ACCESSIBLE AND EFFICIENT SCREENING OF MULTICLASS CONTAMINANTS IN FOOD

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INTRODUCTION

In recent years, the world's production and consumption of grains and cereals has maintained steady growth, while the price per tonne has shown some fluctuation.[1] Agricultural, environmental and naturally occurring contaminants in these commodities are regulated around the globe to ensure the final produce is safe for human consumption. Therefore, the need for multi analyte screening procedures to efficiently detect violating residues, in an accessible and cost effective manner, is ever increasing.

Routine testing laboratories continue to strive for efficient and reliable sample throughput methodologies, where generic analytical conditions are essential. Limitations, however, may exist due to the complexity of sample matrices and differing physicochemical characteristics of contaminating compounds, thus requiring replication of work, to ensure all residues of interest can be targeted and detected.

In this work we present a simplified extraction procedure, allowing for the reliable detection of residues at their regulated limits by liquid chromatography coupled with tandem quadrupole mass spectrometry, utilising a novel ionisation interface, UniSpray. This novel ionisation source allows for multimode ionisation of both polar and non-polar analytes, in a single injection. **Figure 1** shows the mode of ion formation, where the high velocity droplet stream generated at atmospheric pressure allows for increased ionisation and sampling efficiency. [2]

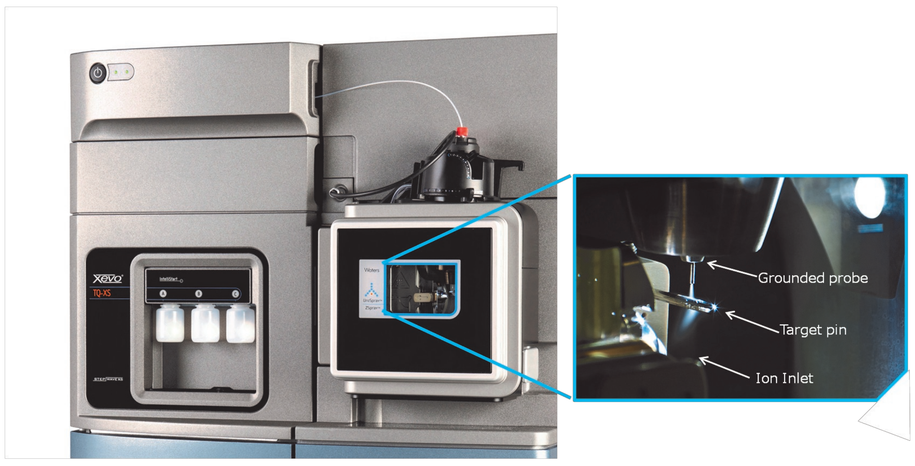


Figure 1. *UniSpray ion source on Xevo TQ-XS, where the nebulised spray, generated by the grounded probe, is directed at the stainless steel target pin held at a high voltage. Interaction with this target creates a fine spray of charged droplets allowing for more efficient ionisation and sampling into the ion inlet orifice of the mass spectrometer.*

