

Improved Recoveries for GC/MS/MS Analysis of Pesticide Residues in Cannabis

Using Supel[™] QuE Verde for QuEChERS and SLB[®]-5ms GC Column

One potential approach for the determination of pesticide residues in cannabis is the use of the “quick, easy, cheap, effective, rugged and safe” (QuEChERS) method outlined in AOAC official method 2007.01. In this application, QuEChERS was used in the extraction of pesticides from dried cannabis. For cleanup of the extracts, two different sorbent mixes were evaluated.

Experimental

Dried cannabis was supplied courtesy of Dr. Hari H. Singh, Program Director at the Chemistry and Physiological Systems Research Branch of the National Institute on Drug Abuse at the National Institute of Health. The sample was ground to a fine powder and extracted following the procedure outlined in the conditions section of **Figure 1**. The resulting acetonitrile extract was cleaned using two different sorbents: (1) PSA/C18/ENVI-Carb[™] and (2) Supel[™] QuE Verde. Unspiked and spiked (50 ng/g) samples were prepared. Analysis of the final extracts was done by GC/MS/MS using the GC conditions listed in **Figure 1**. Quantitation was performed against multi-point, matrix-matched calibration curves prepared in unspiked cannabis extract. Separate curves were prepared for each cleanup sorbent.

Results and Discussion

Matrix Removal

Figure 2 shows cannabis extracts before and after each cleanup. As expected, the PSA/C18/ENVI-Carb[™] sorbent mixture removed the most color. The Supel[™] QuE Verde mix removed the green from the cannabis extract, leaving only yellow pigments, and a much lighter colored extract than no cleanup. Extracts were analyzed by GC/MS in full scan mode to evaluate background (**Figures 1 a-c**). The TIC patterns of the extracts, cleaned and uncleaned, appear similar. However, there are some differences in peak amplitude between the chromatograms, and if the sum of the peak areas in the TICs are compared, it is evident that the lowest background was obtained using Supel[™] QuE Verde cleanup.

Figure 2. QuEChERS Extracts of Cannabis With and Without Cleanup

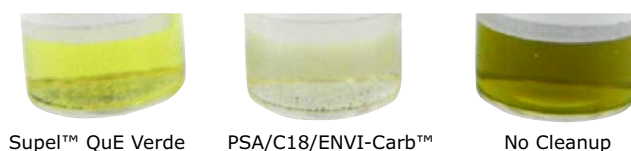


Figure 1. GC/MS Scan Analysis of Cannabis Extract Background (a) with no cleanup, (b) after cleanup with Supel[™] QuE PSA/C18/ENVI-Carb[™], and (c) after cleanup with Supel[™] QuE Verde

sample/matrix: ground cannabis, 1 g
 sample pretreatment: add 10 mL water to sample, allow to sit for 30 min
 extraction tube: Supel[™] QuE Citrate extraction tube (55227-U)
 extraction process: add 10 mL of acetonitrile containing 1% acetic acid; shake 10 min at 2,500 rpm on automated shaker; add contents of Supel[™] QuE citrate extraction tube; shake 1 min; centrifuge at 5,000 rpm for 5 min; remove supernatant
 cleanup tube: Supel[™] QuE Verde, 2 mL cleanup tube (55447-U)
 cleanup process: transfer 1 mL of supernatant to Supel[™] QuE Verde cleanup tube; shake for 2 min; centrifuge at 5,000 rpm for 5 min; remove supernatant and place in amber low adsorption vial for GC/MS/MS analysis.

column: SLB[®]-5ms, 30 m x 0.25 mm I.D., 0.25 μm (28471-U)
 oven: 50 °C (2 min), 8 °C/min to 320 °C (5 min)
 inj. temp.: 250 °C
 detector: MSD, full scan, m/z 45-500
 MSD interface: 320 °C
 carrier gas: helium, 1.4 mL/min constant
 injection: 1 μL, splitless (splitter open at 0.75 min)
 liner: 4 mm I.D., split/splitless type, single taper wool packed FocusLiner[™] design (2879901-U)
 instrument: Agilent[®] 7890/7000B GC/MS/MS

