EVOQ® DART-TQ+ enables fast, sensitive pesticide analysis in food

Highlights

This application note covers fast and sensitive pesticide residue analysis on the EVOQ® DART-TQ+ mass spectrometer.

- Quantify and confirm more pesticide residues in less time than ever before
- Streamlined sample to report workflow
- Robust design provides fast result generation with high uptime

Keywords:
Triple Quad; Pesticides; Food Analysis; Food Safety

Introduction

In many parts of the world, as the population continues to grow and demand for food increases, the continued use of pesticides in agriculture is seen as essential. However, pesticides pose potential risks to human and animal health if not responsibly managed in both fresh and processed animal feed and food products.

In the EU, the SANTE 11312/2021 guidelines set out the maximum residue level (MRL) legally permitted in or on food or animal feed. In the US, the Environmental Protection Agency (EPA), establishes 'tolerances' of pesticides, which are listed in 40 code of federal regulations (CFR) Part 180. There are also internationally agreed MRLs under Codex Alimentarius.

Producers are responsible for ensuring their products comply, resulting in costly and potentially brand-damaging warnings and penalties if they do not. However, establishing compliance often involves complex analytical approaches, which may be time and resource intensive. In addition, certain food matrices can be difficult to analyze, making reliable, reproducible, and sensitive results a significant challenge for testing laboratories.

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Enabling faster, more sensitive analysis

Typically, food testing laboratories use triple quadrupole (TQ) liquid chromatography-mass spectrometry (LC-MS) instruments in Multiple Reaction Monitoring (MRM) mode for pesticide analysis but, given that some compounds show low sensitivity with LC, often gas chromatography (GC) methodologies are also required.

When analyzing a large number of compounds per run, typical MRM performance may be compromised by the speed of the electronics and overall design of the triple quadrupole mass spectrometer. Not all the generated ions can be analyzed within a standard run time; therefore, to achieve the required sensitivity, either the analysis time must be extended, or the analysis must be run in just one polarity requiring two runs per sample. If both positive and negative polarities are monitored in the same analysis, extra time is needed to make positive/negative alterations required to analyze some compound classes in the sample. Against this background, a quicker and more robust method is required to speed up time to result.

While the EVOQ® DART-TQ+ is the world's first and only triple quad with a fully integrated direct analysis in real time (DART) ion source, capable of screening samples in less than 30 seconds, pesticide screens that have an extremely large number of compounds in a single assay benefit from the time of separation provided by conventional LC-MS.

With the EVOQ® DART-TQ+ users can easily switch between the DART and VIP-HESI (Vacuum Insulated Probe-Heated Electrospray) ion sources extending the utility of this TQ built for small molecule analysis.

Designed with extremely fast electronics the EVOQ® DART-TQ+ provides fast acquisition speed of up to 1,000 MRMs/second. This results in the ability to analyze many co-eluting pesticides with no loss of sensitivity. The EVOQ® DART-TQ+ can analyze over 500 analytes (with at least 2 MRM transition for every analyte) in less then 10 minutes acquisition time, in the same run, including pesticides that ionize in positive and negative modes, and maintain high performance.

Screening of compounds in one analysis in positive and negative mode

To demonstrate the ability of the EVOQ® DART-TQ+ to screen compounds in the same analysis with effectively positive and negative mode, a multi-target method containing 1104 MRM transitions for 500 analytes (both detected in positive and negative mode) has been developed (Figure 1). The speed of analysis is sufficient to generate a high number of data points in and around the peak – an essential requirement for accurate analysis.

