RAPID SCREENING OF DRINKING WATER FOR MULTIPLE PESTICIDE RESIDUES BY UPLC-TOF MS

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OVERVIEW

- There is an increasing requirement to investigate unknown as well as targeted pesticide analytes
- The technique should be sensitive and selective, and applicable to a large number compounds with minimal sample preparation
- Data processing should be fast and efficient
- Chromatography is performed by ACQUITY™ UPLC™
- For high sensitivity full spectral detection, LCT Premier™ is employed
- Compounds not amenable to ESI^+ ionisation are simultaneously acquired in ESI^- mode.
- A library of known compounds is used to screen the results within ChromaLynx™ chromatographic deconvolution software

INTRODUCTION

Recent advances in analytical techniques, as well as changes in the types of compounds and the way in which they are used have lead to a requirement for a rapid and sensitive yet generic pesticide screening method.

Traditionally, GC and LC coupled to either single quad MS or other detectors have been the most commonly employed techniques. However due to their relatively low sensitivity and selectivity, they have required large injection volumes or more sample preparation. More recently, the advanced technology of triple quadrupole MS/MS analysers has been used to attain low detection levels and the increased selectivity provided by multiple reaction monitoring (MRM) type experiments has enabled the analysis of complex matrices without extensive clean-up. These advantages have made MS/MS the method of choice for low level quantitation and confirmation for a large number of targeted compounds.

Setting up methods for the selected analytes is time consuming and the analysis is inherently targeted towards a limited number of compounds. This has lead concerned analysts to ask what other potentially harmful, non-targeted analytes may be in the samples and has resulted in the demand for an analytical method which is sensitive and selective, but not specific.

A new time of flight mass spectrometer (LCT Premier™) offers the solution in that it has unmatched full-scan sensitivity coupled with high resolution mass spectra. This means that any ionisable component in a sample will be exact mass-measured and its elemental composition can be calculated or confirmed to <3 ppm.

ACQUITY UPLC™ is a novel ultra-performance liquid chromatograph utilizing 1.7 µm stationary phase particles in a high pressure system. This provides a very fast, high resolution separation which helps to increase the sensitivity of the method and eliminate matrix interference arising from minimal sample preparation.

When coupled, these new technologies provide a very powerful analysis rich in information. The data provided are subject to interrogation by ChromaLynx™ software which de-convolutes the chromatograms and displays the mass-measured spectra from each peak. These can then be compared against a library of target analytes or used to help determine the identity of an unknown compound.

METHODS

LC Conditions

LC System:	Waters® ACQUITY UPLC™	
Mobile Phase A:	5% aqueous MeOH + 2mM $CH_3CO_2NH_4$	
Mobile Phase B:	95% aqueous MeOH + 2mM $CH_3CO_2NH_4$	
Column:	ACQUITY UPLC™ BEH C_{18} 1.7 µm, 2.1 x 100 mm	
Flow Rate:	0.45 mL/min	
Injection Volume:	20 µL	
Column Temp:	40 °C	
Gradient:	t = 0 min	0% B
	t = 8.5 min	100% B
	t = 11 min	100% B
	t = 11.1 min	0% B
	t = 13.5 min	0% B

MS Conditions

Mass Spectrometer:	Waters® Micromass LCT Premier
Ionisation Mode:	Electrospray +/- switching
Capillary Voltage:	1000 V
Source Temperature:	120 °C
Desolvation Temp:	400°C
Gas Flow:	600 L/hr
Mass Range:	50—1000 Da
Acquisition Time:	0.25 s/function
Nominal Calibration:	$NaCH_2O_2$ in pos. and neg. modes
LockSpray™ reference:	Leucine Enkephalin
	$[M+H]^+$ = 556.2771 Da
	$[M-H]^-$ = 554.2615 Da

RESULTS & DISCUSSION

Figure 1 shows the base peak intensity chromatograms from the analysis of drinking water spiked with 92 pesticide residues at a concentration of 100 ppb. Six of the components ionise exclusively in negative mode, and both traces are shown to illustrate the simultaneous acquisition of all spiked pesticides in positive and negative mode.

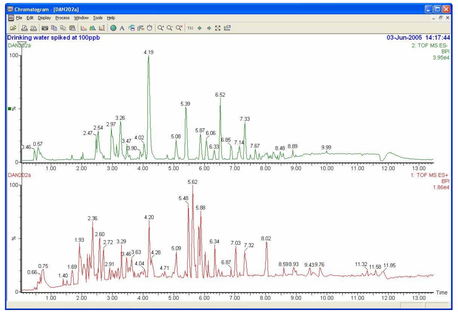

Fig 1. Positive and negative ion BPI chromatograms of drinking water spiked at 100 ppb

The chromatographic peaks here are typically ~5 s. Figure 2 shows a typical combined spectrum of Diuron, together with its elemental composition calculation. It is clear there are a number of possibilities within 5 ppm of the measured mass, so the observed isotope pattern is compared to a theoretical model using i-FIT™ software. In this case, although not the closest match by exact mass (3.4 ppm) the correct formula is displayed as the highest rank, since its isotope pattern is the closest match.

