APPLICATION NOTE 65901

# Pesticide residues screening and quantitation analysis in olive oil using an Orbitrap Exploris 240 HRMS

Authors: Francesca Barbetti[1], Charles Yang[2], Debora D'Addonna[3], Christian Klaas[4]
[1]ISVEA S.r.L., Siena, Italy
[2]Thermo Fisher Scientific, San Jose, CA
[3]Thermo Fisher Scientific, Radano, Italy
[4]Thermo Fisher Scientific, Bremen, Germany

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## Goal

To develop and test a multi-residue instrument method that can be applied for high-throughput quantitation and unknown screening of pesticide residues in food matrices at or below the current legislative requirements. A high-resolution, accurate-mass (HRAM) mass spectrometer was operated in Full Scan-Data-Independent Acquisition (DIA) mode and using a Thermo Scientific™ AcquireX™ Background Exclusion workflow, providing an option for full spectrum filtering, retrospective analysis, and multi-parameter-based compound identification. The method was tested on over 400 target pesticides, in positive and negative mode, with an option for future extension to a larger number of analytes.

## Introduction

The demand for quick and simple analysis of large numbers of samples in agriculture applications is growing yearly. Throughout the world, pesticides are used to control pests that are harmful to crops, humans, and animals. These substances can pose a significant health threat, and therefore need to be accurately detected at the levels required by governmental authorities. Typically, maximum residue levels for pesticides in different products of plant and animal origin are set at low part-per-billion (ppb) levels. The current regulations present significant analytical challenges with respect to the low limits of quantification and high number of target analytes.

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Most routine LC-based methods usually employ triple quadrupole mass spectrometry. In recent years, Thermo Scientific™ Orbitrap™ mass analyzers have become available, providing higher confidence in compound identification and confirmation along with quantitative capabilities comparable to triple quadrupole MS/MS. Mass accuracy (typically below 5 ppm) minimizes interferences from co-eluting analytes and matrix co-extractives, and thus reduces the potential for false positive and negative results. This work describes the method performance parameters using the latest benchtop LC-Orbitrap instrument, the Thermo Scientific™ Orbitrap Exploris™ 240 mass spectrometer and its application to screening hundreds of target analytes at or below legislative levels (maximum residue levels – MRLs) in olive oil matrix.

## Experimental

### Reagents, all Fisher Scientific

- Acetonitrile, uHPLC-MS grade (P/N A956-1)
- Ammonium formate >99% (P/N A115-50)
- Methanol, uHPLC-MS grade (P/N A458-1)
- Formic acid, extra pure for HPLC (P/N 28905)
- Water, uHPLC-MS grade (P/N W8-1)

### Consumables

- Thermo Scientific™ HPLC Vial (P/N A4954-010)
- Thermo Scientific™ National™ 10 mm Wide Opening Screw Caps and Septa (P/N C4010-60A)
- Thermo Scientific™ Accucore™ aQ column, 100 × 2.1 mm, 2.6 µm (P/N 17326-102130)

### Standards

Pesticides were purchased from Ultra Scientific. See results tables for the identity of all pesticides investigated for targeted analysis.

### Sample preparation

Olive oil was purchased from a local market and analyzed for background levels of pesticides. Approximately 5 g of olive oil was weighed into a 50 mL conical tube. Then, 10 mL of acetonitrile, 6 mL of water, and 100 µL of internal standard were added to the tube. This mixture was capped and shaken vigorously for 5 minutes. A Thermo Scientific™ QuEChERS™ salt slim pack (4000 mg $MgSO_4$, 1000 mg NaCl, 500 mg $Na_2$ citrate and 1000 mg $Na_3$ citrate), which includes all the salts required for the extraction process, was added. The mixture was shaken for about 1 minute and then centrifuged at >3300 rpm for 15 minutes. A 2 mL aliquot of the supernatant was aspirated and filtered through a 0.45 µm filter into a vial. The recovered supernatant was passed through a lipid removal cartridge into an HPLC vial and spiked with the necessary calibration levels. A 1 µL injection was made with the Thermo Scientific™ Vanquish™ Flex Binary UHPLC system equipped with a Thermo Scientific™ Accucore™ aQ reversed phase column.

### Calibration standard preparation

A MegaMix high stock standard was prepared by taking 10 µL from each vial (~1000 µg/mL) and adding them together. For calibration, a 5-level calibration set was prepared by post-spiking the control olive oil extract with the mixture at concentrations ranging from 0.5 to 500 (0.5, 1.0, 5, 10, 500) ppb. All calibration levels were injected six times.

### Instrument analysis

Sample analysis was carried out on a Vanquish Flex Binary UHPLC system coupled to an Orbitrap Exploris 240 mass spectrometer.

### HPLC parameters

| | |
|---|---|
| Column temperature | 30 °C |
| Flow rate | 300 µL/min |
| Total run time | 15 min |
| Injection volume | 1 µL |
| Column | Accucore aQ, 100 × 2.1 mm, 2.6 µm |
| Mobile phases | A: Water with 5 mM ammonium formate, 0.1% formic acid<br>B: Methanol with 5 mM ammonium formate, 0.1% formic acid |
| Gradient | Table 1 |

**Table 1. HPLC gradient run program**

| Time [min] | Flow rate [mL/min] | A% | B% | Curve |
|---|---|---|---|---|
| 0.0 | 0.300 | 98 | 2 | 5 |
| 1.0 | 0.300 | 98 | 2 | 5 |
| 2.0 | 0.300 | 50 | 50 | 5 |
| 9.0 | 0.300 | 2 | 98 | 5 |
| 12.0 | 0.300 | 2 | 98 | 5 |
| 12.1 | 0.300 | 98 | 2 | 5 |
| 15.0 | 0.300 | 98 | 2 | 5 |

### Orbitrap Exploris 240 MS settings

| | |
|---|---|
| Spray voltage | 3.5 kV Pos / 2.5 kV Neg |
| Sheath gas | 30 arb |
| Aux gas | 6 arb |
| Sweep gas | 1 arb |
| Capillary temperature | 290 °C |
| Vaporizer temperature | 350 °C |
| Ion polarity | Pos / Neg switching |
| Full scan mass range | 110 – 1100 *m/z* |
| Full scan resolution | 45,000 |
| Data-Independent Acquisition (DIA) resolution | 30,000 |
| HCD collision energy | Stepped 18, 35, 60 |

### Data acquisition and processing

Data were acquired and processed using Thermo Scientific™ TraceFinder™ software to ensure full automation from instrument setup to raw data collection, processing, and reporting. Data acquired from DIA were analyzed with an extraction mass tolerance of ≤5 ppm for both precursor and product ions. Analytes were quantified based on full scan data. In addition, confirmation of target pesticides was performed using DIA fragment matching against a curated, high-resolution spectral library. The Thermo Scientific™ AcquireX™ Background Exclusion workflow was applied, and the data was extracted with a mass tolerance of ≤5 ppm for both precursor and product ions. Analytes were first confirmed using a targeted list of pesticides from a compound database and matched with the spectral library. All unknown pesticides were automatically passed to the unknown workflow in TraceFinder software to search online compound databases as well as other local databases.

## Results and discussion

Simplified in-house validation for screening and semi-quantitative methods was carried out on targeted pesticides. The linearity of the calibration curves was assessed over the range from 0.5 to 500 ng/mL to demonstrate the potential of the method for quantitative analysis. Method selectivity was evaluated by comparison of blank olive oil and spiked samples (n=6). The evaluation was based on accurate precursor *m/z* value of the analyte at the specified retention time window (±0.1 min). Full scan quantitation based upon mono-isotopic match, presence of fragment ions (FI), and high-resolution curated pesticide spectral library search (LS) was additionally applied for confirmation according to References 1 and 2. Acceptance values were set to less than or equal to 5 ppm for mass accuracy (FS and $MS^2$), ± 0.1 min for retention time, reproducibility at LOQ ≤15%, at least one fragment ion present, and for passing LS matching a report out of greater than or equal to 60% and a $r^2 \geq 0.9000$. The established values are shown in Table 2.

The methodology showed excellent reproducibility in terms of a) consistent peak shapes and robust column life, with over 250 injections and b) consistent peak response over time. Figure 1 shows select pesticides across the retention time range of the method (0–8 minutes), for 250 injections with a retention shift of less than 0.1 min. Figure 2 shows a chromatogram of a 10 ppb matrix-matched standard (MMS) for a method containing over 500 pesticides with positive and negative polarity switching occurring throughout the run. Enough data points were obtained across each peak for accurate quantitation.

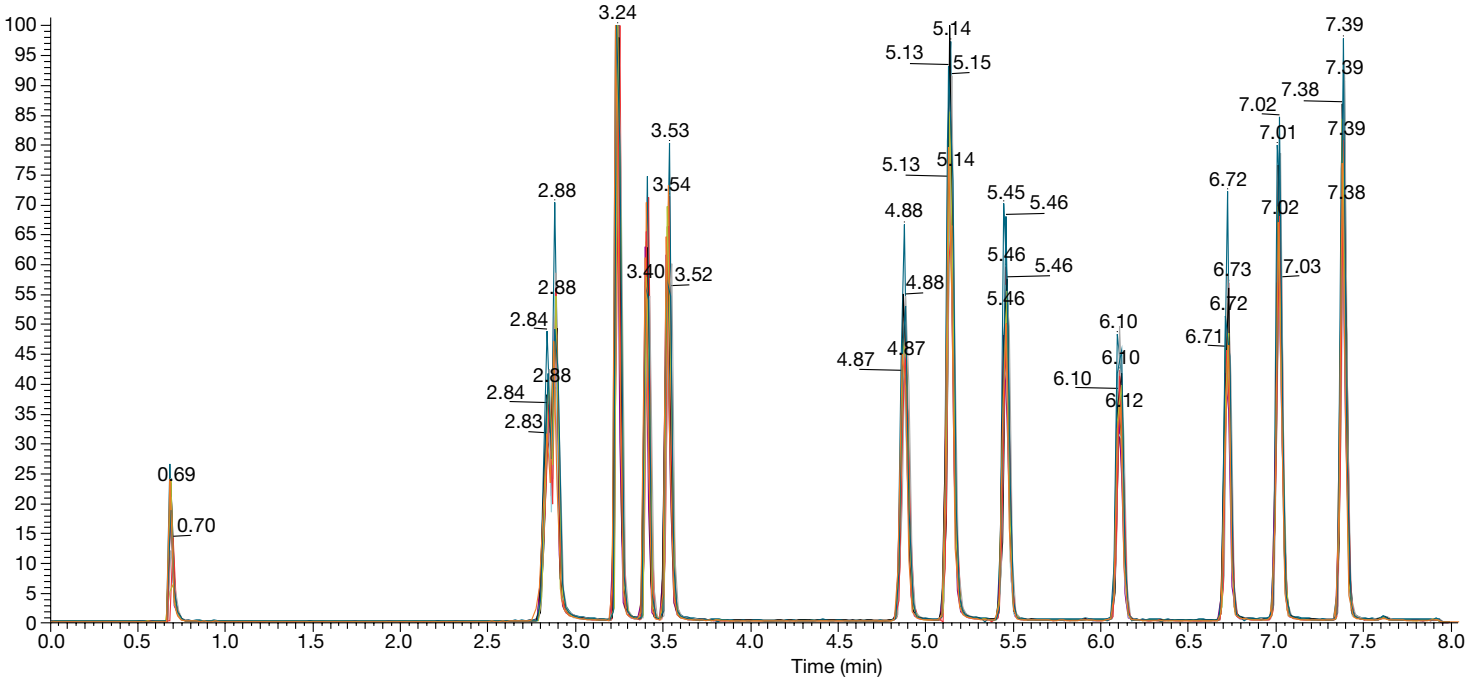


**Figure 1. Robust LC-MS reproducibility of pesticides spiked in olive oil, selected pesticides (overlay of injections 1 to 250) with extracted mass tolerance of 3 ppm**