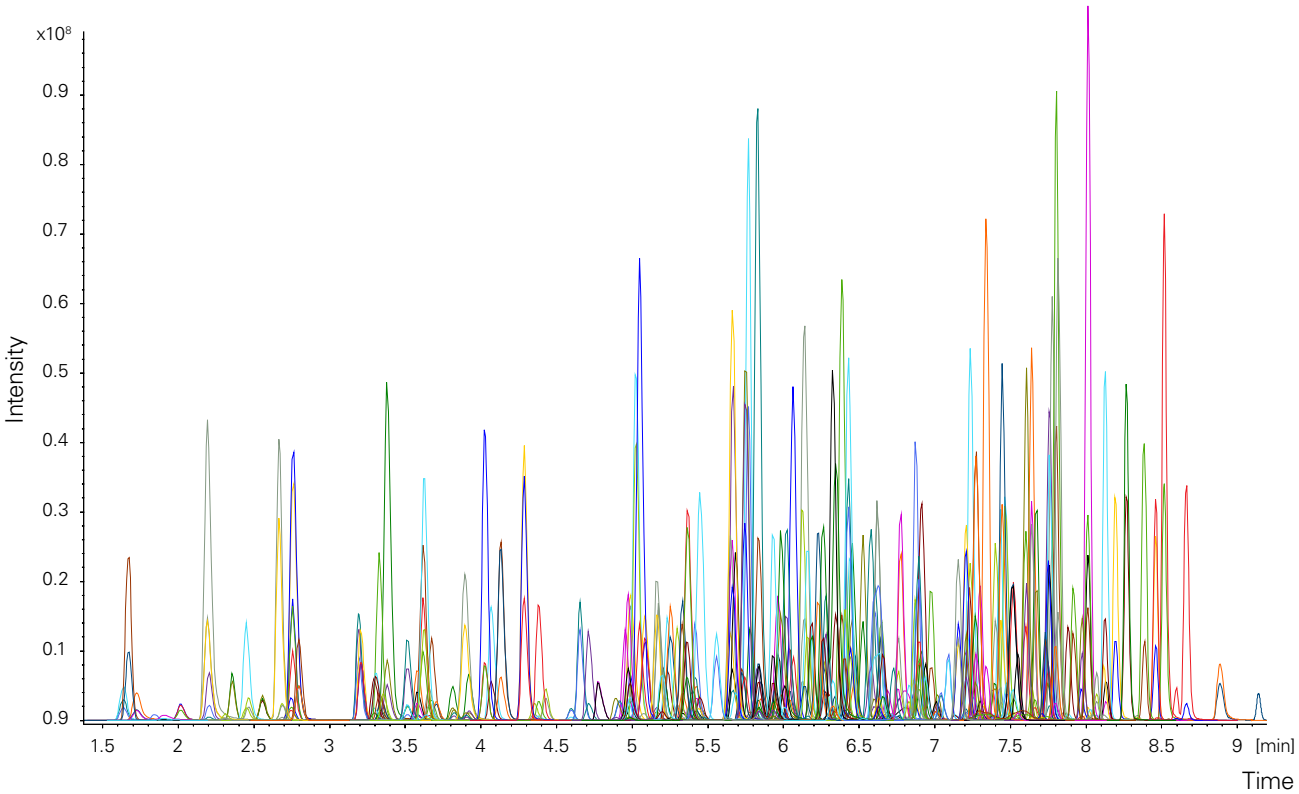


Figure 1. Analysis of pesticides maintaining sensitivity using a method with 500 analytes (+/-) and 1104 transitions.

High speed, high sensitivity, no compromises

To demonstrate the ability of the EVOQ® DART-TQ+ to acquire data at a very high speed without sensitivity compromises, two analyses were completed, each with a different number of compounds, and including positive and negative analytes. The data shows that the same peak intensity and signal stability is achieved in the two runs (Figure 2).

Figures 2A and B show Espirotetramat Enol and Figures 2C and D show Flufenoxuron.

