EXPLORING THE ANALYTICAL SCOPE OF PESTICIDES, IONIZABLE IN A SINGLE INJECTION BY LC-MS/MS

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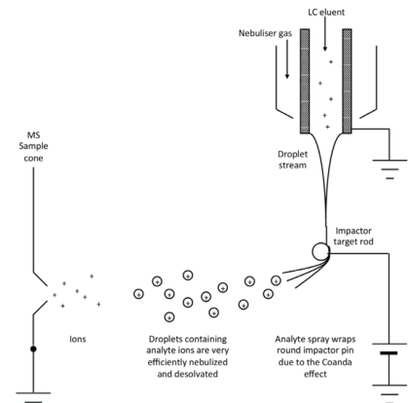
INTRODUCTION

The invention of the atmospheric pressure ionization has revolutionised the world of analytical testing, enabling liquid chromatography, coupled with mass spectrometry to become mainstream and the gold standard in many routine laboratories requiring high throughput quantitative analysis. Electrospray ionization has almost become the default atmospheric pressure ionization source in these environments, due to its broad coverage of molecular weights and capabilities to ionize highly polar to mid polar compounds.[1] In this work, an alternative ionization source, UniSpray, is investigated across a number of experiments for the analysis of various pesticides across relevant food and water samples.



UniSpray's process of ionization is shown in the schematic, where unlike ESI, the capillary is grounded. Instead the voltage is applied to the impactor pin placed within the source chamber. As the eluent spray wraps around this pin, analyte ions are efficiently nebulized and desolvated, thus allowing for improved ionization and sensitivity. In this poster we summarise a number of investigations carried out to explore how these improvements in sensitivity can positively influence method performance in the determination of pesticides and metabolites.

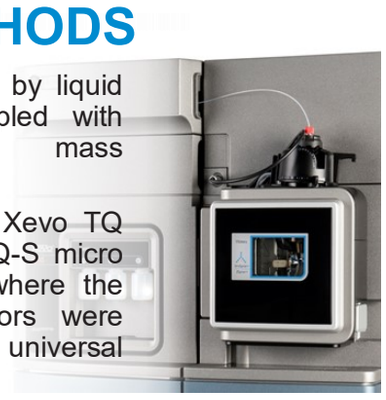
METHODS

QuEChERS extraction was applied to a variety of foodstuffs, comparing the performance by electrospray and UniSpray ionization.

Solvent based and matrix matched calibration standards, along with food and water extracts were analysed by both ionization modes to investigate the method performance, in terms of linearity, detection, repeatability, matrix effects and scope of analytes ionized.

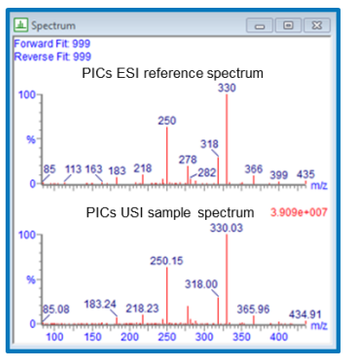
All samples were analysed by liquid chromatography (LC) coupled with tandem quadrupole mass spectrometry (MS/MS).

In this work, a number of Xevo TQ instruments (Xevo TQD, TQ-S micro and TQ-XS) were used, where the ESI and USI source doors were readily interchanged on the universal source design.



Initial investigations showed similar spectra are achieved by ESI and USI. Therefore, the same MRM transitions were applied using both ionization techniques.

The spectra shown gives an example of fipronil sulfone under ES and US ionisation modes.



RESULTS AND DISCUSSION

Sensitivity

In a study of 42 insecticides in eggs, the sensitivity, in terms of peak area achieved under ESI and USI were compared.

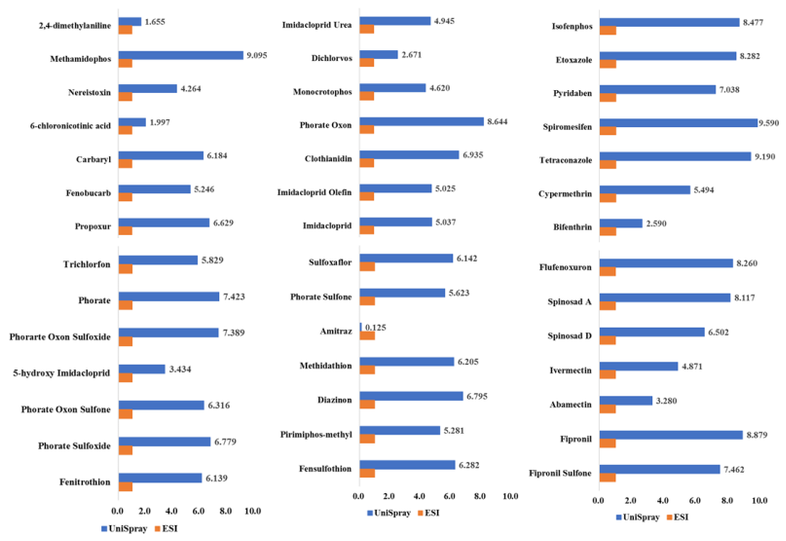


Figure 1. USI peak area normalised against ESI for 42 insecticides at 0.05 mg/kg in egg.

