

Ultra-sensitive detection of pesticides in drinking water with a simple, rapid, and high quality analysis.

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INTRODUCTION

Rapid and highly sensitive analysis of drinking water is essential in protecting human health and well-being. The assurance of clean, safe drinking water has become more critical given the potential of accidental or intentional contamination, which has increased in recent years.

Monitoring for harmful substances in drinking water, or water used in products intended for consumption is required to ensure the exposure of the consumer is limited. Apart from the duty of care to consumers, organizations have regulatory testing imposed on them to ensure a safe product is delivered. The World Health Organization (WHO) publishes guidelines for drinking water quality and these are used as the basis of much of the drinking water regulation across the globe.

Highly efficient water treatment processes allow the effective removal of the majority pesticides that have entered water sources but drinking water regulations still require testing to ultra trace concentrations. To report results to regulators they must be of high quality to conform to international standards such as ISO17025.

This requirement has led to multiple approaches for enriching samples before instrumental analysis, with solid phase extraction prior to LC/MS/MS a popular choice. In addition to this, online pre-concentration and large volume injection using specialized injection systems have been used to introduce samples to LC/MS/MS systems. These techniques can be very successful but can add time, resource and complexity to the analysis.

Cleaner aqueous samples such as drinking water are highly compatible for direct injection onto a LC/MS/MS system but large multi-analyte determinations require extremely fast systems with ultra-sensitive detection.

Described here is the application of direct injection UPLC LC/MS/MS to the rapid, high quality and ultra-sensitive analysis of multiple pesticides in drinking water.

METHODS

Sample preparation

Na₂S₂O₃ was added to drinking water samples to 200 mg/L to ensure dechlorination. 1.0 mL aliquots were transferred into amber glass LC/MS certified vials and presented for analysis.

UPLC Conditions

Column: ACQUITY UPLC BEH C₁₈, 1.7 μm, 2.1 x100mm
Flow rate: 0.5 mL/min (gradient Table 1)
Injection vol: 100 μL (Full loop)
Mobile phase A: 98:2 H₂O : MeOH + 0.1% HCOOH
Mobile phase B: MeOH + 0.1% HCOOH

Xevo TQ-S Conditions

Ionisation mode: ESI+
Capillary voltage: 0.6 kV
Source temperature: 150 °C
Desolvation temperature: 650 °C
Cone gas flow: 150 L/Hr
Desolvation gas flow: 1200 L/Hr
Acquisition Mode: MRM with RADAR enabled

Time (min)	Flow rate (mL/min)	%A	%B	Curve
Initial	0.50	90	10	0
0.25	0.50	90	10	6
7.75	0.50	2	98	6
8.50	0.50	2	98	6
8.51	0.50	90	10	6
10.00	0.50	90	10	6

Table 1. ACQUITY UPLC gradient.

RESULTS & DISCUSSION

Direct injection of drinking water samples on to the Xevo TQ-S eliminated the need for sample preparation prior to analysis. Direct injection was performed using a standard ACQUITY using standard 2 mL ACQUITY autosampler vials.

Rapid ACQUITY UPLC separations allowed a high throughput analysis with all analytes of interest eluting before 7.5 minutes and a total run time of 10 minutes for each sample. Separations of 81 typically analysed pesticides were performed and an overlaid MRM total ion chromatogram is shown in Figure 1.

