# A High-Throughput Approach to Multi-Matrix Food Testing Using QuEChERS and Tandem GC/MS

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### Introduction

High throughput food laboratories using QuEChERS for multi-residue analysis in a variety of matrices face significant challenges since not all matrices will yield the same level of co-extractives. Nonvolatile co-extractives can contaminate the system and limit sample throughput. One approach is to replace dispersive SPE with a SPE cartridge containing an increased amount of an appropriate sorbent to increase capacity; however this requires a conditioning step, vacuum/positive pressure system, and evaporation of eluted volume - all of which are avoided by utilizing QuEChERS methodology. We have implemented a simple strategy when using a "just enough" sample purification technique such as QuEChERS in order that difficult samples may be handled in a cost-effective and efficient manner without loss in recovery. This involves a second dispersive step in series in order to streamline multi-matrix sample preparation.

### **Experimental**

#### Source of Methodology

The entire method, including sample preparation, is based on an external laboratory's production protocol. This currently calls for one d-SPE step and the ESTD method without the use of analyte protectants. In the study presented here, the ISTD anthracene-D10 was monitored and the use of protectants was evaluated.

#### Preparation of Winter Squash Extracts at 2xL00

15 g of homogenized winter squash (Robot Coupe; no dry ice) was placed into a 50 mL PP centrifuge tube.

#### Pre-extraction spiked samples:

Spike homogenized sample in the tube with 32xLOQ stock standard to yield a 2xLOQ/g final sample. Add anthracene-D10 to yield 200 ppb in the final extract. Mix.

Add 2 ceramic homogenizers, 15 mL acetonitrile, vortex 1 minute

Add AOAC QuEChERS extraction salt packet (6 g MgSO<sub>4</sub>, 1.5 g Na Acetate, PN 5982-6755), shake vigorously for 1 minute, centrifuge 4000 rpm, 5 minutes.

• For 1x d-SPE:

Transfer 9 mL of ACN extract to 15 mL dispersive-SPE tube (400 mg PSA and 1200 mg MgSO<sub>4</sub>, PN 5982-5058), vortex 1 min, centrifuge 4000 rpm, 5 minutes.

Transfer to silanized GCMS vial PN 5183-2072 for analysis. QS to 1.0 mL with 500 ppb each 3-ethoxy-1,2-propanediol and L-gulonic acid-y-lactone (protectants).

### **Experimental cont.**

For 2x d-SPE:

Transfer 5 mL of ACN extract from the 1x d-SPE step to a 15 mL dispersive SPE tube (400 mg PSA and 1200 mg MgSO<sub>4</sub>, PN 5982-5058), vortex 1 min, centrifuge 4000 rpm, 5 min. Transfer to silanized GCMS vial for analysis. OS to 1.0 mL with 500 ppb each 3-ethoxy-1,2-propanediol and L-gulonic acid-y-lactone (protectants).

#### Post-extraction spiked samples

Spike blank extracted sample with stock standard to yield a 2xLOQ/q sample. QS to 1 mL with 200 ppb anthracene-D10 and 500 ppb each 3-ethoxy-1,2-propanediol and L-gulonic acid-y-lactone.

### GC-MS/MS Analysis by EI-MRM

Analysis was performed on an Agilent 7890A Gas Chromatograph coupled to a 7000B Triple Quadrupole Mass Spectrometer equipped with a Multi Mode Inlet and Purged Ultimate Union used for back flushing the column. The union was placed between two HP-5MSUI columns of dimensions 5m x 0.25mm x 0.25µm and 15m x 0.25mm x 0.25µm (PN 19091S-431UI). The inlet was programmed in cold splitless mode from 60 to 280°C at 725°C/min. and 1 µL was injected. A 2 mm dimpled liner (PN 5190-2296) was used. The oven was programmed to reach 310°C in constant flow mode. A two minute post-run back flush commenced at 26.6 min.

The MS source temperature was 310°C. An EM gain of 80 was used for this analysis. MRM transitions were distributed among nineteen time segments.

#### **Recovery and Precision Experiments**

Percent recovery was calculated by comparing analyte response obtained with pre-extraction spiked samples to those of post-extraction spikes for both 1x d-SPE and 2x d-SPE extracts:

#### Peak Area Pre-sniked /Peak Area Post-sniked x 100

%RSDs were calculated for each of the four sample types using multiple injections performed on the same day: preand post-spiked 1x d-SPE extract and pre- and post-spiked 2x d-SPE extract (see table).

Recovery and same-day precision results presented in the table were obtained after over 100 injections were made on the GC columns. Over 740 injections of similar samples had been made on the MS source.

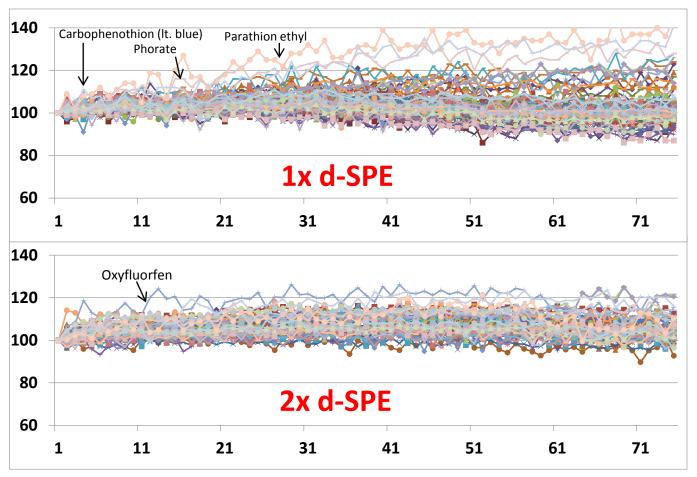
Comparison of techniques by inter-day consecutive injections was performed with new GC columns and liners for each set in order to better control these variables.