Method with 240 pesticides

Method with 500 pesticides

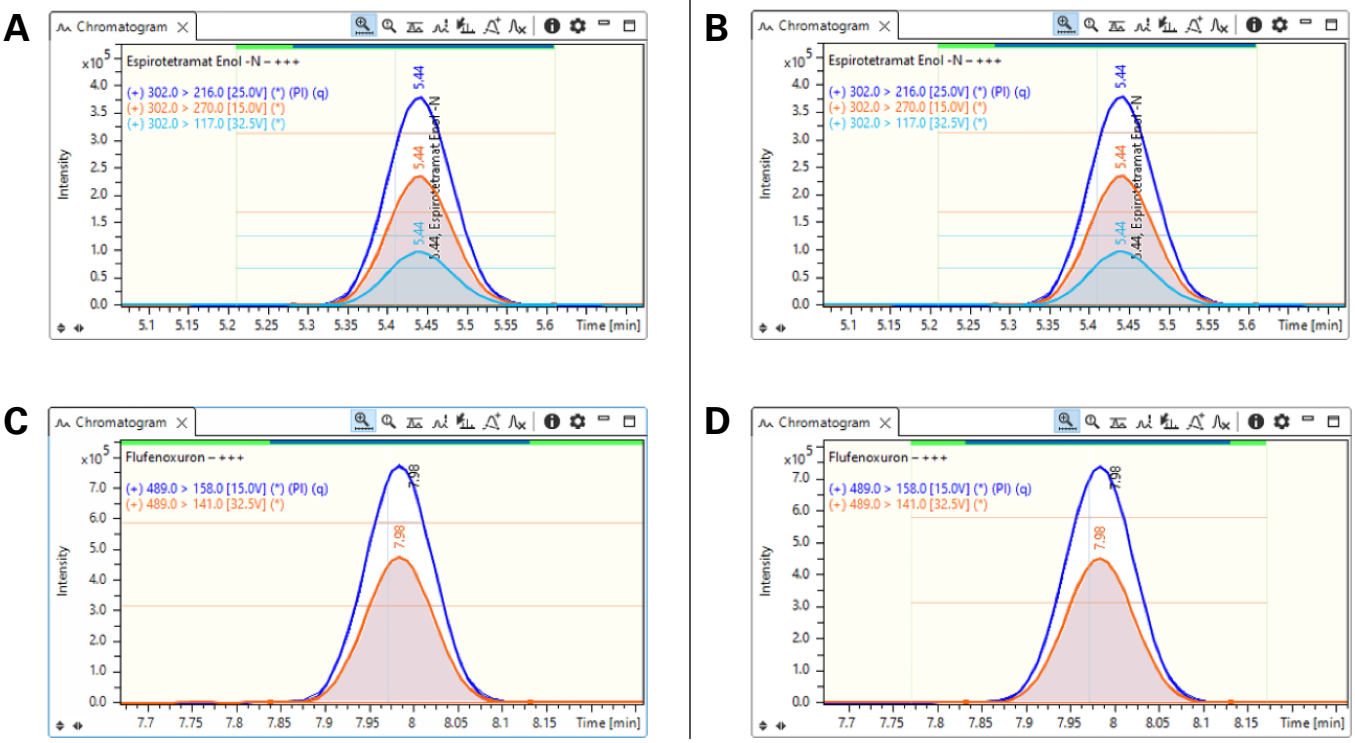


Figure 2. A: Espirotetramat Enol; Method with 240 pesticides (23 negative). Minimum scan time: 15.5 milliseconds. B: Espirotetramat Enol; Method with 500 pesticides (44 negative). Minimum scan time: 11.7 milliseconds. C: Flufenoxuron; Method with 240 pesticides (23 negative). Minimum scan time: 15.5 milliseconds. D: Flufenoxuron; Method with 500 pesticides (44 negative). Minimum scan time: 11.7 milliseconds.

Additionally, to assess signal stability across various acquisition speeds, injections were conducted with increasing scanning speed (reducing scan time) in a method involving 500 pesticides (both positive and negative modes). Figure 3 presents the results for one of the pesticides at different acquisition speeds.

