## Supplemental information for

"Automated mini-column solid-phase extraction cleanup for rapid analysis of chemical contaminants in foods by low-pressure gas chromatography – tandem mass spectrometry"

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# Automated Mini-SPE of QuEChERS **Reagent Blank** Extracts GC-MS Full Scan m/z 100-500, 1 µL injection including **APs**



Water in extracts when MgSO<sub>4</sub> not included in SPE yields worse cleanup

# **30 mg C<sub>18</sub>+Z-Sep+CarbonX** Mini-SPE of QuEChERS **Kale** Extracts GC-MS Full Scan m/z 100-500, 1 µL injection including APs



Conclusion: Not much cleanup, but 200-300 µL is ok

# **30 mg C<sub>18</sub>+Z-Sep+CarbonX** Mini-SPE of QuEChERS **Salmon** Extracts GC-MS Full Scan *m/z* 100-500, 1 μL injection including APs



**Conclusion: Not much cleanup** 

# **30 mg C<sub>18</sub>+Z-Sep+CarbonX** Mini-SPE of QuEChERS **Pork** Extracts GC-MS Full Scan m/z 100-500, 1 µL injection including APs



**Conclusion: Not much cleanup** 

# **30 mg C<sub>18</sub>+Z-Sep+CarbonX** Mini-SPE of QuEChERS **Avocado** Extracts GC-MS Full Scan *m/z* 100-500, 1 μL injection including APs



**Conclusion: Not much cleanup** 

## **30 mg C<sub>18</sub>+Z-Sep+CarbonX** Mini-SPE of QuEChERS **Kale** Extracts <u>UV/Vis Absorbance Results</u>



## **30 mg C<sub>18</sub>+Z-Sep+CarbonX** Mini-SPE of QuEChERS **Salmon** Extracts <u>UV/Vis Absorbance Results</u>



## **45 mg MgSO<sub>4</sub>+C<sub>18</sub>+PSA+CarbonX** Mini-SPE of **Salmon** Extracts

UV/Vis Absorbance Results



## **30 mg C<sub>18</sub>+Z-Sep+CarbonX** Mini-SPE of QuEChERS **Pork** Extracts <u>UV/Vis Absorbance Results</u>



### **45 mg MgSO<sub>4</sub>+C<sub>18</sub>+PSA+CarbonX** Mini-SPE of QuEChERS **Pork** Extracts

UV/Vis Absorbance Results



## **30 mg C<sub>18</sub>+Z-Sep+CarbonX** Mini-SPE of QuEChERS **Avocado** Extracts <u>UV/Vis Absorbance Results</u>



## 45 mg MgSO<sub>4</sub>+C<sub>18</sub>+PSA+CarbonX Mini-SPE of Avocado Extracts

UV/Vis Absorbance Results





## **30 mg C<sub>18</sub>+Z-Sep+CarbonX** Mini-SPE of QuEChERS **Kale** Extracts Chlorophyll Removal and HCB Results vs. Extract Vol. Added



Conclusion: 200 µL extract needed for 80% HCB elution

### **30 mg C<sub>18</sub>+Z-Sep+CarbonX** Mini-SPE of QuEChERS Extracts

Recovery vs. Extract Vol. Added



**Conclusion:** most analytes were not retained by the sorbents

### **30 mg C<sub>18</sub>+Z-Sep+CarbonX** Mini-SPE of QuEChERS Extracts

Recovery vs. Extract Vol. Added



**Conclusion: 300 µL extract needed for >70% elution of PBDEs** 

### **45 mg MgSO<sub>4</sub>+C<sub>18</sub>+PSA+CarbonX ITSP of QuEChERS Extracts**

Recovery vs. Extract Vol. Added



Conclusion: 300 µL extract needed for >70% elution of PBDEs

## **30 mg C<sub>18</sub>+Z-Sep+CarbonX** Mini-SPE of QuEChERS Extracts

Recovery vs. Extract Vol. Added



Conclusion: ≥600 µL extract needed for full elution of PAHs

### **45 mg MgSO<sub>4</sub>+C<sub>18</sub>+PSA+CarbonX** Mini-SPE of QuEChERS Extracts <u>Recovery vs. Extract Vol. Added</u>



**Conclusion:** ≥600 µL extract needed for full elution of PAHs

<u>Relative Recovery Differences for the Analytes in Mini-SPE</u> for the 300  $\mu$ L Extract Volumes vs. Avg. 600  $\mu$ L Result with 45 mg mini-cartridge results – 30 mg mini-cartridge results (n = 12 for 4 matrices)



**Conclusion:** Similar results using either mini-cartridge

## Validation Experiments

Determine performance results in the use of automated mini-SPE cleanup in the LPGC-MS/MS analysis of pesticides and other contaminants in QuEChERS extracts of 10 different matrices.