METHODS

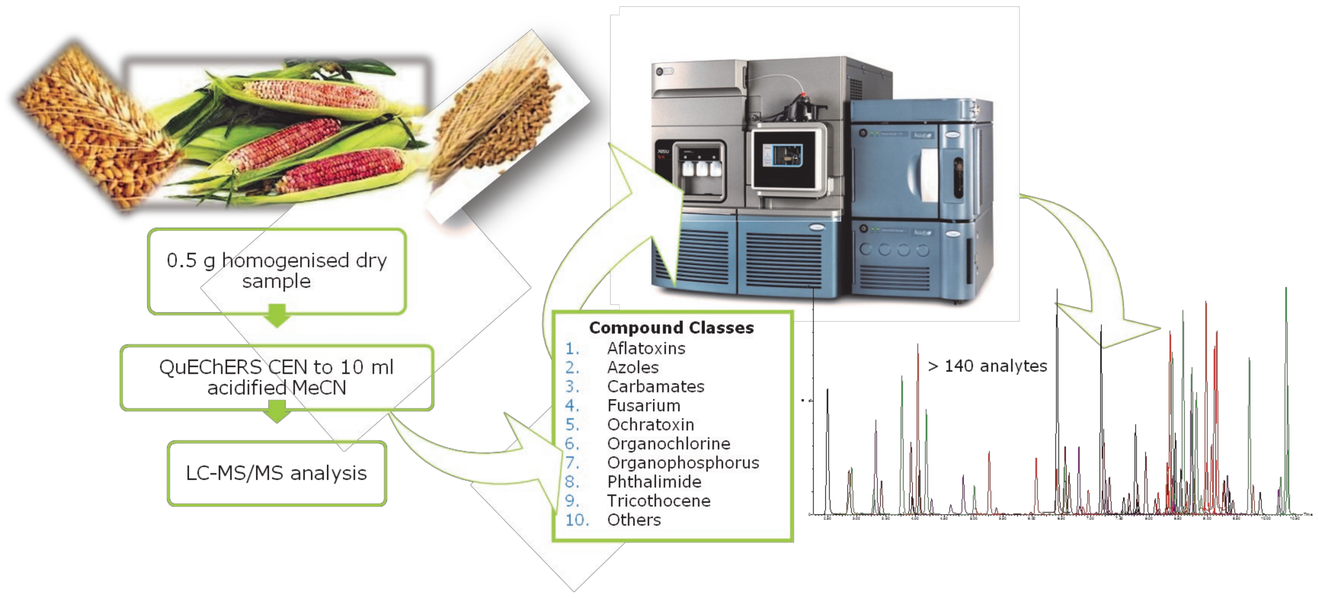


Figure 2. *Generic, single step QuEChERS clean up was applied to samples of barley, red corn and wheat, spiked with over 140 analytes (including mycotoxins and pesticides) and presented for LC-US-MS/MS analysis.*

LC Conditions

- LC System: Waters ACQUITY I-Class
- Column: ACQUITY UPLC BEH C_{18} 2.1 x 100 mm, 1.7 µm
- Column Temp: 45°C
- Sample Temp: 4°C
- Flow Rate: 0.450 mL/min.
- Mobile Phase A: 0.1 % formic acid in water
- Mobile Phase B: 0.1 % formic acid in methanol
- Total run time: 17 min
- Injection volume: 1 µL
- Gradient:

Time (min)	A (%)	B (%)	Curve
0	98	2	6
0.25	98	2	6
12.25	1	99	6
13.0	1	99	6
13.01	98	2	6
17	98	2	6

MS Parameters

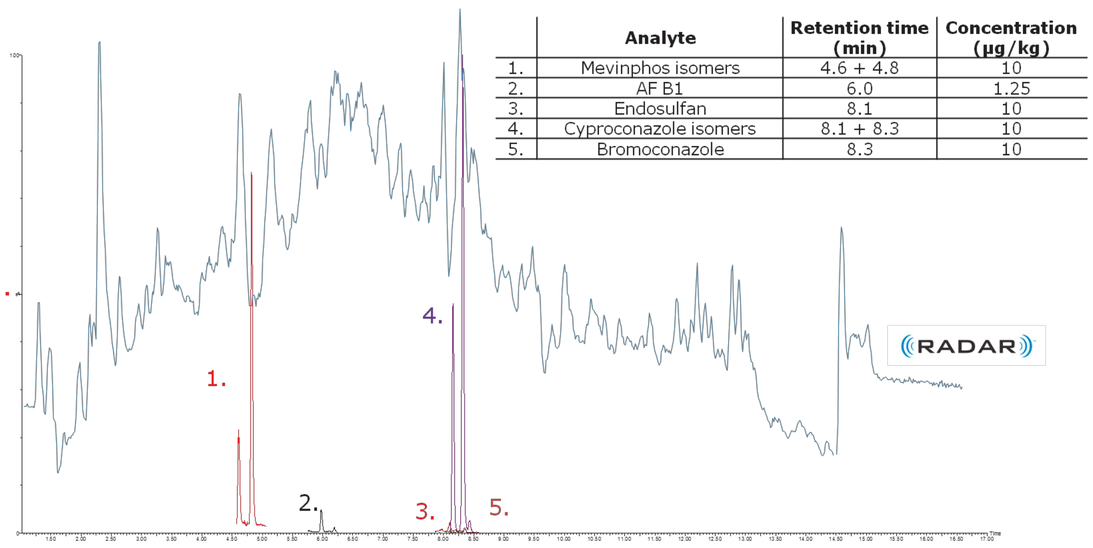
- MS System: Xevo TQ-XS
- Ionisation mode: UniSpray (US^+)
- Capillary voltage: 1 kV
- Desolvation temperature: 550 ° C
- Desolvation gas flow: 1000 l/hr
- Source temperature: 120 ° C
- Cone gas flow: 150 l/hr
- Acquisition mode: MRMs obtained from QuanPedia™

RESULTS AND DISCUSSION

A simple, efficient and sensitive method for the screening of commonly targeted contaminants in foods has been developed, where proof of the method's principle has been applied to the complex commodities of dry cereal and grains. One hundred and forty one analytes were spiked into barley, wheat and red corn to regulated permitted limits. All pesticide residues, including organohalogenated, carbamates, phthalimide, azoles and many others were spiked to 0.01 $mg.kg^{-1}$, while mycotoxin residues were spiked at varying concentrations from 1.25 $\mu g.kg^{-1}$ (for AF B1) to 500 $\mu g.kg^{-1}$ (for deoxynivalenol).

Simplified sample clean up was employed, allowing for efficient analyte extraction under generic conditions. Despite matrix complexity, regulatory limits were readily detected utilising the high sensitivity afforded by the Xevo TQ-XS tandem quadrupole MS. This is shown in **Figure 3**, where a full scan acquired simultaneously with the MRM functions shows excelled sensitivity and selectivity for a selection of residues of interest.