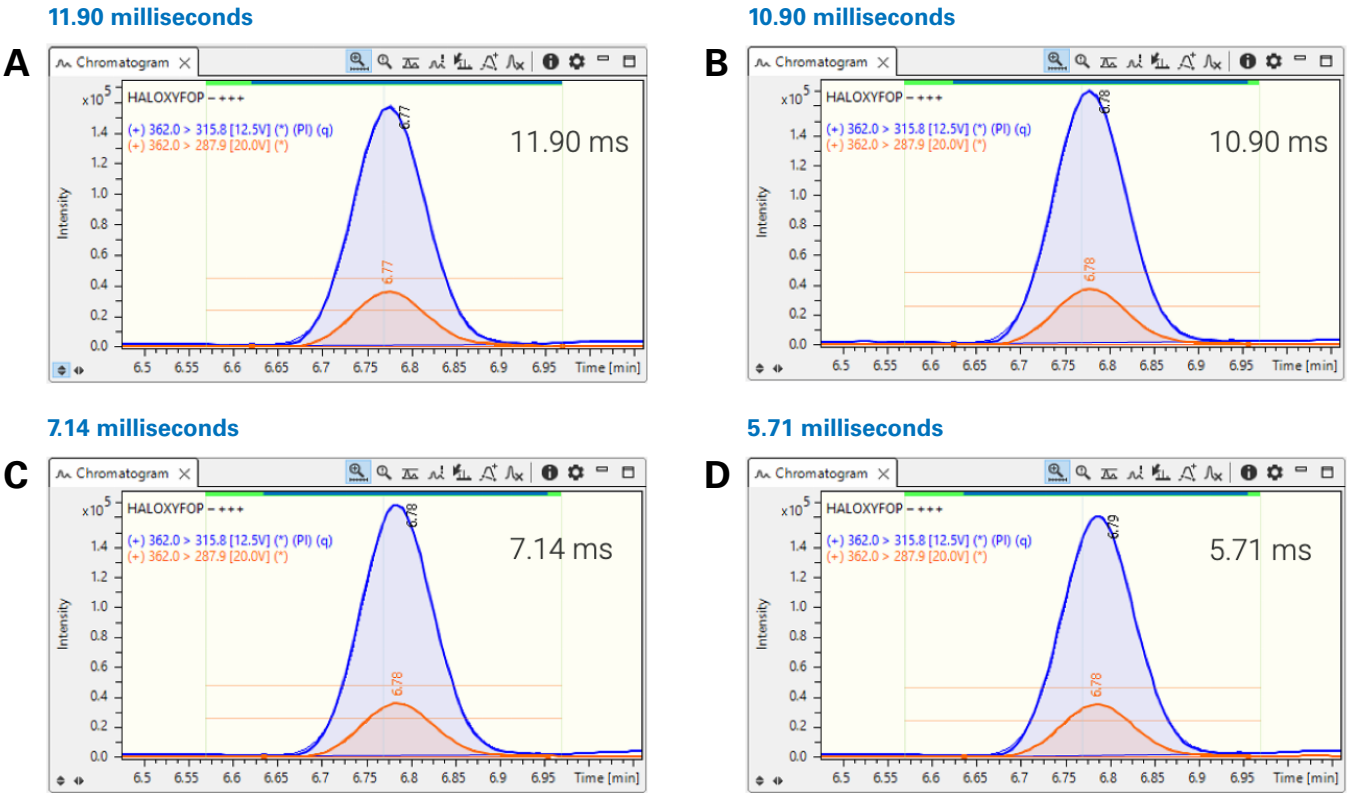
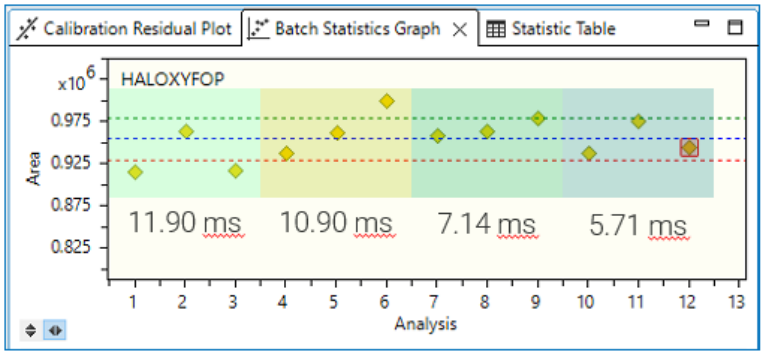