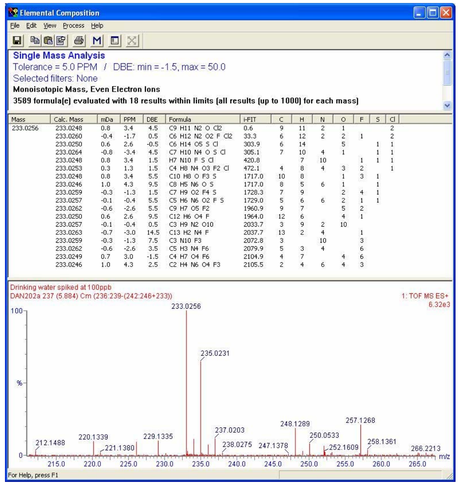

Figure 2. Spectrum and EleComp report for Diuron, ranked by closest isotope ratio fit

Where specific analytes are targeted, an extracted ion chromatogram (XIC) can be displayed and a signal-to-noise calculation made. This gives an indication of the sensitivity of the method, and because of the high mass accuracy of the instrument, 30 ppm windows can be used to optimise this. By plotting such a narrow mass range, the selectivity of the method is greatly increased over other MS techniques, and this advantage could be used to introduce a confirmatory step.

When screening a sample for unexpected compounds, it becomes difficult to pick out individual ions, especially where the matrix is complicated or the concentration of the analyte low. In such cases, it is useful to process the data using ChromaLynx™ chromatographic deconvolution software. This will automatically plot the XIC's of up to eight most intense ions at each data point and display the spectrum for each peak. The exact mass spectrum can then be either interrogated to elucidate an elemental composition as discussed above, or compared against a library of spectra obtained from standards. Each library entry will include mass, formula, retention time and polarity/cone voltage information, all of which can be used to filter the 'hit list' and effectively minimise the occurrence of false positive results. Figure 3 shows the ChromaLynx™ browser indicating the presence of a mixture of pesticides in drinking water.

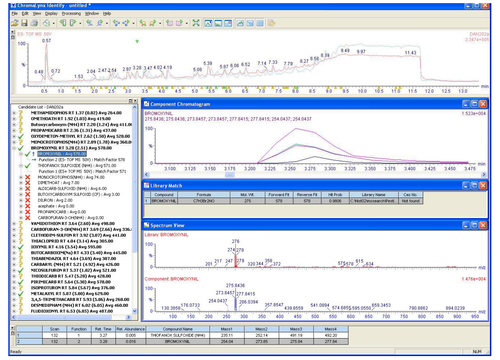

Figure 3. ChromaLynx Browser window showing screening results

This report from ChromaLynx™ clearly presents all the information required from a screening analysis. The positive and negative ion chromatograms are displayed at the top, with green or yellow markers to signify where a peak has been found. These correspond to the results on the left which show that a spectrum has been matched with one or more library entries. The match is given a score based on the number of corresponding spectral peaks and their relative intensities, and is marked as found (green) if this score is above a user-defined value. Below a certain value, a red cross indicates that the score is insufficient to provide a match, and this spectrum can then be interrogated to define the compound responsible. Where this score is between the two values, a yellow ? is displayed to indicate a tentative hit.

ToF MS has not previously had sufficient dynamic range to perform any more than basic quantitative functions. The LCT Premier™ has inbuilt Dynamic Range Enhancement (DRE) which allows quantification to be performed as easily as with more conventional analysers. Figure 4 below shows an example of the quantification of carbaril performed in positive/negative switching mode with DRE.

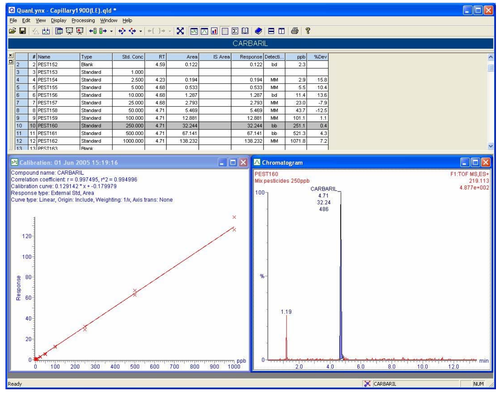

Figure 4. Quantification of Carbaril in +/- switching mode with Dynamic Range Enhancement

CONCLUSIONS

- ACQUITY™ UPLC™ provides a fast chromatographic run with good resolution so as to minimise interference from co-eluting peaks
- High mass-accuracy MS spectra provided by the LCT Premier™ mass spectrometer allow confirmation of targeted compounds and to help identify unknowns
- ChromaLynx™ software performs automated deconvolution of complex chromatographic data to provide simplified results
- The use of a mass spectral library within this software efficiently automates screening for known compounds
- Further work should extend the library to contain as many contaminants as possible, and investigate the use of exact-mass fragments formed by in-source CID for confirmation purposes

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