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應用手冊

Multi-Residue Pesticide Analysis in Ginseng Powder: Optimized Cleanup After QuEChERS Extraction for UPLC-MS/MS And GC-MS/MS Analysis

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Abstract

This application note presents QuEChERS extraction and SPE-based cleanup strategies for multi-residue pesticide analysis of American ginseng powder, a highly resinous root material commonly used as an herbal supplement.

Benefits

- Rapid QuEChERS extraction of ginseng powder.
- Simple, fast dSPE cleanup prior to UPLC-MS/MS analysis; cleaner extracts mean less time spent on routine instrument maintenance.
- Straightforward SPE cleanup for GC-MS/MS analysis for longer column life and less injection port maintenance.

- Atmospheric pressure ionization for GC-MS/MS (APGC).
- Excellent performance for both UPLC-MS and APGC-MS using the Xevo TQ-S Mass Spectrometer – only 30 minutes to convert from LC to GC operation with no source venting required.

Introduction

The QuEChERS methods have simplified and streamlined sample preparation for pesticide analysis. Although effective for fruits, vegetables and many other types of samples there are challenges when this technique is applied to dried commodities. This is the second in a series of application notes that illustrate sample preparation for dried commodities. The first application note discussed the analysis of dried tea, a highly resinous leaf material.[1] This application note presents QuEChERS extraction and SPE-based cleanup strategies for multi-residue pesticide analysis of American ginseng powder, a highly resinous root material commonly used as an herbal supplement. For the analysis of dried ginseng powder, the sample is first equilibrated with water before extraction using the DisQuE pouch for CEN QuEChERS. Aliquots are then taken for cleanup and chromatographic analysis; one aliquot is subjected to a dSPE cleanup specific for determination of base/neutral pesticides by UPLC-MS/MS. A second aliquot is taken and subjected to an SPE cartridge cleanup optimized for determination of base/neutral pesticides by GC-MS/MS analysis. Recovery data for target pesticides extracted from ginseng powder will be presented using these cleanup protocols.

Experimental

UPLC conditions

System:	ACQUITY UPLC I-Class
Column:	ACQUITY UPLC BEH C_{18}, 2.1 x 100 mm, 1.7 µm
Injection Volume:	5 µL

Temperature:	45 °C
Mobile Phase A:	10 mM ammonium acetate in water (pH 5.0)
Mobile Phase B:	10 mM ammonium acetate in methanol
Flowrate:	0.45 mL/min
Gradient:	10% B initial and hold to 0.25 minutes, linear gradient to 99% B at 12.25 minutes, hold to 13.0 minutes, back to 10% B at 13.1 minutes, hold and re-equilibrate until 17 minutes

MS conditions for UPLC

Instrument:	Xevo TQ-S
Mode:	Electrospray positive and negative (ES+, ES-)
Capillary:	3.0 kV
Extractor:	3.0 V
Source temp.:	150 °C
Cone gas:	150 L/hr
Desolvation temp.:	500 °C
Desolvation gas:	1000 L/hr
Collision gas (Argon):	0.18 mL/min

GC conditions

Instrument:	Agilent 7890
Column:	J&W DB% MS 30 m x 0.25 mm x 0.25 µm
Injection volume:	2 µL splitless
Flowrate:	2.0 mL/min helium (constant flow)
Temperature program:	80 °C initial, hold for 0.5 min, 12 °C/min to 300 °C and hold for 10 min

MS conditions for APGC

Instrument:	Xevo TQ-S
Mode:	API positive
Corona:	2.2 µA
Source temperature:	150 °C
Probe temperature:	450 °C
Cone gas:	170 L/hr
Aux gas:	250 L/hr
Nebulizer gas:	4.0 Bar
Collision gas (Argon):	0.18 mL/min

LC-MS/MS cone and collision parameters, as well as MRM transitions used for this study are presented in Table 1. GC-MS/MS cone and collision parameters and MRM transitions used for this study are presented in Table 2.