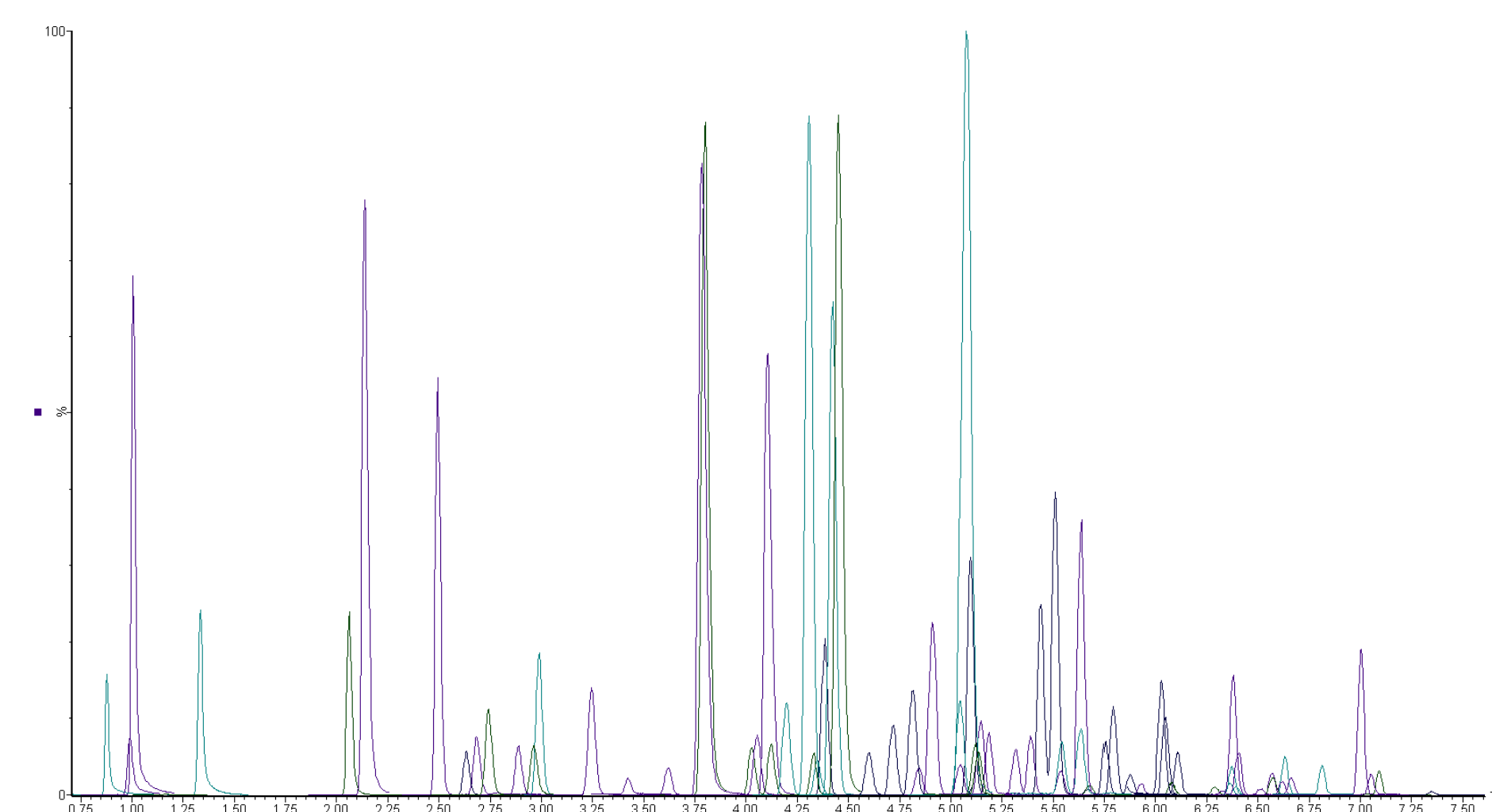


Figure 1. Overlaid MRM chromatograms of the 81 pesticides analysed.

Ultra-sensitive pesticide detection

Detection of pesticides to extremely low concentrations was achieved using direct injection-Xevo TQ-S. This level of sensitivity allowed detection of pesticides to parts-per-quadrillion (ppq) or pg/L. Figure 2 shows detection of a selection of pesticides in a water sample spiked at 200 ppq (pg/L). This is 500 times below the EU requirement.

The capability to measure to this level allows real background concentrations of contaminants to be observed and monitored. This can aid trending in sample points and batches and allows better understanding of final product quality.

