MULTIRESIDUE PESTICIDE ANALYSIS IN FRUIT AND VEGETABLE COMMODITIES USING BOTH UPLC AND APGC ON A SINGLE MASS SPECTROMETER PLATFORM

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INTRODUCTION

Hundreds of pesticides are commercially available and approved for use on various crops making pesticide residue analysis an important component of ensuring food safety. Maximum Residue Levels (MRLs) are set at the highest level of pesticide that would be expected to be found in that crop when it has been treated in line with good agricultural practice. National authorities control and enforce MRLs by testing samples for pesticide residue levels using analytical surveillance programs. These programs check for compliance with MRLs, assess dietary exposure, and check for use of unauthorized pesticides. The food industry also carries out its own due diligence analyses. With the large amount of pesticides available for use, it is important to be able to rapidly and reliably analyze samples for many pesticides in a single method. Mass spectrometry coupled with both gas (GC) and liquid chromatography (LC) is needed to provide comprehensive analysis of a wide range of pesticide residues with sufficient sensitivity to meet global MRL regulations. The use of Quick, Easy, Cheap, Efficient, Rugged and Safe (QuEChERS) sample extraction and clean up has streamlined analytical efficiencies for multi residue analyses.[1] The advantage of ultra performance liquid chromatography (UPLC) coupled with tandem quadrupole mass spectrometry (MS/MS) for multi residue pesticide analysis is widely reported.[2] More recently the use of GC-MS/MS operated at atmospheric pressure (APGC) has been shown to offer significant improvements in performance over electron impact (EI) for challenging pesticides, in terms of selectivity, specificity and speed of analysis.[3, 4] For this analysis, a single workflow for multi residue analysis of pesticides is demonstrated on a variety of fruit and vegetable samples on the same tandem quadrupole MS instrument, with less than 30 minutes needed to switch between chromatographic inlets. The performance of the method is highlighted in terms of sensitivity, repeatability, and linearity for both LC and GC in compliance with the SANTE guidelines (11945/2015) for pesticide analysis.[5]

Figure 1. Xevo TQ-S micro with the Universal Source allowing for UPLC and APGC analysis on the same mass spectrometer.

METHODS

Commodities Studied

Four different classes of food commodities were studied:


Lemon – high acid content


Celery – high water content


Kale – high water content


Corn – high starch/protein content

Pesticide Residue Classes

Each analysis method (APGC and UPLC) contained approximately 200 pesticide residues from various classes.

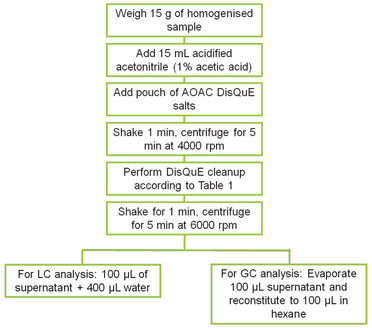
The classes of pesticides studied in the UPLC analysis include:

- Organophosphorus
- Carbamates
- Organonitrogen

The classes of pesticides studied in the APGC analysis include:

- Organophosphorus
- Organochlorine
- Organonitrogen
- Pyrethroids
- Herbicide Methyl Esters

Sample Extraction and Cleanup



Sample	MgSO4	PSA	GCB	Volume
Celery	150 mg	25 mg	7.5 mg	1 mL
Lemon	150 mg	25 mg	-	1 mL
Corn	150 mg	25 mg	-	1 mL
Kale	900 mg	150 mg	150 mg	6 mL

Table 1. dSPE cleanup conditions used for each sample matrix.

Method Generation and Management using QuanPedia

MS Methods, TargetLynx Processing Methods, and UPLC Methods were generated and maintained using QuanPedia databases.

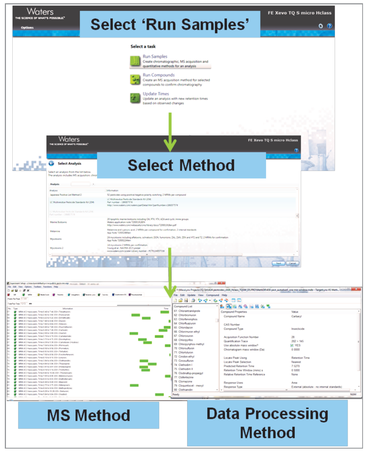


Figure 2. Xevo TQ-S micro with the Universal Source allowing for UPLC and APGC analysis on the same mass spectrometer.

UPLC-MS/MS Parameters

LC System: ACQUITY UPLC H Class
Column: ACQUITY BEH C18 2.1 x 100 mm, 1.7um
Mobile Phase A: Water + 10 mM ammonium acetate
Mobile Phase B: Methanol + 10 mM ammonium acetate
MS System: Xevo TQ-S micro
Ionization Mode: ESI+

APGC-MS/MS Parameters

GC System: 7890A
Autosampler: CTC PAL RTC
Column: 30 m x 0.25 mm x 0.25 µm Rxi-5MS
MS System: Xevo TQ-S micro
Ionization mode: API+
Ionization mechanism: **Proton transfer** (3 vials of water in source)

For full method details, see Waters application note 720006013en

Fast Scanning Speeds of Xevo TQ-S micro

Each analysis method contained approximately 200 pesticide residues acquiring at least 2 MRM transitions per compound. The mass spectrometer must be able to rapidly scan through all of the MRM channels to acquire the required data.

