

Application News

High Performance Liquid Chromatograph Mass Spectrometer

Applying Non-Targeted Analysis to Food Safety Pesticide Screening

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User Benefits

- ◆ Food commodities were measured by LC/QTOF mass spectrometry using a modified Pretreatment Optimised Injection Sequence (POISE) to enhance retention and peak shape of polar analytes.
- ◆ Non-targeted analysis (NTA) software, LabSolutions Insight™ Profiler, was applied to perform feature detection, data alignment, and compound identification and successfully detected 280 test compounds at MRL concentration of 10 µg/kg.
- ◆ Additional compounds outside the scope of routine analysis were identified using in-house and third-party repositories.

Introduction

Residual pesticide analysis is central to food safety, yet conventional targeted quantitation with LC/TQ or GC/MS is inherently limited to predefined analyte panels. Although these platforms provide high sensitivity and quantitative precision, expanding coverage requires labour-intensive method development, optimisation, and validation. To address the growing chemical complexity of agrochemical residues, workflows are increasingly adopting high-resolution mass spectrometry (HRMS) based non-targeted acquisition strategies. These strategies enable simultaneous targeted quantitation and large-scale suspect screening within a single experiment.

In this study, a unified LC/QTOF acquisition workflow was developed to support both targeted quantitation and non-targeted screening at scale. Leveraging large, curated screening databases and advanced data processing with the LabSolutions Insight Profiler software application, the method facilitates high-confidence identification of both known and previously unmonitored pesticide residues. This integrated strategy significantly enhances analytical coverage while maintaining data integrity, offering a scalable solution for next-generation multi-residue analysis in complex food matrices.

To test the capability of non-targeted analysis (NTA), a matrix sample (olive oil) was spiked at a concentration of 10 µg/kg, a concentration typically defined as the maximum reporting limit (MRL) for most pesticides. Analysis was then extended to unknown samples to determine if additional compounds could be identified outside the scope of routine analysis.

Materials and Methods

Analysis included a selection of unknown test samples of various commodities previously quantified by LC/TQ. Quality Control (QC) samples spiked with a panel of compounds were also included. Samples were prepared using a standard QuEChERS method.

To enhance peak shape and retention of polar analytes, sample injection used a modified POISE method in which 1 µL of sample was mixed with 10 µL water, repeated four times, totalling a 4 µL sample injection. Analytical conditions were maintained the same as the LC/TQ analysis where applicable; LC/QTOF data acquisition utilised a non-targeted data independent acquisition (DIA) method in positive ion mode (Table 1).

Data Processing

Data were processed using LabSolutions Insight Profiler software which performed feature detection, alignment and screening using large scale suspect lists for compound identification. Pre-defined processing parameters were used that included non-targeted feature detection, alignment, identification and batch processing (Fig. 2). Compounds were identified using a curated Shimadzu pesticide database containing over 500 compounds. Third-party libraries were also used, including the Food Safety Mass Spectral Library (Wageningen University)¹.