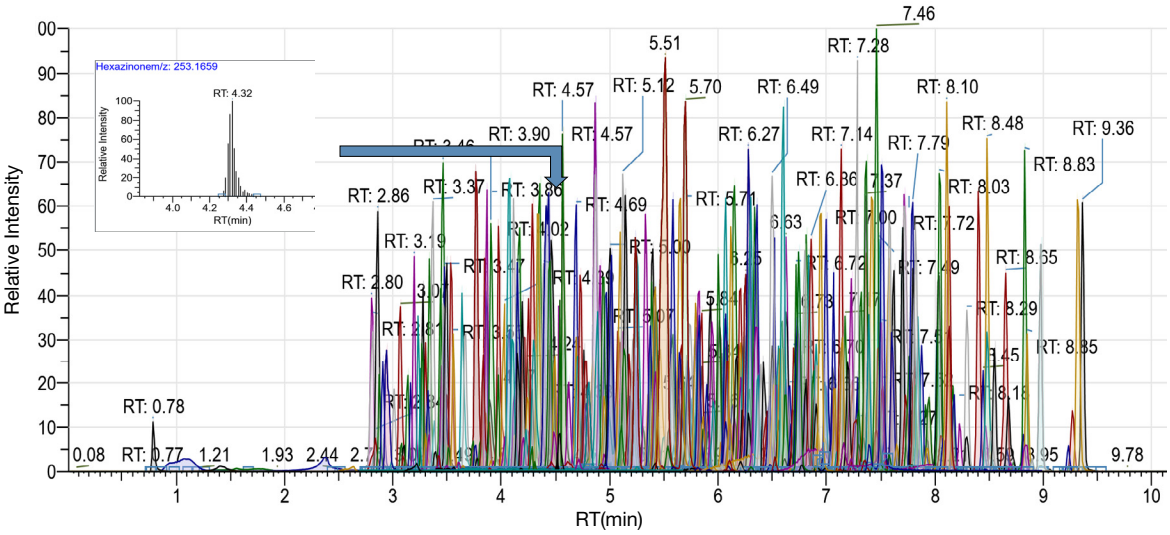


**Figure 2. Chromatogram of over 500 pesticides in 15 min in olive oil MMS spiked at 10 ppb. The peak highlighted at 4.32 min is hexazinone showing over 11 scans across the Full Scan quantitation ion used for the analysis.**

The implementation of the AcquireX Background Exclusion workflow also helps in identification of unknown contaminants using a unique routine to automatically create an exclusion list based on LC-MS analysis of the matrix blank. The instrument method is automatically updated with the exclusion list, so that when subsequent samples are analyzed, $MS^2$ experiments are not performed on matrix background signals. As a result, more cycle time is spent on triggering $MS^2$ on the relevant ions of interest. This is groundbreaking for data processing because it is minimizing false positives and negatives. Utilizing TraceFinder software, these new acquired data files can be quickly used and data processing performed for known and unknown screening workflows. TraceFinder software can easily go from a known to an unknown workflow by simply selecting a check box (Figure 3). The software can be set to search multiple spectral libraries, along with online spectral databases such as ChemSpider by simply selecting the Exhaustive Search Feature option (Figure 4).

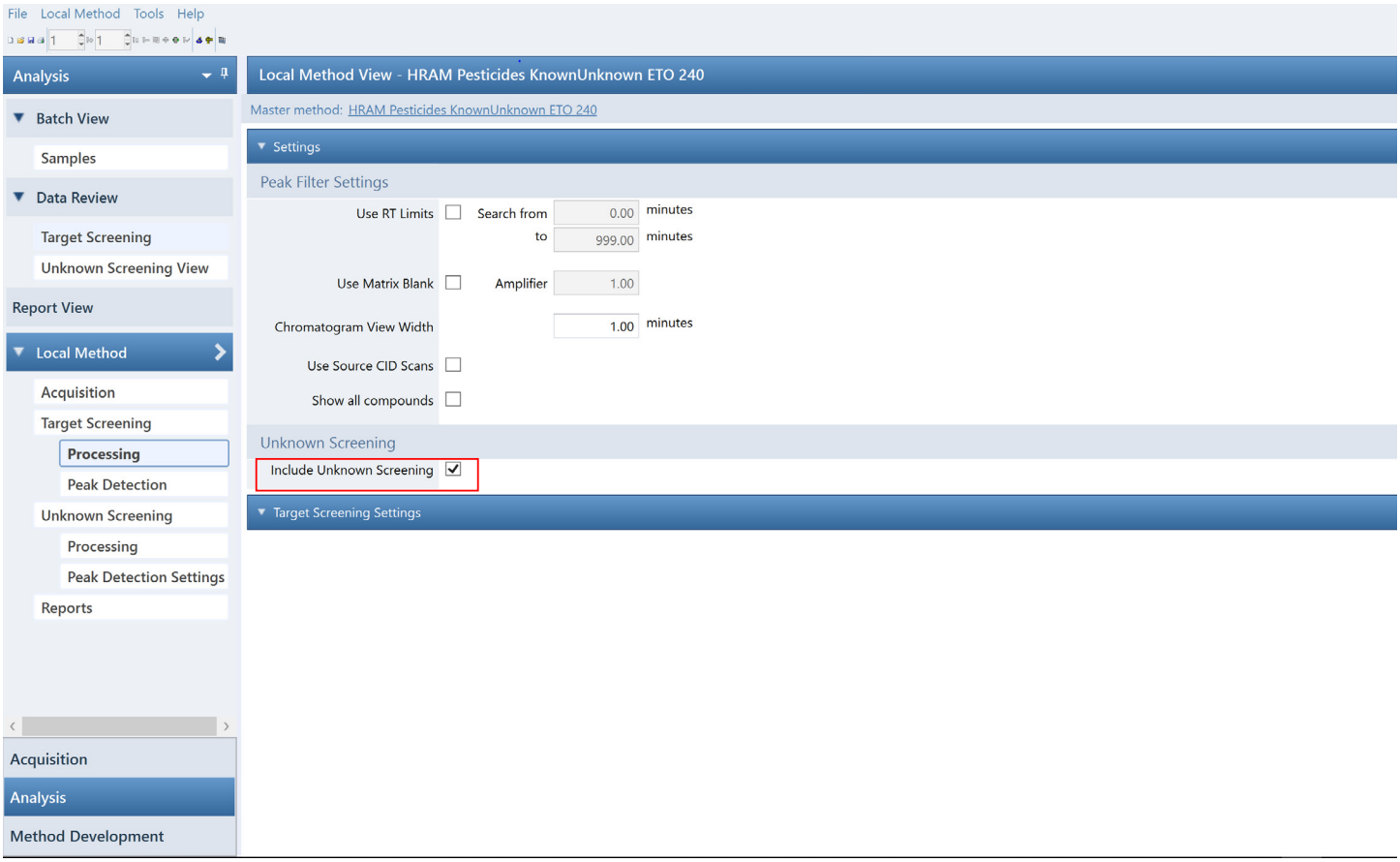


**Figure 3. TraceFinder software easy configuration from known screening workflow to immediately activate unknown screening workflow with a check**

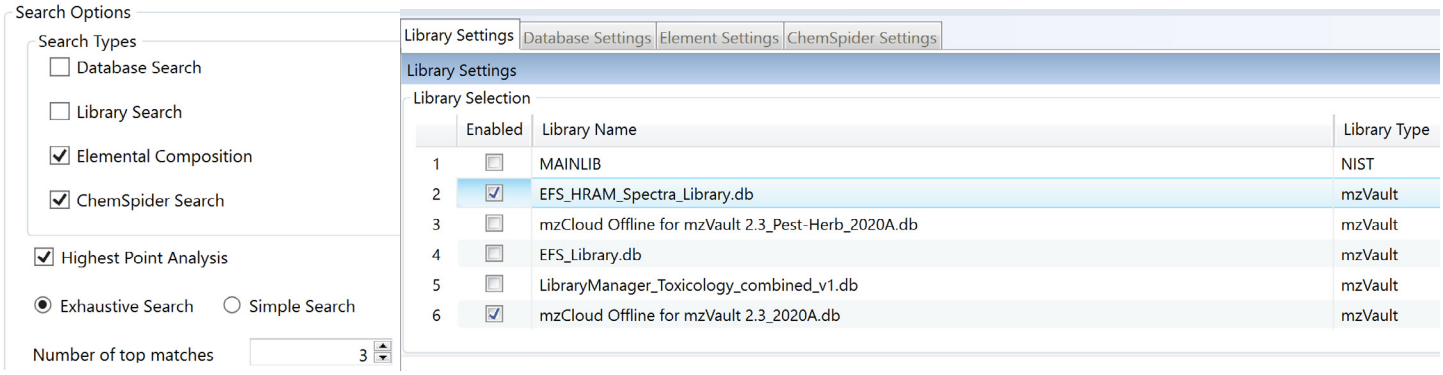


**Figure 4. Unknown search parameters are easily activated by checking the box. The capability to search multiple localized mzCloud curated spectral libraries gives you the confidence of the exact match.**

This feature ensures that the best results are displayed based on the search criteria selected. Figure 5 shows the quick and easy data review section of the targeted screening workflow with sortable grids and detailed information at the bottom. Chlorpyrifos (highlighted) is shown as an example of consistent mass measurement accuracy of the Orbitrap Exploris 240 mass spectrometer. Only those compounds that were not identified in the targeted screening workflow will be automatically moved into the unknown workflow for further investigation. An example of this is shown in Figure 6 for compounds moved into the unknown screening workflow. In many cases, the ChemSpider database was used to identify and label the most likely hits with the corresponding elemental composition. Many unknowns were identified as fatty oil (oleic acid) chemicals from olive oil (e.g., palmitoleic acid and myristoleic acid). A unique compound called erucamide was also identified, and research shows that it is a "slip additive" that is most commonly used in plastics and was later used as lubricants (Figure 7).

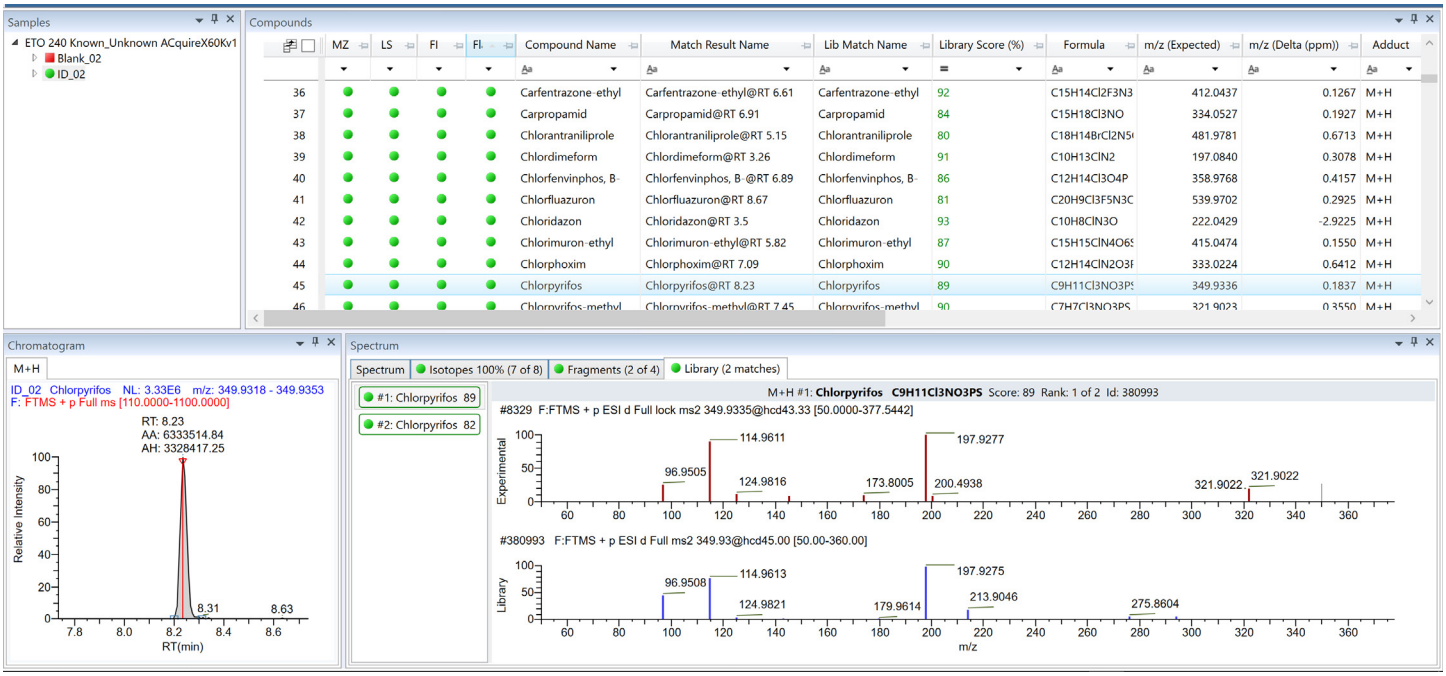


**Figure 5. Quick overview of targeted compound detection for chlorpyrifos with library scoring of 89% and Δppm of 0.1837**