Sample preparation

QuEChERS extraction

Place 2 g ginseng powder and 10 mL reagent water into a 50 mL centrifuge tube. Let soak and equilibrate for 30 minutes. Add 10 mL acetonitrile, cap and vortex for 10 seconds and then shake well for a 1 minute. Add contents of DisQuE pouch for CEN QuEChERS and shake well for 1 minute. Centrifuge the sample at 4000 RPM (rcf 3250 x g) for 5 minutes and collect the supernatant. Aliquots of the supernatant are used for SPE cleanups.

dSPE cleanup for pesticides analysis by LC-MS

Place 1 mL of QuEChERS extract into 2 mL DisQuE dSPE tube (150 mg $MgSO_4$/25 mg PSA/25 mg C_{18}, p/n 186004832). Add 7 mg graphitized carbon black (GCB), vortex for 10 seconds and shake for 1 minute. Centrifuge the sample at 12000 RPM (rcf 13400 x g) for 4 minutes and collect the supernatant. Transfer 200 µL of supernatant to a LC-MS cetified vial and dilute to 1.0 mL with mobile phase A for LC-MS.

SPE cleanup for pesticides analysis by GC-MS

Dilute 1 mL of QuEChERS extract with 10 mL 3:1 acetone/toluene. Install a Sep-Pak PSA/carbon SPE cartridge on vacuum manifold with collection vessel in place. Place 200 mg anhydrous $MgSO_4$ atop the cartridge frit. Pass all of the diluted extract through cartridge and collect. Rinse the cartridge with 2 mL 3:1 acetone/toluene and collect (combine with pass-through fraction above). Evaporate to just below 0.5 mL, add 2 mL toluene and evaporate to 0.5 mL.

Results and Discussion

Figure 1 shows a typical UPLC-MS/MS chromatogram obtained from a 10 ppb spiked sample of ginseng; the selected compound is triazophos. Figure 2 shows a typical APGC-MS/MS chromatogram obtained from a 10 ppb spiked sample of ginseng; the selected compound is diazinon.

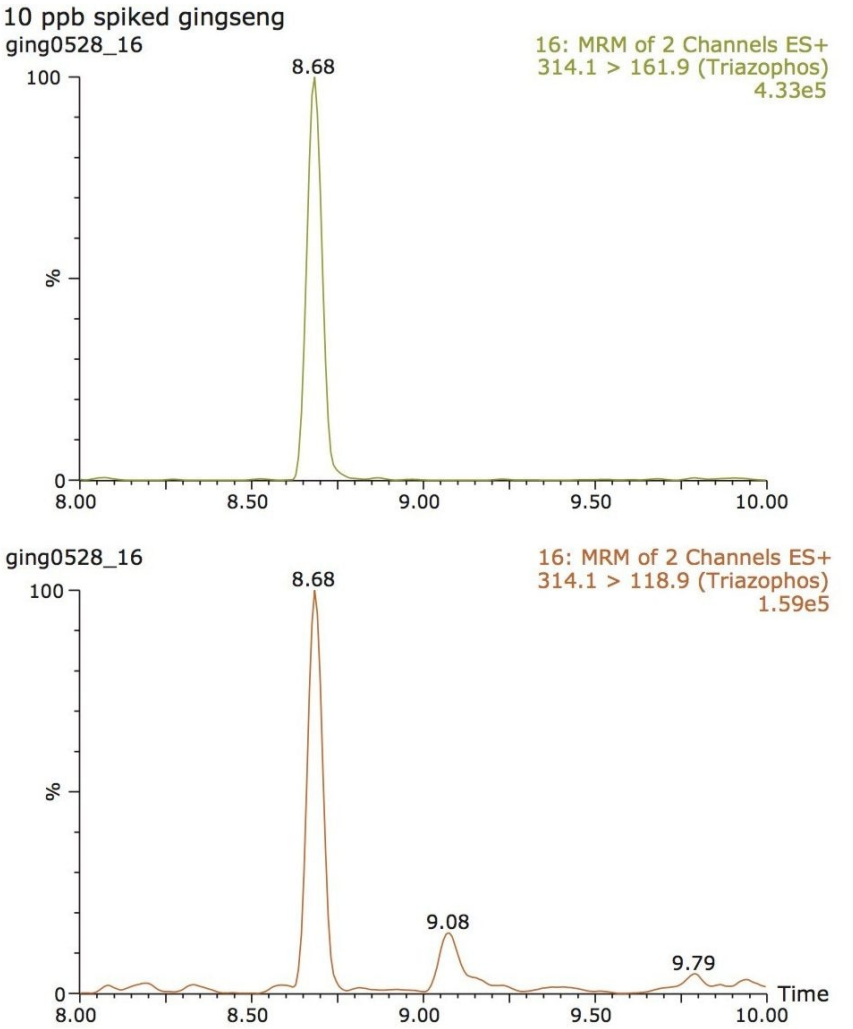

Figure 1. LC-MS/MS analysis of ginseng, 10 ppb triazophos (transition for quantitation on top).