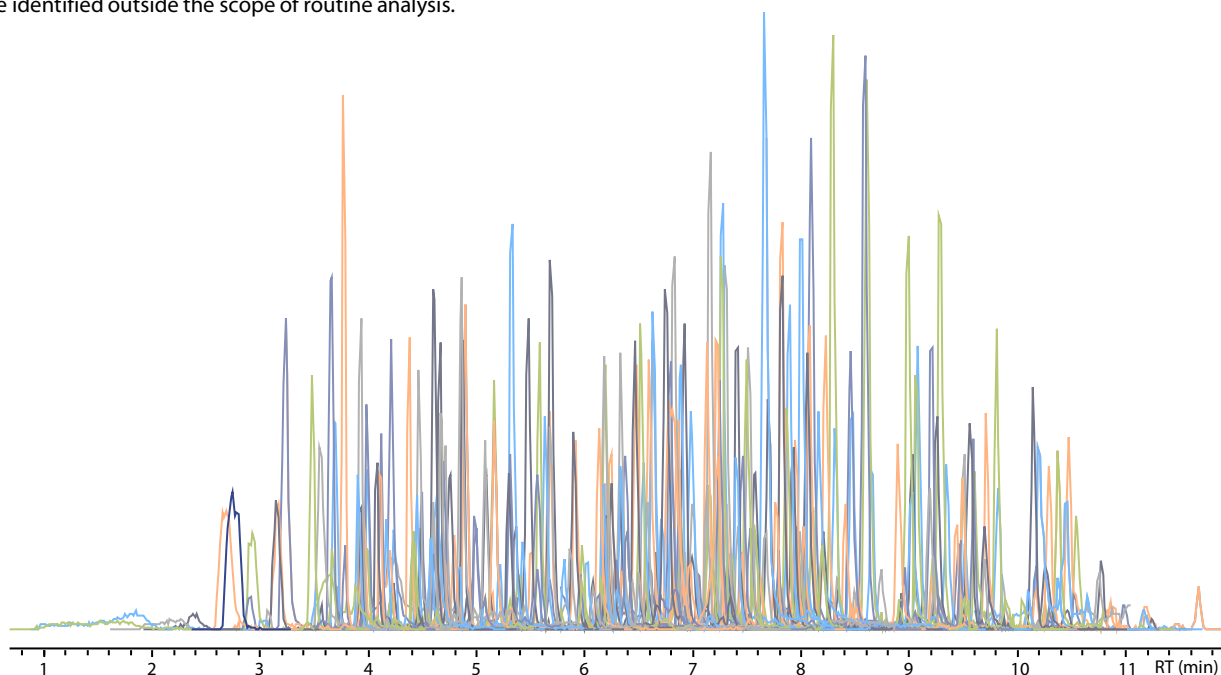


Fig. 1 Extracted ion chromatograms of 280 pesticides spiked into olive oil at 10 µg/kg.

These were successfully found using non-targeted feature detection. The concentration broadly corresponds to the EU maximum reporting limit (MRL) in many food commodities therefore demonstrating the application was fit for purpose for a broad panel of compounds at meaningful concentration levels.

Data Acquisition

LC method and ion source parameters from the validated residual pesticide LC/TQ method were directly transferred to the LC/QTOF. The LC/QTOF method was optimized for pesticide analysis with MS and DIA-MS/MS.

Table 1. Analytical conditions.

[UHPLC conditions] (Nexera X2)	
Column	Shim-pack Velox Biphenyl (2.1x100 mm 2.7 µm) + Biphenyl guard column (2.1x5 mm 2.7 µm); maintained at 45 °C
Flow Rate	0.4 mL/min
Mobile Phase	A: Water + 2 mM ammonium formate + 0.004% formic acid B: Methanol + 2 mM ammonium formate + 0.004% formic acid
Rinse (R0 / R1 / R2) (R3)	IPA:MeOH:MeCN:H ₂ O (1:1:1:1) + 1% formic acid Methanol + 1% acetic acid
Gradient	3.5% B (0-0.1 min) → 13% B (1 min) → 50% B (3 min) → 100% B (12-14 min) → 3.5% B (14.1-16.4 min)
Injection	4 µL; autosampler set to 12 °C
[MS conditions] (LCMS-9050)	
Interface	300 °C, 1.5 kV (ESI+)
Heat block, DL	400 °C, 250 °C
Gas flow rates	Nebulizing gas 2 L/min; Heating gas 15 L/min Drying gas 5 L/min
MS	TOF-MS (m/z 140-925)
MS/MS	DIA-MS/MS (m/z 40-1000, 31 events, 29 msec), CE 5-55 V (1 second cycle time)

Feature Detection and Alignment

Detects and aligns all ion signals that behave as a peak.

Statistics

Applied to find ion signals of significance and to remove ions of high variance in QC samples when used.

