EVALUATING SYSTEM PERFORMANCE DURING ROUTINE ANALYSIS OF FOOD COMMODITIES FOR PESTICIDE RESIDUES

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Dimple Shah,[1] Jodi-Anne Wood,[1] Simon Hird [2] and Eimear McCall [2]
1 Waters Corporation, Milford, MA, USA;   2 Waters Corporation, Wilmslow, United Kingdom.

INTRODUCTION

The analysis of pesticide residues remains of critical demand in food contaminant laboratories, where, due to the physiochemical properties of the various analytes across commodities under analysis, many challenges in the analytical workflow can impact efficiency. From sample processing through to data analysis and interpretation, **this poster summarises the system's performance looking at representative food samples from five commodity groups. While 552 compounds were targeted in this method, the data reported focuses on 256 analytes, selected based on EC Regulation 2019/533/EU.[1] Where appropriate, SANTE/12682/2019 guidelines [2] are referenced to interpret the method performance and influence decisions maximizing the system's performance.**

METHODS

Representative samples from each of the commodity groups were purchased from local retail outlets, including high-water content (spinach), high acid with high-water content (strawberry), high oil with very low water content (soybean), high protein with low water and fat content (wheat flour) and difficult or unique (black tea) commodity groups.

Samples were extracted using QuEChERS CEN methodology, diluted and analysed by LC-MS/MS. A time windowed multiple reaction monitoring (MRM) method containing more than 500 compounds was created from the Quanpedia database.

Replicate injections were run for each commodity at three concentration levels (0.005, 0.01 and 0.05 mg/kg), bracketed between matrix matched calibration curves (0.0001 to 0.1 mg/kg), without the use of internal standard.
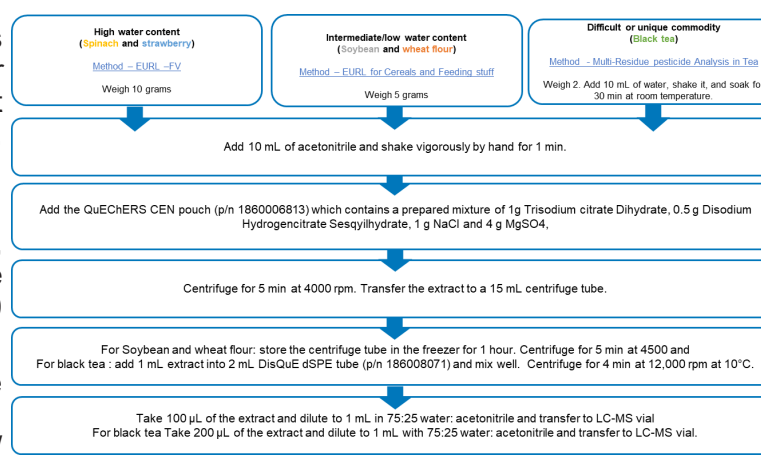

Figure 1. Summary of sample preparation

LC-MS/MS:

LC system: ACQUITY UPLC IClass PLUS with FL SM

Column: ACQUITY HSS T3 2.1 x 100 mm (186003539)

Post injector mixing kit: 50 µL extension loop (430002012)

Injection volume: 5 µL

MS instrument: Xevo TQ-XS

Ionisation: Electrospray

Polarity: Positive and negative (switching)

Acquisition: Time windowed MRM (at least 2 transitions per analyte)

RESULTS AND DISCUSSION

The performance of the LC-MS/MS method was assessed in terms of retention, retention time stability, calibration linearity, instrument method precision and matrix effects. Focussing on a selection of 256 analytes, these results are summaried and discussed here.
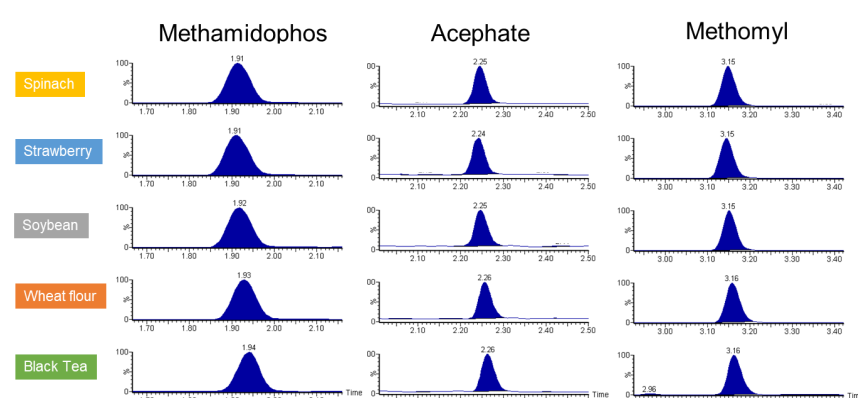

Figure 2. Excellent retention, peak shape and stability was observed for the more polar, first eluting compounds in this method across commodities.