Further enhancements in analytical efficiencies are demonstrated in **Figure 4**, where traditional gas chromatography amenable compounds are detected at regulated maximum residue limits by LC-MS/MS utilising the novel multimode ionisation source.



	Analyte	Retention time (min)	Concentration (µg/kg)
1.	Mevinphos isomers	4.6 + 4.8	10
2.	AF B1	6.0	1.25
3.	Endosulfan	8.1	10
4.	Cyproconazole isomers	8.1 + 8.3	10
5.	Bromoconazole	8.3	10

Figure 3. *High sensitivity of MS/MS allows for the detection of analytes at ≤10 $\mu g.kg^{-1}$ in red corn QuEChERS extract, despite complexity of the matrix shown in the RADAR (full scan) acquisition. Simple, generic extraction provides efficient clean up while allowing for multi class and multi residues to be detected at permitted regulatory limits in complex matrices.*

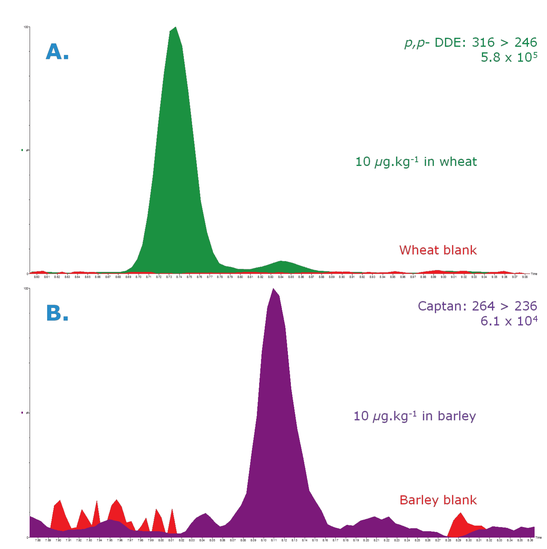


Figure 4. *Unique ionisation afforded by the UniSpray ion source provides extension to scope for traditionally termed LC– and/ or GC– amenable compounds in a single injection where **A.** p,p-DDE and **B.** captan are detected at 10 $\mu g.kg^{-1}$ in wheat and barley, respectively.*

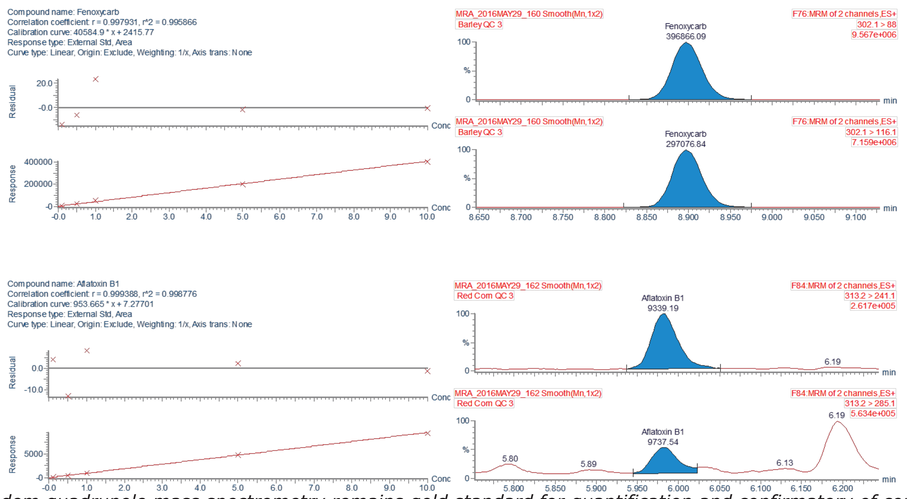


Figure 5. *Tandem quadrupole mass spectrometry remains gold standard for quantification and confirmatory of contaminant residues in food matrices. Quantification and confirmatory traces are shown for fenoxycarb (in barley) and aflatoxin B1 (in red corn), along with example of the calibration curves.*

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CONCLUSIONS

✓ A single extraction and centrifugation method provided simplified sample clean up of cereals prior to LC-MS/MS analysis for the targeted screening of agricultural, environmental and naturally occurring contaminants.

✓ Multiple classes of residues were targeted in a single injection, including organohalogenated, carbamates, tricothocenes, aflatoxins.

✓ Coupling LC with a high sensitivity MS/MS and the multimode ionisation source, UniSpray, a novel screening method of multiple compound classes in complex commodities has been developed to below the regulatory limits.

References

1. Committee for the Common Organisation of Agricultural Matters Agri C4, April 2016; http://ec.europa.eu/agriculture/cereals/presentations/cereals-oilseeds/market-situation-cereals_en.pdf
2. Poster 290 – Instrumentation: New Developments in Ionization and Sampling, An Aerodynamic Perspective on Impactor API Sources, Steve Bajic, Waters Corporation, Wilmslow, UK.