ROUTINE DETERMINATION OF HIGHLY POLAR CATIONIC PESTICIDES AND PLANT GROWTH REGULATORS BY LC-MS/MS

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INTRODUCTION

This poster highlights a modern, alternative solution, which provides excellent retention, separation and detection for a range of polar anionic pesticides, using the Anionic Polar Pesticide Column on a standard UPLC-MS/MS (ACQUITY IClass with Xevo TQ-S micro) platform. Considering the analytical quality control criteria of SANTE/12682/2019, steps to ensure a robust and reliable LC-MS/MS method are discussed.[1] With a desire to maximize efficiencies and ability to extract multiple polar analytes using a single method, this approach looks at extending the analytical scope from the traditional glyphosate, glufosinate and AMPA target list. In developing these methods, consideration was given to the main renowned challenges:

1. **Retention**: Highly polar, low molecular weight compounds can create challenges for reversed phase C_{18} columns.
2. **Separation**: Expanding the scope of analytes, including metabolites, increases the importance for baseline chromatographic separation.
3. **Detection**: Required limits of detection vary depending on the commodity, compound and residue definition, typically in crude extracts.
4. **Reliability**: Methodology should prove reliable, ensuring incurred residues are readily determined with confidence in the routine laboratory, without requiring specialised training or time intensive workflow.

METHODS

All samples were purchased from local retail outlets, homogenized and extracted using a version of the EURL Quick Polar Pesticides (QuPPe) extraction method. [2] All linearity data reported is matrix matched standards, while QCs were spiked prior to extraction. Full sample extraction and method details are available. For more information, scan the QR code below or visit **www.waters.com/polarpesticides**.

RESULTS AND DISCUSSION

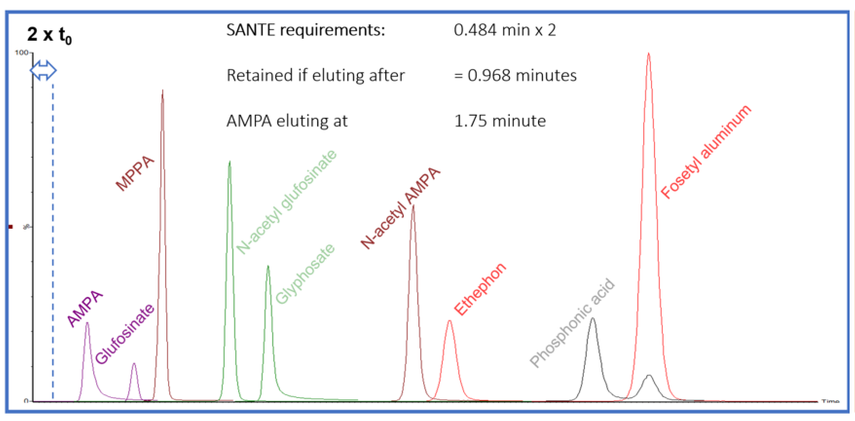


Figure 1. The SANTE guidelines state that 2 x the column void (t_0) volume represents retention. AMPA, the first analyte to elute, is shown to retain, as it elutes > 0.968 mins. Achieving retention allows additional flexibility and control in the method.

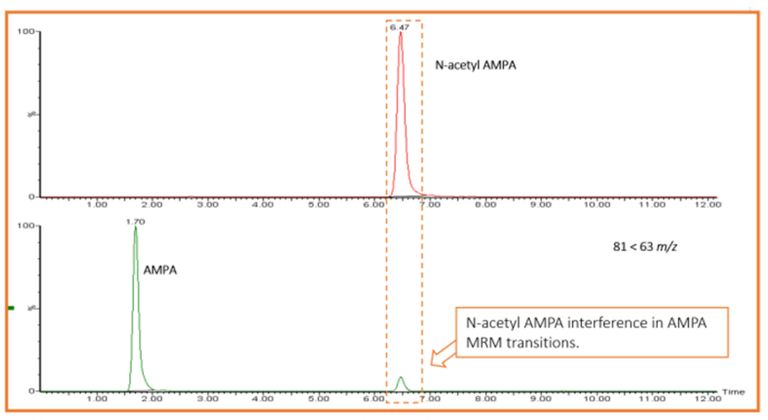


Figure 2. Baseline separation of many critical pairs is essential to avoid false detections from isobaric interferences. An example is shown for AMPA and its metabolite.