Figure 3. Acquisition of several compounds with the same sensitivity and stable ion ratio with either a few or several milliseconds of scan time. A: 11.90 milliseconds acquisition speed; B: 10.90 milliseconds acquisition speed; C: 7.14 milliseconds acquisition speed ; D : 5.71 milliseconds acquisition speed.

Statistical analysis showed that even with different acquisition speeds, including polarity switching, the reproducibility within 10 consecutive injections was 2.60% (Figure 4).

The ability of the instrument to maintain both sensitivity and reproducibility at very low scan times allows for further extension of the multi-residue pesticide method with additional hundreds of compounds.



Analyte Name	Property	Area of PI
HALOXYFOP	%RSD	2.60

Figure 4. Area vs. number of consecutive injections.

Analytical figures of merit

In order to evaluate the key analytical figures of merit of the EVOQ® DART-TQ+, a cucumber QuEChERS extract (1 g/mL) was spiked with a pesticide mixture.

1. **LINEARITY** was evaluated with different calibration levels: 0.2, 0.5, 2, 5, 10, 20 and 50 ppb. Figure 5 shows Cyflufenamid in a real matrix (weighting: 1/x) and the residual values. Relative deviations of the of the observed and theoretical concentrations (Residual %) are well within the desired +/- 20% range.

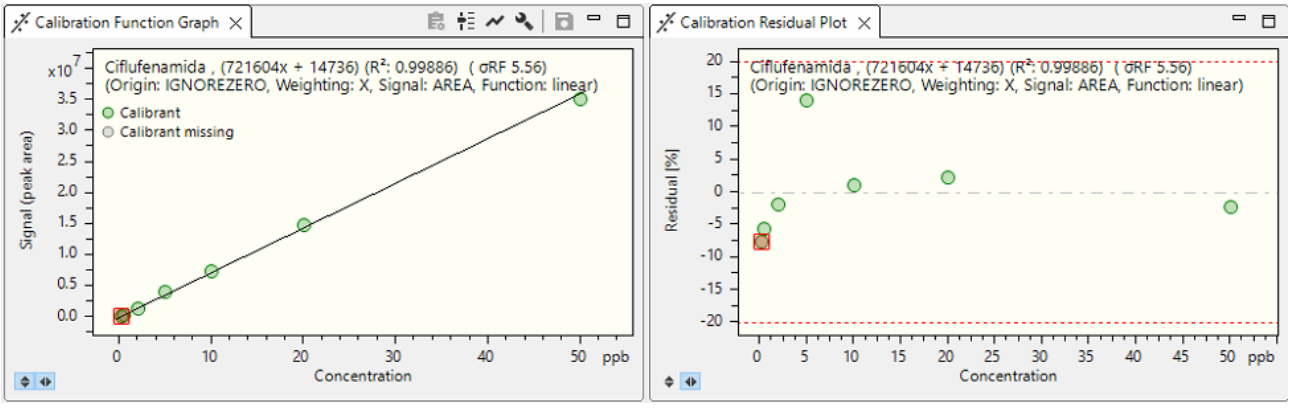


Figure 5. Cyflufenamid in a real matrix (weighting: 1/x) and (right graphic) the residual values.

2. **SENSITIVITY** was determined for a range of analytes at, or close to, the lower limit of quantitation (LLOQ). Signal-to-noise ratio was greater than 10 for the lowest calibration level. Figure 6 shows an example chromatogram, with Carbendazim analysis demonstrating excellent sensitivity at the limit of quantitation – 0.2 ppb – in this case.

