UTILIZING ION MOBILITY ENABLED HIGH RESOLUTION MASS SPECTROMETRY FOR FOOD CONTAMINANT SCREENING

Naren Meruva[1], Lauren Mullin[1,2], Adam Ladak[1], Gareth Cleland[1], Joe Romano[1]
[1]Waters Corporation, 34 Maple Street, Milford MA 01757 USA
[2]MTM Research Centre, Örebro University, Örebro SE-70182 Sweden

Waters
THE SCIENCE OF WHAT'S POSSIBLE.®

INTRODUCTION

Food companies and authorities are under pressure to develop screening methods capable of detecting a broad spectrum of contaminants in a single analytical run. High Resolution Mass Spectrometry (HRMS) is being utilized in order to perform food screening and expand the scope of current food testing. Unlike traditional tandem quadrupole screening that utilizes multiple reaction monitoring (MRM) acquisitions, HRMS is an untargeted screening technique which collects all of the data to allow the detection of potentially a limitless number of contaminants. In addition to the high level of selectivity through the acquisition of full spectra with accurate mass and isotopic information for both precursor and product ions in a single run, HRMS systems equipped with ion mobility separation (IMS) offer extra dimensions of separation and confirmation using collisional cross section (CCS) measurements. The determination of the CCS of an ion is extrapolated from the observed drift time as the ion passes through the drift cell. In this work an IMS HRMS was utilized to screen for contaminants in fruits and vegetables subjected to QuEChERS extraction. The advantages of ion mobility and CCS for food screening are demonstrated.

MATERIALS AND METHOD

LC Conditions
LC System: Waters ACQUITY I-Class
Column: ACQUITY UPLC BEH C18 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: 10mM ammonium acetate (pH5.0) in Water
Mobile Phase B: 10mM ammonium acetate (pH 5.0) in MeOH

Gradient:	Min.	Flow Rate	%A	%B
	Initial	0.450	98.0	2.0
	0.25	0.450	98.0	2.0
	12.25	0.450	1.0	99.0
	13.00	0.450	1.0	99.0
	13.01	0.450	98.0	2.0
	17.00	0.450	98.0	2.0

Total run time: 17 min
Injection volume: 5 µL

LC/MS Ionization Conditions
Ionization Mode: ESI+
Capillary (kV): 1.0
Sample Cone (V): 20.0
Source Temperature: 120°C
Desolvation Temperature: 550°C
Cone Gas Flow: 50 L/Hr
Desolvation Gas Flow: 1000 L/Hr
Acquisition range: 50-1200 m/z
Scan time: 0.25 sec
Lockmass: LeuEnk (556.2771m/z)

IM/MS Conditions
System: Waters VION IMS QTof
Collision Energy ramp: 20 to 55 eV
Acquisition Range: 50-1200 m/z
Acquisition rate: 8 spectra/second
IMS Drift Gas: N_2

Software
UNIFI scientific information system

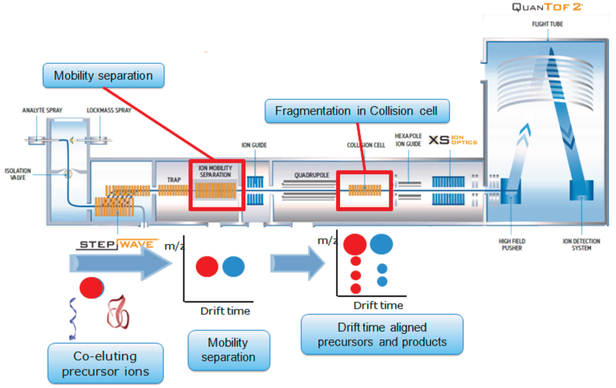

Figure 1: Schematic of the VION IMS QTof. The example shows two co-eluting species being separated in the drift cell under Nitrogen gas. The reason for the separation is due to the different shape or collisional cross section of each species. Fragmentation is also performed every other scan to provide fragment ion information. The fragments are aligned with the precursor as they share the same drift time.

RESULTS AND DISCUSSION

The sample extracts were screened against a scientific library with, as part of the acquisition and processing software UNIFI. The scientific library holds a number of properties including the expected retention time, molecular formula, structure, expected fragments and expected CCS value. The combination of all these properties allows added confidence in the detection of a contaminant in a sample. The data was acquired and processed within UNIFI and data filters were used to show the desired data. Figure 2 shows a typical workflow view within

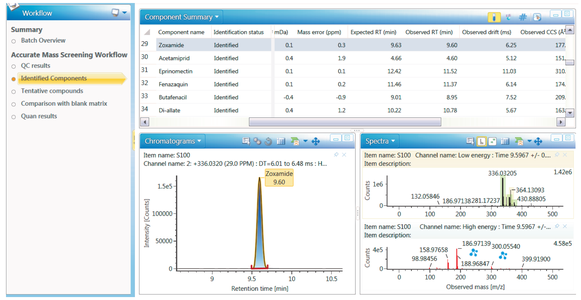

Figure 2: UNIFI workflow view of identified compounds in strawberry within 0.25 minutes of the expected retention time, 3 ppm mass error and 1 observed fragment.

