Evaluation of Different QuEChERS Methods for Multi Residue Analysis in Fruits and Vegetables.

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INTRODUCTION

QuEChERS is a popular worldwide method for multi-residue analysis of pesticides in fruits and vegetables. This poster presents comparison data obtained using the original method from Anastassiades et. al. (2003) and the buffered QuEChERS methods.

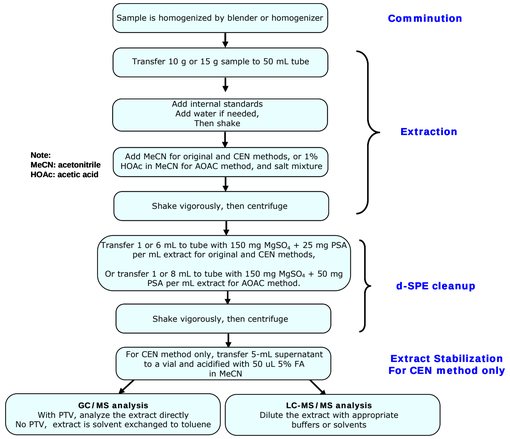
Sample is first extracted with acetonitrile, followed by a liquid-liquid partitioning induced by adding $MgSO_4$ and NaCl. After centrifugation, the matrix cleanup and the removal of residual water from the extract is accomplished in one step called dispersive solid phase extraction (d-SPE) by using primary secondary amine (PSA) sorbent and $MgSO_4$. There are two buffered QuEChERS procedures were adopted to improve the recoveries of certain pesticides by the addition of buffers during the extraction and partitioning step. AOAC Official Method 2007.01 uses an acetate buffer while many EU countries use citrate buffer. Modifications have also been employed in the d-SPE cleanup step. In addition to PSA, C18 bonded silica could be added to samples with relatively high fat content, and graphitized carbon black (GCB) is very effective in removing high levels of pigments, such as chlorophyll or carotinoid, in samples. The analysis is performed using UPLC with tandem MS (multiple reaction monitoring) and/or GC-MS (selected ion recording, SIR) to detect low ppb levels of residue pesticides in various products.

METHODS

Extraction Tube of Original and Buffered QuEChERS Methods.

	Sample Size	Solvent	Tube Content
AOAC Method 2007.01 Acetate Buffer	15 g	15 mL 1 % acetic acid in Acetonitrile	6 g $MgSO_4$ 1.5 g sodium acetate
CEN Method 15662 citrate Buffer	10 g	10 mL acetonitrile	4 g $MgSO_4$ 1 g NaCl 1.5 g sodium citrate
Validation of Original QuEChERS Method Lehotay *et al. (2005)*	15 g	15 mL acetonitrile	6 g $MgSO_4$ 1.5 g NaCl
Original QuEChERS Method Anastassiades *et al. (2003)*	10 g	10 mL acetonitrile	4 g $MgSO_4$ 1 g NaCl

Sample Preparation Protocol of QuEChERS



UPLC® - MS/MS

LC System: Waters ACQUITY UPLC® System
Column: ACQUITY UPLC BEH C18, 2.1 x 100 mm, 1.7 µm
Column Temp: 40 °C
Sample Temp: 4 °C
Injection Volume: 15 µL
Mobile Phase A: Water + 0.1% formic acid
Mobile Phase B: Methanol + 0.1% formic acid
Gradient:

Time	Flow rate mL/min	A%	B%
0.00	0.3	75	25
0.25	0.3	75	25
7.75	0.3	0	100
8.50	0.3	0	100
8.51	0.5	75	25
10.50	0.5	75	25
11.00	0.3	75	25

MS System: Waters ACQUITY® TQ Detector

Ionization mode: Positive electrospray (ESI+)
Acquisition: Multiple reaction monitoring (MRM)

GC-MS

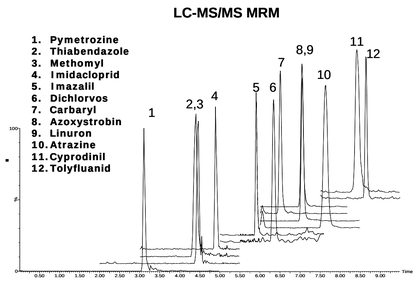
GC-Conditions

Instrument :	Agilent 6890N GC
Column:	RTX-5MS, 30 m x 0.25 mm 0.25 µm film)
Carrier gas:	Helium
Flow rate:	1.0 mL/min
Temp. program:	Initial 100° C, hold 1 min, then 10°C/min to 320° C, hold for 7 minute
Injection Volume:	2 µL splitless