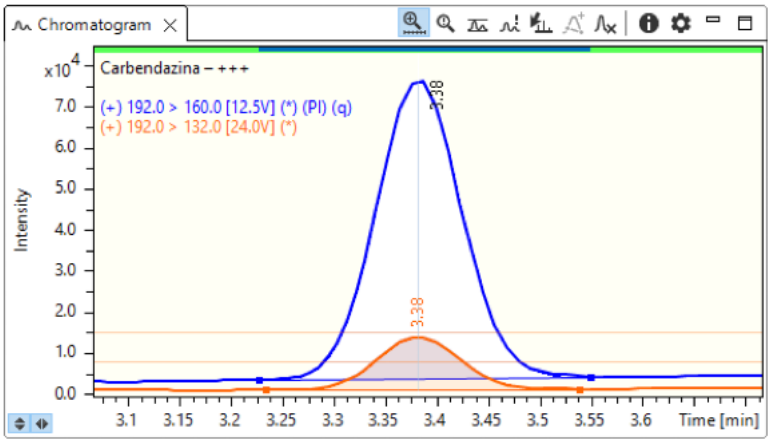


Figure 6. Carbendazim chromatogram in matrix (2 µL injection volume) at LLOQ (0.2 ppb).

Due to the high sensitivity of the instrument, samples and standards can be diluted to reduce any matrix effect. This means less interference, and that one matrix can be used to calibrate different (similar) samples. As a result, the lab can achieve a higher throughput and less maintenance and downtime compared with other, less sensitive instruments.

3. **REPEATABILITY** was estimated using the relative standard deviation (RSD) value for the area of ten consecutive injections in matrix of the 5 ppb and 50 ppb standards. Figure 7 shows that for 5 ppb, most of the pesticides were below 15% and for 50 ppb, all were below 15%.

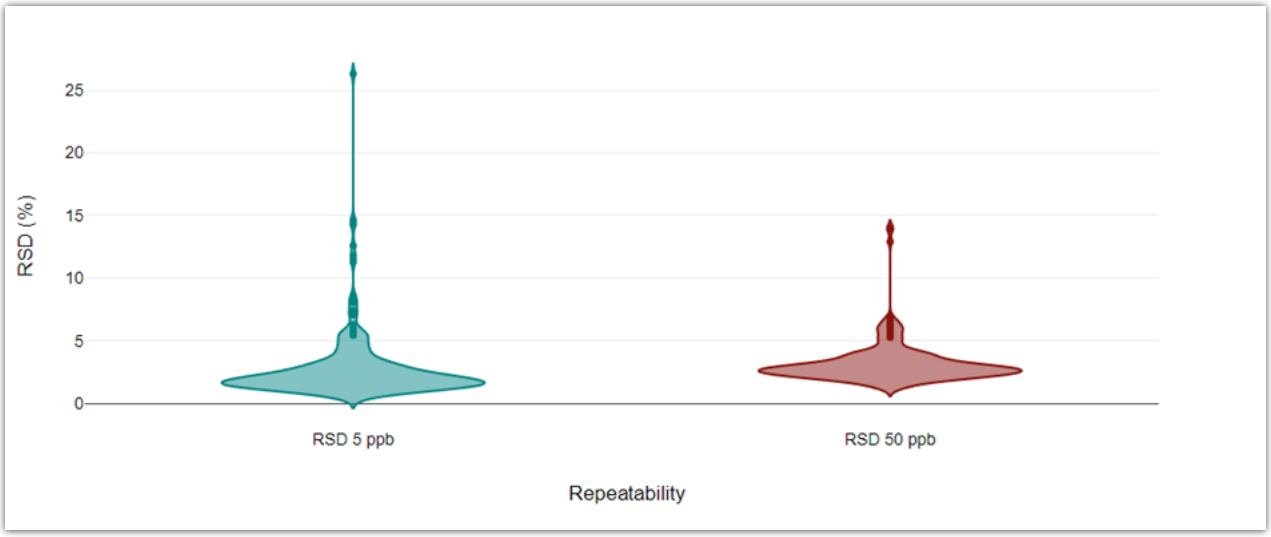


Figure 7. EVOQ® DART-TQ⁺ signal stability in matrix.