### **Recovery and Precision for One vs. Two QuEChERS d-SPE Steps**

(pt)   (pt-s)(pte Post-Spite Prost-Spite Post-Spite Post-Post-Post-Post-Post-Post-Post-Post-					% <b>R</b> e	% Recovery % RSDs					Δ %RSD	
(pp)   Pre-spite   Post-Spite   Pre-spite   Post-Spite   Pre-spite   Prespite   Pre-spite   Pr		RT	m/z	Conc.	1x d-SPE	2x d-SPE	1x d-SPE		2x d-SPE		1x - 2x d-SPE	
Dichlobenii   5.08   170.9 > 136.0   20   88   89   0.4   1.2   0.4   0.4   0.1     THPI   7.26   131.1 > 80.1   60   84   84   1.1   0.8   1.2   2.4   0.0   1.4     PCB   minite   7.32   248.4 > 141.9   10   73   81   0.8   1.6   2.4   1.8   1.6   2.4   1.8   1.6   2.4   1.8   1.6   2.4   1.8   1.6   2.4   1.8   1.6   2.4   1.8   1.6   2.4   1.8   1.6   2.4   1.8   1.6   2.4   1.8   1.6   1.5   2.6   1.8   1.6   1.5   2.6   1.8   1.0   0.6   1.5   2.0   4.2   0.4   2.0   1.1   1.0   0.1   0.0   1.6   1.5   2.0   4.2   0.4   2.0   1.6   1.5   2.0   4.2   0.4   2.0   1.1   1.3   1.1   1.0   <			-	(ppb)			-	-	-	-	Pre-spike	Post-Spike
Thří   7.26   151 1 - 80.1   60   84   84   1.1   0.8   1.2   2.8   0.01   2     PCB   7.99   248.8 > 141.9   10   79   81   0.8   1.6   2.4   1.8   1.6   2.4   1.8   1.6   2.4   1.8   1.6   2.4   1.8   1.1   1.7   0.2   0.2     Chorpropham   9.88   12.2   2.0   88   102   3.0   1.8   6.6   2.8   3.6   -     Ethaffuralini   10.50   366.1 - 2.84.1   30   88   104   3.4   1.5   6.8   2.5   -3.4   -1.4   -0.6   0.0     Alpha-MHC   10.57   2.18.8 - 183.0   10   88   99   0.7   1.2   1.1   1.8   1.0   8.8   90   9   2.8   1.2   1.1   1.1   1.0   1.0   1.0   1.0   1.0   1.0   1.0   1.0   1.0   1.0   1.0 <t< td=""><td>Dichlobenil</td><td>5.08</td><td>170.9 -&gt; 136.0</td><td>20</td><td>88</td><td>89</td><td></td><td></td><td></td><td></td><td>0</td><td>0.7</td></t<>	Dichlobenil	5.08	170.9 -> 136.0	20	88	89					0	0.7
1-Naphthol   7.72   144.1 > 115.1   40   72   68   1.5   3.1   3.3   2.3   1.8   0.6     Diphenylamine   9.45   161.1 > 157.1   20   83   84   0.9   1.2   0.7   1.7   1.0   0.2   2.4   1.7   0.2   2.4     Chloprophan   9.85   11.3   3.5   8.3   0.4   3.4   0.5   6.6   2.4   3.5   6.8   2.5   3.4   3.5     Chloprophanti   0.55   260.0 > 75.0   202   1.0   8.8   1.0   3.4   1.5   6.8   2.5   3.4   3.5   3.5   3.4   3.5   3.5   3.4   3.5   3.5   3.4   3.5   3.5   3.4   3.5   3.5   3.4   3.5   3.5   3.4   3.5   3.5   3.4   3.5   3.4   3.5   3.4   3.5   3.4   3.5   3.4   3.5   3.4   3.5   3.4   3.5   3.4   3.5	•											1.0
PCE 7.99 24.8 5.41.9 10 79 81 0.8 1.6 1.7 0.2 0.7   Chlorpropham 9.98 21.2 0.71 1.0 1.7 0.2 0.7   Chlorpropham 9.98 21.2 0.17 0.1 1.7 0.2 0.6   Chlorpropham 9.98 21.2 0.13 6.6 2.8 3.6 0.1   Triffuratin 10.50 306.3 226.1 1.8 0.6 1.8 6.6 2.8 3.6 1.1 1.7 0.7 <td></td> <td>-2.0 0.7</td>												-2.0 0.7
Diphenylamine   9.45   16.1 - 167.1   20   83   84   0.9   1.2   0.7   1.7   0.2   0.7     Ethaffuralin   10.00   276.0 - 202.2   40   88   102   3.0   1.8   6.6   2.8   -3.6   -3.6     Phorate   10.55   260.0 - 75.0   20   89   92   1.2   2.6   1.8   1.9   -0.6   0.0     alpha-BHC   10.57   228.8 - 213.9   10   79   79   0.7   2.2   1.1   3.1   1.1   -0.1   -0.6     Dicioran   10.90   255.9 - 21.4   4.0   91   99   1.6   1.5   2.0   4.2   4.4   -0.1     Dicioran   11.69   248.9 - 28.8   20   86   92   1.6   2.8   1.1   1.0   0.0   -1.6   2.8   1.1   0.0   1.1   1.0   1.1   1.1   0.0   1.1   1.0   1.0   1.0   1.0   1.0   1.0<	•											-0.3
Ethalfuralin   10.20   226.0 - 202.2   40   88   102   3.0   1.8   6.6   2.8   3.6   -     Phorate   10.55   260.0 - 75.0   20   89   92   1.2   2.6   1.8   1.9   -0.6   0   0     alpha-BHC   10.75   28.8 - 213.9   10   79   79   0.7   2.2   1.1   3.1   1.1   0.1   0     Olcloran   10.90   205.9 - 213.4   40   91   99   1.6   1.5   2.0   4.2   0.4   1.0   1.0   0     Dicloran   1.60   28.8   91   90   91   1.6   2.8   4.1   1.6   1.0   0   0   0   0.1   0.0   0.1   0.0   0.1   1.0   0.0   0.0   0.0   1.0   1.0   0.0   0.0   0.0   0.0   0.0   0.0   0.0   0.0   0.0   0.0   0.0   0.0   0.0   0.0												-0.6