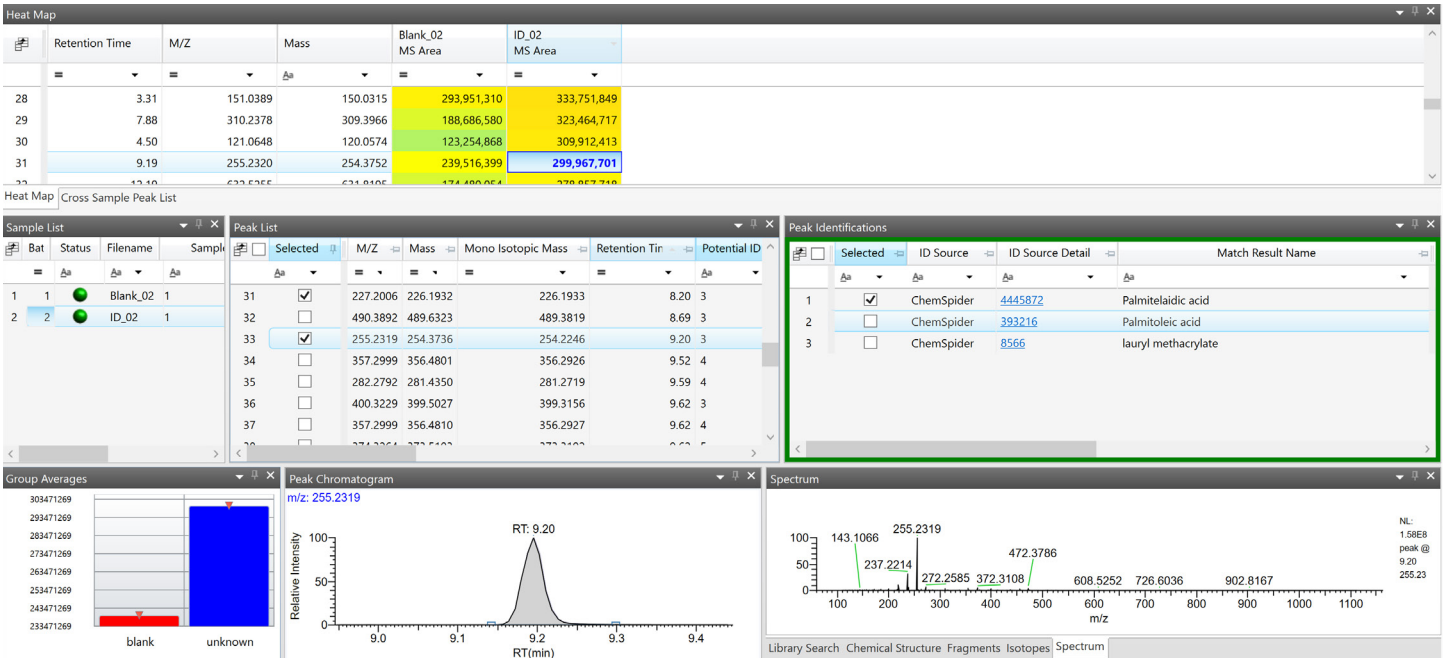


**Figure 6. Quick overview of unknown screening where identification is quickly listed. Here is a highlighted example of palmitoleic acid found in the sample, a fatty acid in olive oil that was not being targeted.**

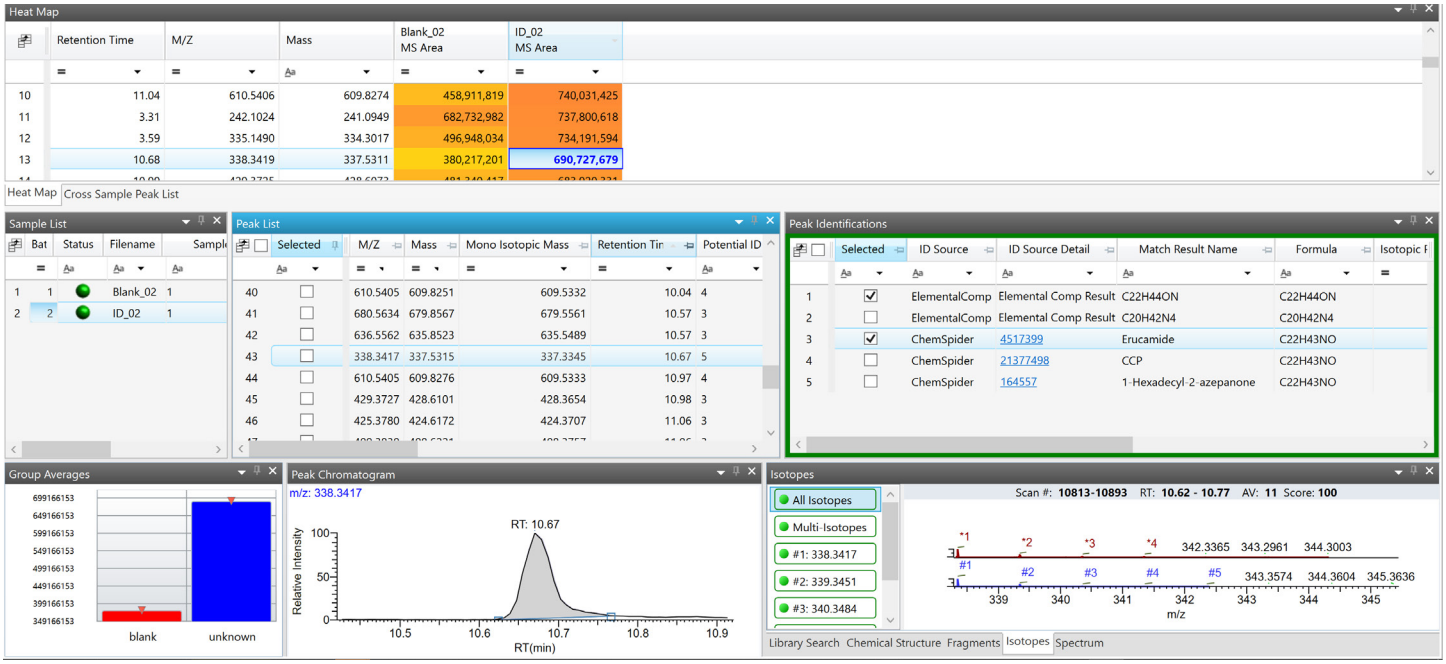


**Figure 7. Quick overview of unknown screening that found enucamide, a lubricant in olive oil**

Figure 8 shows calibration curves for ametryn and fenazaquin from 0.5 to 100 and 0.5 to 500 ppb, respectively. Over 95% of the pesticides studied had calibration curves with $r^2 > 0.950$ (Table 2). Confirmation fragment ions are displayed in the middle of each panel at 1 and 0.5 ppb for each pesticide, with indicator colors (green) easily visible to show passing fragment ion and curated Thermo Scientific™ mzCloud™ local spectral library criteria. A polarity switching method of over 500 pesticides was developed and optimized to ensure that at least one fragment ion was detected per compound. LOQs were determined as outlined by the SANTE/11813/2017 guidelines, with results shown in Figure 9.

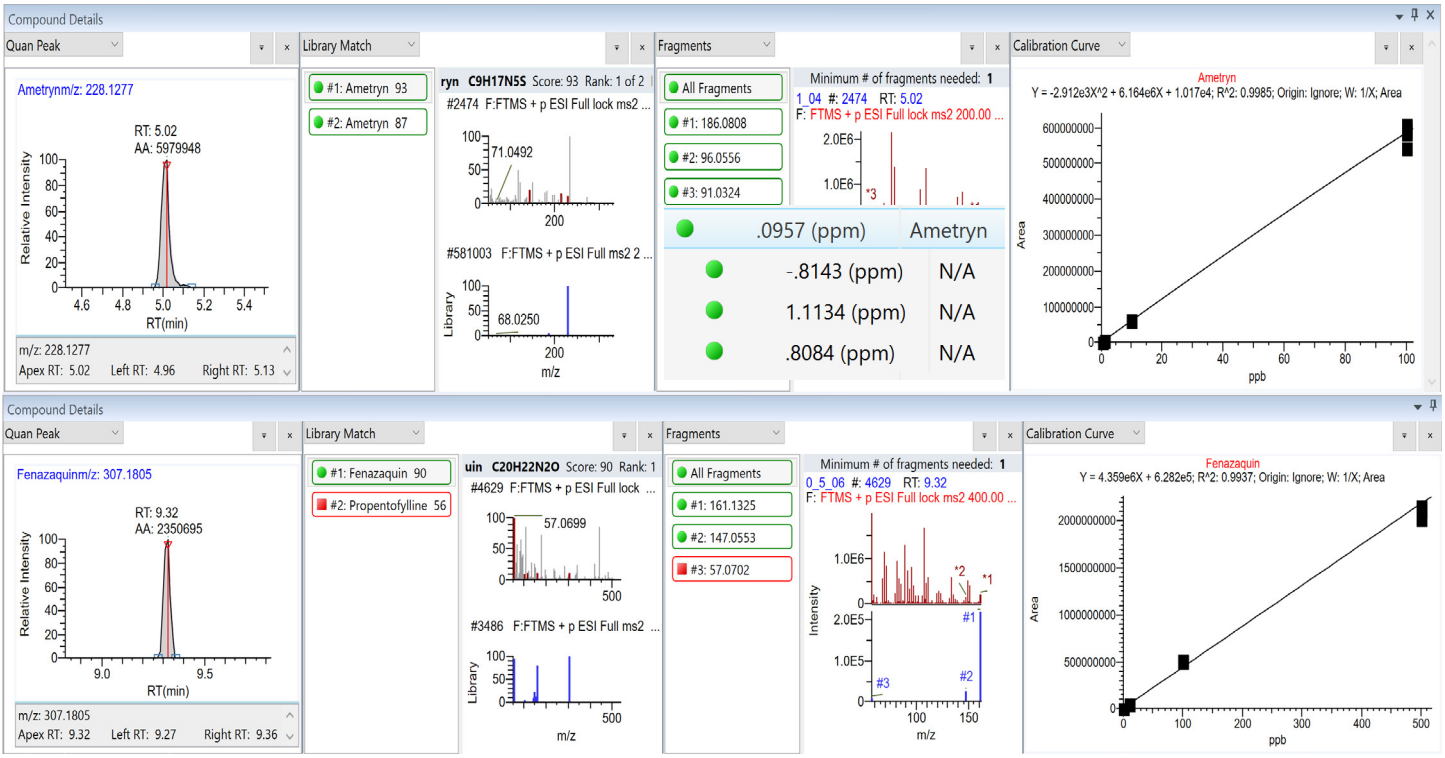


**Figure 8. Quantitation ions and confirming ion in MMS in olive oil, along with calibration range from 0.5 to 100 (500) ppb in TraceFinder software for ametryn at 1 ppb and fenazquin at 0.5 ppb, which shows excellent $r^2$, $MS^2$ fragment ion matching. The technique allows for confident quantitation and screening with confirmation well below the MRL concentration.**