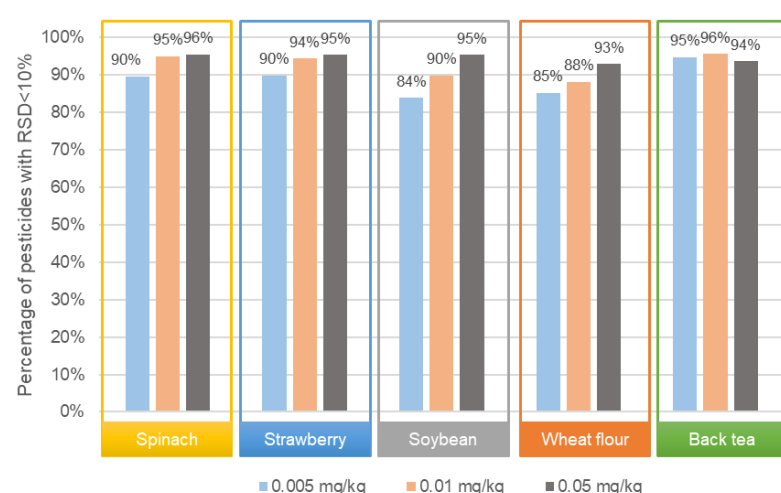**Figure 3.** The percentage of pesticides with RSDs <10% for matrix matched spikes. The LOD (defined here as S/N >10 for both MRMs) for the majority of compounds was 0.005 mg/kg; >90% for spinach, strawberry and soybean, 79% for wheat and 83% for tea.
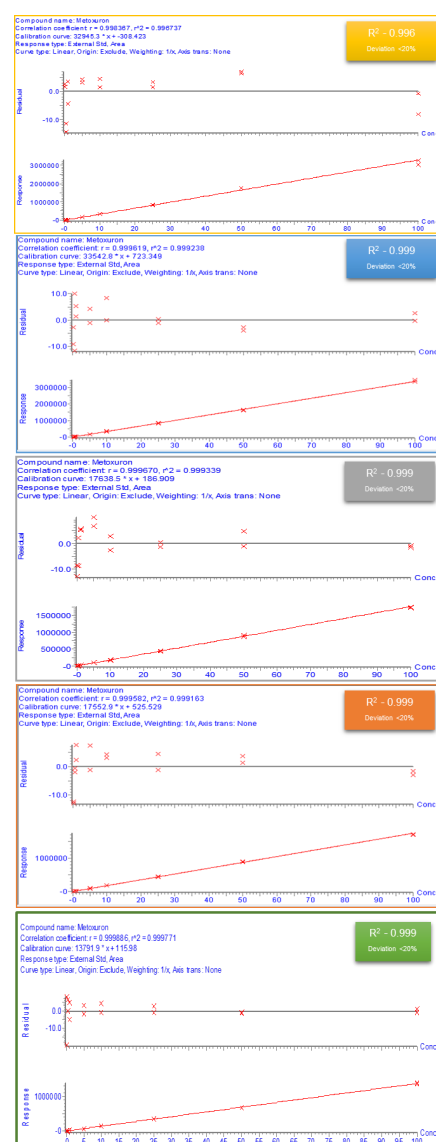