Triffundin 10.50 306.1-264.1 30 88 104 3.4 1.5 6.8 2.5 3.4 -1   Phorate 10.57 218.8-218.5 10 87 89 0.8 1.2 1.1 2.7 -0.3 -1   Dicloran 10.00 205.5-212.6 40 91 99 1.6 1.5 2.0 4.2 -0.4 -2   Clomazone 11.45 2041.1-107.2 15 88 89 1.2 1.1 1.13 1.1 -1.1 0   PCN8 11.65 29.89-28.8 20 86 99 1.6 2.8 3.4 1.6 -1.8 -1.8 -0   Anthracene-D10 11.80 188.0-106.1 200 94 97 0.4 1.2 0.7 0.5 -0.3 0 0   Fonofos 11.52 23.10-212.0 10 90 96 1.7 1.7 2.7 1.5 -1.0 0 0 0 0 0 0 0 0 0 0 0 0	• •											0
Phorete   10.55   20.0   20   89   92   1.2   2.6   1.8   1.9   0.6   0     HCB   10.75   228.8 > 213.9   10   79   79   77   2.2   1.7   1.8   1.0   0.0 <td< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>-1.0 -1.1</td></td<>												-1.0 -1.1
alpha-BHC 10.57 218.8 > 183.0 10 87 89 0.8 1.1 1.2 77 1.8 1.0 0   Dicloran 10.90 205.9 > 124.0 40 91 99 1.6 1.5 2.0 4.2 4.0 4.0   Undane 11.50 218.8 > 183.0 10 88 90 0.2 2.3 2.1 2.1 1.1 1.3 1.1 0.1 1.0   PCNB 11.50 228.8 > 236.8 20 86 91 1.6 2.8 3.4 1.6 1.8 1.0 1.8 1.0 90 96 1.7 1.7 2.7 1.5 1.0 0   Pronamide 11.82 246.0 > 106.1 10 89 92 0.7 2.1 1.9 1.4 4.1 0.0   Pronamide 11.2 2.6 1.3 2.9 2.6 1.3 2.9 2.6 1.3 2.9 2.0 1.0 2.0 1.0 1.0 2.0 1.0 1.0 2.0 1.0 1.0 1.0 1.0												0.7
Dicloran 10.90 205.9 - 124.0 40 91 91 96 1.5 2.0 4.2 4.0 4.2   Clomazone 11.50 218.8 - 183.0 10 88 90 0.9 2.3 2.1												-1.5
Clomazone 11.45 2041-5172 15 88 89 1.2 1.1 1.3 1.1 -0.1 PCN   PCNB 11.65 218.8-318.0 10 88 90 0.9 2.3 2.1 2.1 -1.1 0.1 91   ProMofs 11.65 234.9-236.8 20 86 93 1.6 2.8 3.4 1.6 -1.0 0 0   Anthracene-D10 11.80 188.0-160.1 200 94 97 0.4 1.2 0.7 0.5 -0.3 0   Fonofs 11.82 246.0-160.1 10 89 92 0.7 2.1 1.4 2.9 2.6 -1.8 -1 0.3 0.3 1.6 1.2 1.4 2.9 2.6 -1.8 -1 0.3 0.6 0.3 1.6 1.2 1.6 0.9 1.4 -2.2 1.6 0.9 1.4 -2.2 1.6 0.4 1.0 1.6 1.5 1.0 1.6 1.5 1.0 1.6 1.5 1.0 1.6 1.5												0.4
Lindane 11.50 218.8 > 183.0 10 88 90 0.9 2.3 2.1 2.1 2.1 2.1 1.1 0   PCNB 11.65 291.0 > 128.0 10 90 96 1.7 1.7 2.7 1.5 1.0 0   Anthracence-D10 11.80 188.0 > 160.1 10 98 92 0.7 2.1 1.9 1.4 1.1 0 0 0 0 0 1.1 1.9 1.4 1.1 0 0 0 0 1.1 1.4 2.2 0												-2.7 0
PCNB 11.65 294.9 > 236.8 20 86 93 1.6 2.8 3.4 1.6 1.8 1.6 1.8 1.6 1.8 1.6 1.8 1.6 1.8 1.6 1.80 1.80 1.80 1.80 1.80 1.80 94 97 0.4 1.1 0 0   Pronamide 11.96 172.9 > 145.1 10 88 94 1.1 1.4 2.9 2.6 -1.8 -1.7 1.7 1.8 1.4 2.2 1.4 -1.4 2.9 2.6 -1.8 -1.7 1.7 1.8 1.4 2.9 2.6 -1.8 -1.7 1.7 1.8 -1.7 1.7 1.4 2.9 2.6 -1.8 -1.7 1.7 1.4 2.2 2.6 -1.8 -1.6 -1.6 -1.4 -1.8 -1.7 <t< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>0.2</td></t<>												0.2
Anthraceme-D10   11.80   188.0 > 160.1   200   94   97   0.4   1.2   0.7   0.5   -0.3   0     Fonofos   11.82   266.0 > 109.1   10   88   94   1.1   1.4   2.9   2.6   -1.8   -1     Terbacii   12.8   160.9 > 144.1   20   88   92   1.3   2.4   3.5   1.4   0.3   0     Trailate   12.50   267.9 > 184.1   20   88   90   1.2   1.6   0.9   1.4   0.3   0   0   1.0   -10   -												1.3
								1.7		1.5	-1.0	0.2
Pronamide 11.96 172.9 > 146.1 10 88 94 1.1 1.4 2.9 2.6 1.8 2.7   Terbacil 12.38 160 > > 144.1 20 88 90 1.2 1.6 0.9 1.4 0.3 0   Triallate 12.67 197.1 > 141.0 20 89 93 1.1 2.4 2.3 1.6 1.2 0   Chorpyrifos Methyl 13.40 286.0 > 270.9 50 88 96 2.8 1.1 3.9 2.9 1.0 0   Vinciozolin 13.45 286.0 > 270.9 50 88 96 2.8 1.1 4.0 3.7 2.6 0   Heptachlor 13.47 271.1 > 28.8.3 25 89 91 2.0 2.4 2.2 2.4 -0.2 1.5 -7   Aldrin 13.83 244.1 > 58.2 25 88 92 2.3 2.0 0.4 1.5 1.9 0   Aldrin 14.40 207.1 > 54.1 60 86 91 0.8 1.9 2												0.6
Terbacil12.38160.9 > 14.15088921.32.43.51.4-2.21Triallate12.60267.9 > 18.12089931.12.42.31.61.40.30Chioryprifos Methyl13.40286.0 > 27.95088962.81.13.92.91.0-1Vinclozolin13.45284.9 > 212.02091921.44.14.03.7-2.60Heptachlor13.47272.1 > 256.92085902.11.43.21.7-1.1-0Ametryn13.75227.1 > 55.32589912.02.42.22.4-0.2-0.2Fenchlorphos13.81244.9 > 27.001089930.81.62.43.0-1.5-1.9Prometryn13.85241.1 > 55.22588922.32.00.41.51.90Aldrin14.39262.8 > 193.12079841.43.02.22.2-0.80Bromacil14.40207.1 > 54.16086910.81.92.12.31.30.4-1.40Dicofol-p.p (degr.1)14.80291.1 > 105.120811073.02.65.03.6-2-1.30MGK-264 I15.38164.1 > 86.11091900.71.32.77.8												0.7 -1.3