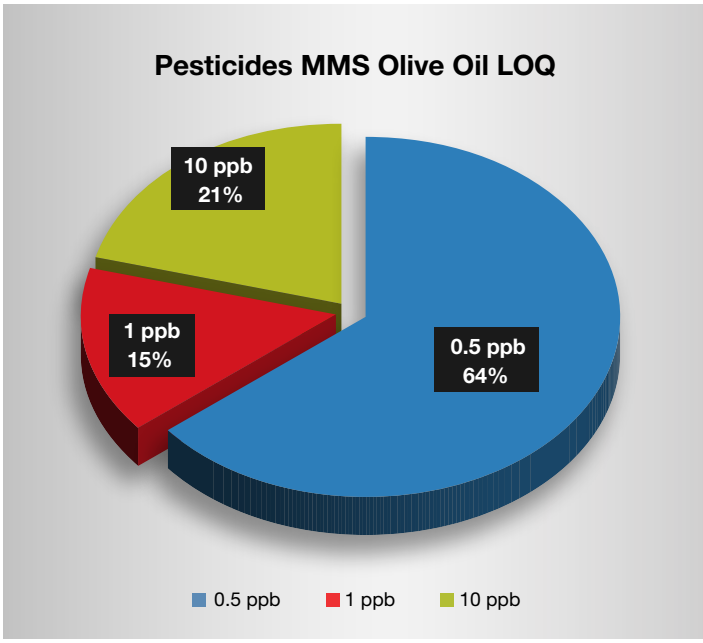


**Figure 9. LOQs of pesticides in MMS in olive oil obtained following the SANTE guidelines for the screening method of over 400 pesticides**

## Conclusion

Large pesticide panels for quantitative analysis at levels at or below EU MRLs have been shown to provide excellent sensitivity and robustness in a routine laboratory setting for olive oil matrix. In addition, TraceFinder software gives you the flexibility to screen for unknown contaminants in the sample. The capability of searching online databases enables identification of unknowns due to the excellent mass accuracy and high resolving power of the Orbitrap Exploris 240 mass spectrometer, significantly lowering the number of extraneous ID possibilities. The new AcquireX Background Exclusion workflow, utilizing the automatic update of an instrument method with an exclusion list created from a blank matrix injection, allows elimination of unwanted background ions in $MS^2$ for real samples, making identification more reliable. Currently ongoing work is required to evaluate the performance of the residues in matrix extracted spikes (MES) extracts.

## Acknowledgements

We would like to thank ISVEA and the local Thermo Fisher Scientific team for the support in developing the method.

### References

1. Method Validation & Quality Control Procedures for Pesticide Residues Analysis in Food & Feed. *EU Reference Libraries for Residues of Pesticides*. http://www.eurl-pesticides.eu/docs/public/tmplt_article.asp?CntID=727
2. Acceptance Criteria for Confirmation of Identity of Chemical Residues using Exact Mass Data for the FDA FVM Program. *US Food & Drug Administration Office of Foods and Veterinary Medicine*. September **2015**.

Table 2. Name of compound, $r^2$, concentration LOQ, RT, Δppm, %RSD, FI, and Library Score

| Compound | R^2 | LOQ conc. (ppb) | Actual RT (min) | Δ *m/z* (ppm) | %RSD | % CV | LS | FI | Library score (%) |
|---|---|---|---|---|---|---|---|---|---|
| 2,6-Dichlorobenzamide | 0.956 | 1.0 | 3.16 | -0.555 | 10.01 | 6.07 | Pass | Pass | 100 |
| Acephate | 0.999 | 1.0 | 2.61 | 0.748 | 11.14 | 16.41 | Pass | Pass | 86 |
| Acetamiprid | 0.998 | 0.5 | 3.47 | -0.372 | 9.22 | 8.79 | Pass | Pass | 95 |
| Acetochlor | 0.990 | 1.0 | 6.29 | -0.267 | 9.65 | 11.84 | Pass | Pass | 98 |
| Acibenzolar-S-methyl | 0.996 | 1.0 | 6.28 | -1.782 | 8.84 | 10.53 | Pass | Pass | 90 |
| Alachlor | 0.990 | 1.0 | 6.29 | -0.267 | 9.65 | 11.84 | Pass | Pass | 98 |
| Aldicarb-sulfoxide | 0.998 | 0.5 | 2.84 | -0.156 | 3.58 | 4.13 | Pass | Pass | 88 |
| Allethrin | 1.000 | 0.5 | 7.95 | 0.185 | 9.54 | 8.11 | Pass | Pass | 89 |
| Ametryn | 0.980 | 0.5 | 5.00 | -0.172 | 4.35 | 4.81 | Pass | Pass | 87 |
| Amicarbazone | 0.999 | 10.0 | 4.04 | 0.181 | 6.87 | 7.18 | Pass | Pass | 90 |
| Aminocarb | 0.999 | 0.5 | 2.82 | -0.372 | 3.49 | 4.05 | Pass | Pass | 96 |
| Ancymidol | 0.998 | 0.5 | 4.25 | 0.706 | 9.04 | 8.52 | Pass | Pass | 90 |
| Anilofos | 0.999 | 0.5 | 6.81 | 2.288 | 10.71 | 9.98 | Pass | Pass | 77 |
| Aspon | 0.999 | 0.5 | 8.48 | 0.029 | 3.84 | 3.88 | Pass | Pass | 92 |
| Asulam | 0.998 | 0.5 | 2.88 | -0.282 | 2.95 | 2.62 | Pass | Pass | 100 |
| Atrazine | 0.999 | 0.5 | 4.87 | -0.029 | 4.3 | 3.08 | Pass | Pass | 100 |
| Azaconazole | 0.999 | 0.5 | 5.23 | 0.341 | 4.54 | 4.49 | Pass | Pass | 86 |
| Azamethiphos | 0.998 | 0.5 | 4.03 | 0.553 | 7.86 | 5.95 | Pass | Pass | 84 |
| Azinphos-ethyl | 0.997 | 1.0 | 6.28 | -0.199 | 5.24 | 5.42 | Pass | Pass | 86 |
| Azinphos-methyl | 0.998 | 10.0 | 5.38 | 1.380 | 6.71 | 6.28 | Pass | Pass | 90 |
| Aziprotryne | 0.999 | 0.5 | 5.93 | 0.493 | 1.17 | 1.59 | Pass | Pass | 82 |
| Azoxystrobin | 0.999 | 0.5 | 5.39 | -0.341 | 2.29 | 2.5 | Pass | Pass | 100 |
| Barban | 0.994 | 10.0 | 5.94 | -0.036 | 13.46 | 12.15 | Pass | Pass | 62 |
| Beflubutamid | 0.999 | 0.5 | 6.74 | 0.117 | 2.71 | 2.23 | Pass | Pass | 86 |
| Benalaxyl | 0.999 | 0.5 | 6.84 | -0.159 | 5.67 | 6.04 | Pass | Pass | 98 |
| Bendiocarb | 0.999 | 0.5 | 4.17 | 0.094 | 4.56 | 3.74 | Pass | Pass | 99 |
| Benodanil | 0.998 | 1.0 | 4.79 | -0.295 | 13.82 | 11.99 | Pass | Pass | 66 |
| Benoxacor | 0.999 | 0.5 | 5.31 | 0.807 | 9.73 | 9.97 | Pass | Pass | 85 |
| Bensulide | 0.999 | 0.5 | 6.55 | -0.155 | 6.18 | 5.01 | Pass | Pass | 93 |
| Benthiavalicarb-isopropyl | 0.998 | 0.5 | 5.82 | -0.411 | 4.48 | 4.34 | Pass | Pass | 88 |
| Benzofenap | 0.999 | 0.5 | 7.62 | 0.086 | 2.63 | 2.54 | Pass | Pass | 95 |
| Benzoylprop-ethyl | 0.998 | 0.5 | 6.91 | -0.343 | 5.95 | 4.87 | Pass | Pass | 98 |
| Bioresmethrin | 0.999 | 0.5 | 8.98 | -0.194 | 4.85 | 4.62 | Pass | Pass | 88 |
| Boscalid | 0.998 | 0.5 | 5.71 | -1.224 | 5.2 | 4.68 | Pass | Pass | 100 |
| Brodifacoum | 1.000 | 0.5 | 9.27 | 1.171 | 7.84 | 7.64 | Pass | Pass | 86 |
| Bromacil | 0.997 | 0.5 | 4.19 | 0.918 | 12.99 | 13.41 | Pass | Pass | 97 |
| Bromfenvinphos-ethyl | 0.999 | 0.5 | 6.99 | -0.430 | 5.39 | 5.28 | Pass | Pass | 85 |
| Bupirimate | 0.999 | 0.5 | 6.15 | 0.079 | 3.77 | 4.65 | Pass | Pass | 93 |
| Buprofezin | 0.998 | 0.5 | 7.79 | 0.273 | 2.16 | 2.65 | Pass | Pass | 96 |
| Butachlor | 0.974 | 100.0 | 8.00 | 0.017 | 12.62 | 11.61 | Pass | Pass | 91 |
| Butafenacil_M+NH4 | 0.999 | 0.5 | 6.04 | 0.144 | 5 | 4.24 | Pass | Pass | 88 |
| Butralin | 0.999 | 0.5 | 8.47 | 0.556 | 7.06 | 7.87 | Pass | Pass | 90 |
| Buturon | 0.997 | 0.5 | 4.97 | 0.766 | 4.18 | 3.55 | Pass | Pass | 87 |
| Butylate | 0.999 | 1.0 | 7.65 | -1.082 | 10.05 | 15.49 | Pass | Pass | 93 |

Table 2. Name of compound, $r^2$, concentration LOQ, RT, Δppm, %RSD, FI, and Library Score