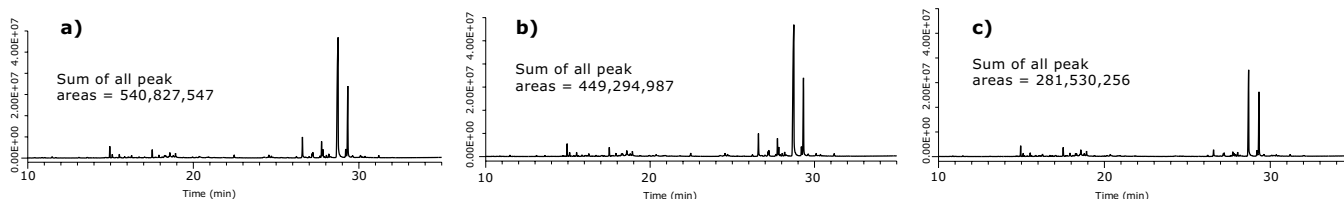
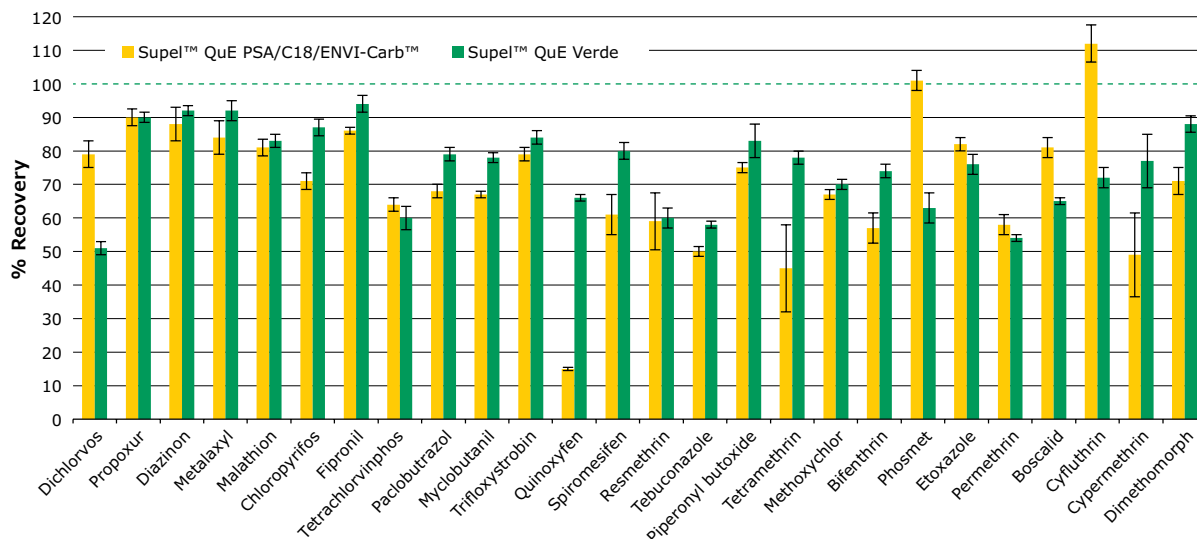


Figure 3. Comparison of Pesticide Recovery and Reproducibility After Cleanup, for Spiked Cannabis Samples (n=3)



Recovery and Reproducibility

The average recoveries obtained from 50 ng/g spiked cannabis samples are summarized in **Figure 3**. Recoveries were generally better using the Supel™ QuE Verde cleanup for many of the pesticides, especially the pyrethroid pesticides and triazole fungicides. The organophosphorus pesticides showed mixed results, with some such as chlorpyrifos showing better recovery from Supel™ QuE Verde, and others such as phosmet showing better recovery using PSA/C18/ENVI-Carb™. Quinoxifen showed very poor recovery after cleanup with PSA/C18/ENVI-Carb™. This compound has some planar character to its structure, which resulted in strong retention on the ENVI-Carb™, and thus reduced recovery. The pesticide synergist piperonyl butoxide, of interest in relation to cannabis production, showed >70% recovery using both cleanups, but better recovery after Supel™ QuE Verde compared to PSA/C18/ENVI-Carb™ cleanup. Reproducibility, determined as % RSD for n=3 spiked replicates, was generally very good for both cleanups. The exceptions were tetramethrin and cypermethrin, which had RSD values >20% after PSA/C18/ENVI-Carb™ cleanup.

Conclusions

As demonstrated here, QuEChERS is a viable approach for the analysis of pesticide residues in cannabis. Many compounds of interest, including piperonyl butoxide, show good recovery and reproducibility by this extraction technique. For cleanup of QuEChERS extracts of cannabis, the use of graphitized carbon is recommended for removal of chlorophyll. However, as

evidenced by the recovery of quinoxifen in **Figure 3**, traditional GCBs such as ENVI-Carb™ will reduce the recovery of pesticides with planar structures. Supel™ QuE Verde, which contains PSA, Z-Sep+ and an improved GCB, can be used to reduce pigmentation while improving recoveries of these compounds.

Compared to conventional PSA/C18/GCB cleanup, cannabis extracts cleaned with the Supel™ QuE Verde mixture showed lower GC/MS background, and better recoveries for many pesticides.

Featured and Related Products

Description	Qty/pk	Mfr No.	Thomas No.
Supel™ QuE QuEChERS Products			
Verde Cleanup Tube, 2 mL	100	55447-U	CHM01W399
PSA/C18/ENVI-Carb™ (AOAC) Tube, 2 mL	100	55289-U	---
Citrate Extraction Tube, 12 mL	50	55227-U	21A00L830
Empty Centrifuge Tube, 50 mL	50	55248-U	---
Capillary GC Column			
SLB®-5ms, 30 m x 0.25 mm I.D., 0.25 µm		28471-U	21A00L230
Standards			
A complete listing of pesticide standards is available at SigmaAldrich.com/standards			
Solvent			
Acetonitrile, for HPLC, ≥ 99.9%		34851	---



© 2020 Merck KGaA, Darmstadt, Germany and/or its affiliates. All Rights Reserved. MilliporeSigma, the vibrant M, Supelco, ENVI-Carb, SLB and Supel are trademarks of Merck KGaA, Darmstadt, Germany or its affiliates. All other trademarks are the property of their respective owners. Detailed information on trademarks is available via publicly accessible resources.

MS_AN5191EN
2017-08266
01/2020