As the data was collected using alternating scans between low and elevated collision energy, both precursor and product ion spectra were collected simultaneously. By utilizing IMS the precursor and product ion spectra were aligned showing only the spectra associated with the same retention (min.) and drift (ms) time. This produces cleaner spectra that make it easier to confirm known compounds and elucidate unknowns in matrix samples. Figure 3 shows an example of spectral clean up achieved with ion mobility.

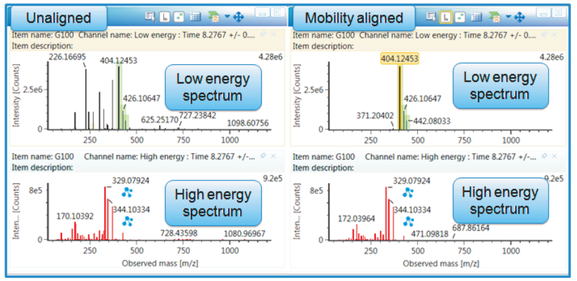

Figure 3: Example of Azoxystrobin detected in a green grape sample showing the advantages of mobility spectral alignment.

Although the library contained over 500 targets, there were contaminants found in the sample not present in the library. In order to identify components of interest a blank was compared to the suspect sample which is shown in Figure 4. The peaks that were not present in the blank were submitted to the elucidation toolset within UNIFI, following spectral clean-up. In the elucidation toolset elemental composition, data base searching and fragment match is performed. If a number of hits are found for a suspected contaminant, the results are automatically ranked within the software. Compounds can be submitted in batches for elucidation and results added to the scientific library for following screening experiments. Figure 5 shows the results from the elucidation of a peak that was not in the scientific library. In this case the time to obtain this result was less than 20 seconds.

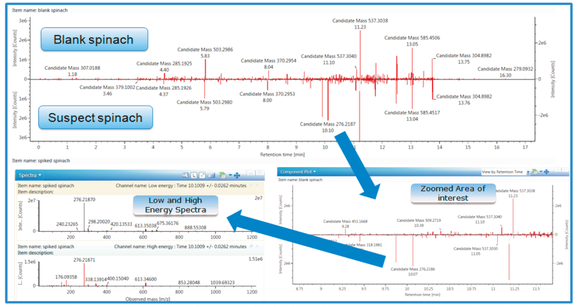

Figure 4: Binary comparison of a spinach blank and a suspect spinach sample and selection of large contaminant peak.

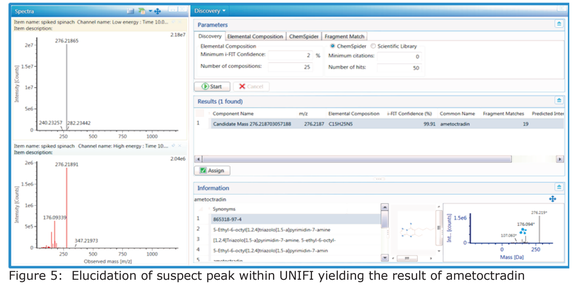

Figure 5: Elucidation of suspect peak within UNIFI yielding the result of ametoctradin

As well as the advantage of spectral clean up ion mobility separation allows CCS measurements to be made. The samples were screened against known CCS values and used as a further point of confirmation. In figure 6 the identification of five pesticides is shown in a spinach sample. Two of the five pesticides were confirmed with CCS despite not having any confirmed fragments due to their low level in the sample. 100 pesticides were run at between 1 and 100 ppb in solvent standards in order to ensure the CCS values were maintained at all concentrations. Figure 7 shows that the CCS values had RSDs less than 1% across the concentration range for all pesticides.

	Component name	Retention Time Error (min)	Mass error (ppm)	Observed CCS (Å²)	Expected CCS (Å²)	Collision cross section delta (%)	Expected Fragments Found	Response	Adducts
1	Flonicamid	-0.09	0.7	142.63	144.24	-1.12	0	1872	+H
2	Dinotefuran	0.00	0.8	144.32	146.02	-1.16	0	7368	+Na
3	Chlorantraniliprole	-0.14	0.1	201.33	204.38	-1.49	2	55631	+Na, +H
4	Metalfumizone	-0.07	0.9	210.74	214.34	-1.68	1	6359	+H
5	Atrazine	-0.10	0.3	145.36	148.52	-2.13	1	19211	+H

Figure 6: Identification of pesticides in a spinach sample using retention, mass accuracy and

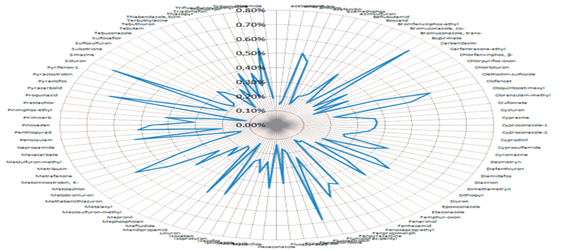

Figure 7: Reproducibility of CCS values for 100 pesticides over a concentration range of 1 to 100 ppb

CONCLUSIONS

- **HRMS coupled with IMS allows untargeted data independent analysis to be performed in food screening samples and expands the scope of screening**
- **Spectral clean up offered with ion mobility separation allows easier identification of targets and elucidation of unknowns**
- **The use of UNIFI software allows screening of targets and elucidation of unknowns to be performed without the need for multiple processing software**
- **Using CCS values in contaminant screening offers a unique point of identification**

TO DOWNLOAD A COPY OF THIS POSTER, VISIT WWW.WATERS.COM/POSTERS