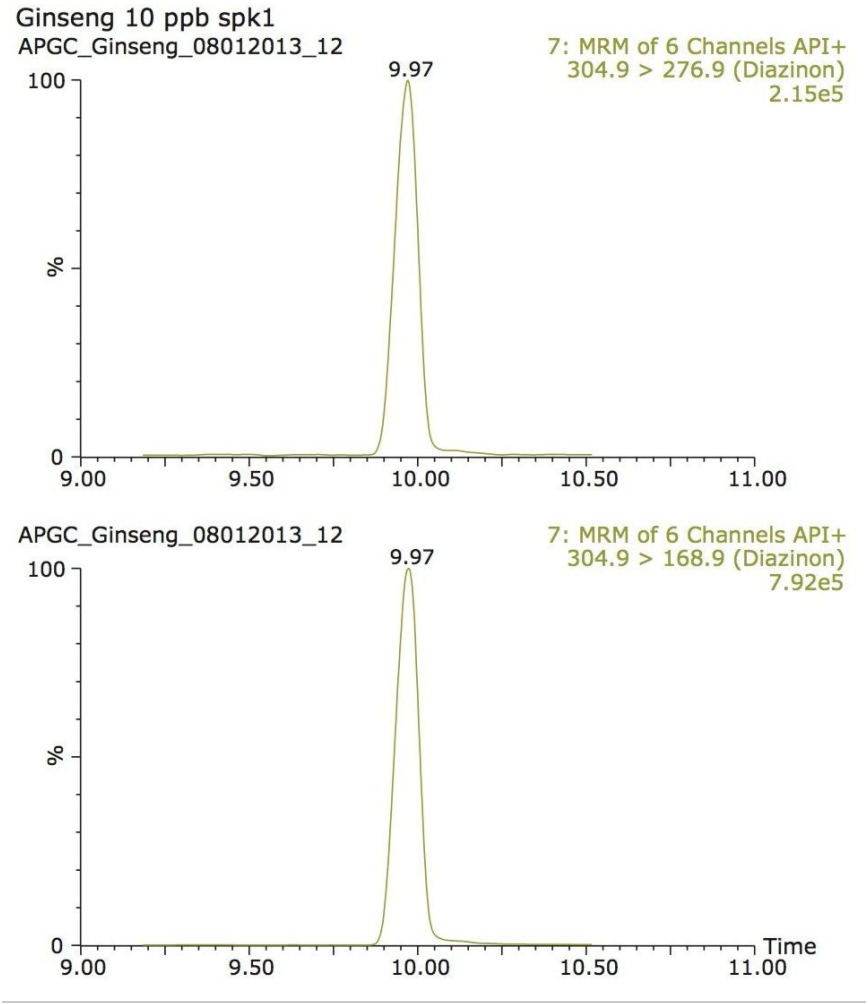

Figure 2. APGC-MS/MS analysis of ginseng, 10 ppb diazinon (transition for quantitation on top).

Recovery data for this study are presented in Tables 1 and 2 and were determined by comparison of the peak areas for samples spiked into the sample matrix prior to sample preparation with the peak areas for samples spiked after all sample preparation steps.

UPLC-MS/MS (dSPE Cleanup)