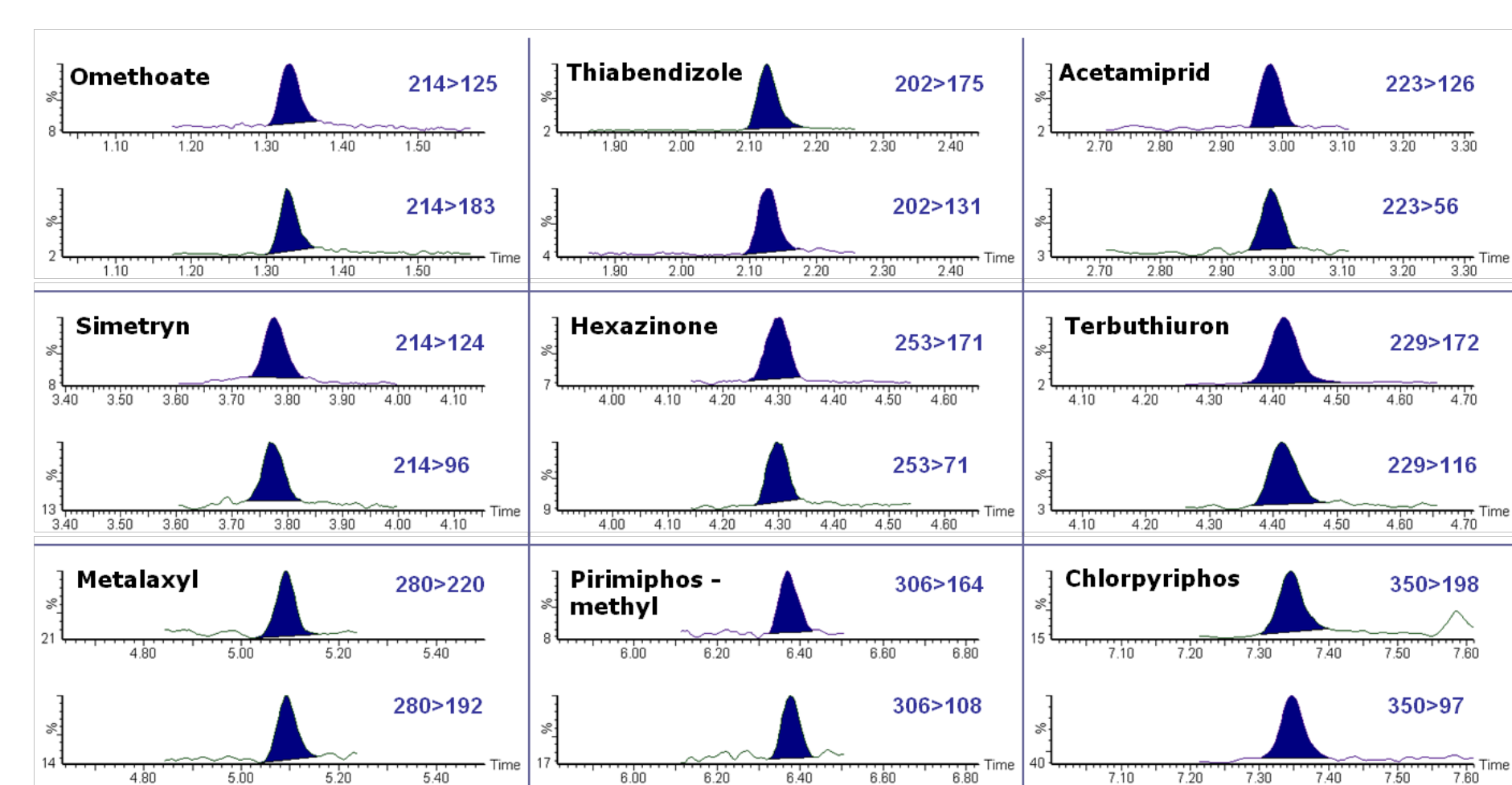


Figure 2. Detection of a selection of pesticides in a water sample spiked at 200 ppq (pg/L).

Linearity and Precision

External calibration (7 point with replicates at each point) of target analytes was performed at concentrations around the common regulatory level for pesticides (100 ng/L). Good linearity was achieved for all compounds analysed with typical coefficient of determinations (r²) of >0.995.

The removal of variables that are introduced during sample preparation combined with the precision of the ACQUITY XEVO TQ-S allowed very precise measurements in drinking water. Peak area precision was tested at 100 ng/L fortified QC samples over 32 injections. Table 2 shows peak area precision for different compounds from a variety of pesticide types from these QC samples. This instilled a high degree of confidence in reported results.

Class	Compound	%RSD (n=32)
Triazine herbicides	Ametryn	1.39
	Terbutryn	1.96
	Cyanazine	1.26
	Atrazine	1.46
	Simetryn	1.78
Fungicides	Spiroxamine	1.85
	Kresoxim Methyl	4.29
	Azoxystrobin	2.19
	Dimethomorph	4.14
	Pyraclostrobin	4.18
Phenylurea herbicides	Chlorotoluron	0.59
	Siduron	1.24
	Monuron	1.56
	Monolinuron	1.09
	Diuron	1.24
Organophosphorous pesticides	Diclotophos	0.94
	Heptenophos	1.47
	Mevinphos	2.34
	Tetrachlorvinphos	2.47
	Chlorfenvinphos	3.67
Organothiophosphorous pesticides	Omethoate	1.22
	Demeton S Methyl	1.50
	Azinphos Methyl	2.48
	Dimethoate	2.27
	Ethoprophos	2.31

Table 2. Peak area precision data for 32 injections of 100 ng/L QC samples showing different compounds from a variety of pesticide classes.

Background Matrix Monitoring using RADAR enabled MS methods

The simultaneously acquired full scan data (using RADAR enabled MRM method) allowed observation of the matrix challenge for every individual sample injected. With simultaneous full scan capability matrix components that co-elute with MRM target analytes can be investigated by interrogating the "always available" spectral data.

Figure 3 shows RADAR enabled acquisition of drinking water sample spiked at 100 ng/L. Light blue colored chromatogram is MS2 base peak intensity (BPI) full scan chromatogram. Also shown overlaid is a selection of simultaneously acquired pesticide MRMs. The mass spectrum (Figure 3 inset) shows intense background ions of a component that elutes over a broad region in the chromatogram. This co-elutes with a target analyte and highlights a component that may cause some matrix effect.

