

Exceptional Recoveries of Planar Pesticides From Spinach and Fresh Oregano

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

Recently a “Quick, Easy, Cheap, Effective, Rugged, and Safe” (QuEChERS) cleanup method has been developed with the use of Supel™ QuE Verde, a sorbent combination containing an improved graphitized carbon black (GCB), Z-Sep+, and primary-secondary amine (PSA). This sorbent combination has been shown to provide improved recovery of planar pesticides over current QuEChERS sorbents while maintaining sufficient color removal in high chlorophyll matrices. The GC/MS analysis of select planar pesticides from spinach and oregano extracts is described herein.

Experimental

QuEChERS extraction and cleanup was performed in a similar fashion to that outlined in the AOAC International Official Method 2007.01.¹ Organic spinach and freshly picked oregano were extracted with acetonitrile. The procedure outlined in **Figure 1** fully describes the extraction and cleanup procedure for use with the 2 mL tubes. The acetonitrile extract was spiked with a mixture predominantly composed of planar pesticides in acetonitrile to a concentration of 50 ng/mL. Extractions were performed in triplicate. Analysis of the final extracts was done by GC/MS using the GC conditions listed in **Figure 1**.

Figure 1. Chromatograms of Planar Pesticides in (a) Spinach and (b) Fresh Oregano After Cleanup With Supel™ QuE Verde

sample/matrix: (a) homogenized organic spinach, 10 g;
(b) homogenized fresh oregano, 10 g

extraction tube: Supel™ QuE Acetate extraction tube (55234-U)

extraction process: add 10 mL of acetonitrile to homogenized spinach or oregano in 50 mL centrifuge tube (55248-U); add contents of Supel™ QuE Acetate extraction tube; shake 2 min at 2,500 rpm on automated shaker; centrifuge at 3,500 rpm for 5 min; spike supernatant with a mixture of planar pesticides in acetonitrile to a concentration of 50 ng/mL

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 at 2,500 rpm on automated shaker; centrifuge at 3,000 rpm for 3 min; remove supernatant and place in amber low adsorption vial for GC/MS analysis

column: SLB®-5ms, 20 m × 0.18 mm I.D., 0.18 μm (28564-U)

oven: 60 °C (1 min), 8 °C/min to 300 °C (10 min)

inj. temp.: 250 °C

detector: MSD, selected ion mode (SIM)

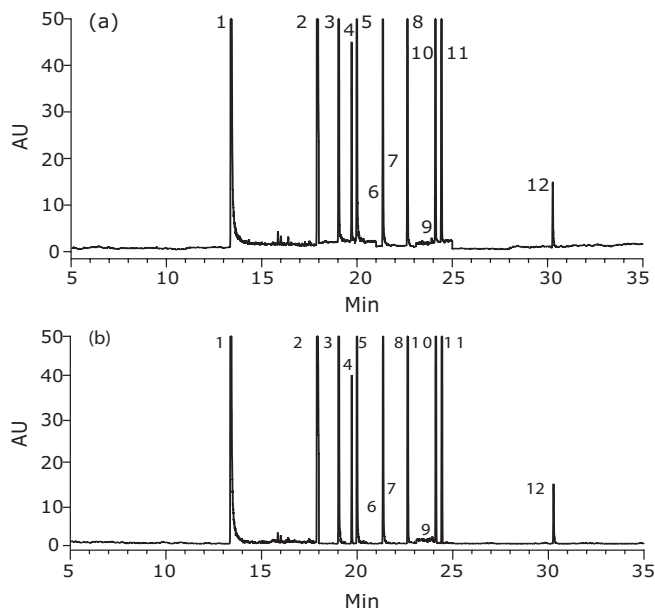
MSD interface: 325 °C

carrier gas: helium, 0.7 mL/min constant

injection: 1 μL, splitless (splitter open at 0.75 min)

liner: 2.3 mm I.D., split/splitless type, single taper wool packed FocusLiner™ design (2879901-U)

- | | |
|-----------------------------|-----------------|
| 1. 2,6-Dichlorobenzonitrile | 7. Metribuzin |
| 2. Diphenylamine | 8. Dacthal |
| 3. Hexachlorobenzene | 9. Folpet |
| 4. Pentachloronitrobenzene | 10. γ-Chlordane |
| 5. Terbutylazine | 11. α-Chlordane |
| 6. Chlorothalonil | 12. Coumaphos |



Results and Discussion

Background was evaluated by analysis of the final extracts by GC/MS in full scan mode. The analysis of the spiked extracts in selected ion mode (SIM) revealed that the Supel™ QuE Verde cleanup removed enough matrix interferences to easily identify and quantitate all 12 residues in a mixture containing planar pesticides (Figure 1).