| Compound | R^2 | LOQ conc. (ppb) | Actual RT (min) | Δ *m/z* (ppm) | %RSD | % CV | LS | FI | Library score (%) |
|---|---|---|---|---|---|---|---|---|---|
| Carbendazim | 0.999 | 0.5 | 3.19 | 0.406 | 6.78 | 6.57 | Pass | Pass | 95 |
| Carbetamide | 0.998 | 0.5 | 3.96 | 0.890 | 12.84 | 13.56 | Pass | Pass | 97 |
| Carbofuran | 0.998 | 1.0 | 4.16 | 0.011 | 11.18 | 9.56 | Pass | Pass | 100 |
| Carbofuran, 3OH- | 0.998 | 0.5 | 3.38 | 0.945 | 5.62 | 5.07 | Pass | Pass | 96 |
| Carboxin | 0.997 | 1.0 | 4.46 | -0.281 | 3.47 | 2.39 | Pass | Pass | 91 |
| Carfentrazone-ethyl | 0.994 | 0.5 | 6.60 | -0.021 | 9.41 | 7.1 | Pass | Pass | 95 |
| Carpropamid | 0.999 | 0.5 | 6.90 | -0.447 | 5.07 | 4.5 | Pass | Pass | 93 |
| Chlorantraniliprole | 0.997 | 1.0 | 5.15 | -1.798 | 10.59 | 9.87 | Pass | Pass | 83 |
| Chlorbromuron | 0.999 | 0.5 | 5.90 | 0.622 | 2.43 | 2.3 | Pass | Pass | 85 |
| Chlorfenvinphos, B- | 0.998 | 0.5 | 6.89 | 0.246 | 5.08 | 5.35 | Pass | Pass | 86 |
| Chlorfluazuron | 0.998 | 10.0 | 8.65 | 0.745 | 3.51 | 3.37 | Pass | Pass | 74 |
| Chloridazon | 0.988 | 10.0 | 3.49 | -2.098 | 8.33 | 5.84 | Pass | Pass | 96 |
| Chlorimuron-ethyl | 0.998 | 0.5 | 5.80 | -0.360 | 3.29 | 3.27 | Pass | Pass | 87 |
| Chloroxuron | 0.999 | 0.5 | 6.20 | -0.009 | 4.59 | 4.14 | Pass | Pass | 85 |
| Chlorphoxim | 0.999 | 0.5 | 7.08 | 0.458 | 6.79 | 5.76 | Pass | Pass | 92 |
| Chlorpyrifos | 0.999 | 0.5 | 8.23 | 0.358 | 6.25 | 4.99 | Pass | Pass | 91 |
| Chlorpyrifos-methyl | 0.998 | 10.0 | 7.44 | -0.119 | 8.11 | 8.39 | Pass | Pass | 100 |
| Chlorsulfuron | 0.998 | 0.5 | 4.38 | 1.647 | 10.28 | 9.73 | Pass | Pass | 84 |
| Chlortoluron | 0.998 | 0.5 | 4.88 | -0.509 | 5.56 | 4.31 | Pass | Pass | 95 |
| Cinidon-ethyl | 0.999 | 0.5 | 8.08 | -0.645 | 8.32 | 8.76 | Pass | Pass | 73 |
| Cinosulfuron | 0.991 | 100.0 | 3.90 | 0.266 | 8.85 | 8.28 | Pass | Pass | 90 |
| Clethodim | 0.997 | 0.5 | 7.52 | -0.098 | 5.32 | 3.29 | Pass | Pass | 83 |
| Clodinafop-propargyl | 0.997 | 0.5 | 6.60 | -0.086 | 6.37 | 4.5 | Pass | Pass | 92 |
| Clofentezine | 0.988 | 0.5 | 7.51 | 0.058 | 12.5 | 4.56 | Pass | Pass | 79 |
| Clomazone | 1.000 | 0.5 | 5.37 | -0.688 | 2.22 | 2.2 | Pass | Pass | 100 |
| Cloquintocet-mexyl | 0.999 | 0.5 | 8.13 | 0.116 | 5.62 | 6.37 | Pass | Pass | 96 |
| Clothianidin | 0.998 | 10.0 | 3.32 | 0.148 | 6.82 | 6.64 | Pass | Pass | 89 |
| Coumaphos | 0.999 | 1.0 | 6.98 | 0.221 | 13.38 | 13.35 | Pass | Pass | 89 |
| Coumatetralyl | 0.997 | 0.5 | 6.27 | 0.306 | 5.71 | 4.24 | Pass | Pass | 97 |
| Crimidine | 0.998 | 1.0 | 3.86 | 1.500 | 5.88 | 7.99 | Pass | Pass | 89 |
| Cumyluron | 0.998 | 0.5 | 6.06 | -0.353 | 1.21 | 0.94 | Pass | Pass | 95 |
| Cyanazine | 0.998 | 1.0 | 3.97 | 0.436 | 9.32 | 8.35 | Pass | Pass | 100 |
| Cyazofamid | 0.998 | 0.5 | 6.36 | 0.228 | 4.38 | 3.1 | Pass | Pass | 85 |
| Cyclanilide | 0.993 | 10.0 | 6.37 | 0.463 | 4.99 | 4.79 | Pass | Pass | 86 |
| Cycloate | 0.999 | 0.5 | 7.39 | -0.835 | 4.09 | 5.21 | Pass | Pass | 94 |
| Cyclosulfamuron | 0.999 | 0.5 | 6.20 | -0.206 | 4.05 | 3.72 | Pass | Pass | 93 |
| Cycloxydim | 0.999 | 0.5 | 7.58 | -0.011 | 2.46 | 2.03 | Pass | Pass | 88 |
| Cycluron | 0.999 | 1.0 | 5.15 | -0.735 | 10.8 | 9.85 | Pass | Pass | 98 |
| Cyflufenamid | 0.996 | 0.5 | 7.05 | -0.453 | 7.05 | 3.67 | Pass | Pass | 84 |
| Cyprazine | 0.998 | 0.5 | 4.88 | 0.574 | 5.14 | 3.48 | Pass | Pass | 84 |
| Cyproconazole | 0.998 | 0.5 | 5.85 | 0.537 | 9.3 | 8.13 | Pass | Pass | 98 |
| Cyprodinil | 0.998 | 0.5 | 6.86 | 0.519 | 2.65 | 3.27 | Pass | Pass | 100 |
| Cyromazine | 1.000 | 1.0 | 2.37 | -2.810 | 1.61 | 3.57 | Pass | Pass | 89 |
| DEF | 1.000 | 0.5 | 8.83 | 0.240 | 4.91 | 4.51 | Pass | Pass | 92 |

Table 2. Name of compound, $r^2$, concentration LOQ, RT, Δppm, %RSD, FI, and Library Score

| Compound | R^2 | LOQ conc. (ppb) | Actual RT (min) | Δ *m/z* (ppm) | %RSD | % CV | LS | FI | Library score (%) |
|---|---|---|---|---|---|---|---|---|---|
| Demeton | 0.998 | 0.5 | 5.33 | 3.039 | 7.06 | 10.07 | Pass | Pass | 97 |
| Demeton-S (disulfoton oxon) | 0.998 | 0.5 | 5.33 | 3.039 | 7.06 | 10.07 | Pass | Pass | 86 |
| Demeton-S-methyl-sulfone | 0.997 | 1.0 | 3.10 | -0.037 | 7.89 | 7.97 | Pass | Pass | 84 |
| Desmetryn | 0.999 | 0.5 | 4.44 | -0.066 | 4.06 | 4.17 | Pass | Pass | 92 |
| Diafenthiuron | 0.998 | 1.0 | 8.52 | 0.699 | 3.67 | 5.46 | Pass | Pass | 78 |
| Dialifor | 0.999 | 0.5 | 7.28 | -0.062 | 4.96 | 4.59 | Pass | Pass | 88 |
| Diallate | 0.995 | 100.0 | 7.46 | -1.826 | 6.99 | 6.49 | Pass | Pass | 78 |
| Dibutyl phthalate | 0.998 | 10.0 | 7.51 | -0.007 | 4.52 | 2.68 | Pass | Pass | 87 |
| Dibutyl succinate | 0.999 | 10.0 | 6.70 | 0.256 | 2.8 | 2.67 | Pass | Pass | 99 |
| Dichlofluanid | 0.984 | 100.0 | 6.15 | 2.090 | 9.08 | 8.25 | Pass | Pass | 89 |
| Dichlorvos | 0.999 | 0.5 | 4.21 | 1.132 | 7.5 | 10.47 | Pass | Pass | 87 |
| Diclobutrazol | 0.999 | 0.5 | 6.66 | -0.780 | 5.4 | 4.94 | Pass | Pass | 88 |
| Diclosulam | 0.988 | 10.0 | 4.48 | -0.338 | 5.57 | 5.48 | Pass | Pass | 83 |
| Diethyl toluamide | 0.995 | 1.0 | 4.92 | -0.554 | 14.95 | 7.33 | Pass | Pass | 90 |
| Difenacoum | 0.999 | 0.5 | 8.66 | 0.594 | 7.46 | 7.14 | Pass | Pass | 94 |
| Difenoconazole | 0.999 | 0.5 | 7.41 | 0.427 | 8.09 | 6.54 | Pass | Pass | 100 |
| Difenoxuron | 0.999 | 0.5 | 5.10 | 0.488 | 5.27 | 4.54 | Pass | Pass | 87 |
| Diflubenzuron | 0.999 | 0.5 | 6.67 | 0.285 | 9.27 | 6.72 | Pass | Pass | 95 |
| Diflufenican | 0.997 | 10.0 | 7.56 | -0.284 | 11.58 | 9.18 | Pass | Pass | 100 |
| Dimefuron | 0.999 | 0.5 | 5.18 | -1.841 | 7.97 | 5.94 | Pass | Pass | 97 |
| Dimepiperate | 0.997 | 0.5 | 7.45 | 0.356 | 5.6 | 9.5 | Pass | Pass | 88 |
| Dimethachlor | 0.997 | 0.5 | 5.12 | 0.292 | 4.25 | 3.93 | Pass | Pass | 100 |
| Dimethametryn | 0.998 | 0.5 | 6.28 | 0.188 | 2.3 | 2.99 | Pass | Pass | 88 |
| Dimethenamid | 0.998 | 0.5 | 5.57 | -0.037 | 1.16 | 1.21 | Pass | Pass | 100 |
| Dimethirimol | 0.998 | 0.5 | 3.76 | 0.460 | 7.67 | 8.1 | Pass | Pass | 92 |
| Dimethoate | 0.997 | 0.5 | 3.45 | -0.146 | 6.38 | 5.07 | Pass | Pass | 97 |
| Dimethomorph | 0.997 | 0.5 | 5.79 | -0.152 | 8.99 | 6.12 | Pass | Pass | 97 |
| Diniconazole | 0.999 | 0.5 | 7.29 | 0.696 | 3.85 | 3.37 | Pass | Pass | 93 |
| Dinotefuran | 0.999 | 0.5 | 2.91 | -0.194 | 6.61 | 6.6 | Pass | Pass | 87 |
| Dioxacarb | 0.997 | 0.5 | 3.41 | -2.561 | 1.72 | 1.61 | Pass | Pass | 89 |
| Diphenamid | 0.998 | 0.5 | 5.13 | -1.142 | 5.4 | 5.4 | Pass | Pass | 87 |
| Dipropetryn | 0.998 | 0.5 | 6.28 | 0.188 | 2.3 | 2.99 | Pass | Pass | 81 |
| Disulfoton sulfone | 0.998 | 0.5 | 4.73 | 0.079 | 2.67 | 2.5 | Pass | Pass | 89 |
| Dithiopyr | 0.996 | 0.5 | 7.52 | -0.497 | 9.91 | 5.72 | Pass | Pass | 84 |
| Diuron | 0.998 | 0.5 | 5.24 | 0.991 | 3.02 | 2.28 | Pass | Pass | 100 |
| DMST | 0.999 | 0.5 | 4.28 | -0.358 | 4.02 | 3.83 | Pass | Pass | 97 |
| Dodemorph | 0.999 | 1.0 | 5.09 | 0.123 | 4.67 | 4.75 | Pass | Pass | 91 |
| Dodine | 0.999 | 0.5 | 7.29 | 0.015 | 7.94 | 10.61 | Pass | Pass | 93 |
| D-Trans-allethrin | 1.000 | 0.5 | 7.95 | 0.185 | 9.54 | 8.11 | Pass | Pass | 93 |
| Edifenphos | 0.998 | 0.5 | 6.81 | 0.684 | 8.81 | 6.63 | Pass | Pass | 81 |
| Emamectin benzoate | 0.999 | 0.5 | 8.04 | 0.766 | 4.29 | 5.4 | Pass | Pass | 88 |
| Epoxiconazole | 0.999 | 0.5 | 6.39 | 0.072 | 6.87 | 5.15 | Pass | Pass | 99 |
| EPTC | 0.999 | 1.0 | 6.62 | -1.139 | 5.78 | 9.22 | Pass | Pass | 87 |
| Ethiofencarb | 0.986 | 0.5 | 4.54 | -0.944 | 11.83 | 10.26 | Pass | Pass | 88 |