Triallate 12.50 267.9 - 184.1 20 88 90 1.2 1.6 0.9 1.4 0.3 0   Chlorpyrifos Methyl 13.40 286.0 - 270.9 50 88 96 2.8 1.1 3.9 2.9 -1.0 0   Vinclozolin 13.45 224.3 - 226.0 20 91 92 1.4 4.1 4.0 3.7 -2.6 0   Heptachlor 13.47 27.1 - 528.3 25 89 91 2.0 2.4 2.2 2.4 0.2 -1.1 -1.1 -2.6 0   Ametryn 13.75 227.1 - 58.3 25 89 91 2.0 2.4 2.2 2.4 0.2 -2 -0.8 0 -1.4 0.3 1.5 1.9 0 0 -1.4 0.0 -1.4 0.0 -1.5 1.4 0.3 1.6 1.4 0.3 1.6 1.4 0.3 1.6 1.4 0.3 1.6 1.4 0.3 1.6 1.4 0.3 1.6 1.4 0.3 1.1 1.8 <t< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>1.0</td></t<>												1.0
		12.50	267.9 -> 184.1	20	88	90	1.2	1.6	0.9	1.4		0.2
Vinciozolin13.45284.9 > 212.02091921.44.14.03.7-2.60Heptachlor13.47272.1 > 25.8.32585902.11.43.21.7-1.1-0Ametryn13.75227.1 > 58.32589912.02.42.22.4-0.2-0.2Fenchlorphos13.81284.9 > 27.01089930.81.62.43.0-1.5-1.9Prometryn13.85241.3 > 58.22588922.32.00.41.51.90Aldrin14.3926.8 > 193.12079841.43.02.22.2-0.80Bromacil14.4027.1 > 54.16086910.81.92.12.3-1.4-0Dicofol-p, (degr.)14.80249.9 > 193.13585891.21.83.01.1-1.80DCPA (Dacthal)14.89291.1 > 109.120911073.02.65.03.6-2-2-2Cyprodinyl15.78164.1 > 80.11091940.71.32.72.2-0.4-0MGK-264 I15.76352.8 > 262.92083881.84.14.72.0-2.82.5MGK-264 II15.76352.8 > 262.92083831.84.14.72.0-2.82.6												0.8
Heptachlor13.47272.1 $\rightarrow$ 226.92085902.11.43.21.7-1.1-1.1Ametryn13.75227.1 $\rightarrow$ 58.32589912.02.42.22.4-0.2Prometryn13.81244.9 $\rightarrow$ 27.01089930.81.62.43.0-1.5-1.5Prometryn13.85241.1 $\rightarrow$ 58.22588922.32.00.41.51.90.8Aldrin14.3926.8 $\rightarrow$ 193.12079841.43.02.22.20.80.0Bromacil14.40207.1 $\rightarrow$ 54.16086910.81.01.61.5-1.40.0Dicofol-p.p. (degr.)14.66238.1 $\rightarrow$ 162.12086940.31.01.61.5-1.40.0Dicofol-p.p. (degr.)14.80291.1 $\rightarrow$ 109.120911073.02.65.03.6-2-2.0-2.0Cyprodinyl15.73223.9 $\rightarrow$ 208.21588910.62.02.22.4-1.6-0.4Heptachlor Epoxide15.76352.8 $\rightarrow$ 262.92083881.84.14.72.0-2.82.2Pendimethalin15.96252.1 $\rightarrow$ 162.135911061.32.77.83.4-6.5-0.4Chordane-Trans16.54372.8 $\rightarrow$ 265.81084850.82.5	•••••••••••••••••••••••••••••••••••••••											-1.9
Ametryn   13.75   227.1 > 58.3   25   89   91   2.0   2.4   2.2   2.4   -0.2     Fenchlorphos   13.81   284.9 > 270.0   10   89   93   0.8   1.6   2.4   3.0   1.5   -1     Prometryn   13.85   241.1 > 55.2   25   88   92   2.3   2.0   0.4   1.5   1.9   0.8     Bromacil   14.40   207.1 > 54.1   60   86   91   0.8   1.9   2.1   2.3   1.4   0.0   1.5   -1.4   0.0     Dicofol-p.p(degr.)   14.80   291.1 > 109.1   20   91   107   3.0   2.6   5.0   3.6   -2   -1   0     DCPA (Dacthal)   14.90   300.8 > 222.9   10   88   89   0.5   1.4   3.3   1.4   -2.7   0     MGK-Z64 I   15.76   352.8 > 262.9   20   83   88   1.8   4.1   4.7   2.0   -2.8												0.4 -0.3
Prometryn   13.85   241.1 > 58.2   25   88   92   2.3   2.0   0.4   1.5   1.9   0     Aldrin   14.39   262.8 > 193.1   20   79   84   1.4   3.0   2.2   2.2   -0.8     Bromacil   14.40   207.1 > 54.1   60   86   91   0.8   1.9   2.1   2.3   1.3   -1.3     Dicofol-p.p (degr.)   14.80   249.9 > 133.1   35   85   89   1.2   1.8   3.0   1.1   -1.8   0     Parathion Ethyl   14.89   291.1 > 109.1   20   91   107   3.0   2.6   5.0   3.6   -2   -1.0     DCPA (Dacthal)   14.90   300.8 > 222.9   10   88   89   0.5   1.4   3.3   1.4   -2.7   2.0   -2   2.0   -4   -1.6   -6   -2   -2.0   -1.3   -2   -2.0   -4   -6.5   -0.0   -2.0   -2.8   -2.6	-											0