Screening and Identification

Using large scale screening lists and multiple libraries to identify ion signals of interest.

Batch

A single, configurable workflow integrates feature detection, alignment, and compound identification, enabling automated batch processing for non-targeted analysis.

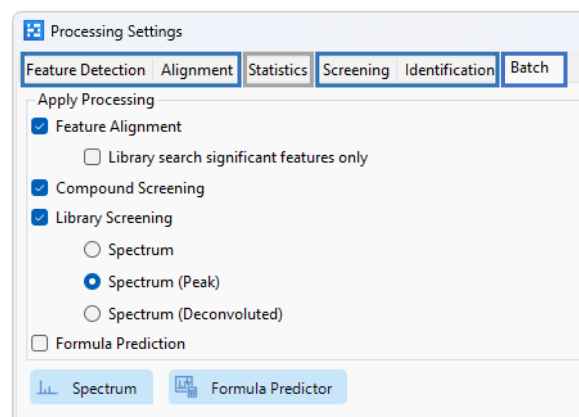


Fig. 2 LabSolutions Insight Profiler processing settings.

In this example pre-defined settings were loaded before all data files were processed as a single batch from which a cascade of automated data analysis steps were performed. Because data analysis did not involve predefined sample groups, statistical analysis was not applied.

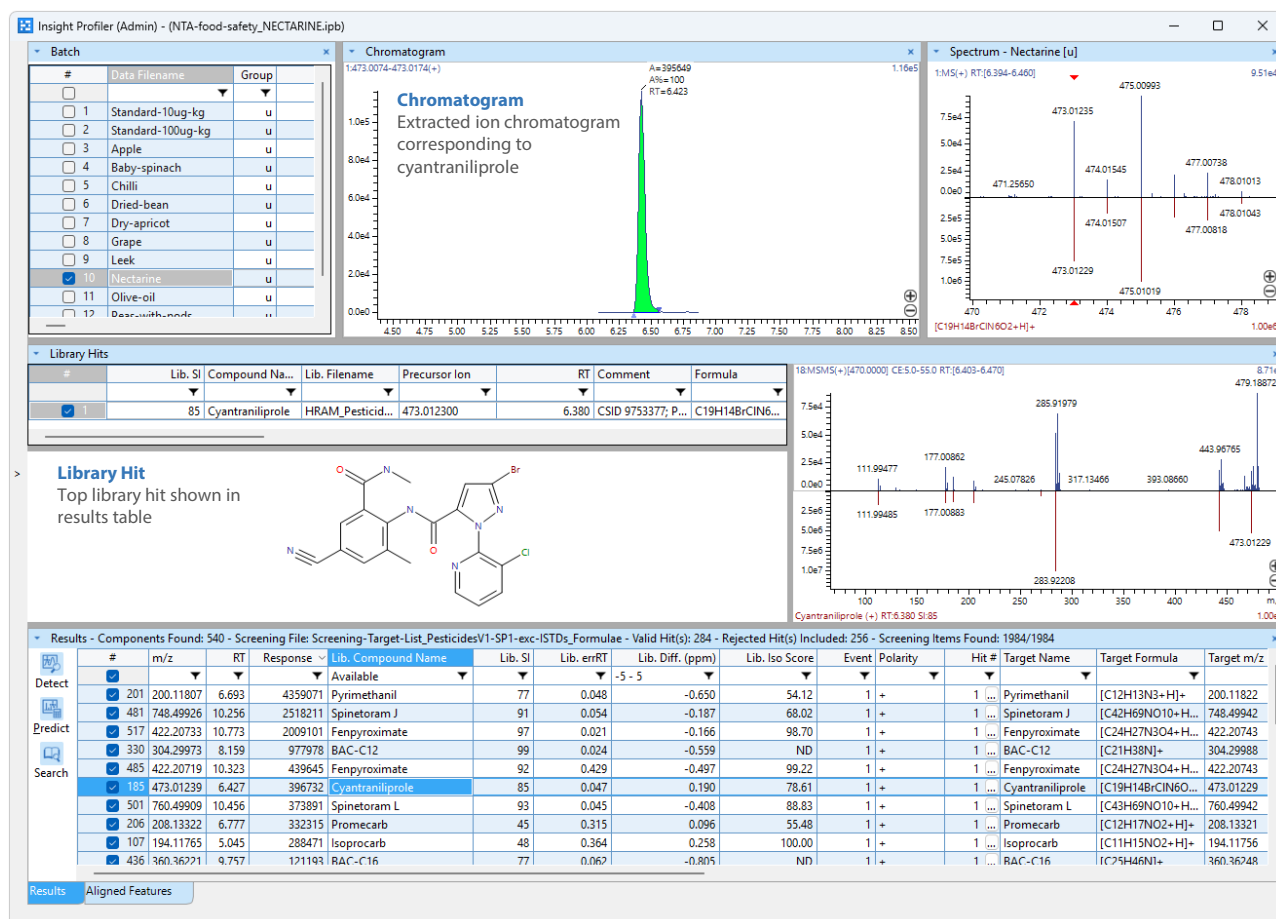


Fig. 3 LabSolutions Insight Profiler software. In this example non-targeted detection of cyantraniliprole is shown in a nectarine sample using an in-house LC/QTOF pesticide library containing over 500 registered compounds.

■Results

The LabSolutions Insight Profiler processing method was configured to detect features with a “low” response; each feature must have a summed spectral intensity over 10,000 to be considered. Features were identified using MS/MS libraries and large-scale screening lists. To test the capability of NTA, a test sample was analysed containing 280 pesticides spiked into olive oil matrix at a concentration of 10 µg/kg. All compounds were previously confirmed to meet SANTE HRMS quantitative guidelines². NTA successfully detected and identified all 280 pesticide parent ions, with MS/MS spectral library matching (Fig. 1).

NTA was also applied to a selection of unknown samples previously measured by LC/TQ quantitation to determine if any additional compounds could be identified outside a target panel routinely applied for multiresidue LC-MS analysis. NTA confirmed the presence of several compounds (Table 2), including the neonicotinoid, acetamiprid, which was detected in four samples (Fig. 4). Although levels were very high in baby spinach the MRL for this food commodity is 3 mg/kg.

