC-TOFMS; For complete conditions, visit www.restek.com and enter GC_FF1204 in the search.

RESTEK
Pure Chromatography

Questions about this or any other Restek® product?
Contact us or your local Restek® representative (www.restek.com/contact-us).

Restek® patents and trademarks are the property of Restek Corporation. (See www.restek.com/Patents-Trademarks for full list.) Other trademarks in Restek® literature or on its website are the property of their respective owners. Restek® registered trademarks are registered in the U.S. and may also be registered in other countries.

© 2014 Restek Corporation. All rights reserved. Printed in the U.S.A.

www.restek.com

Lit. Cat.# FFAR1950-UNV