Table 2. Name of compound, $r^2$, concentration LOQ, RT, Δppm, %RSD, FI, and Library Score

| Compound | R^2 | LOQ conc. (ppb) | Actual RT (min) | Δ *m/z* (ppm) | %RSD | % CV | LS | FI | Library score (%) |
|---|---|---|---|---|---|---|---|---|---|
| Ethion | 1.000 | 0.5 | 8.02 | -0.282 | 0.55 | 0.5 | Pass | Pass | 92 |
| Ethiprole | 0.998 | 0.5 | 5.55 | -0.003 | 2.77 | 2.56 | Pass | Pass | 83 |
| Ethirimol | 0.998 | 0.5 | 3.76 | 0.460 | 7.67 | 8.1 | Pass | Pass | 84 |
| Ethofumesate | 0.998 | 0.5 | 5.44 | -0.258 | 5.77 | 4.46 | Pass | Pass | 93 |
| Ethoprophos | 0.998 | 0.5 | 6.28 | 0.168 | 2.71 | 2.6 | Pass | Pass | 92 |
| Ethoxyquin | 0.998 | 0.5 | 4.85 | 0.307 | 5.94 | 8.99 | Pass | Pass | 93 |
| Etofenprox | 0.999 | 0.5 | 9.37 | 0.235 | 3.75 | 3.91 | Pass | Pass | 91 |
| Etoxazole | 1.000 | 0.5 | 8.40 | 0.032 | 3.88 | 4.27 | Pass | Pass | 95 |
| Fenamidone | 0.998 | 0.5 | 5.54 | 0.020 | 4.55 | 4.61 | Pass | Pass | 90 |
| Fenamiphos | 0.999 | 0.5 | 6.50 | 0.662 | 5.88 | 5.08 | Pass | Pass | 84 |
| Fenamiphos-sulfone | 0.998 | 1.0 | 4.25 | 0.440 | 5.67 | 5.2 | Pass | Pass | 73 |
| Fenamiphos-sulfoxide | 0.999 | 0.5 | 4.16 | -0.059 | 8.3 | 6.38 | Pass | Pass | 74 |
| Fenarimol | 0.990 | 0.5 | 6.20 | -0.438 | 8.01 | 3.61 | Pass | Pass | 90 |
| Fenazaquin | 0.994 | 0.5 | 9.32 | -0.427 | 2.44 | 1.78 | Pass | Pass | 87 |
| Fenbuconazole | 0.998 | 0.5 | 6.44 | -0.423 | 6.12 | 4.37 | Pass | Pass | 92 |
| Fenfuram | 0.938 | 1.0 | 4.55 | -0.992 | 5.54 | 2.93 | Pass | Pass | 97 |
| Fenhexamid | 0.988 | 1.0 | 6.06 | 0.346 | 4.05 | 2.73 | Pass | Pass | 95 |
| Fenoxanil | 0.999 | 0.5 | 6.45 | -0.255 | 4.94 | 4.46 | Pass | Pass | 89 |
| Fenoxycarb | 0.997 | 0.5 | 6.59 | -0.229 | 5.79 | 3.58 | Pass | Pass | 97 |
| Fenpropidin | 0.999 | 0.5 | 5.25 | -0.669 | 4.87 | 5.24 | Pass | Pass | 100 |
| Fenpropimorph | 0.999 | 0.5 | 5.41 | 0.698 | 2.59 | 2.92 | Pass | Pass | 100 |
| Fenpyroximate | 0.999 | 0.5 | 8.64 | 0.574 | 3.46 | 3.4 | Pass | Pass | 100 |
| Fensulfothion | 0.998 | 10.0 | 4.95 | 0.731 | 6.75 | 6.64 | Pass | Pass | 85 |
| Fenthion | 0.998 | 1.0 | 6.92 | 0.813 | 7.13 | 7.04 | Pass | Pass | 65 |
| Fenthion-sulfoxide | 0.998 | 0.5 | 4.39 | -0.184 | 10.1 | 8.03 | Pass | Pass | 84 |
| Fentrazamide | 0.998 | 1.0 | 6.80 | -1.866 | 8.78 | 8.35 | Pass | Pass | 95 |
| Fenuron | 0.998 | 0.5 | 3.46 | -0.314 | 2.95 | 3.01 | Pass | Pass | 96 |
| Flamprop Isopropyl | 0.997 | 0.5 | 6.83 | -0.271 | 7.41 | 5.02 | Pass | Pass | 84 |
| Flamprop-methyl | 0.999 | 0.5 | 5.94 | -0.235 | 2.43 | 2.53 | Pass | Pass | 80 |
| Fluazifop-butyl | 0.998 | 0.5 | 7.71 | 0.248 | 4.41 | 4.05 | Pass | Pass | 98 |
| Fluazifop-P-butyl | 0.998 | 0.5 | 7.71 | 0.248 | 4.41 | 4.05 | Pass | Pass | 98 |
| Fluazuron | 0.999 | 0.5 | 8.16 | -0.349 | 4.04 | 3.74 | Pass | Pass | 92 |
| Flufenacet | 0.998 | 0.5 | 6.20 | -0.362 | 6.28 | 5.16 | Pass | Pass | 97 |
| Flumetsulam | 0.997 | 0.5 | 3.32 | -1.004 | 9.95 | 6.99 | Pass | Pass | 92 |
| Fluometuron | 0.998 | 0.5 | 4.68 | 0.305 | 5.08 | 4.62 | Pass | Pass | 94 |
| Fluopyram | 0.998 | 0.5 | 6.07 | -0.332 | 3.69 | 2.89 | Pass | Pass | 88 |
| Fluoxastrobin | 0.999 | 0.5 | 6.06 | 0.219 | 6.62 | 5.42 | Pass | Pass | 95 |
| Fluridone | 0.999 | 0.5 | 5.33 | 0.050 | 3.11 | 3.25 | Pass | Pass | 87 |
| Fluroxypyr | 0.987 | 500.0 | 3.96 | 0.793 | 1.46 | 1.41 | Pass | Pass | 94 |
| Flurtamone | 0.997 | 0.5 | 5.59 | -0.062 | 2.71 | 2.82 | Pass | Pass | 97 |
| Flusilazole | 0.998 | 0.5 | 6.56 | 0.467 | 4.42 | 3.48 | Pass | Pass | 97 |
| Fluthiacet-methyl | 1.000 | 0.5 | 6.76 | -0.053 | 2.47 | 2.3 | Pass | Pass | 85 |
| Flutolanil | 0.998 | 0.5 | 5.78 | -0.046 | 6.09 | 5.22 | Pass | Pass | 98 |
| Flutriafol | 0.999 | 0.5 | 4.79 | -1.701 | 8.33 | 7.35 | Pass | Pass | 90 |

Table 2. Name of compound, $r^2$, concentration LOQ, RT, Δppm, %RSD, FI, and Library Score

| Compound | R^2 | LOQ conc. (ppb) | Actual RT (min) | Δ *m/z* (ppm) | %RSD | % CV | LS | FI | Library score (%) |
|---|---|---|---|---|---|---|---|---|---|
| Fluxapyroxad | 0.996 | 0.5 | 5.82 | -0.105 | 5.73 | 3.42 | Pass | Pass | 86 |
| Forchlorfenuron | 0.998 | 0.5 | 5.13 | -0.871 | 8.63 | 8.62 | Pass | Pass | 94 |
| Fosthiazate | 0.985 | 0.5 | 4.60 | -0.060 | 6.98 | 6.4 | Pass | Pass | 89 |
| Fuberidazole | 0.998 | 0.5 | 3.45 | -0.505 | 3.67 | 3.58 | Pass | Pass | 88 |
| Furalaxyl | 0.998 | 0.5 | 5.42 | -0.330 | 2.58 | 2.37 | Pass | Pass | 97 |
| Furathiocarb | 0.998 | 0.5 | 7.73 | -0.177 | 3.34 | 3.45 | Pass | Pass | 89 |
| Griseofulvin | 0.998 | 0.5 | 4.79 | 0.529 | 5.89 | 5.01 | Pass | Pass | 61 |
| Halofenozide | 0.996 | 10.0 | 5.60 | -0.066 | 4.2 | 3.91 | Pass | Pass | 84 |
| Haloxyfop-2-ethoxyethyl | 0.998 | 0.5 | 7.63 | -0.501 | 2.43 | 2.55 | Pass | Pass | 89 |
| Heptenophos | 0.999 | 0.5 | 5.10 | 0.437 | 3.8 | 3.44 | Pass | Pass | 91 |
| Hexaconazole | 0.999 | 0.5 | 7.01 | -0.152 | 5.85 | 4.47 | Pass | Pass | 91 |
| Hexazinone | 0.957 | 0.5 | 4.30 | 0.155 | 7.93 | 4.97 | Pass | Pass | 97 |
| Hexythiazox | 0.999 | 0.5 | 8.18 | 0.750 | 5.87 | 5.52 | Pass | Pass | 97 |
| Hydramethylnon | 0.998 | 0.5 | 7.49 | 0.050 | 8.91 | 7.2 | Pass | Pass | 86 |
| Imazalil | 0.998 | 0.5 | 4.70 | -0.298 | 4.47 | 5.32 | Pass | Pass | 88 |
| Imazamox | 0.997 | 0.5 | 3.47 | -0.976 | 6.27 | 6.36 | Pass | Pass | 100 |
| Imazapic | 0.999 | 0.5 | 3.53 | -0.637 | 6.02 | 5.6 | Pass | Pass | 89 |
| Imazaquin | 0.998 | 0.5 | 4.16 | 0.024 | 7.48 | 6.41 | Pass | Pass | 98 |
| Imidacloprid | 0.961 | 100.0 | 3.30 | 0.558 | 4.82 | 4.45 | Pass | Pass | 96 |
| Inabenfide | 0.997 | 0.5 | 5.60 | -0.457 | 4.35 | 3.41 | Pass | Pass | 84 |
| Indoxacarb | 0.999 | 0.5 | 7.34 | 0.140 | 7.22 | 5.29 | Pass | Pass | 82 |
| Ipconazole | 0.995 | 0.5 | 7.52 | 0.245 | 6.79 | 3.67 | Pass | Pass | 90 |
| Iprobenfos | 0.998 | 0.5 | 6.64 | -0.130 | 3.81 | 4.21 | Pass | Pass | 97 |
| Iprovalicarb | 0.999 | 0.5 | 6.14 | 0.332 | 4.11 | 4.4 | Pass | Pass | 96 |
| Isazofos | 0.997 | 0.5 | 6.00 | 0.098 | 2.01 | 2.36 | Pass | Pass | 96 |
| Isomethiozin | 0.999 | 0.5 | 6.80 | 1.158 | 3.7 | 3.59 | Pass | Pass | 94 |
| Isoprocarb | 0.999 | 100.0 | 4.80 | -1.054 | 2.97 | 2.8 | Pass | Pass | 97 |
| Isoprothiolane | 0.999 | 0.5 | 5.84 | -0.000 | 1.56 | 1.97 | Pass | Pass | 86 |
| Isoproturon | 0.999 | 0.5 | 5.00 | 0.050 | 6.29 | 5.72 | Pass | Pass | 95 |
| Isopyrazam | 0.999 | 0.5 | 7.37 | -0.079 | 8.9 | 7.74 | Pass | Pass | 89 |
| Isouron | 0.997 | 0.5 | 4.37 | 0.112 | 7.74 | 7.66 | Pass | Pass | 91 |
| Isoxadifen-ethyl | 0.995 | 0.5 | 6.60 | 0.079 | 4.28 | 2.78 | Pass | Pass | 79 |
| Isoxaflutole | 0.997 | 10.0 | 4.91 | 0.390 | 12.1 | 10.67 | Pass | Pass | 90 |
| Isoxathion | 0.998 | 0.5 | 7.14 | 0.665 | 2.75 | 2.96 | Pass | Pass | 89 |
| Kadethrin | 0.998 | 0.5 | 7.50 | 0.179 | 15 | 14.77 | Pass | Pass | 89 |
| Kresoxim-methyl | 0.998 | 0.5 | 6.62 | 0.071 | 4.57 | 4.72 | Pass | Pass | 84 |
| Lactofen | 0.998 | 0.5 | 7.82 | -0.588 | 13.42 | 9.55 | Pass | Pass | 85 |
| Lenacil | 0.994 | 10.0 | 4.93 | 1.250 | 5.33 | 5.32 | Pass | Pass | 100 |
| Linuron | 0.999 | 0.5 | 5.72 | 0.432 | 5.06 | 4.78 | Pass | Pass | 97 |
| Malathion | 0.998 | 0.5 | 5.82 | -0.661 | 3.14 | 3.55 | Pass | Pass | 88 |
| Mandipropamid | 0.996 | 0.5 | 5.67 | 0.301 | 7.9 | 5.67 | Pass | Pass | 91 |
| Mecarbam | 0.999 | 0.5 | 6.20 | -0.289 | 3.44 | 3.32 | Pass | Pass | 92 |
| Mefenpyr-diethyl | 0.998 | 0.5 | 6.91 | -0.368 | 5.76 | 6.1 | Pass | Pass | 97 |
| Mefluidide | 0.997 | 0.5 | 4.21 | 0.880 | 7.3 | 5.11 | Pass | Pass | 85 |