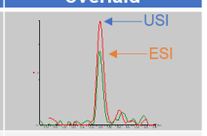
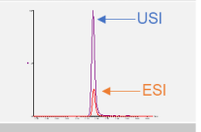
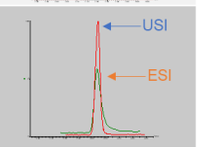
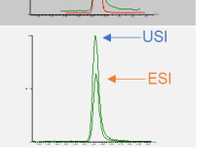
While matrix matched calibration was employed in this study (USI achieving similar results to ESI), Galani, *et al.* reported reduced matrix effects for 81 pesticides in a number of sample types (scan the QR code below for more information).[2]

Repeatability

In a study of 44 antiparasitic pesticides, the improvements in sensitivity were evaluated, where on average, improvements of 2.4 and 1.9 times were observed for peak area and s:n respectively.

Figure 2. Representative analytes from the study for replicates (*n*=5) at 0.05 mg/kg in porcine liver are summarised.

With increased peak area achieved by USI, the %RSDs between replicates are significantly tighter. Overlaid chromatograms also depict the increase in peak area, showing similar isobaric interferences in both ionisation modes.

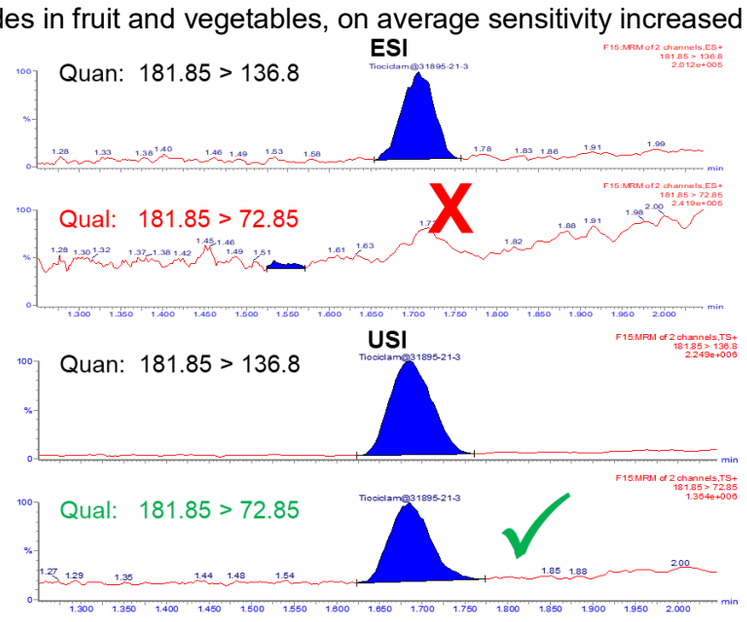
Analyte	Peak area USI gains	S:N USI gains	USI % RSD	ESI %RSD	Chromatograms overlaid
Clorsulon	1.75	2.81	7.18	20.59	
Rafoxanide	3.33	2.55	4.36	6.51	
Albendazole Sulfoxide	2.52	2.41	0.83	1.15	
Cambendazole	1.71	2.05	1.87	2.83	

Identification

In a study of over 300 pesticides in fruit and vegetables, on average sensitivity increased by 3.5 times (in terms of peak area).

Figure 3. Increased sensitivity achieved by UniSpray generated a second transition, absent under traditional ESI.

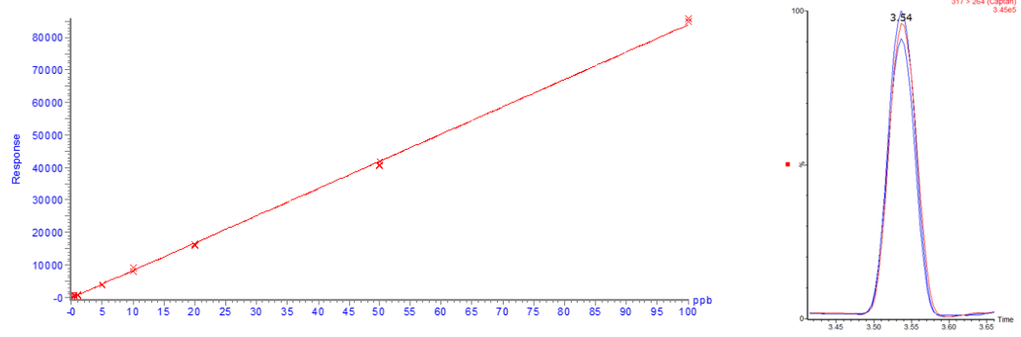
UniSpray allowed for the identification of thiocyclam in cucumber at 0.003 mg/kg, where all retention times and ion ratios were within permitted tolerances of ±0.1 minute and ±30% of the reference standards, respectively.



Analytical scope

Compounds known to be challenging by traditional GC analysis were investigated, including captan, folpet and their metabolites. Results are summarised for captan in kale following traditional QuEChERS extraction and cleanup..[3]

Figure 4. Linearity of captan in matrix matched calibrants is summarised, over a range of 0.005 to 0.1 mg/kg, where all was within tolerance (R^2 > 0.995 and residuals < 20%). Also shown is an example of the chromatography achieved for 0.01 mg/kg captan in kale.



CONCLUSION

- **UniSpray has been found to offer improvements in ionisation efficiency, allowing gains in sensitivity when placed on Xevo MS instruments.**
- **Improvements in sensitivity yield true benefits where repeatability between injections is improved, confidence in analyte identification increased and matrix effects reduced.**
- **This increased efficiency in ionisation has also delivered benefits in the scope of analytes now analysable by LC-MS/MS, with a single ionisation source, thus improving workflow efficiencies and overall confidence in detections.**

Scan the QR bar code for more information

REFERENCES

1.Whitepaper on atmospheric pressure ionisation sources: Available here
2.Captan, Folpet and metabolites by LC-MS/MS poster: Available here
3.Galani J.H.Y., Houbraken M., Van Hulle M., Spanoghe P. *Anal Bioanal Chem* **411,** 5099–5113 (2019): Available here

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