Other compounds included pyrimethanil, a broad-spectrum fungicide, which was detected at very high levels in nectarine. Grape was found to contain boscalid, fluopyram, penconazole and pyrimethanil. All compounds were positively identified using an in-house HRMS Pesticide Library. Using third-party libraries to extend the chemical search space further, acetamiprid-N-dimethyl, propamocarb N-oxide and dimethomorph were also detected using the Food Safety Mass Spectral Library (Wageningen University).

Detecting acetamiprid-N-dimethyl and propamocarb N-oxide reflects the growing need to consider pesticide metabolites in routine quantitative workflows. The detection of dimethomorph is also of note as it highlights the need to search for compounds of regulatory relevance outside current prioritized target lists. Dimethomorph is a systemic fungicide whose approval was not renewed by the European Union in 2024 following concerns regarding, among other factors, its potential effects on human reproductive health, while its use remains authorised in the UK until 31 January 2030 (Fig. 5).

Table 2. Compounds detected using non-targeted data processing in unknown samples

In the upper table the LC/QTOF data processing method detected and identified pesticides included in the validated routine LC/TQ targeted method. The same processing method also identified additional pesticides not routinely quantified using an in-house LC/QTOF pesticide library by MS/MS verification. Acetamiprid-N-dimethyl (DM), propamocarb N-oxide and dimethomorph (bold) were identified using the Food Safety Mass Spectral Library (Wageningen University).