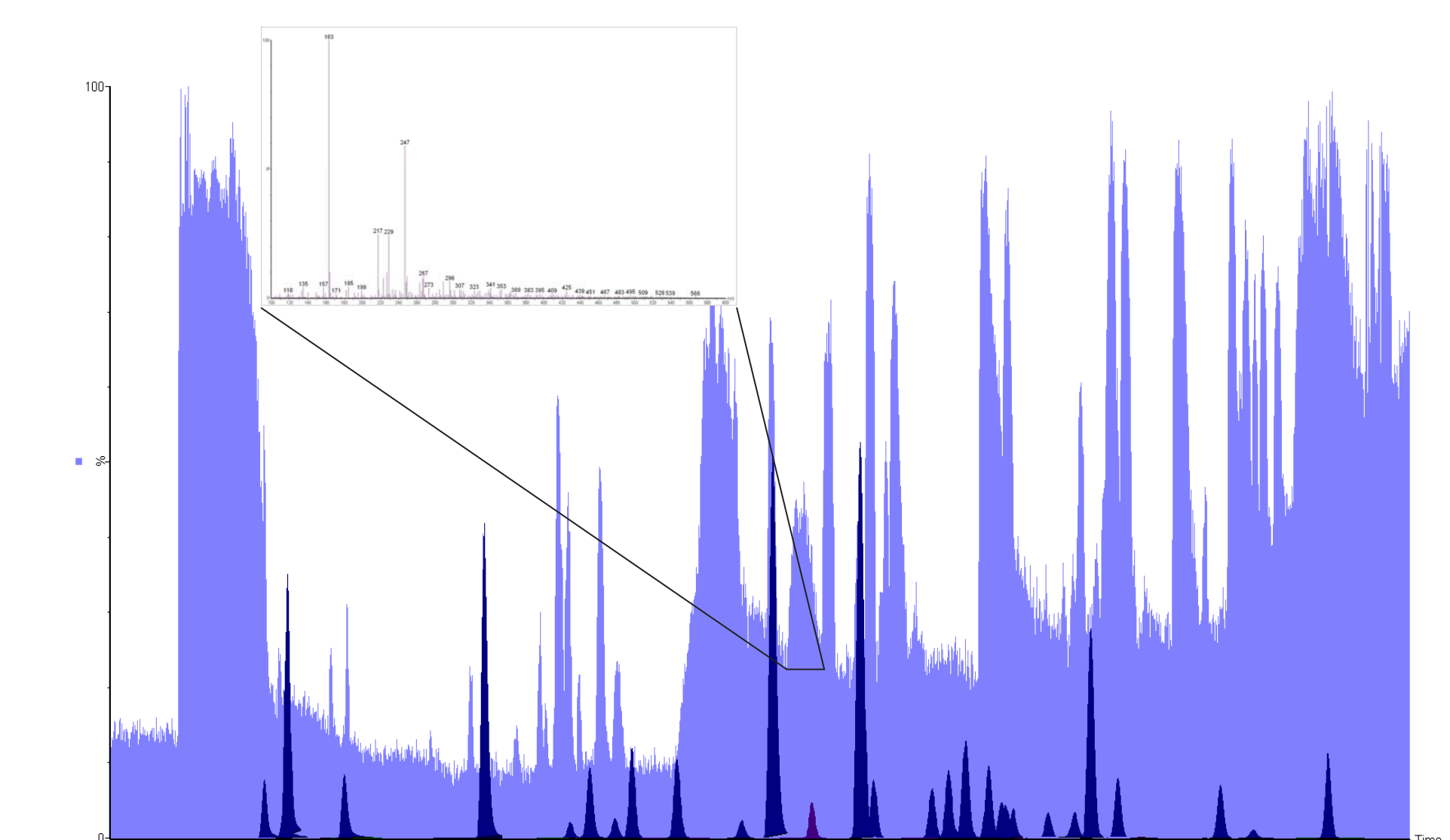


Figure 3. RADAR enabled acquisition of drinking water sample spiked at 100 ng/L. Light blue colored chromatogram is MS2 full scan BPI with spectrum from a region of co-elution (inset). Also shown overlaid is a selection of simultaneously acquired pesticide MRMs.

CONCLUSIONS

Using direct injection on Xevo TQ-S removes sample preparation and enables a simple, high-throughput analysis of pesticides in drinking water.

This is possible with ultra sensitive detection down to ppq (pg/L) concentrations to enable real background concentrations in samples to be observed.

Ultra-sensitivity facilitates a high quality analysis with high precision and comfortable quantitation around the regulatory concentrations. This in turn instills confidence in the data reported.

The RADAR mode of acquisition enables the collection of spectral information on background components in the sample matrix whilst simultaneously collecting MRM data. This can help identify areas of potential ion suppression, observe untargeted contaminants and aid in the development of matrix reduction strategies.