Pesticide	MRL ppb (EU)	RT min	MRM *m/z* (Cone V, Collision eV)		%Recovery (n=6) @10, 100 ppb (% RSD)	
Acephate	50	1.37	184.1 > 125.1 (8,18)	184.1 > 143.0 (8,8)	118 (39)	110 (8)
Acetamiprid	100	4.08	223.0 > 126.0 (30,20)	223.0 > 56.1 (30,15)	122 (6)	124 (5)
Azoxystrobin	50	8.08	404.1 > 344.2 (20,25)	404.1 > 372.1 (20,10)	101 (9)	104 (6)
Boscalid	500	8.30	342.9 > 307.0 (30,20)	342.9 > 139.9 (30,20)	105 (20)	108 (7)
Carbaryl	50	6.45	202.0 > 145 (30,10)	202.0 > 127 (30,26)	113 (13)	146 (4)
Carfentrazone-ethyl	20	9.31	412.0 > 346.0 (30,24)	412.0 > 266.0 (30,18)	91 (8)	134 (3)
Chlorantraniliprole	20	7.72	484.0 > 453.0 (35,20)	484.0 > 283.9 (35,10)	84 (25)	106 (6)
Clothianidin	70	3.57	250.0 > 169.0 (30,12)	250.0 > 132.0 (30,17)	108 (33)	108 (7)
Cyprodinil	1000	9.39	226.0 > 93.0 (40,33)	226.0 > 108.0 (40,30)	91 (16)	115 (6)
Diazinon	50	9.53	305.1 > 169.0 (30,22)	305.1 > 96.9 (30,35)	108 (7)	107 (8)
DimethomorphE	50*	8.55	388.1 > 300.9 (30,20)	388.1 > 165.0 (30,40)	99 (12)	106 (7)
DimethomorphZ	50*	8.23	388.1 > 300.9 (30,20)	388.1 > 165.0 (30,40)	98 (19)	97 (8)
Fluopicolide	20	8.39	383.0 > 173.0 (15,20)	385.0 > 174.9 (15,20)	97 (15)	101 (2)
Fenhexamid	100	8.83	302.1 > 97.2 (32,22)	302.1 > 55.3 (32,38)	106 (11)	107 (8)
Fenamidone	50	8.21	312.1 > 236.1 (30,16)	312.1 > 92.0 (30,25)	112 (11)	103 (5)
Imidacloprid	50	3.55	256.1 > 175.1 (30,19)	256.1 > 209.1 (30,16)	92 (19)	116 (6)
Metalaxyl	100	7.33	280.1 > 220.1 (30,13)	280.1 > 192.1 (30,17)	109 (6)	112 (4)
Novaluron	10	10.31	493.0 > 158.0 (30,19)	493 > 141.0 (30,40)	79 (14)	106 (6)
Pyrethrins	50	11.19	329.3 > 161.1 (20,15)	329.3 > 142.9 (20,15)	81 (29)	125 (10)
Pyrimethanil	10	7.93	200.0 > 107.0 (42,24)	200.0 > 82.0 (42,24)	109 (4)	120 (4)
Pyriproxifen	50	10.71	322.1 > 96.0 (30,14)	322.1 > 227.1 (30,14)	115 (6)	106 (6)
Pyroclostrobin	50	9.72	388.1 > 163.0 (30,25)	388.1 > 193.9 (30,12)	96 (11)	95 (7)
Sethoxydim	100	9.69	328.2 > 178.1 (15,20)	328.2 > 282.2 (15,15)	101 (12)	84 (5)
Spinosad A	50	10.95	732.6 > 142.0 (40,50)	732.6 > 98.1 (40,50)	105 (12)	110 (8)
Spinosad D	50	11.35	732.6 > 142.0 (40,50)	732.6 > 98.1 (40,50)	88 (22)	91 (5)
Thiamethoxam	20000 (20US)	2.73	292.0 > 181.0 (30,22)	292.0 > 211.0 (30,13)	114 (22)	110 (10)
Triazophos	20	8.86	314.1 > 161.9 (30,18)	314.1 > 118.9 (30,35)	106 (6)	110 (5)
Trifloxystrobin	50	10.16	409.0 > 186.0 (30,16)	409.0 > 145.0 (30,40)	96 (4)	97 (4)

** sum of isomers*

Table 1. UPLC-MS/MS recovery data

APGC-MS/MS (PSA/Carbon Cartridge Cleanup)