Unknown sample analysis

Compounds positively identified by LC/QTOF analysis which are included in a routine LC/TQ targeted method

Baby-spinach	Dried-bean	Dry-apricot	Grape	Leek	Nectarine
Abamectin B1a	Acephate	Dodine	Ametoctradin	Azoxystrobin	Acetamiprid
Acetamiprid	Acetamiprid	Acetamiprid	Fenhexamid	Propamocarb	Azoxystrobin
Azoxystrobin	Azoxystrobin	Nicotine	Fluopicolide	Spirotetramat met.	Cyantraniliprole
Chlorantraniliprole	Chlorantraniliprole	Thiacloprid	Spiroxamine		Fenpyroximate
Fluopicolide	Clothianidin				Spinetoram J
Metolcarb	Cyantraniliprole				Spinetoram L
Propamocarb	Imibenconazole				Sulfoxaflor
	Methamidophos				
	Thiamethoxam				

Compounds positively identified by non-targeted screening by LC/QTOF which are outside the scope of a routine LC/TQ method

Baby-spinach	Dried-bean	Dry-apricot	Grape	Leek	Nectarine
Acetamiprid DM		Tebuconazole	Boscalid	Difenoconazole	Pyrimethanil
Propamocarb N-Ox		Trifloxystrobin	Dimethomorph		
			Fluopyram		
			Penconazole		
			Pyrimethanil		

Acetamiprid [C10H11ClN4+H]⁺ m/z 223.07450 RT 4.723

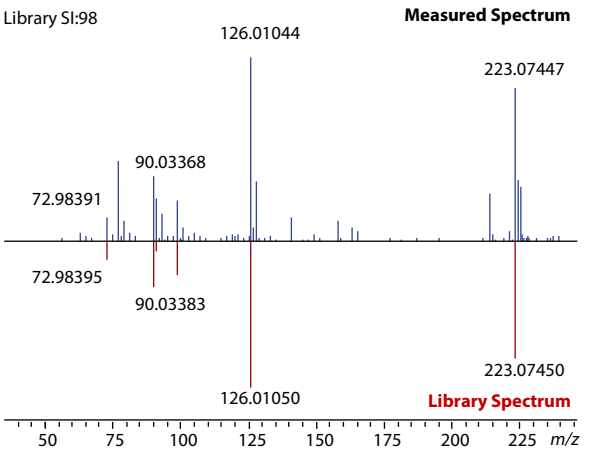
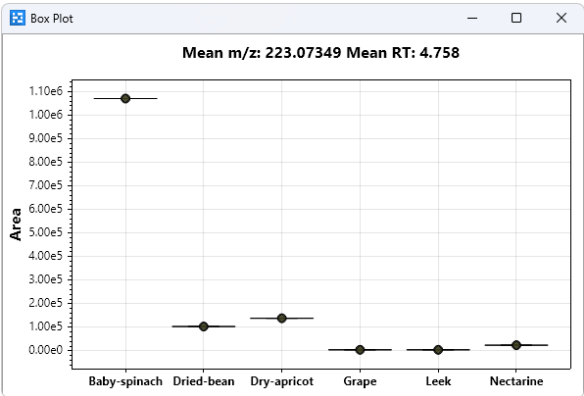


Fig. 4 Box plot and library identification of the neonicotinoid acetamiprid. This compound was detected in four of the unknown samples and identified with high confidence using an in-house LC/QTOF pesticide library.

