Sample Preparation Protocol of QuEChERS GC-MS

QuEChERS is a popular worldwide method for multi-residue analysis of pesticides in fruits and vegetables. This protocol 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 MgSO₄ and NaCl. After centrifugation, the matrix cleanup and the removal of residual solvents is performed. The sample is then re-dissolved in MeCN:acetonitrile (1:1) and analyzed.

**QuEChERS approach** is the most popular analytical technique for the multi-residue pesticide analysis. In addition to the original QuEChERS method, there are less buffered methods available. Buffered methods performed well for multi-residue analysis. The buffered method in most cases performed better than the original method. This is common for all three commodities of high water content, dry commodities such as salt or flour, acid sensitive pesticides due to the buffer giving different recoveries than the original method. For CEN method only 0.50 1.00 1.50 2.00 2.50 3.00 3.50 4.00 4.50 5.00 5.50 6.00 6.50 7.00 7.50 8.00 8.50 9.00 % Recovery 20 40 60 80 0.00 0.3 75 25 0.25 0.3 75 25 7.75 0.3 0 100 8.00 0.3 0 100 8.51 0.5 75 25 10.00 0.5 75 25 11.00 0.3 0 100

**Neutral, Acidic and Basic Pesticides**: Different recoveries were obtained for neutral, acidic and basic pesticides. The buffer gave different recoveries from the original method in various products. The analysis is performed using UPLC with tandem MS recording, SIR to detect low ppb levels of residue pesticides in various products.

**Column**: ACQUITY UPLC BEH C₁₈, 2.1 x 100 mm, 1.7 μm

**Stationary Phase**: 1.5 g sodium acetate

**Mobile Phase A**: Water + 0.1% formic acid

**Mobile Phase B**: Methanol + 0.1% formic acid

**GC-Conditions**
- Instrument: Agilent 6890 N GC
- Column: RTX-SMS, 30 m x 0.25 mm
- Flow rate: 1.0 mL/min
- Temperature: 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 ACQUITY UPLC® TQ Detector
- Introduction: Positive electrospray (ES+) Acquisition: Multiple reaction monitoring (MRM)

**Overview**: Multiple Reaction Monitoring (MRM) Chromatograms of Pesticides Fortified at 20 μg/g in Grape Extract.

**RESULTS**

**DISCUSSION**

QuEChERS methods are generally excellent for most of the pesticides. Non-ionic matrix such as fruits and vegetables. For the samples with relatively high level of fat content, such as avocado, C₁₈ sorbent (Trifunctionally Bonded C₁₈ EIC) was added to the d-SPE cleanup tube. The recoveries of some pesticides are improved as shown in Figure 1. As demonstrated in Figure 2, in the extract of avocado, the buffered QuEChERS method maintaining constant pH in acetonitrile extract, is better for some base sensitive pesticides such as tolyfluanid. This is common for all three commodities, avocado (Figure 2), salt (Figure 3), and grapes (Figure 4), as the buffer gives a better clean up of extract if GC-MS is the choice of analysis. As QuEChERS approach is designed for commodities of high water content, dry commodities such as salt or flour, acidic and basic pesticides are better preserved by the buffer giving different recoveries than the original method. 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 less buffered methods available. Buffered methods performed well for multi-residue analysis. The buffered method in most cases performed better than the original method. This is common for all three commodities of high water content, dry commodities such as salt or flour, acid sensitive pesticides due to the buffer giving different recoveries from the original method. For CEN method only.

**REFERENCE**

1. Anastassiades et al. (2003)
2. HPLC Protocols for Rapid UPLC-MS and GC-MS Determination of Acidic Pesticides in QuEChERS Extracts; Michael S. Young and Jeremy C. Shla, Florida Pesticide Residue Workshop 2008.