Aldrin14.39 $262.8 > 193.1$ 2079841.43.02.22.20.80Bromacil14.40 $207.1 > 54.1$ 6086910.81.92.12.3-1.3-1.3-1.0Metolachlor14.66 $2381.3 > 162.1$ 2086940.31.01.61.5-1.4-0Dicofol-p.p (degr.)14.80 $249.9 > 139.1$ 3585891.21.83.01.1-1.80Parathion Ethyl14.89 $291.1 > 109.1$ 20911073.02.65.03.6-2-20DCPA (Dacthal)14.90 $30.8 > 222.9$ 1088890.51.43.31.4-2.70MGK-264 I15.76 $352.8 > 262.9$ 2083881.84.14.72.0-2.82Pendimethalin15.76 $552.4 > 262.9$ 2083881.84.14.72.0-2.82Pendimethalin15.96 $521.4 > 162.1$ 35911061.32.77.83.4-6.5-0Folpet*16.29 $259.8 > 130.1$ 10363422.611.412.35.810.35Endosulfan I16.85 $372.8 > 265.8$ 1086873.53.53.63.2-0.10Dicdrin17.30 $271.1 > 72.1$ 5086900.91.21.	•		284.9 -> 270.0	10								-1.4
	•											0.4
$\begin{array}{c c c c c c c c c c c c c c c c c c c $												0.7 -0.3
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DCPA (Dacthai) 14.90 300.8 > 222.9 10 88 89 0.5 1.4 3.3 1.4 -2.7 0   MGK-264 I 15.38 164.1 > 80.1 10 91 94 0.7 1.3 2.7 2.2 -2.0 -1.6   Cyprodinyl 15.73 223.9 > 208.2 15 88 91 0.6 2.0 2.2 2.4 -1.6 -0   Heptachlor Epoxide 15.76 352.8 > 262.9 20 83 88 1.8 4.1 4.7 2.0 -2.8 2   MGK-264 II 15.78 164.1 > 98.1 10 89 93 0.8 3.0 1.2 3.2 -0.4 -0.4   Pendimethalin 15.96 252.1 > 162.1 35 91 106 1.3 2.7 7.8 3.4 -6.5 -0.4 -0.4 -0.4 -0.4 -0.4 -0.4 -0.4 -0.4 -0.4 -0.4 -0.4 -0.4 -0.4 -0.4 -0.4 -0.2 -0.4 -0.2 -0.4 -0.2 -0.4 -0.2 -0.4 <td< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>0.7</td></td<>												0.7
MGK-264115.38164.1 $\rightarrow$ 80.11091940.71.32.72.22.01Cyprodinyl15.73223.9 $\rightarrow$ 208.21588910.62.02.22.4-1.6-0Heptachlor Epoxide15.76352.8 $\rightarrow$ 262.92083881.84.14.72.0-2.82MGK-264 II15.78164.1 $\rightarrow$ 98.11089930.83.01.23.2-0.4-0.5Pendimethalin15.96252.1 $\rightarrow$ 162.135911061.32.77.83.4-6.5-0Folpet*16.29259.8 $\rightarrow$ 130.110363422.611.412.35.810.35Chlordane-Trans16.54372.8 $\rightarrow$ 265.81084850.82.51.23.8-0.10Napropamide17.30271.1 $\rightarrow$ 72.15086900.91.21.10.8-0.20Dieldrin17.50262.7 $\rightarrow$ 193.14086873.22.62.2-0.40DDF-p,p17.70318.0 $\rightarrow$ 246.01082820.62.81.12.6-0.50Endrin18.10262.7 $\rightarrow$ 193.12082881.73.81.42.7-0.6-0.5DDT-p,p18.71234.9 $\rightarrow$ 165.120929010.07.32.14.37.92<												-1.1
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Heptachlor Epoxide   15.76   352.8 -> 262.9   20   83   88   1.8   4.1   4.7   2.0   -2.8   2     MGK-264 II   15.78   164.1 -> 98.1   10   89   93   0.8   3.0   1.2   3.2   -0.4   -0.5     Pendimethalin   15.96   252.1 -> 162.1   35   91   106   1.3   2.7   7.8   3.4   -6.5   -0.5     Folpet*   16.29   259.8 >130.1   10   36   34   22.6   11.4   12.3   5.8   10.3   5     Chlordane-Trans   16.54   372.8 > 265.8   10   84   85   0.8   2.5   1.2   3.8   -0.4   -0.4     Chlordane-Cis   16.99   372.8 > 265.8   10   86   87   3.5   3.6   3.2   -0.1   0     Napropamide   17.30   271.1 ->72.1   50   86   90   0.9   1.2   1.1   0.8   -0.2   -0.4   0												-1.0 -0.4
MGK-264 II15.78164.1 $\rightarrow$ 98.11089930.83.01.23.2-0.4-0.4Pendimethalin15.96252.1 $\rightarrow$ 162.135911061.32.77.83.4-6.5-6.5Folpet*16.29259.8 $\rightarrow$ 130.110363422.611.412.35.810.35.7Chlordane-Trans16.54372.8 $\rightarrow$ 265.81084850.82.51.23.8-0.4-1Endosulfan I16.85238.8 $\rightarrow$ 204.04087901.22.93.62.4-2.40Napropamide17.30271.1 $\rightarrow$ 72.15086900.91.21.10.8-0.20Dieldrin17.50262.7 $\rightarrow$ 193.14086872.22.92.62.2-0.40DDE-p,p17.70318.0 $\rightarrow$ 246.01082820.62.81.12.6-0.50Endrin18.10262.7 $\rightarrow$ 193.12082881.73.81.42.70.31Oxyfluorfen18.14252.1 $\rightarrow$ 146.250871081.32.84.92.5-3.70DDT-p,p18.71234.9 $\rightarrow$ 165.120929010.07.32.14.27.93DDT-p,p18.51234.9 $\rightarrow$ 165.120929010.07.22.14.37.92 </td <td></td> <td>2.1</td>												2.1
Folpet*16.29259.8 -> 130.110363422.611.412.35.810.355Chlordane-Trans16.54372.8 -> 265.81084850.82.51.23.8-0.4-1Endosulfan I16.85238.8 -> 204.04087901.22.93.62.4-2.400Chlordane-Cis16.99372.8 -> 265.81086873.53.53.63.2-0.100Dieldrin17.30271.1 -> 72.15086900.91.21.10.8-0.200Dieldrin17.50262.7 -> 193.14086872.22.92.62.2-0.400DDE-p,p17.70318.0 -> 246.01082820.62.81.12.6-0.500Cxyfluorfen18.14252.1 -> 146.250871081.32.84.92.5-3.70.6DDT-p,p18.51234.9 -> 165.120929010.07.32.14.27.93DDD-p,p18.71234.9 -> 165.110919010.07.22.14.37.92Oxadixyl18.80163.1 -> 132.23587900.41.20.61.1-0.20DDT-p,p18.71234.9 -> 165.110919010.07.22.14.37.92	MGK-264 II		164.1 -> 98.1	10	89	93	0.8	3.0			-0.4	-0.2