Removal of the majority of the green pigment from the spinach and oregano extracts was observed after cleanup with Supel™ QuE Verde. Total chlorophyll removal was evaluated using a spectrophotometer by measuring absorbance at 664 nm, 647 nm, and 630 nm, and comparing the processed extracts to the initial acetonitrile extract of each plant material. In all cases, chlorophyll removal was 95% or greater.

Average analyte recoveries obtained from 50 ng/mL spiked spinach and oregano extracts using 2 mL Supel™ QuE Verde cleanup tubes are summarized in Figure 2. Recoveries were in the range of 70% to 120% for all of the planar pesticides tested in both matrices. Reproducibility, determined as %RSD for n=3 spiked replicates, was very good for both matrices. Each pesticide exhibited a %RSD value less than 5% with the exception chlorothalonil, which had a %RSD value of 20%.

Conclusion

The general consensus among food analysts regarding analytical method performance requires pesticide recovery to be between 70% and 120%, and chlorophyll removal to be 95% or greater.

Because of the strong interaction between planar pesticides and the planar surfaces of GCB, there remains a

compromise between color removal and analyte recovery, especially regarding the most planar pesticides such as hexachlorobenzene and chlorothalonil. Supel™ QuE Verde combines a novel carbon with zirconia coated silica (Z-Sep+) to provide an optimum balance between planar pesticide recovery and color removal. As shown in this application, QuEChERS cleanup using Supel™ QuE Verde, may be used prior to GC/MS analysis to provide sufficient chlorophyll removal while maintaining excellent recovery of planar pesticides from spinach and oregano matrices.

Reference

1. AOAC Official Method 2007.01, Pesticide Residues in Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate.

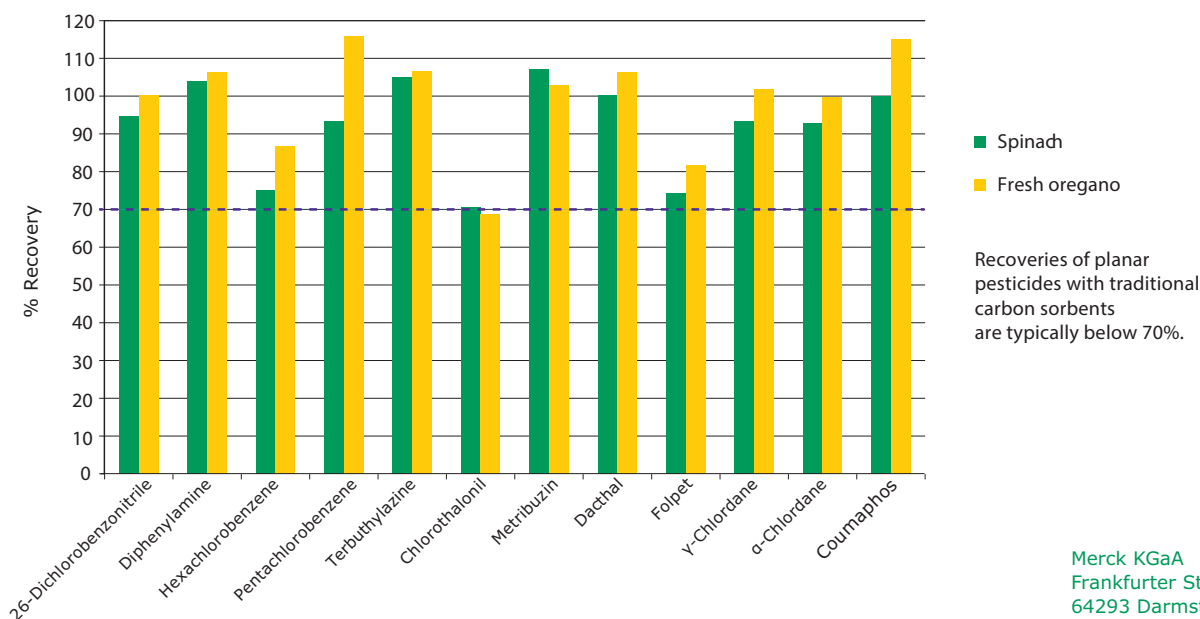
Featured Products

Description	Cat. No.
Supel™ QuE QuEChERS Products	
Verde Cleanup Tube, 2 mL, 100 ea	55447-U
Verde Cleanup Tube, 15 mL, 50 ea	55442-U
Acetate Extraction Tube, 15 mL, 50 ea	55234-U
Empty Centrifuge Tube, 50 mL, 50 ea	55248-U
Columns	
SLB®-5ms Capillary GC Column, 20 m × 0.18 mm I.D., 0.18 µm	28564-U
Accessories	
Inlet Liner, Split/Splitless Type, Single Taper FocusLiner Design (wool packed)	2879901-U

Related Information

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Figure 2. Average Percent Recoveries From Spinach and Oregano Extracts Spiked at 50 ng/mL After Cleanup With the 2 mL Supel™ QuE Verde Tube (n=3). Note: Recoveries with traditional carbon sorbents are typically below 70%



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