Used mini-cartridges showing removal of chlorophyll and other matrix components

Final extract volumes = 278  $\pm$  5  $\mu$ L (n = 255) after 50  $\mu$ L addition of APs (and/MeCN) solution



Injection liner and septa after the 5 day experiment including 230 matrix extracts of diverse commodities

A little "dirt" here and there, but the analyte protectants did their job and results still looked great from start to finish.

Coumaphos in salmon after 230 injections of QuEChERS matrix extracts using mini-SPE **No internal standard** needed to still yield R<sup>2</sup> = 0.999 calibration curve



25 ng/mL std in salmon extract

#### Methamidophos Results (vs. atrazine-d5 IS) – all 325 analyses combined!



10 ng/mL std in kale

#### Acephate Results (vs. atrazine-d5 IS) – all 325 analyses combined!



25 ng/mL std in orange

#### Omethoate Results (vs. atrazine-d5 IS) – all 325 analyses combined!



5 ng/mL std in carrot

#### Dicrotophos Results (vs. atrazine-d5 IS) – all 325 analyses combined!



5 ng/mL std in pork

#### Dimethoate Results (vs. atrazine-d5 IS) – all 325 analyses combined!



5 ng/mL std in kiwi

#### Carbofuran Results (vs. atrazine-d5 IS) – all 325 analyses combined!



10 ng/mL std in orange

#### Diazinon Results (vs. atrazine-d5 IS) – all 325 analyses combined!



10 ng/mL std in wheat

#### Chlorothalonil Results (vs. atrazine-d5 IS) – all 325 analyses combined!



5 ng/mL std in basil

Chlorothalonil 5 ng/mL calibration standards over the course of 5 days (inj. #) RO = reagent-only; ion ratios within horizontal lines <  $|\pm 10\%|$  of ref. ratio



Matrix contamination of system from canned black olive extracts slowly dissipated during sequence, but did not cause instrument or analytical performance problems.

#### Chlorpyrifos Results (vs. atrazine-d5 IS) – all 325 analyses combined!



5 ng/mL std in black olive

#### Cyprodinil Results (vs. atrazine-d5 IS) – all 325 analyses combined!



5 ng/mL std in black olive

#### TBECH Results (vs. atrazine-d5) – all 325 analyses combined!



10 ng/mL in wheat grain

#### Thiabendazole Results (vs. atrazine-d5) – all 325 analyses combined!



5 ng/mL in salmon

#### Flutriafol Results (vs. atrazine-d5 IS) – all 325 analyses combined!



5 ng/mL std in kale

#### Imazalil Results (vs. atrazine-d5) – all 325 analyses combined!



5 ng/mL std in apple

#### Myclobutanil Results (vs. atrazine-d5 IS) – all 325 analyses combined!



5 ng/mL std in apple

#### Endosulfan II Results (vs. atrazine-d5 IS) – all 325 analyses combined!



5 ng/mL std in apple

#### Endosulfan Sulfate Results (vs. atrazine-d5 IS) – all 325 analyses combined!



10 ng/mL std in orange

Endosulfan sulfate 5 ng/mL reagent-only and matrix-matched calibration standards



LOQ ≈2 ng/mL in all matrices; even after 325 injections, including 230 food extracts

#### Bifenthrin Results (vs. atrazine-d5 IS) – all 325 analyses combined!



5 ng/mL std in basil

#### Benzo(b+k)fluoranthene (vs. benzo(a)pyrene-d12 IS) – all 325 analyses combined!



#### (Es)fenvalerate Results (vs. atrazine-d5 IS) – all 325 analyses combined!



10 ng/mL std in orange

a ghost peak occurs in orange 1 injection later

#### Dechlorane Plus Results (vs. FBDE 126 IS) – all 325 analyses combined!



5 ng/mL std in wheat grain