Pesticide	MRL ppb (EU)	RT min	MRM *m/z* (Cone V, Collision eV)		%Recovery (n=6) @10, 100 ppb (% RSD)	
Acephate	50	6.60	183.8 > 94.8 (10,20)	183.8 > 142.8 (10,10)	66 (6)	62 (5)
Bifenthrin	100	15.97	242.8 > 122.9 (20,10)	242.8 > 154.9 (20,10)	86 (20)	122 (15)
Carfentrazone ethyl	20	14.85	411.7 > 276.8 (20,30)	411.7 > 301.8 (20,30)	85 (8)	74 (7)
Chlorpyrifos methyl	100	10.90	321.6 > 124.7 (35,20)	321.6 > 289.6 (35,10)	73 (4)	77 (7)
Chlorfenapyr	50000	14.03	408.7 > 270.8 (20,20)	408.7 > 378.7 (20,10)	74 (6)	82 (5)
Diazinon	50	9.98	304.9 > 168.9 (20,20)	304.9 > 276.9 (20,10)	88 (6)	81 (5)
Deltamethrin	5000	20.40	505.6 > 252.7 (20,20)	505.6 > 280.7 (20,10)	LOQ	72 (9)
Fenvalerate	50	19.54	419.8 > 124.8 (10,40)	419.8 > 166.8 (10,10)	61 (4)	75 (9)
L-Cyhalothrin	1000	16.95	449.8 > 196.8 (15,20)	449.8 > 224.8 (15,10)	77 (8)	77 (16)
Propetamphos	100 (US)	9.76	281.9 > 137.8 (10,20)	281.9 > 194.8 (10,10)	83 (13)	79 (9)
Pyriproxyfen	50	16.67	321.9 > 95.8 (10,20)	321.9 > 184.8 (10,20)	79 (11)	76 (8)
Phenothrin	50	16.45	350.9 > 182.8 (20,40)	350.9 > 248.8 (20,20)	77 (8)	88 (9)
Resmethrin	200	15.46	338.9 > 170.9 (25,10)	338.9 > 292.9 (25,10)	52 (9)	56 (10)
Trifluralin	50	8.76	335.9 > 235.8 (30,10)	335.9 > 251.8 (30,20)	81 (6)	79 (7)

Table 2. APGC-MS/MS recovery data

A modified QuEChERS method was used for this study. The ginseng powder sample is first mixed with water and allowed to equilibrate before the addition of acetonitrile and QuEChERS salts. This procedure was shown to be effective for extraction of a wide range of pesticide residues from ginseng. An aliquot of the QuEChERS extract was cleaned up using dSPE prior to LC-MS analysis. Figure 3 shows the cleanup obtained; most of the colored matrix compounds are removed and therefore will not be deposited on the cone. Another aliquot of the QuEChERS extract was cleaned up using an SPE cartridge (carbon/PSA) prior to GC-MS analysis. Without the SPE cleanup, only a few sampled could be analyzed by GC-MS before injection port and column maintenance was required; after SPE cleanup hundreds of samples were analyzed without any routine maintenance.

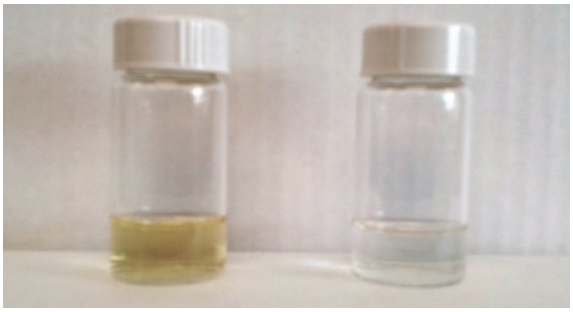

Figure 3. QuEChERS extracts obtained from powdered ginseng; without dSPE cleanup (left) and with dSPE cleanup (right)

Conclusion

- The modified QuEChERS approach was effective for recovery of a wide range of pesticides from ginseng powder.
- dSPE provided cleanup suitable for UPLC-MS/MS analysis.
- A PSA/carbon cartridge based SPE cleanup was highly effective for GC-MS/MS analysis using APGC-MS.
- One Xevo TQ-S Mass Spectrometer can be shared to provide excellent performance for both UPLC-MS and APGC-MS.
- Only 30 minutes are required to convert from LC to GC interface.
- No venting of the mass spectrometer is required for the conversion.

References

1. Multi-Residue Pesticide Analysis in Tea: Optimized Cleanup After QuEChERS Extraction for UPLC-MS/MS and GC-MS/MS Analysis, Waters Application Note 720004819EN.

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ACQUITY UPLC I-Class System <https://www.waters.com/waters/en_US/UPLC-inlet-to-MS-with-the-best-dispersion/nav.htm?cid=134613317>

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