

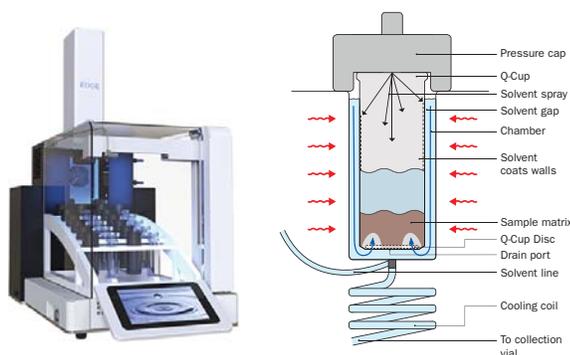
Rapid Extraction, Cleanup and Determination of Multiple Pesticide Residues in Difficult Matrices Utilizing Energized Dispersive Extraction and UPLC MS/MS

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Introduction

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. Some matrices, such as avocado or hops, can be very difficult to work with and their extraction is a manual and tedious process that is a bottleneck. An alternative to the QuEChERS method that both helps improve pesticide recoveries in difficult matrices while also offering a more rapid and efficient process would be beneficial to the modern world. A new sample preparation technology, Energized Dispersive Extraction, paired with UPLC MS/MS analysis that allows for extraction, cleanup, filtration and analysis in less than fifteen minutes of difficult matrices is described.

Energized Dispersive Extraction



Q-Cup Technology combines the processes of Pressurized Fluid Extraction and Dispersive Solid Phase Extraction into one instrument.

Extraction of Pesticides

EDGE Method

Sample extraction and sample clean up together

1. Add dSPE sorbent (same material can be used as in cleanup of the QuEChERS method) and transfer 15 g homogenized food sample to Q-Cup
2. Place Q-Cup in the EDGE
3. Run the 5 min EDGE method: 30 mL extraction at 100 °C
4. Transfer extract to a vial for concurrent analysis

AOAC 2007.01 Method Procedure

Sample extraction

1. Transfer 15 g homogenized sample to 50 mL centrifuge tube
2. Add 15 mL 1% acetic acid in acetonitrile + 1.5 g NaAc + 6 g MgSO₄
3. Shake vigorously 1 min
4. Centrifuge > 1500 U/min for 1 min

Sample Cleanup

1. Transfer 1-8 mL of acetonitrile layer to tube with 150 mg MgSO₄ + 50 mg PSA per mL extract
2. Shake vigorously 30 sec
3. Centrifuge > 1500 U/min for 1 min
4. Transfer supernatant to a vial for concurrent analysis

Hops Extracts



UPLC Conditions

- Waters Acquity UPLC BEH C18 1.7 µm 2.1 x 50 mm column
- 5 µL injections
- Mobile Phase A: 10 mM Ammonium Acetate in Water
- Mobile Phase B: 5 mM Ammonium Acetate in Methanol

Time (min)	Flow Rate (mL/min)	%A	%B
Initial	0.25	95	5
2	0.25	95	5
6	0.25	60	40
12	0.25	10	90
14	0.25	10	90
16	0.25	95	5

- Quantitation was based on a 7 point multi-level calibration curve using Multiple Reactions Monitoring

MS/MS Conditions

Canadian Pesticide Mix 4 in LCMS Acetonitrile

Name	Transition	Cone Voltage (V)
Acephate	143	16
Chlorpyrifos	97	24
Coumaphos	227	50
Diazinon	169	24
Dichlorvos	109	34
Dimethoate	199	30
Prophos	131	36
Etofenprox	177	60
Etoxazole	141	54
Terrazole	105	52
Fensulfthion	281	32
Fenthion	169	32
Malathion	127	30
Methyl parathion	125	36
Mevinphos	127	26
Imidan (Phosmet)	160	30
Spiroxamine	144	36
Tetrachlorvinphos (Z)	127	42
Thiophanate-methyl	151	28

Pesticide Recovery Data

Name	Recovery (n=3)	% RSD (n=3)
Acephate	136	16
Chlorpyrifos	98	24
Coumaphos	98	50
Diazinon	103	24
Dichlorvos	97	34
Dimethoate	94	30
Prophos	121	36
Etofenprox	103	60
Etoxazole	114	54
Terrazole	103	52
Fensulfthion	64	32
Fenthion	100	32
Malathion	88	30
Methyl parathion	96	36
Mevinphos	107	26
Imidan (Phosmet)	93	30
Spiroxamine	88	36
Tetrachlorvinphos (Z)	95	42
Thiophanate-methyl	117	28

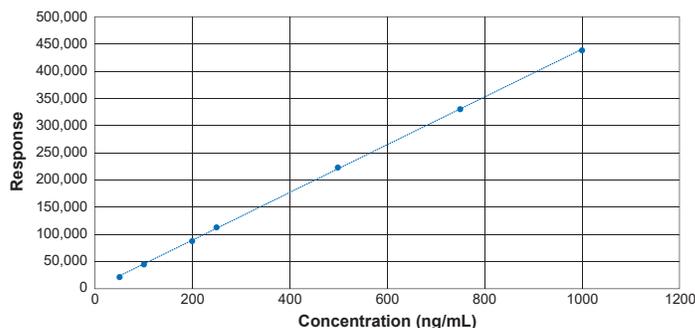
- MS System: Waters Acquity H Class, Xevo TQD
- Ionization Mode: ESI+
- Capillary Voltage: 0.10kV
- Source temp: 150 °C
- Probe temp: 600 °C
- Sampling Rate: 10Hz

- 16 out of 19 compounds with %RSD values of 7 or less
- The three compounds with higher %RSD values are most likely due to matrix interference.

Pesticide Analysis

Matrix Match Hops Calibration Curve

Compound name: Diazinon
Correlation coefficient: r = 0.999949
Calibration curve: y = 439.71x + 867.14



Conclusions

The new energized dispersive extraction method for the extraction of pesticides from difficult food matrices yielded comparable or better recoveries compared to QuEChERS. Furthermore; the new energized dispersive method offered faster run times, and a automated simplified approach compared to alternative methods. Combined with a rapid UPLC MS/MS method, extraction and analysis of the samples is completed in under fifteen minutes. Energized dispersive extraction offers a good and economical option for the extraction of pesticides from all types of food matrices.