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LC–MS/MS DETERMINATION OF INSECTICIDE RESIDUES IN PEAR FRUITS ASSOCIATED WITH CACOPSYLLA PYRI MANAGEMENT

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Abstract. *Pear psyllid, Cacopsylla pyri (L.), is a major constraint to pear production in Europe, including Serbia, because feeding on fruits and honeydew contamination reduce its quality and complicate crop protection. Chemical control therefore needs to be accompanied by reliable residue monitoring and measures that conserve natural enemies. This study describes a QuEChERS-based liquid chromatography–tandem mass spectrometry (LC–MS/MS) workflow for determining spirodiclofen, spirotetramat, spinetoram, deltamethrin, diflubenzuron, abamectin, and chlorantraniliprole in pear fruits. Sample preparation involved a 10 g test portion, internal-standard addition, extraction with 10 mL acetonitrile, salt-assisted partitioning, and dispersive solid-phase extraction. The reported instrumental procedure used electrospray ionization and multiple reaction monitoring, with matrix-matched calibration. According to the experimental summary, recoveries for the investigated pesticides were within 70–120%, coefficients of determination exceeded 0.99, and the limit of quantification was 0.01 mg/kg. The comparative chromatogram shows a fortified sample and four pear extracts with a prominent shared signal and fewer conspicuous secondary signals in the fruit extracts. These observations support a qualitative comparison of chromatographic profiles but do not establish pesticide identities or concentrations without transition-specific data. The experimental summary reports residues below the maximum residue limits applied in the original assessment; independent verification requires the individual concentrations and the applicable residue definitions and limits. The findings support the use of residue analysis alongside integrated pear psyllid management, while emphasizing the distinction between analytical performance, regulatory compliance, and dietary risk assessment.*

Keywords*: pear psyllid; pesticide residues; QuEChERS; LC–MS/MS; matrix-matched calibration; integrated pest management*

INTRODUCTION

The common pear psyllid, *Cacopsylla pyri* (L.) (Hemiptera: *Psyllidae*), is among the most important arthropod pests of European pear orchards. Its economic significance reflects both direct feeding and indirect contamination of fruit. Sap removal and feeding-associated injury can weaken shoots, whereas honeydew favors sooty mold development and reduces the marketability of otherwise harvestable fruit. Pear psyllids also include vectors of the pear-decline phytoplasma, adding a plant-health dimension to population management (CIVOLANI et al., 2023a). The practical objective is consequently to protect marketable yield while avoiding unnecessary pesticide applications.

The pest is particularly relevant to intensive pear production in Serbia and neighboring countries. Across the Western Balkans, chemical control remains important, although the potential of indigenous predators and parasitoids is incompletely exploited (KRNDIJA et al., 2024). Damage varies with infestation timing, orchard management, cultivar, and the effectiveness of natural regulation. Preventive management should begin with orchard monitoring and practices that limit favorable conditions for population growth. Balanced fertilization, canopy management, and preservation of suitable surrounding vegetation can form part of a broader strategy, together with selective interventions timed to susceptible pest

stages. A whole-ecosystem approach considers pest suppression, natural enemies, and crop development jointly (REEVES et al., 2024a). Recent modeling further indicates that pear flowering, psyllid generations, and earwig activity can shift at different rates under warming. Treatment timing therefore needs to follow observed phenology rather than a fixed calendar (REEVES et al., 2025).

Physical and mineral-based interventions offer options for reducing reliance on conventional insecticides. In a Croatian field study, an integrated insecticide program provided 84–95% efficacy, whereas processed kaolin achieved 37–71%, with substantial variation between years (TOMAŠ et al., 2022). In northern Italy, potassium bicarbonate treatments reduced juvenile *C. pyri* populations, reaching mortality of up to 89% at the infestation peak, although spirotetramat remained more effective (CIVOLANI et al., 2023b). In Serbia, researchers have been evaluated spirodiclofen, spirotetramat, and carboxymethyl cellulose-B against C. pyri, documenting the continuing need to assess control options under local conditions (NAĐ AND MARINKOVIĆ, 2022). These findings support context-specific integration of alternative measures; they do not establish equivalent performance across orchards or authorize their use outside locally approved conditions.