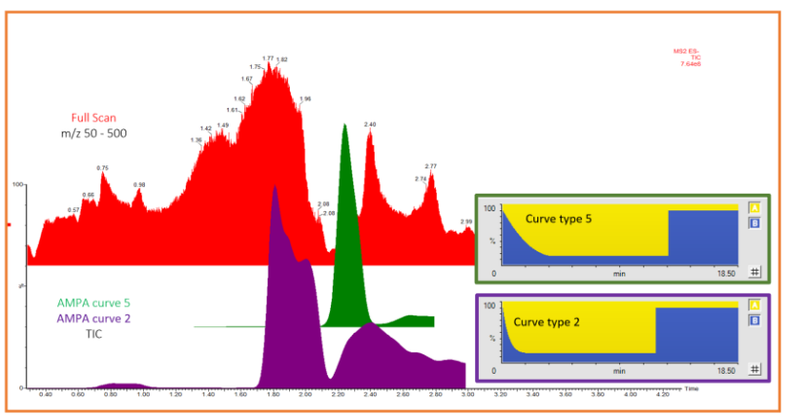
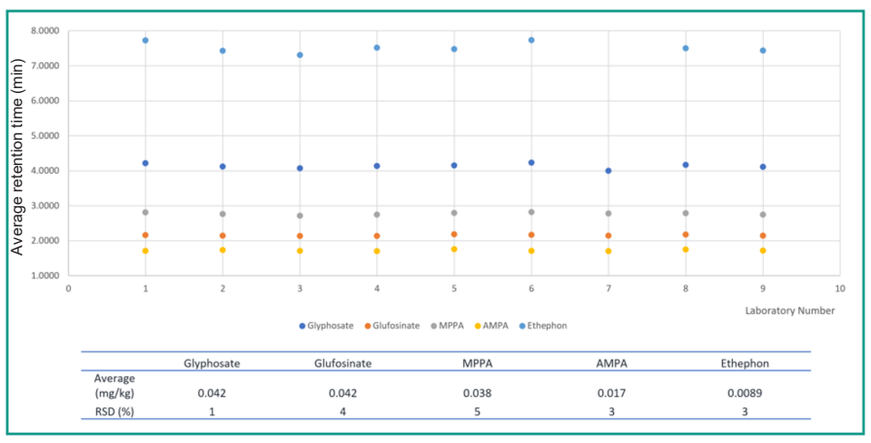
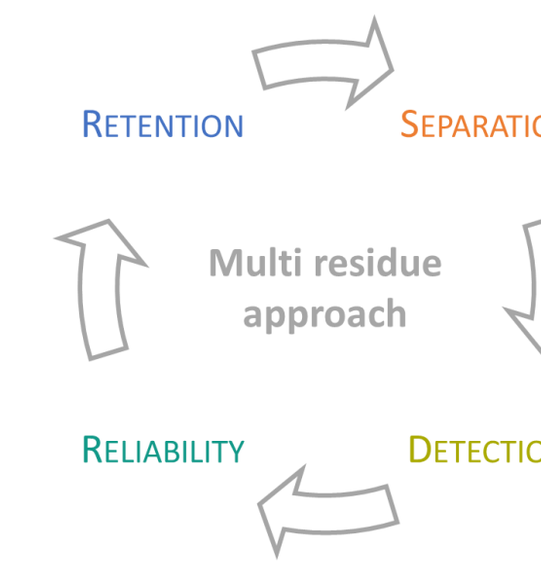


Figure 3. AMPA demonstrates significant matrix suppression across commodity types. In this example, co-extractives from wheat cause significant chromatographic and detection issues. Benefiting from the excellent retention, minor changes to the gradient (shallower profile) allowed for the analyte to be moved away from isobaric interferences, thus improving peak shape and sensitivity of AMPA.



	Glyphosate	Glufosinate	MPPA	AMPA	Ethephon
Average (mg/kg)	0.042	0.042	0.038	0.017	0.0089
RSD (%)	1	4	5	3	3

Figure 7. A small study was carried out across 9 Waters laboratories (8 countries), where matrix matched standards and unknown samples were analysed for a priority scope of analytes. Excellent agreement was achieved by all labs, in terms of the spiked concentration, along with repeatability of the retention times across systems.