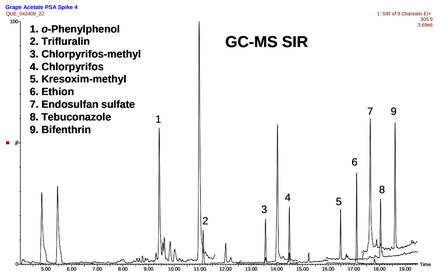
MS System: Waters Quattro micro™ GC MS

Ionization mode:	Electron Impact (70 eV)
Acquisition:	Single Ion Recording (SIR) Mode

Overlap Multiple Reaction Monitoring (MRM) Chromatograms of Pesticides Fortified at 20 µg/g in Avocado Extract.



Overlap Single Ion Recording (SIR) Chromatograms of Pesticides Fortified at 20 µg/g in Grape Extract.



RESULTS

Figure 1.

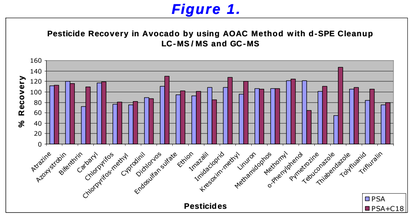


Figure 2.

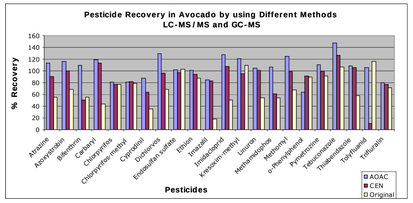


Figure 3.

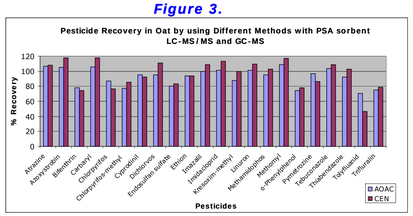
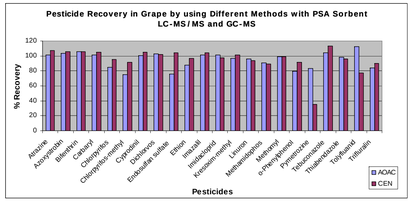


Figure 4.



DISCUSSION

QuEChERS methods are generally excellent for most of the pesticides in non-fatty matrix such as fruits and vegetables. For the samples with relatively high level of fat content, such as avocado, C18 sorbent (Trifunctionally Bonded C18 Silica) was added to the d-SPE cleanup tube. The recoveries of some pesticide are improved as shown in Figure 1.

As demonstrated in Figure 2, in the extract of avocado, the non-buffered original method is not suitable for basic and acid sensitive pesticides. Both buffered methods, acetate and citrate buffers, give higher recoveries than the original method. The AOAC method maintaining consistent pH in acetonitrile extract, is better for some base sensitive pesticides such as tolyfluanid. This is common for all three commodities, avocado (Figure 2), oat (Figure 3), and grape (Figure 4). In general, the CEN method give better clean up of extract if GC-MS is the choice of analysis.

As QuEChERS approach is designed for commodity consists of high water content, dry commodities such as oat or flour, adding water is necessary to achieve the optimization condition of QuEChERS approach. For oat extraction, 15 g of water is added to the 50-mL tube containing 7.5 g of well homogenized oat. After the sample is rest for 10 minutes, acidic acetonitrile and salts are added to the tube for extraction.

Acid sensitive pesticide, pymetrozine, is better preserved by the AOAC method using acetate buffer as demonstrated in grape extract in Figure 4.

CONCLUSION

QuEChERS approach is the most popular analytical technique for the multi-residue pesticide analysis. In addition to the original QuEChERS method, there are two buffered methods, CEN method 15662 and AOAC Official method. Both buffered methods performed well for multiresidue pesticides analysis in most commodities. AOAC method is better for the base sensitive pesticides due to the buffer giving consistent pH throughout extraction and d-SPE cleanup procedure..

REFERENCE

1. Lehotay, JAOAC Int. 90(2) 2007, 485-520.
2. "SPE Protocols for Rapid UPLC-MS and GC-MS Determination of Acidic Pesticides in QuEChERS Extracts", Michael S. Young and Jeremy C. Shia, Florida Pesticide Residue Workshop 2008.

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