Biological control is supported by predatory bugs, earwigs, lacewings, ladybirds, and parasitoids. Regional records include *Anthocoris nemoralis*, *Trechnites insidiosus*, and *Prionomitus mitratus* (KRNDIJA et al., 2024). Laboratory experiments showed a type II functional response of *A. nemoralis* to *C. pyri* and no significant overall change in prey consumption across the tested temperatures (REEVES et al., 2023). Experiments with *A. nemoralis* and *Forficula auricularia* also showed that interactions between natural enemies depend on prey availability and spatial separation (REEVES ET AL., 2024b). Preserving these organisms requires attention to pesticide selectivity: aged spinetoram, spinosad, and indoxacarb residues affected earwig survival or behavior in experimental assessments (NIEDOBOVÁ ET AL., 2024).

Residue monitoring addresses a separate outcome of crop protection: the chemical composition of harvested fruit. A Serbian-market survey analyzed 2,164 samples of 46 fruit species and reported residues at or above 0.01 mg/kg in 62.57% of samples; 4.67% exceeded the Serbian MRLs used in that assessment. For pears, exceedances were reported in six of 95 samples (KECOJEVIĆ et al., 2025). These figures concern a market-monitoring population and cannot be transferred directly to an individual orchard trial. Nevertheless, they illustrate why visual fruit quality and successful pest control do not replace chemical analysis.

Pears contain co-extractives that can influence extraction selectivity and mass-spectrometric response. QuEChERS extraction and appropriate cleanup provide a practical basis for multiresidue determination, but the method must be validated for the matrix and target analytes (ZHANG et al., 2025). The present study aimed to describe the supplied LC–MS/MS workflow, summarize its reported validation characteristics, examine the comparative chromatographic profiles of four pear extracts, and discuss the residue findings in relation to contemporary *C. pyri* management. Pest-control efficacy and residue dissipation were not measured by the chromatographic comparison itself.

MATERIAL AND METHODS

Study material and analytical scope

Pear fruits originated from the crop-protection study described in the accompanying experimental summary as following Good Agricultural Practice (GAP). The analytical panel comprised spirodiclofen, spirotetramat, spinetoram, deltamethrin, diflubenzuron, abamectin,

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and chlorantraniliprole. Four pear-extract traces were supplied, labeled Kruska-1.d, Kruska-2.d, Kruska-3.d, and Kruska-4.d. They were assessed alongside the trace 15753-sp2.d, identified in the accompanying material as a fortified sample. These identifiers were retained as sample labels; they were not treated as evidence of four independent field replicates or four distinct insecticide treatments.

Sample preparation

A 10 g pear test portion was supplemented with an internal standard (IS), followed by addition of 10 mL acetonitrile (ACN). QuEChERS extraction salts were added, and the sample was centrifuged for 5 min at 4,000 rpm. A 6 mL aliquot of the resulting extract was subjected to dispersive solid-phase extraction (dSPE). Cleanup used primary–secondary amine (PSA), magnesium sulfate ($MgSO_4$), and C18 sorbent, as specified in the supplied scheme. After a second centrifugation for 5 min at 4,000 rpm, 2 mL of the cleaned extract was transferred into an analytical vial. This sequence preserves the quantities and centrifugation conditions shown in the experimental workflow.

Chromatographic determination and quality control

Separation, detection, and quantification were performed by LC–MS/MS. The experimental description states that positive electrospray ionization (ESI) and multiple reaction monitoring (MRM) were used. Quantification relied on matrix-matched calibration with an internal standard. The supplied chromatographic export is labeled "+/−ESI TIC MRM"; this label is retained in Figure 1 and requires confirmation against the acquisition method. The abbreviation MRM denotes multiple reaction monitoring, rather than "multiresidue reaction monitoring."

Validation was reported to follow SANTE/11312/2021. The available summary provides recovery limits, coefficients of determination (R^2), and the limit of quantification (LOQ). These metrics were transcribed without reconstructing unreported calibration levels, replicate numbers, precision values, or measurement uncertainty. The relevant guidance distinguishes satisfactory recovery and precision from instrumental identification and calibration requirements (European Commission, 2021). The version actually used for the experiment must be specified; the current version is SANTE/11312/2021 v2026 (European Commission, 2025). A later revision cannot be retrospectively described as the protocol used in an earlier experiment.

Data interpretation

Chromatograms were compared descriptively using the displayed acquisition-time axis (approximately 0–16.5 min) and count scales. Approximate signal positions and heights were read visually; they are not substitutes for instrument-exported retention times or integrated peak areas. Concentrations and statistical differences were not calculated because transition-specific integration and calibration results were unavailable. The statement that detections were below MRLs was treated as a reported outcome of the original analysis. Independent compliance assessment requires concentrations in mg/kg, the relevant commodity and residue definition, and the applicable jurisdiction and date. The EU database provides substance- and commodity-specific information for such checks (European Commission, 2026).