4. **REPRODUCIBILITY** was evaluated using the concentration calculated from real samples analyzed on different days with several injections in between. Table 1 shows the reference concentration* and the results obtained with EVOQ® DART-TQ+. In this study, 250 samples were analyzed without any instrument maintenance between runs. The results show a high level of reproducibility.

Table 1. Summary of real samples that were analyzed and quantified with different calibration curves on different days.

Sample	Pesticides detected	Reference*	Cal. Curve 1	Cal. Curve 2	Cal. Curve 3	Cal. Curve 4	Cal. Curve 5
641	Proamocarb Cyazofamide	11 ppb 6 ppb	10 ppb 8 ppb	12 ppb 10 ppb	12 ppb 9 ppb	12 ppb 11 ppb	12 ppb 11 ppb
647	Fluopriam Proamocarb	57 ppb** 41 ppb	43 ppb 38 ppb	43 ppb 39 ppb	47 ppb** 38 ppb	48 ppb** 37 ppb	48 ppb** 37 ppb
636	Proamocar Azoxystrobin Fluopriam	22 ppb 20 ppb 10 ppb	19 ppb 17 ppb 9 ppb	20 ppb 20 ppb 10 ppb	19 ppb 22 ppb 10 ppb	19 ppb 20 ppb 10 ppb	20 ppb 22 ppb 11 ppb
749	Fluonicamid Acetamiprid	36 ppb 12 ppb	37 ppb 11 ppb	36 ppb 13 ppb	39 ppb 13 ppb	37 ppb 11 ppb	39 ppb 13 ppb

*Reference value provided by an accredited laboratory for pesticides analysis. Samples were extracted, analyzed and shipped for EVOQ® DART TQ+ analysis. Pesticide stability in the extract is not taken into consideration.

** Values above the highest calibration level, sample should be diluted.

Software

Bruker provides a high-quality pesticide reference library, including retention times, two MRM transitions and ion ratio for more than 500 pesticides. The library is updated regularly.

MRM Method Builder: The EVOQ DART-TQ+ MRM Builder removes the need to know the MRM transition, lets the software set up the method and manage the TQ duty cycle. The software automatically finds the precursor ion, product ions and optimal collision energies.

MRM method setup is easy. Users simply type the name of the compound and the system autofills the MRM information, saving time and resources to quickly generate the methods required.

Exception-based data-review software makes it easier to highlight sample data that does not meet preset method criteria.

Conclusion

As pressure on the world's food chain mounts, pesticides are indispensable to farmers and growers who need to control pests, diseases, and weeds to maximize yields and keep up with demand. Screening and analyzing food samples for pesticides is a critical food quality and safety requirement, and labs need analytical tools that provide the required sensitivity and improved speed.

The EVOQ® DART-TQ+ is an easy-to-use, small footprint (40 cm) benchtop system engineered for small molecule screening and quantitation with exceptional speed, ultra-high sensitivity, and reduced chemical noise. It easily switches from the integrated DART source to the VIP-HESI source in seconds.

EVOQ® DART-TQ+ offers advantages over current standard practice for pesticide analysis in food:

- Ready to use method for multi-residue pesticide screening and quantitation for more than 500 target analytes in 14.5 minute sample-to-sample time
- Superior sensitivity with more compounds per analysis or more datapoints for each chromatographic peak
- A good linear dynamic range for standards between 0.2 – 50 ppb for most of the compounds in the mixture
- Excellent repeatability, even when operating at maximum speed
- Optimum robustness verified with an inter-day validation without any instrument maintenance.

References

[1] Analytical quality control and method validation procedures for pesticide residues analysis in food and feed, SANTE 11312/2021 (2022).

[2] https://www.ecfr.gov/current/title-40/chapter-I/subchapter-E/part-180

[3] https://www.fao.org/fao-who-codexalimentarius/thematic-areas/pesticides/en/#c452840

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