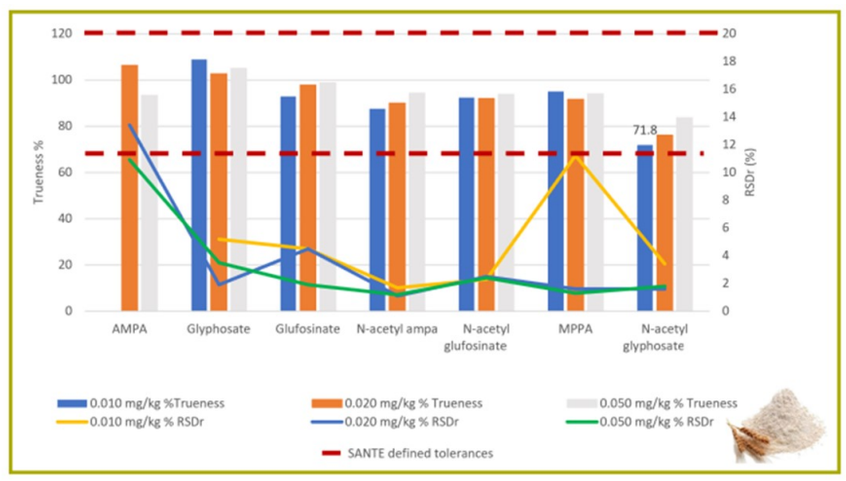


Figure 4. Method detection, in terms of trueness and repeatability are shown for replicate samples prepared at 3 concentrations in wheat, spiked prior to extraction at 0.01 mg/kg and 2x and 5x. All trueness was within the 70 to 120 % range (primary y-axis) and %RSD < 15% (secondary y-axis). Similar results were obtained across other foodstuffs, where all recoveries and repeatability of the targeted analytes were within defined SANTE guidelines tolerances.

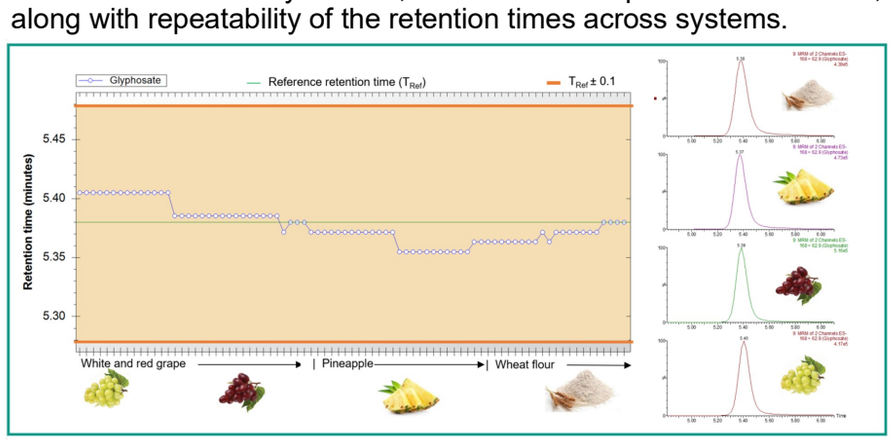


Figure 6. Summarising a number of foodstuffs analysed, excellent stability was achieved in terms of retention time and peak shape for all analytes. Example is shown for glyphosate.

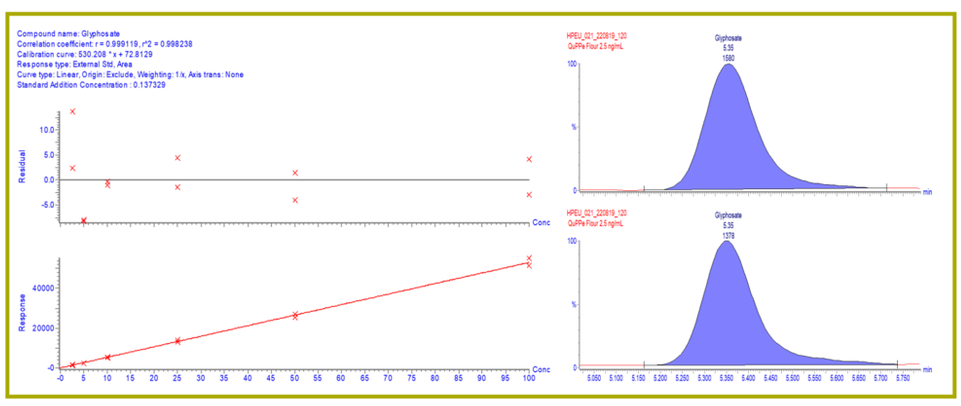


Figure 5. Example of detection– quantitation, linearity and sensitivity– results are shown for glyphosate over a bracketed matrix matched calibration curve and chromatography equivalent to 0.01 mg/kg in wheat.

For results achieved in other commodity groups, scan the QR code below.

CONCLUSION

- **A simple method, ensuring reliability, for the determination of anionic highly polar pesticides has been developed for routine operation on standard UPLC-MS/MS, using the Anionic Polar Pesticide Column.**
- **Methodology has focussed around retaining, resolving and quantifying these physiochemically challenging compounds, enabling reliable and sensitive detection, far exceeding the current MRLs.**
- **Small does not have to limit capabilities– delivering purpose driven performance, the determination, with confidence, of these small molecular weight, highly polar, anionic pesticides is now becoming routine.**

Scan the QR bar code for more information

REFERENCES

1.SANTE/12682/2019 : Available here
2.European Commission (2019) QuPPe Method: Available here

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