Introduction
The utility of ultra performance liquid chromatography – orthogonal acceleration time-of-flight mass spectrometry (UPLC TOFMS) for the quantitative analysis of over 100 pesticides targeted in strawberry is demonstrated. The Wildlife Incident Investigation Scheme (WIIS) operated in Scotland by SASA also uses this methodology to investigate poisoning and intoxication of wildlife, beneficial insects, companion animals and livestock where there is evidence to indicate that pesticides or biocides may have been involved.

Accurate mass measurement of +ve and -ve ions allowed their extraction following full mass range data acquisition with negligible interference from background or co-eluting species observed during UPLC gradient separation (in a cycle time of just 6.5 minutes).

Extracted ion data was used to construct calibration curves and to detect and identify any residues.

Pesticides in Food

Ultra Performance Liquid Chromatography
UPLC was performed using a Waters ACQUITY Ultra-Performance LC System with gradient elution.

Mass Spectrometry – MSMS
Electrospray ionisation was achieved using a Quattro Premier XE tandem mass spectrometer (Waters Corporation) operated in +ve and -ve ion polarity switching mode during multiple reaction monitoring (MRM) acquisition in accordance with time-scheduled sequencing.

Mass Spectrometry – TOFMS
An orthogonal acceleration time-of-flight mass spectrometer with an electrospray ionisation interface was used (LCT Premier-XE or Synapt MS, Waters Corporation). Data acquisition was performed using either +ve or -ve ion mode over a mass range of m/z 50 to 1000 at a nominal instrument resolution of 11500 (FWHM).

UPLC MSMS Analysis
A single UPLC MSMS experiment acquires data for over 100 pesticides plus internal standards in 6.5 minutes and comprises 7 consecutive acquisition groups in +ve ion mode and 3 acquisition groups in +ve ion mode.

UPLC TOF MS Analysis
It is extremely difficult to identify analyte peaks associated with target or other species of interest at such low concentrations by visual inspection alone. Extraction of ions is essential and the chromatographic/mass resolving power of UPLC TOFMS presents a powerful combination capable of optimum selectivity.

Results
Residues of 9 different pesticides were successfully detected in the strawberry samples (STR1 & STR2) using UPLC TOFMS.

Table 1: Comparison of UPLC TOFMS and UPLC MSMS results

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<th>Pesticide</th>
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<th>UPLC MSMS</th>
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Table 2: UPLC TOFMS and MSMS details

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The results obtained using TOFMS were in excellent agreement with screen and confirmation results determined by UPLC MSMS.

Conclusion
No significant differences in sensitivity or mass accuracy were apparent when comparing results obtained from the LCT Premier-XE and Synapt MS systems.

Full mass range spectral data acquisition of pesticides and poisons present in complex mixtures that were separated by ultra performance liquid chromatography was readily achieved using TOFMS and electrospray ionisation in just 6.5 minutes total cycle time.

+ve or -ve ions that are accurately mass measured in ‘real time’ can be subsequently extracted from the condensed chromatographic data sets using narrow mass windows, typically 15 m/z units.

Quantitation of pesticide multi-residues and wildlife poisons using UPLC TOFMS and UPLC method transfer between TOFMS and MSMS systems was straightforward and results obtained following analysis of real samples compared favourably with results obtained from our established and validated MSMS method.

Wildlife poisoning
Exposure to anticoagulant rodenticides
Measurement of trace levels of rodenticides can provide an indication of wildlife species at risk from secondary poisoning e.g. following ingestion of dead or dying rodents.

Pesticide abuse / wildlife poisoning
The carbamate insecticide carbofuran has been identified as a poison used in targeting several species including golden eagle, buzzard, red kite and peregrine falcon.

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