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $												-0.7
Endosulfan I16.85238.8 -> 204.04087901.22.93.62.4-2.40Chlordane-Cis16.99372.8 -> 265.81086873.53.53.63.2-0.10Napropamide17.30271.1 -> 72.15086900.91.21.10.8-0.20Dieldrin17.50262.7 -> 193.14086872.22.92.62.2-0.40DDE-p.p17.70318.0 -> 246.01082820.62.81.12.6-0.50Endrin18.10262.7 -> 193.12082881.73.81.42.70.31Oxyfluorfen18.14252.1 -> 146.250871081.32.84.92.5-3.70Endosulfan II18.35238.8 -> 204.06086873.02.43.72.7-0.6-0DDT-p.p18.51234.9 -> 165.120929010.07.32.14.27.93DDD-p.p18.71234.9 -> 165.110919010.07.22.14.37.92Oxadixyl18.80163.1 -> 132.23587900.41.20.61.1-0.20Carbophenothion19.30342.1 -> 157.120911002.12.83.01.9-1.00Pip												5.6 -1.3
Chlordane-Cis 16.99 372.8 -> 265.8 10 86 87 3.5 3.5 3.6 3.2 -0.1 0   Napropamide 17.30 271.1 -> 72.1 50 86 90 0.9 1.2 1.1 0.8 -0.2 00   Dieldrin 17.50 262.7 -> 193.1 40 86 87 2.2 2.9 2.6 2.2 -0.4 00   DDE-p,p 17.70 318.0 -> 246.0 10 82 82 0.6 2.8 1.1 2.6 -0.5 00   Endrin 18.10 262.7 -> 193.1 20 82 88 1.7 3.8 1.4 2.7 0.3 11   Oxyfluorfen 18.14 252.1 -> 146.2 50 87 108 1.3 2.8 4.9 2.5 -3.7 0.6 -0.6   DDT-p,p 18.51 234.9 -> 165.1 20 92 90 10.0 7.3 2.1 4.2 7.9 3   DDT-p,p 18.71 234.9 -> 165.1 10 91 90 0.0 7.2												0.5
Napropamide   17.30   271.1 -> 72.1   50   86   90   0.9   1.2   1.1   0.8   -0.2   0     Dieldrin   17.50   262.7 -> 193.1   40   86   87   2.2   2.9   2.6   2.2   -0.4   00     DDE-p,p   17.70   318.0 -> 246.0   10   82   82   0.6   2.8   1.1   2.6   -0.5   00     Endrin   18.10   262.7 -> 193.1   20   82   88   1.7   3.8   1.4   2.7   0.3   1     Oxyfluorfen   18.14   252.1 -> 146.2   50   87   108   1.3   2.8   4.9   2.5   -3.7   0.0     Endosulfan II   18.35   238.8 - 204.0   60   86   87   3.0   2.4   3.7   2.7   -0.6   0.0     DDT-p,p   18.71   234.9 -> 165.1   20   92   90   10.0   7.2   2.1   4.3   7.9   2.0   0xadixyl   18.80 <td></td> <td>0.3</td>												0.3
DDE-p,p 17.70 318.0 -> 246.0 10 82 82 0.6 2.8 1.1 2.6 -0.5 0   Endrin 18.10 262.7 -> 193.1 20 82 88 1.7 3.8 1.4 2.7 0.3 11   Oxyfluorfen 18.14 252.1 -> 146.2 50 87 108 1.3 2.8 4.9 2.5 -3.7 00   Endosulfan II 18.35 238.8 -> 204.0 60 86 87 3.0 2.4 3.7 2.7 -0.6 -0.6   DDT-p,p 18.51 234.9 -> 165.1 20 92 90 10.0 7.3 2.1 4.2 7.9 3   DDD-p,p 18.71 234.9 -> 165.1 10 91 90 10.0 7.2 2.1 4.3 7.9 2.0   Oxadixyl 18.80 163.1 -> 132.2 35 87 90 0.4 1.2 0.6 1.1 -0.2 0   Carbophenothion 19.30 342.1 -> 157.1 20 91 100 2.1 2.8 3.0	Napropamide	17.30	271.1 -> 72.1	50	86		0.9	1.2	1.1	0.8	-0.2	0.4
Endrin18.10262.7 > 193.12082881.73.81.42.70.31Oxyfluorfen18.14252.1 > 146.250871081.32.84.92.5-3.70Endosulfan II18.35238.8 > 204.06086873.02.43.72.7-0.6-0DDT-p,p18.51234.9 > 165.120929010.07.32.14.27.93DDD-p,p18.71234.9 > 165.110919010.07.22.14.37.92Oxadixyl18.80163.1 > 132.23587900.41.20.61.1-0.20Carbophenothion19.30342.1 > 157.120911002.12.83.01.9-1.00Endosulfan Sulfate19.32271.8 > 237.02089951.32.41.82.0-0.50Piperonyl Butoxide20.10176.1 > 103.11592991.12.61.11.401Iprodione20.40313.9 - 56.22090964.44.32.83.31.61Methoxychlor-p,p20.70227.1 > 169.260849410.06.61.12.28.94Tetradifon21.05228.8 > 79.04087901.83.33.01.4-1.21												0.7
Oxyfluorfen18.14252.1 -> 146.250871081.32.84.92.5-3.70Endosulfan II18.35238.8 -> 204.06086873.02.43.72.7-0.6-0DDT-p,p18.51234.9 -> 165.120929010.07.32.14.27.93DDD-p,p18.71234.9 -> 165.110919010.07.22.14.37.92Oxadixyl18.80163.1 -> 132.23587900.41.20.61.1-0.20Carbophenothion19.30342.1 -> 157.120911002.12.83.01.9-1.00Endosulfan Sulfate19.32271.8 -> 237.02089951.32.41.82.0-0.50Piperonyl Butoxide20.10176.1 -> 103.11592991.12.61.11.401Iprodione20.40313.9 -> 56.22090964.44.32.83.31.61Methoxychlor-p,p20.70227.1 -> 169.260849410.06.61.12.28.94Tetradifon21.05228.8 -> 79.04087901.83.33.01.4-1.21Fenarimol21.90219.1 -> 107.25087911.71.81.20.80.51 <td></td> <td>0.2</td>												0.2