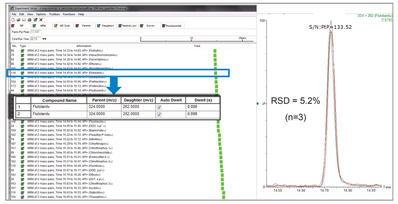


Figure 3. The fast scanning of the Xevo TQ-S micro collects the required data points (minimum 12 points per peak) while maintaining peak quality.

Pesticides in Matrix

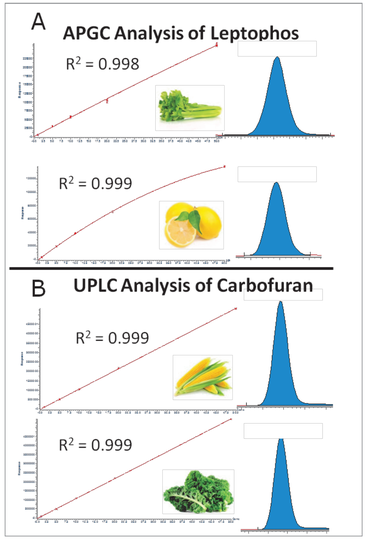


Figure 4. Matrix matched calibration curves and chromatograms for standards at 0.001 mg/kg. (A) APGC analysis of leptophos in celery and lemon, (B) UPLC analysis of carbofuran in corn and kale.

RESULTS AND DISCUSSION

Matrix matched standards were prepared in celery, lemon, corn and kale over a range of 0.001 - 0.050 mg/kg and replicate injections made using the UPLC and APGC methods. The data were fitted with the best fit calibration; for the UPLC data, the response was shown to be linear whereas the APGC response over the range investigated was non-linear and so was fitted with a quadratic calibration. (Figure 4). This is in accordance with the SANTE/11945/2015 guidelines.[5] A majority of the compounds in both analysis methods had correlation coefficient (R^2) values of 0.995 or greater. Residuals from triplicate injections at each calibration point were within ±20%.

Figure 5 demonstrates the percentage of pesticides in each method detected in the spiked matrices at 0.010 mg/kg, but many pesticides could also be detected at 0.001 mg/kg as demonstrated in Figure 4. The precision of the measurements was excellent with more than 90% of the detected pesticides exhibiting RSDs less than 10% (n=3). The exception was the APGC analysis of the kale matrix which had more than 80% of pesticides exhibiting RSDs less than 10% (Figure 6). Ion ratios in matrix were also shown to be within 30% tolerance of the reference values.

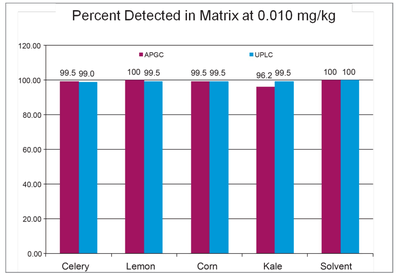


Figure 5. Percentage of pesticides detected in the 0.010 mg/kg standard for each matrix using both APGC and UPLC.

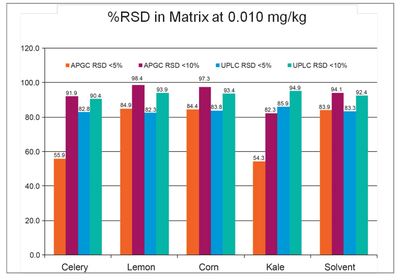


Figure 6. Percentage of compounds detected at 0.010 mg/kg at respective RSDs.

RADAR Provides Another Layer of Information

RADAR allows a full scan to be acquired with MRM transitions and provides extra information in the sample analysis. Figure 7 shows two different matrices spiked with the same concentration of tetrachlorvinphos (red trace). Sample A quantified two times higher than sample B. The full scan data (blue trace) shows a large matrix interference in sample A at the retention time of tetrachlorvinphos which may suggest matrix enhancement as the reason for the difference in qauntitation. This information can help in the development of more extensive sample clean up or change in chromatographic conditions to move the peak of interest away from the matrix interference.

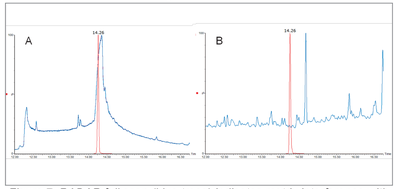


Figure 7. RADAR full scan (blue trace) indicates matrix interference with tetrachlorvinphos MRM (red trace) in sample A, but no interference in sample B.

CONCLUSIONS

- **Complex multi residue pesticide analysis was demonstrated using both UPLC and APGC analysis on the same tandem quadrupole instrument**
- **Instrument methods were generated and maintained using QuanPedia databases making method generation and maintenance fast and simple.**
- **The reliable scanning speed of the TQ-S micro produced accurate and precise measurements for large multi residue methods.**
- **The performance of the analysis complied with the SANTE guidelines for pesticide residue analysis.**
- **Detection at the default maximum residue limit of 0.010 mg/kg was easily achieved for > 99% of pesticides analyzed with good precision (RSDs < 10%) for most analytes in the food samples.**
- **The flexibility of the Universal Source architecture provides access to both UPLC-MS/MS and GC-MS/MS on the same instrument, allowing for an increase of laboratory efficiency, while maintaining required sensitivity and repeatedly.**

References

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