Table 2. Name of compound, $r^2$, concentration LOQ, RT, Δppm, %RSD, FI, and Library Score

| Compound | R^2 | LOQ conc. (ppb) | Actual RT (min) | Δ *m/z* (ppm) | %RSD | % CV | LS | FI | Library score (%) |
|---|---|---|---|---|---|---|---|---|---|
| Mepanipyrim | 0.999 | 0.5 | 6.49 | 0.431 | 2.31 | 3.04 | Pass | Pass | 91 |
| Mephospholan | 0.997 | 0.5 | 4.07 | 0.369 | 8.23 | 8.06 | Pass | Pass | 83 |
| Mepronil | 0.999 | 0.5 | 5.84 | -0.095 | 1.96 | 1.72 | Pass | Pass | 87 |
| Metaflumizone | 0.998 | 1.0 | 7.92 | -0.280 | 12.23 | 13.22 | Pass | Pass | 75 |
| Metalaxyl | 0.999 | 0.5 | 4.87 | -0.227 | 3.8 | 3.44 | Pass | Pass | 97 |
| Metalaxyl-M | 0.999 | 0.5 | 4.87 | -0.227 | 3.8 | 3.44 | Pass | Pass | 97 |
| Metamitron | 0.984 | 100.0 | 3.51 | -0.436 | 11 | 4.66 | Pass | Pass | 98 |
| Metazachlor | 0.998 | 0.5 | 4.86 | 0.544 | 6.22 | 6.89 | Pass | Pass | 95 |
| Metconazole | 0.998 | 0.5 | 7.05 | -0.429 | 3.04 | 2.13 | Pass | Pass | 96 |
| Methabenzthiazuron | 0.999 | 0.5 | 5.21 | -0.528 | 2.69 | 2.65 | Pass | Pass | 82 |
| Methacrifos | 0.999 | 10.0 | 5.22 | -0.153 | 4.83 | 5.91 | Pass | Pass | 85 |
| Methamidophos | 1.000 | 1.0 | 1.80 | -0.888 | 3.87 | 4.46 | Pass | Pass | 80 |
| Methfuroxam | 0.998 | 0.5 | 5.24 | 0.503 | 2.3 | 2.29 | Pass | Pass | 98 |
| Methiocarb | 0.999 | 0.5 | 5.64 | -1.012 | 3.41 | 3.26 | Pass | Pass | 90 |
| Methiocarb-sulfone | 0.992 | 1.0 | 3.46 | 0.503 | 10.77 | 5.29 | Pass | Pass | 88 |
| Methiocarb-sulfoxide | 0.998 | 1.0 | 3.33 | 2.873 | 8.3 | 9.58 | Pass | Pass | 98 |
| Methomyl | 0.989 | 10.0 | 3.09 | -0.446 | 2.91 | 5.94 | Pass | Pass | 98 |
| Methoxyfenozide | 0.998 | 0.5 | 5.90 | -0.207 | 5.95 | 7.15 | Pass | Pass | 100 |
| Metobromuron | 0.998 | 0.5 | 4.96 | -0.157 | 8.21 | 7.43 | Pass | Pass | 90 |
| Metolachlor | 1.000 | 0.5 | 6.36 | -0.020 | 2.79 | 2.94 | Pass | Pass | 100 |
| Metolcarb | 0.998 | 10.0 | 4.00 | -0.564 | 10.45 | 9.78 | Pass | Pass | 96 |
| Metosulam | 0.997 | 0.5 | 4.25 | -0.038 | 10.67 | 10.16 | Pass | Pass | 87 |
| Metoxuron | 0.996 | 0.5 | 3.84 | -0.101 | 6.71 | 5.85 | Pass | Pass | 92 |
| Metrafenone | 0.999 | 0.5 | 7.20 | 0.383 | 3.65 | 3.53 | Pass | Pass | 99 |
| Mexacarbate | 0.999 | 0.5 | 3.40 | -4.222 | 11.59 | 14.79 | Pass | Pass | 82 |
| Molinate | 0.998 | 0.5 | 6.09 | -0.532 | 5.16 | 7.46 | Pass | Pass | 96 |
| Monalide | 0.997 | 0.5 | 6.42 | 0.021 | 2.34 | 2.31 | Pass | Pass | 96 |
| Monolinuron | 0.998 | 0.5 | 4.71 | 0.008 | 5.77 | 5.63 | Pass | Pass | 91 |
| Monuron | 0.998 | 0.5 | 4.26 | 0.578 | 7.25 | 6.04 | Pass | Pass | 100 |
| Myclobutanil | 0.999 | 0.5 | 5.95 | 0.140 | 3.14 | 3 | Pass | Pass | 83 |
| Naled | 0.997 | 10.0 | 5.09 | 1.949 | 12.6 | 11.03 | Pass | Pass | 84 |
| Napropamide | 0.999 | 0.5 | 6.33 | 0.935 | 3.61 | 4.13 | Pass | Pass | 99 |
| Nicotine | 0.994 | 1.0 | 0.79 | -0.245 | 10.54 | 6.05 | Pass | Pass | 95 |
| Novaluron | 0.996 | 1.0 | 7.64 | -0.243 | 2.83 | 2.61 | Pass | Pass | 95 |
| Nuarimol | 0.999 | 0.5 | 5.50 | -0.521 | 4.46 | 4.2 | Pass | Pass | 89 |
| Ofurace | 0.997 | 0.5 | 4.17 | 0.188 | 9.42 | 8.86 | Pass | Pass | 69 |
| Omethoate | 0.999 | 0.5 | 2.82 | -0.431 | 3.91 | 4.47 | Pass | Pass | 93 |
| Orbencarb | 0.999 | 10.0 | 7.15 | 0.318 | 3.69 | 3.77 | Pass | Pass | 97 |
| Oxadiazon | 0.998 | 0.5 | 7.93 | 0.269 | 7.74 | 6.66 | Pass | Pass | 93 |
| Oxadixyl | 0.996 | 0.5 | 3.83 | 0.698 | 7.82 | 8.28 | Pass | Pass | 84 |
| Oxamyl | 0.999 | 10.0 | 2.99 | -0.309 | 2.84 | 3.19 | Pass | Pass | 88 |
| Oxycarboxin | 0.997 | 1.0 | 3.56 | 0.578 | 11.93 | 9.96 | Pass | Pass | 82 |
| Oxydemeton methyl | 0.999 | 0.5 | 3.06 | 0.275 | 8.39 | 8.91 | Pass | Pass | 84 |
| Paclobutrazol | 0.999 | 0.5 | 5.77 | 0.033 | 6.24 | 4.92 | Pass | Pass | 92 |

Table 2. Name of compound, $r^2$, concentration LOQ, RT, Δppm, %RSD, FI, and Library Score

| Compound | R^2 | LOQ conc. (ppb) | Actual RT (min) | Δ *m/z* (ppm) | %RSD | % CV | LS | FI | Library score (%) |
|---|---|---|---|---|---|---|---|---|---|
| Parathion-methyl-oxon | 0.992 | 100.0 | 3.92 | 0.534 | 6.63 | 4.93 | Pass | Pass | 85 |
| Parathion-oxon | 0.998 | 10.0 | 4.79 | 0.741 | 9 | 8.49 | Pass | Pass | 89 |
| Pebulate | 0.999 | 0.5 | 7.27 | 0.536 | 6.46 | 7.28 | Pass | Pass | 92 |
| Penconazole | 0.996 | 0.5 | 6.83 | -0.057 | 7.92 | 4.46 | Pass | Pass | 94 |
| Pencycuron | 0.999 | 0.5 | 7.24 | 0.062 | 3.03 | 3.22 | Pass | Pass | 96 |
| Phenothrin | 0.987 | 10.0 | 9.25 | 0.421 | 11.46 | 7.68 | Pass | Pass | 62 |
| Phenthoate | 0.998 | 0.5 | 6.62 | 0.229 | 5.54 | 4.85 | Pass | Pass | 94 |
| Phorate | 0.996 | 10.0 | 7.14 | 0.861 | 14.41 | 13.9 | Pass | Pass | 85 |
| Phorate-sulfone | 0.999 | 0.5 | 4.77 | 1.314 | 8.1 | 7.31 | Pass | Pass | 86 |
| Phosalone | 0.998 | 0.5 | 7.14 | 0.251 | 4.31 | 3.52 | Pass | Pass | 93 |
| Phosfolan | 0.999 | 1.0 | 3.73 | -0.348 | 8.12 | 8.46 | Pass | Pass | 80 |
| Phosmet | 0.996 | 0.5 | 5.41 | -0.030 | 13.6 | 3.54 | Pass | Pass | 98 |
| Phoxim | 0.998 | 1.0 | 7.08 | 0.786 | 13.4 | 7.07 | Pass | Pass | 92 |
| Picolinafen | 0.998 | 1.0 | 8.12 | 0.133 | 5.13 | 3.28 | Pass | Pass | 94 |
| Picoxystrobin | 0.998 | 0.5 | 6.53 | -0.352 | 3.62 | 5.02 | Pass | Pass | 84 |
| Piperonyl-butoxide | 0.998 | 1.0 | 7.93 | -0.817 | 13.43 | 12.84 | Pass | Pass | 88 |
| Piperophos | 0.999 | 0.5 | 7.37 | -0.229 | 2.79 | 3.27 | Pass | Pass | 94 |
| Pirimicarb | 0.996 | 0.5 | 3.90 | 0.078 | 7.17 | 7.93 | Pass | Pass | 98 |
| Pirimiphos-ethyl | 0.999 | 0.5 | 7.82 | -0.525 | 3.38 | 4.07 | Pass | Pass | 96 |
| Pirimiphos-methyl | 0.984 | 0.5 | 6.99 | -0.111 | 3.11 | 4.33 | Pass | Pass | 100 |
| Pretilachlor | 0.998 | 0.5 | 7.51 | 0.604 | 6.06 | 4.62 | Pass | Pass | 98 |
| Prochloraz | 0.999 | 0.5 | 7.07 | -0.579 | 3.88 | 3.83 | Pass | Pass | 100 |
| Profenofos | 0.997 | 0.5 | 7.74 | 0.146 | 6.76 | 4.19 | Pass | Pass | 95 |
| Prometon | 0.985 | 0.5 | 4.57 | -0.048 | 11.59 | 6.19 | Pass | Pass | 100 |
| Propachlor | 0.996 | 0.5 | 4.94 | 0.043 | 3.94 | 4.44 | Pass | Pass | 100 |
| Propamocarb | 0.998 | 0.5 | 2.87 | -0.756 | 4.83 | 5.16 | Pass | Pass | 98 |
| Propaquizafop | 0.999 | 0.5 | 7.85 | -0.939 | 5.29 | 4.83 | Pass | Pass | 97 |
| Propargite | 0.999 | 0.5 | 8.29 | -0.288 | 3.87 | 3.64 | Pass | Pass | 89 |
| Propazine | 0.999 | 0.5 | 5.51 | 0.262 | 1.92 | 1.95 | Pass | Pass | 100 |
| Propetamphos | 0.998 | 10.0 | 5.94 | 0.130 | 4.26 | 4.4 | Pass | Pass | 90 |
| Propiconazole | 0.998 | 0.5 | 6.99 | -1.080 | 4.53 | 6.81 | Pass | Pass | 98 |
| Propoxur | 0.998 | 10.0 | 4.12 | -0.061 | 3.87 | 3.71 | Pass | Pass | 98 |
| Propyzamide | 0.999 | 0.5 | 5.87 | 0.607 | 3.63 | 3.26 | Pass | Pass | 95 |
| Prosulfocarb | 0.999 | 0.5 | 7.59 | 0.616 | 2.15 | 2.01 | Pass | Pass | 100 |
| Prothioconazole | 0.998 | 10.0 | 6.95 | -1.289 | 4.39 | 4.27 | Pass | Pass | 85 |
| Pymetrozine | 0.999 | 0.5 | 2.84 | -1.480 | 7.8 | 9.1 | Pass | Pass | 91 |
| Pyracarbolid | 0.997 | 0.5 | 4.34 | -0.099 | 5.87 | 5.21 | Pass | Pass | 95 |
| Pyraclofos | 0.999 | 0.5 | 7.13 | 0.284 | 5.04 | 4.35 | Pass | Pass | 96 |
| Pyraclostrobin | 0.999 | 0.5 | 7.07 | -0.065 | 4.4 | 4.4 | Pass | Pass | 97 |
| Pyrazophos | 0.998 | 0.5 | 7.17 | 0.446 | 3.82 | 3.33 | Pass | Pass | 94 |
| Pyrazosulfuron ethyl | 0.999 | 0.5 | 6.16 | 0.117 | 4.8 | 4.61 | Pass | Pass | 89 |
| Pyrazoxyfen | 0.998 | 0.5 | 6.83 | -1.904 | 6.38 | 4.65 | Pass | Pass | 91 |
| Pyributicarb | 0.999 | 0.5 | 8.04 | 0.772 | 3.14 | 3 | Pass | Pass | 97 |
| Pyridaben | 1.000 | 0.5 | 8.84 | -0.314 | 4.7 | 4.68 | Pass | Pass | 98 |