Endosulfan II18.35238.8 -> 204.06086873.02.43.72.7-0.6-0.6DDT-p,p18.51234.9 -> 165.120929010.07.32.14.27.93DDD-p,p18.71234.9 -> 165.110919010.07.22.14.37.92Oxadixyl18.80163.1 -> 132.23587900.41.20.61.1-0.20Carbophenothion19.30342.1 -> 157.120911002.12.83.01.9-1.00Endosulfan Sulfate19.32271.8 -> 237.02089951.32.41.82.0-0.50Piperonyl Butoxide20.10176.1 -> 103.11592991.12.61.11.401Iprodione20.40313.9 -> 56.22090964.44.32.83.31.61Methoxychlor-p,p20.70227.1 -> 169.260849410.06.61.12.28.94Tetradifon21.05228.8 -> 79.04087901.83.33.01.4-1.21Fenarimol21.90219.1 -> 107.25087911.71.81.20.80.51												0.3
DDD-p,p18.71234.9 -> 165.110919010.07.22.14.37.92Oxadixyl18.80163.1 -> 132.23587900.41.20.61.1-0.20Carbophenothion19.30342.1 -> 157.120911002.12.83.01.9-1.00Endosulfan Sulfate19.32271.8 -> 237.02089951.32.41.82.0-0.50Piperonyl Butoxide20.10176.1 -> 103.11592991.12.61.11.401Iprodione20.40313.9 -> 56.22090964.44.32.83.31.61Methoxychlor-p,p20.70227.1 -> 169.260849410.06.61.12.28.94Tetradifon21.05228.8 -> 79.04087901.83.33.01.4-1.21Fenarimol21.90219.1 -> 107.25087911.71.81.20.80.51	Endosulfan II											-0.3
Oxadixyl 18.80 163.1 -> 132.2 35 87 90 0.4 1.2 0.6 1.1 -0.2 0   Carbophenothion 19.30 342.1 -> 157.1 20 91 100 2.1 2.8 3.0 1.9 -1.0 0   Endosulfan Sulfate 19.32 271.8 -> 237.0 20 89 95 1.3 2.4 1.8 2.0 -0.5 0   Piperonyl Butoxide 20.10 176.1 -> 103.1 15 92 99 1.1 2.6 1.1 1.4 0 1   Iprodione 20.40 313.9 -> 56.2 20 90 96 4.4 4.3 2.8 3.3 1.6 1   Methoxychlor-p,p 20.70 227.1 -> 169.2 60 84 94 10.0 6.6 1.1 2.2 8.9 4   Tetradifon 21.05 228.8 -> 79.0 40 87 90 1.8 3.3 3.0 1.4 -1.2 1   Fenarimol 21.90 219.1 -> 107.2 50 87 91 1.7 1.8 <td></td> <td>3.1</td>												3.1
Carbophenothion19.30342.1 -> 157.120911002.12.83.01.9-1.00Endosulfan Sulfate19.32271.8 -> 237.02089951.32.41.82.0-0.50Piperonyl Butoxide20.10176.1 -> 103.11592991.12.61.11.401Iprodione20.40313.9 -> 56.22090964.44.32.83.31.61Methoxychlor-p,p20.70227.1 -> 169.260849410.06.61.12.28.94Tetradifon21.05228.8 -> 79.04087901.83.33.01.4-1.21Fenarimol21.90219.1 -> 107.25087911.71.81.20.80.51												2.9
Endosulfan Sulfate19.32271.8 -> 237.02089951.32.41.82.0-0.50Piperonyl Butoxide20.10176.1 -> 103.11592991.12.61.11.401Iprodione20.40313.9 -> 56.22090964.44.32.83.31.61Methoxychlor-p,p20.70227.1 -> 169.260849410.06.61.12.28.94Tetradifon21.05228.8 -> 79.04087901.83.33.01.4-1.21Fenarimol21.90219.1 -> 107.25087911.71.81.20.80.51	-											0 0.9
Piperonyl Butoxide 20.10 176.1 -> 103.1 15 92 99 1.1 2.6 1.1 1.4 0 1   Iprodione 20.40 313.9 -> 56.2 20 90 96 4.4 4.3 2.8 3.3 1.6 1   Methoxychlor-p,p 20.70 227.1 -> 169.2 60 84 94 10.0 6.6 1.1 2.2 8.9 4   Tetradifon 21.05 228.8 -> 79.0 40 87 90 1.8 3.3 3.0 1.4 -1.2 1   Fenarimol 21.90 219.1 -> 107.2 50 87 91 1.7 1.8 1.2 0.8 0.5 1	•											0.3
Nethoxychlor-p,p20.70227.1 -> 169.260849410.06.61.12.28.94Tetradifon21.05228.8 -> 79.04087901.83.33.01.4-1.21Fenarimol21.90219.1 -> 107.25087911.71.81.20.80.51	Piperonyl Butoxide	20.10	176.1 -> 103.1	15	92	99	1.1	2.6	1.1	1.4	0	1.2
Tetradifon   21.05   228.8 -> 79.0   40   87   90   1.8   3.3   3.0   1.4   -1.2   1     Fenarimol   21.90   219.1 -> 107.2   50   87   91   1.7   1.8   1.2   0.8   0.5   1	•											1.1
Fenarimol   21.90   219.1 -> 107.2   50   87   91   1.7   1.8   1.2   0.8   0.5   1												4.4
												1.9 1.0
	Cyfluthrin	23.18	226.1 -> 206.1	200	93	102	3.1	2.4	3.2	1.2	-0.1	1.2
Fenvalerate [RR,SS] 23.71 167.1 -> 125.1 22 87 101 5.2 4.6 3.8 3.0 1.4 1	Fenvalerate [RR,SS]	23.71	167.1 -> 125.1	22	87	101	5.2	4.6	3.8	3.0	1.4	1.6
Fenvalerate [RS,SR]   23.81   167.1 -> 125.1   28   86   101   5.0   4.3   3.6   3.4   1.4   0     * For complete recovery pH control must be used   *				28	86	101	5.0	4.3	3.6	3.4	1.4	0.9