Figure 4. Matrix matched curves, bracketing the analytical runs yielded $R^2 > 0.99$ and back-calculated concentrations (residuals) $\pm$ 20%. Example shown for metoxuron in spinach, strawberry, soybean, wheat flour and black tea, equivalent to 0.0001 to 0.1 mg/kg.
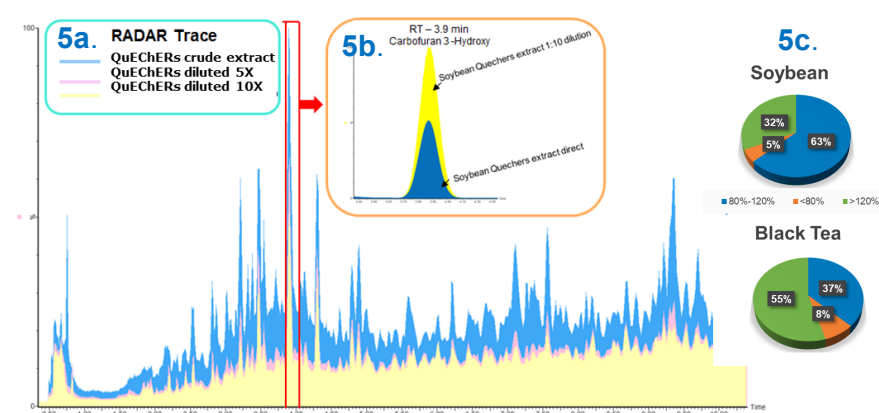

Figure 5. In order to investigate matrix effects, samples were prepared using crude and dilute QuEChERS extracts **5a** RADAR trace of soybean crude, 5X diluted and 10X diluted extracts. **5b** shows chromatogram of carbofuran 3-hydroxy in the crude (blue) and 10X diluted (yellow) extracts, co-eluting with isobaric interference shown in 5a. **5c** Matrix effects were further evaluated by comparing the slope of calibration lines in matrix and solvent. Shown are the effects for soybean, corrected by dilution and matrix matched calibration, while significant enhancement observed in black tea was corrected using dSPE cleanup.
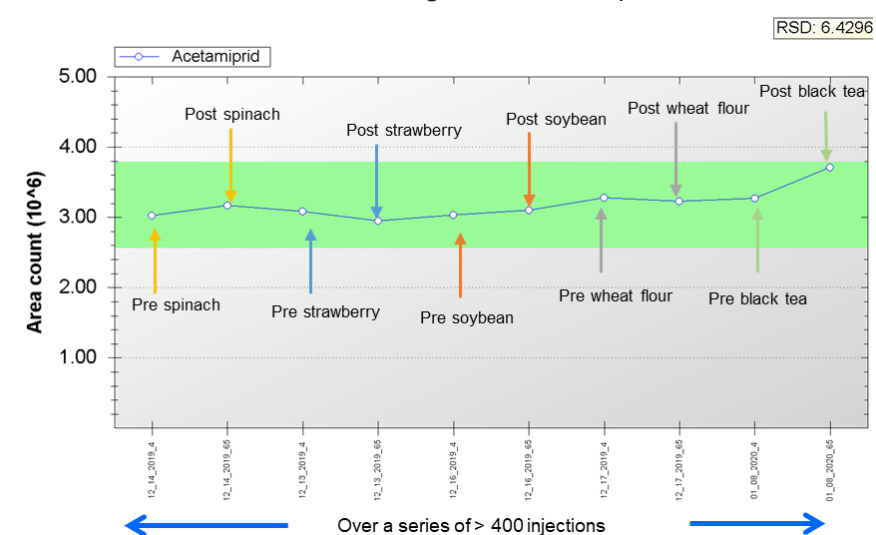

Figure 6. To assess ongoing method and instrument performance, QC samples were injected before and after each commodity batch. Peak area of acetamiprid is plotted, representing 3 days operation, without operator intervention or use of internal standard.

CONCLUSION

- **A multi-residue LC-MS/MS method has been developed for the determination of 552 pesticides and relevant metabolites in representative food commodities.**

- **The performance of the LC-MS/MS method was evaluated for the determination of 256 representative analytes, where the detection of most compounds was achieved at 0.01 mg/kg in matrix matched extracts across all five commodities.**

- **The dilution of the QuEChERS crude extracts reduced the loading of co-extractives into the system and decreases the frequency of routine instrument maintenance. Appropriate sensitivity and peak shape is maintained using the post injector mixing kit** (see Poster PV-27 for more information)**.**

REFERENCES
1. Commission implementing Regulation 2019/533/EU: Available here
2. SANTE/12682/2019 : Available here
3. EURL-FV Multiresidue Method using QuEChERS followed by GC-QqQ/MS/MS and LC-QqQ/MS/MS for Fruits and Vegetables. Available here
4. EURL for cereals and feeding stuff: Determination of pesticide residues in wheat, rye, oat and rice by LC-MS/MS and GC-MS/MS: Available here
5. Multi-Residue Pesticide Analysis in Tea: Optimized Cleanup After QuEChERS Extraction for UPLC-MS/MS and GC-MS/MS: Available here

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