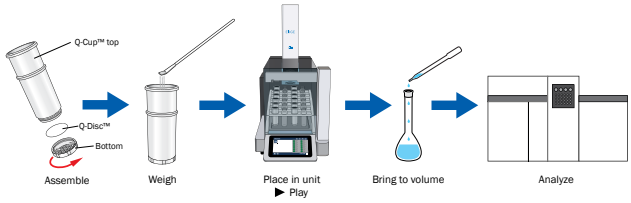
A Rapid, Simple, and Efficient Automated Method for the Extraction of Pesticides from Difficult Food Matrices

A.D. Stell[a], C. S. Cashman[a], [a]CEM Corporation, USA
molecular.support@cem.com

Abstract

In the modern world, consumers increasingly want to know what is in their food and that the substances they are putting in their body are safe. This, along with stringent regulatory requirements, is leading the call for improved extraction of food contaminants such as pesticides. The QuEChERS method has been shown to be practical for pesticide analysis on a number of different sample types. While the QuEChERS method is relatively quick compared to other methods, it is also a manual and tedious process. Herein, a rapid, simple, and efficient automated method for the extraction of difficult food matrices that improves the pesticide extraction process is being reviewed. The extraction of avocados and cranberries is performed on the EDGE and compared to the QuEChERS method. The EDGE method utilizes the same solvent and clean up sorbents as the QuEChERS method, making it a simple transition for labs currently running QuEChERS. The EDGE extraction allows for extraction, cleanup, and filtration in less than ten minutes. Filtration sub 0.3 µm is possible on the EDGE, allowing for direct injection of the extract for UPLC analysis. In this study, extraction of avocado and cranberries was the focus, however; the EDGE extraction method is applicable to many different types of difficult matrices such tea and spices. No matter the matrix on the EDGE the same rapid, simple and efficient automated method is sufficient, leading to good pesticide recovery data. The extraction and determination of multiple pesticide residues from these difficult matrices will be described showing improved recoveries and workflow in comparison to QuEChERS.

EDGE Extraction



1. Assemble Q-Cup sample holder with S1 Q-Disc (allows for sub 0.3µm filtration).
2. Weigh 2.5 g of Q-Matrix Hydra directly into the Q-Cup.
   a. For Cranberries weigh in 250 mg of primary secondary amines (PSA) directly into the C-Cup.
3. Weigh 10 g of homogenized avocado or cranberries directly into Q-Cup.
4. Spike samples with 500 ng of custom pesticide mix from SPEX CertiPrep.
5. Carefully mix contents of the Q-Cup with a glass rod.
6. Wipe glass rod with small piece of Kimwipe, drop into Q-Cup.
7. Place prepared Q-Cup into the EDGE rack alongside 50 mL centrifuge tube for extract collection.
8. Run EDGE extraction method.
9. Confirm extract volume of 40 mL.
10. Transfer to vial for concurrent analysis.

EDGE Extraction Method

Q-Disc: S1 Q-Disc Stack (C9 + G1 + C9 sandwich)

Cycle 1
Extraction Solvent: Acetonitrile w/ 1.0% Acetic Acid (v/v)
Agitation: 02:00 (mm:ss)
Top Add: 25 mL
Bottom Add: 0 mL
Rinse: 5 mL
Temperature: 40 °C
Hold Time: 01:00 (mm:ss)

Cycle 2 (Rinse Only)
Extraction Solvent: Acetonitrile w/ 1.0% Acetic Acid (v/v)
Top Add: 0 mL
Bottom Add: 0 mL
Rinse: 10 mL
Temperature: - - -
Hold Time: - -:- -

Wash 1
Wash Solvent: Acetonitrile w/ 1.0% Acetic Acid (v/v)
Wash Volume: 10 mL
Temperature: 40 °C
Hold: 0:03 (mm:ss)

QuEChERS Extraction

Sample Extraction

1. Transfer 10 g of avocado or cranberries to 50 mL centrifuge tube.
   a. Samples were spiked with 500 ng of custom pesticide mix from SPEX CertiPrep.
2. Add 10 mL 1% acetic acid in acetonitrile, vortex 1 min.
3. Add 1.5 g NaOAc + 6 g $MgSO_4$, shake vigorously 1 min.
4. Centrifuge at 6000 rpm for 5 min.

Sample Cleanup

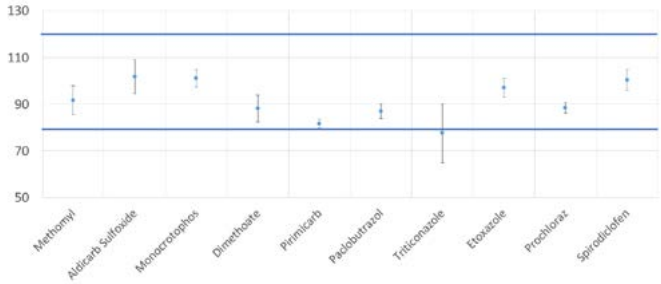
1. Transfer 1 mL of acetonitrile layer to tube with 150 mg $MgSO_4$ + 50 mg PSA.
2. Shake vigorously 1 min.
3. Centrifuge 9000 rpm for 10 min.
4. Transfer supernatant to a vial for concurrent analysis.

UPLC MS/MS Method

- Waters Acquity H Class with Xevo TQD
- Restek ARC-18, 2.7 µm, 100 x 2.1 mm column
- 2 µl injection in acetonitrile
- Temperature: 50 °C
- A: Water with 10 mM Ammonium Acetate and 0.2% Formic Acid
- B: Methanol 10 mM Ammonium Acetate and 0.2% Formic Acid

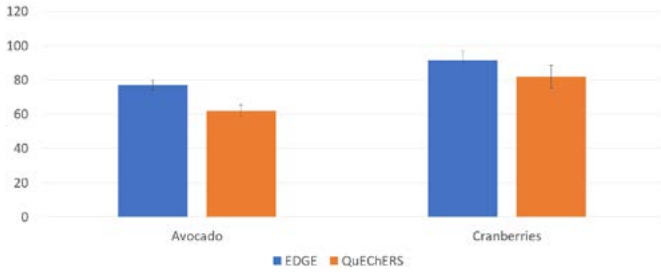
Time (min)	Flow (mL/min)	%A	%B
Initial	0.4	95	5
2	0.4	40	60
4	0.4	25	75
6	0.4	0	100
7	0.4	0	100
7.01	0.4	95	5
9.5	0.4	95	5

EDGE Extraction % Recovery of Pesticides from Cranberries



Acceptable % recovery and RSD values were obtained for all pesticides observed. The % recoveries were determined by a pre and post spike method.

Average % Recovery of Pesticides



Overall higher % recovery was archived using EDGE extraction compared to QuEChERS extraction. The final volume difference between the EDGE and QuEChERS extractions was taken into consideration.

Conclusion

The extraction of avocado and cranberries using the EDGE has proven to be a reliable efficient and robust technique when applied to the various food commodities. With its simple, rapid, and efficient pesticide extraction method, it can be adapted for any food commodity when properly prepared. The incorporation of Q-Matrix Hydra when preparing the sample helps to support the sample, improve dispersion through mixing and remove water. In addition comparable or better recoveries and RSD values were obtained in comparison to the traditional QuEChERS method.