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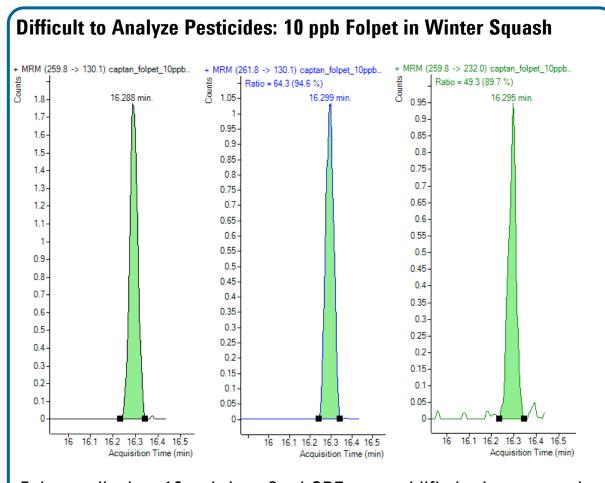
### **Inter-day Precision**



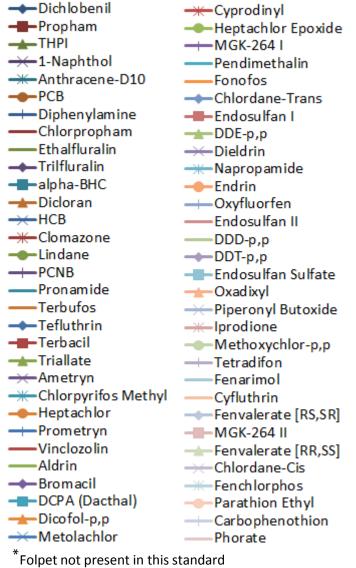
**Stability Over 75 Injections with 1 vs. 2 QuEChERS d-SPE Steps** 

Consecutive injections of post-spiked 2xLOQ winter squash were made over approximately 36 hours. New GC columns and liners were used for each sequence of 75 injections. The MS source had over 740 injections by the end of the 2x d-SPE sequence. Responses are normalized to the first data point.

Highest %RSDs were obtained for carbophenothion (8.5), parathion ethyl (8.4) and phorate (7.0) in the 1x d-SPE sample. Overall averages of %RSDs for the 1x d-SPE and 2x d-SPE samples over 75 injections were 3.4 and 2.6, respectively.



Folpet spiked at 10 ppb into 2x d-SPE non-acidified winter squash extract yielded a %RSD of 5.8 for 8 consecutive injections.



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## Conclusions

- The use of a second d-SPE step results in no loss in recovery
- RSDs did not increase significantly with the possible exception of pendimethalin, which may be stabilized by matrix components
- Performing two d-SPE steps in tandem may be a cost-effective and expeditious means of handing difficult samples

### **Acknowledgements**

The authors wish to thank Inge Biggs and the staff of the California Department of Food & Agriculture for the homogenized samples and pesticide standards and also the many fruitful discussions.