Table 2. Name of compound, $r^2$, concentration LOQ, RT, Δppm, %RSD, FI, and Library Score

| Compound | R^2 | LOQ conc. (ppb) | Actual RT (min) | Δ *m/z* (ppm) | %RSD | % CV | LS | FI | Library score (%) |
|---|---|---|---|---|---|---|---|---|---|
| Pyridaphenthion | 0.999 | 0.5 | 6.01 | -0.387 | 2.59 | 2.43 | Pass | Pass | 96 |
| Pyridate | 0.999 | 1.0 | 9.23 | -0.495 | 4.83 | 6.63 | Pass | Pass | 94 |
| Pyrifenox | 0.998 | 0.5 | 6.17 | -0.078 | 11.62 | 18.29 | Pass | Pass | 96 |
| Pyriftalid | 0.999 | 0.5 | 5.43 | -0.552 | 3.21 | 3.43 | Pass | Pass | 93 |
| Pyrimethanil | 0.999 | 0.5 | 5.74 | 0.026 | 3.12 | 3.96 | Pass | Pass | 100 |
| Pyrimidifen | 0.999 | 0.5 | 8.03 | 0.148 | 1.18 | 1.38 | Pass | Pass | 98 |
| Pyriproxyfen | 0.999 | 0.5 | 8.10 | -0.289 | 2.35 | 2.33 | Pass | Pass | 96 |
| Pyroquilon | 0.951 | 0.5 | 4.45 | -0.268 | 4.48 | 5.12 | Pass | Pass | 94 |
| Pyroxsulam | 0.998 | 0.5 | 4.11 | 0.223 | 4.25 | 4.01 | Pass | Pass | 82 |
| Quinalphos | 1.000 | 0.5 | 6.76 | -0.337 | 2.25 | 2.11 | Pass | Pass | 90 |
| Quinoclamine | 0.919 | 1.0 | 4.23 | -0.313 | 10.58 | 6.12 | Pass | Pass | 92 |
| Quinoxyfen | 0.999 | 0.5 | 8.48 | -0.108 | 3.98 | 4.51 | Pass | Pass | 92 |
| Rabenzazole | 0.996 | 0.5 | 5.01 | -0.241 | 6.72 | 5.84 | Pass | Pass | 90 |
| Resmethrin | 0.999 | 0.5 | 8.98 | -0.194 | 4.85 | 4.62 | Pass | Pass | 78 |
| Rotenone | 0.998 | 0.5 | 6.46 | -0.501 | 3.59 | 2.95 | Pass | Pass | 95 |
| Saflufenacil | 0.997 | 10.0 | 5.23 | 0.176 | 5.96 | 5.65 | Pass | Pass | 84 |
| Schradan | 0.997 | 0.5 | 3.48 | 0.242 | 7.51 | 7.14 | Pass | Pass | 88 |
| Sebuthylazine | 0.999 | 0.5 | 5.51 | 0.262 | 1.92 | 1.95 | Pass | Pass | 95 |
| Secbumeton | 0.983 | 0.5 | 4.57 | -0.048 | 10.04 | 6.19 | Pass | Pass | 100 |
| Sethoxydim | 0.999 | 0.5 | 7.80 | -0.181 | 5.99 | 5.77 | Pass | Pass | 83 |
| Siduron | 0.998 | 0.5 | 5.57 | -1.240 | 5.59 | 4.68 | Pass | Pass | 97 |
| Simeconazole | 0.998 | 0.5 | 6.23 | 0.136 | 6.42 | 4.9 | Pass | Pass | 92 |
| Simetryn | 0.999 | 0.5 | 4.44 | -0.066 | 4.06 | 4.17 | Pass | Pass | 86 |
| Spinetoram 1 | 0.998 | 0.5 | 7.46 | -2.242 | 4.47 | 5.14 | Pass | Pass | 86 |
| Spirodiclofen | 0.999 | 0.5 | 8.54 | 0.116 | 4.46 | 4.63 | Pass | Pass | 96 |
| Spiroxamine | 0.999 | 0.5 | 5.65 | 0.369 | 7.2 | 7.03 | Pass | Pass | 99 |
| Sulcotrione | 0.991 | 100.0 | 3.85 | -1.374 | 12.84 | 13.25 | Pass | Pass | 100 |
| Sulfallate | 0.998 | 10.0 | 6.84 | -0.486 | 7.42 | 8.14 | Pass | Pass | 90 |
| Sulfentrazone | 0.998 | 10.0 | 4.25 | -0.589 | 7.83 | 5.19 | Pass | Pass | 92 |
| Sulfotep | 0.999 | 0.5 | 6.73 | -0.224 | 4.63 | 5.62 | Pass | Pass | 91 |
| Sulprofos | 0.999 | 0.5 | 8.29 | -0.263 | 10.57 | 7.61 | Pass | Pass | 84 |
| Tebuconazole | 0.997 | 0.5 | 6.78 | 0.050 | 14.74 | 4.34 | Pass | Pass | 100 |
| Tebupirimfos | 0.999 | 0.5 | 7.88 | -0.055 | 5.43 | 6.21 | Pass | Pass | 92 |
| Tebutam | 0.999 | 0.5 | 6.36 | 0.138 | 2.04 | 2.2 | Pass | Pass | 99 |
| Tebuthiuron | 0.999 | 0.5 | 4.30 | 1.578 | 7.39 | 7.33 | Pass | Pass | 92 |
| Temephos | 0.999 | 10.0 | 7.99 | -0.568 | 5.85 | 5.93 | Pass | Pass | 90 |
| TEPP | 0.997 | 0.5 | 3.85 | 0.992 | 11.4 | 12.47 | Pass | Pass | 76 |
| Tepraloxydim | 0.998 | 0.5 | 6.15 | 0.468 | 5.76 | 4.25 | Pass | Pass | 82 |
| Terbucarb | 1.000 | 0.5 | 7.37 | -1.768 | 7.57 | 7.63 | Pass | Pass | 99 |
| Terbufos | 0.998 | 10.0 | 7.85 | 3.632 | 11.12 | 11.83 | Pass | Pass | 87 |
| Terbufos_M-C4H7 | 0.997 | 10.0 | 7.85 | 0.590 | 6.56 | 6.83 | Pass | Pass | 84 |
| Terbufos-sulfone | 0.999 | 0.5 | 5.39 | 0.188 | 7.66 | 8.78 | Pass | Pass | 81 |
| Terbumeton | 0.990 | 1.0 | 4.57 | 0.492 | 4.85 | 3.02 | Pass | Pass | 100 |
| Terbuthylazine | 0.997 | 0.5 | 5.70 | -0.070 | 3.35 | 3.03 | Pass | Pass | 100 |

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**Table 2. Name of compound, $r^2$, concentration LOQ, RT, Δppm, %RSD, FI, and Library Score**

| Compound | R^2 | LOQ conc. (ppb) | Actual RT (min) | Δ *m/z* (ppm) | %RSD | % CV | LS | FI | Library score (%) |
|---|---|---|---|---|---|---|---|---|---|
| Terbutryn | 0.997 | 1.0 | 5.79 | 0.176 | 2.87 | 2.94 | Pass | Pass | 100 |
| Tetrachlorvinphos | 0.999 | 0.5 | 6.56 | -0.015 | 4.94 | 4.48 | Pass | Pass | 91 |
| Tetraconazole | 0.998 | 0.5 | 6.28 | -0.168 | 8.89 | 6.81 | Pass | Pass | 93 |
| Tetramethrin | 0.997 | 0.5 | 7.76 | 0.117 | 6.07 | 4.34 | Pass | Pass | 91 |
| Thenylchlor | 0.999 | 0.5 | 6.22 | -0.503 | 3.81 | 4.4 | Pass | Pass | 86 |
| Thiabendazole | 0.999 | 0.5 | 3.45 | -0.101 | 7.15 | 7.59 | Pass | Pass | 96 |
| Thiacloprid | 0.999 | 0.5 | 3.63 | 0.762 | 8.4 | 7.76 | Pass | Pass | 93 |
| Thiazopyr | 0.999 | 0.5 | 6.71 | 0.313 | 4.9 | 5.51 | Pass | Pass | 99 |
| Thifensulfuron-methyl | 0.999 | 0.5 | 4.05 | -0.958 | 11.81 | 12.08 | Pass | Pass | 87 |
| Thiobencarb | 0.999 | 10.0 | 7.15 | 0.318 | 3.7 | 3.77 | Pass | Pass | 86 |
| Thiodicarb | 0.999 | 0.5 | 4.64 | -1.075 | 5.18 | 5.57 | Pass | Pass | 83 |
| Thiofanox sulfoxide | 0.999 | 10.0 | 3.27 | -0.155 | 3.38 | 3.38 | Pass | Pass | 86 |
| Thiophanate-methyl | 0.998 | 0.5 | 4.07 | 1.327 | 5.97 | 6.04 | Pass | Pass | 84 |
| Tolylfluanid | 0.997 | 10.0 | 6.71 | -0.177 | 5.4 | 5.46 | Pass | Pass | 93 |
| Triadimefon | 0.999 | 0.5 | 5.89 | 0.597 | 2.67 | 2.45 | Pass | Pass | 88 |
| Triadimenol | 0.997 | 1.0 | 6.09 | -0.317 | 3.62 | 3.44 | Pass | Pass | 95 |
| Triallate | 0.996 | 10.0 | 8.22 | 0.014 | 6.01 | 6.89 | Pass | Pass | 86 |
| Triazamate | 0.999 | 0.5 | 6.06 | 0.062 | 3.25 | 3.81 | Pass | Pass | 87 |
| Triazophos | 0.998 | 0.5 | 6.12 | 0.246 | 3.26 | 3.44 | Pass | Pass | 94 |
| Tributyl phosphate | 0.999 | 1.0 | 7.49 | 0.216 | 4.17 | 2.49 | Pass | Pass | 89 |
| Tricyclazole | 0.999 | 0.5 | 3.98 | 0.375 | 7.55 | 8.02 | Pass | Pass | 95 |
| Trietazine | 0.998 | 0.5 | 6.25 | 0.063 | 3.97 | 4.97 | Pass | Pass | 100 |
| Trifloxystrobin | 0.999 | 0.5 | 7.37 | -0.316 | 4.79 | 4.55 | Pass | Pass | 96 |
| Triflumizole | 0.999 | 0.5 | 7.62 | -0.221 | 2.96 | 3.76 | Pass | Pass | 93 |
| Triflumuron | 0.991 | 0.5 | 7.13 | 0.132 | 9.29 | 3.75 | Pass | Pass | 98 |
| Tri-Isobutyl phosphate | 0.999 | 1.0 | 7.49 | 0.216 | 4.11 | 2.49 | Pass | Pass | 92 |
| Trinexapac-ethyl | 0.993 | 10.0 | 5.08 | -0.460 | 8.6 | 8.43 | Pass | Pass | 99 |
| Uniconazole | 0.996 | 0.5 | 6.50 | 0.641 | 4.95 | 2.86 | Pass | Pass | 92 |
| Vamidothion | 0.998 | 0.5 | 3.37 | 0.131 | 2.4 | 2.39 | Pass | Pass | 86 |
| Vernolate | 0.999 | 0.5 | 7.27 | 0.536 | 6.46 | 7.28 | Pass | Pass | 92 |
| Warfarin | 0.996 | 0.5 | 5.66 | 0.039 | 6.52 | 4.24 | Pass | Pass | 97 |
| Zinophos | 0.999 | 0.5 | 4.96 | -0.181 | 8.93 | 9.84 | Pass | Pass | 86 |
| Zoxamide | 0.998 | 0.5 | 6.91 | -0.146 | 8.04 | 5.92 | Pass | Pass | 83 |