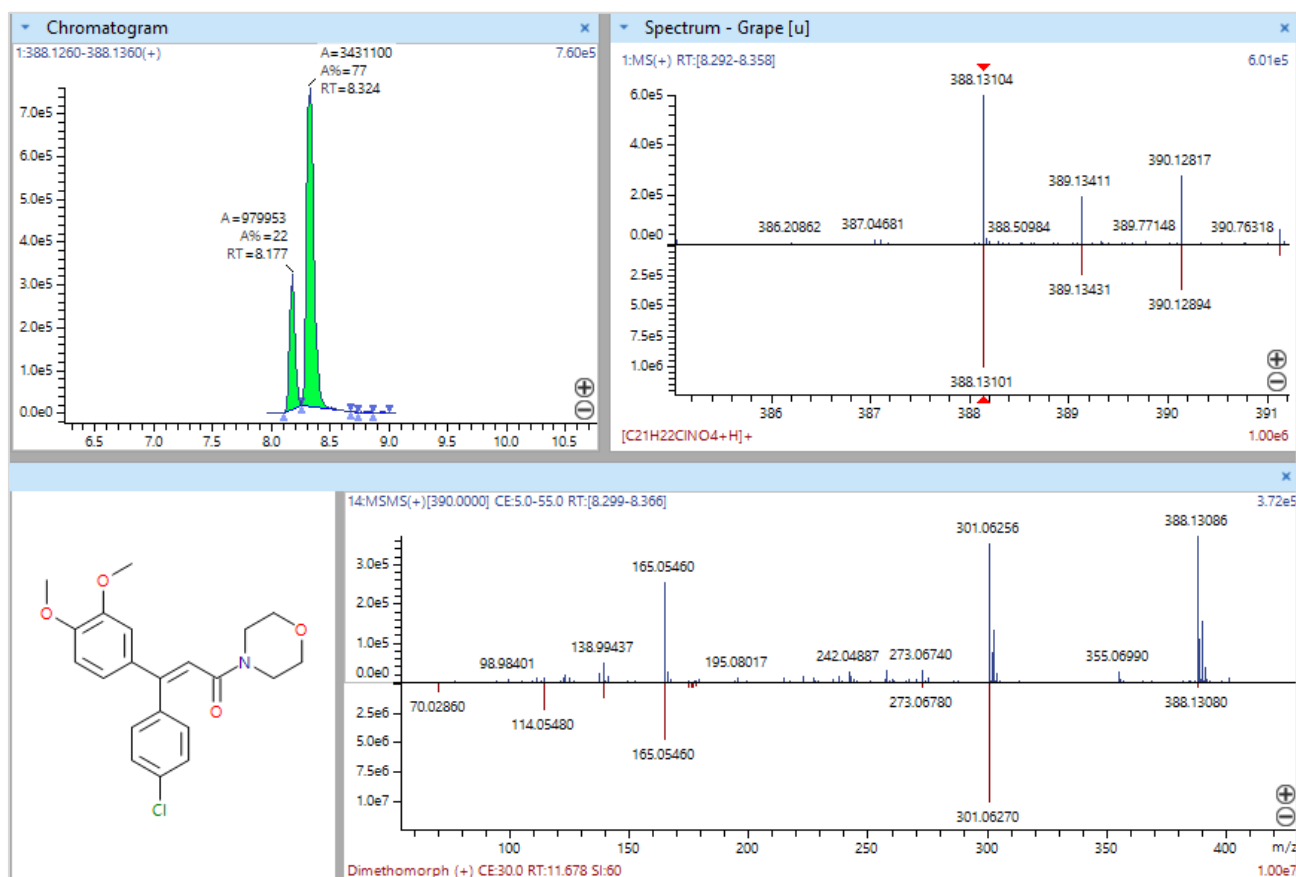


Fig. 5 An example of non-targeted analysis identifying dimethomorph in a grape sample using the Food Safety Mass Spectral Library¹.

Conclusion

The LC/QTOF NTA methodology was successfully applied to a target pesticide panel previously validated on a routine LC/TQ to detect and identify all 280 pesticide compounds at the European Union SANTE Maximum Residue Limit (MRL) of 10 µg/kg. All compounds detected at the MRL were identified by HRMS library matching using an in-house HRMS MS/MS Pesticide Library.

By extending the chemical search space, the same method also detected pesticide compounds outside the target panel including pesticide metabolites and transformation products, and also regulatory-relevant residues such as the detection of dimethomorph.

References

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