RESULTS AND DISCUSSIONS

Reported analytical performance

The experimental summary reports recoveries of 70–120%, $R^2 > 0.99$, and an LOQ of 0.01 mg/kg for all seven investigated pesticides (Table 1). These results indicate reported quantification capability at 10 µg/kg and recoveries within the stated validation interval. However, the interval is an aggregate summary: it does not reveal the recovery of an individual pesticide at each fortification level. Similarly, R^2 alone does not describe calibration residuals, low-level bias, or the adequacy of the selected calibration model. Precision, blank response, confirmation-ion behavior, and measurement uncertainty remain necessary for a complete performance assessment.

Table 1

Analytical performance reported in the supplied experimental summary

Parameter	Reported result	Scope of interpretation
Target panel	Seven insecticides	Spirodiclofen, spirotetramat, spinetoram, deltamethrin, diflubenzuron, abamectin, chlorantraniliprole
Recovery	70–120%	Summary range; individual validation results were not supplied
Calibration	$R^2 > 0.99$	Matrix-matched calibration with IS; range not supplied
LOQ	0.01 mg/kg	Reported for each target pesticide
Residue compliance	Below MRLs	Original study statement; numerical concentrations and reference MRLs not supplied

The workflow is analytically plausible for a multiresidue panel in a fruit matrix. Partitioning into acetonitrile and subsequent cleanup reduce the material entering the LC–MS/MS system, while matrix-matched standards help compensate for matrix-associated response differences. They do not, by themselves, demonstrate complete removal of co-extractives or equal compensation for every pesticide. The pear-focused review by ZHANG et al. (2025) emphasizes the dependence of method performance on extraction and detection conditions. In the present dataset, the reported recoveries support the extraction approach, but additional validation records are needed to evaluate repeatability and the effectiveness of the selected internal standard across the whole panel.

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Interpretation of the comparative chromatograms

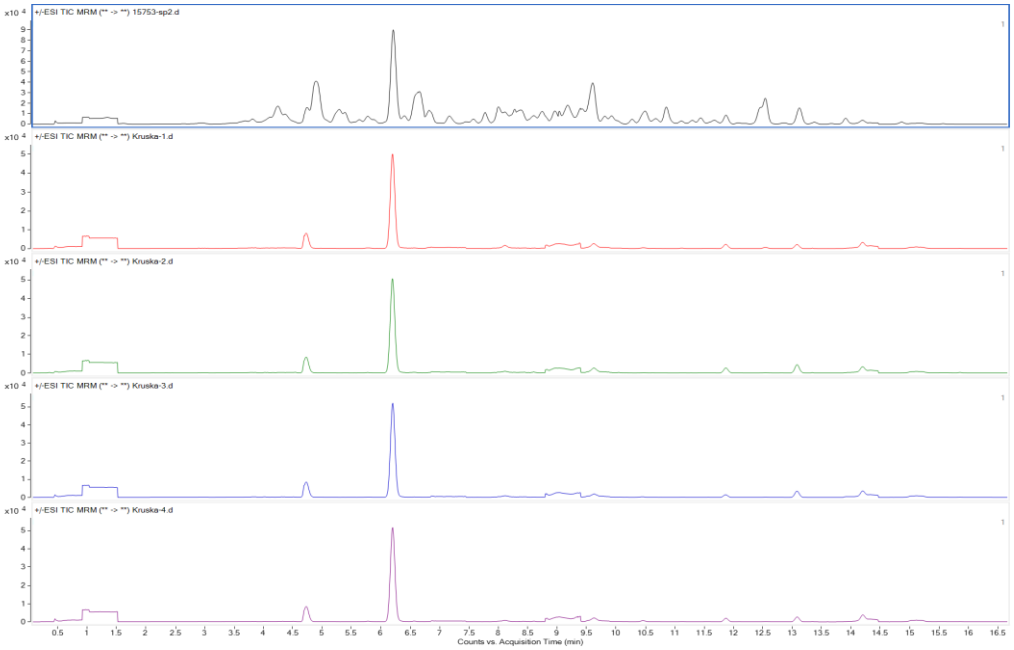


Figure 1. Supplied comparative TIC–MRM chromatograms. Top: fortified sample 15753-sp2.d. Below: pear extracts Kruska-1.d to Kruska-4.d, respectively. The horizontal axis shows acquisition time in minutes; vertical scales show counts × 10^4. Peak labels do not identify individual pesticides

The fortified extract displays several conspicuous signals distributed across the chromatographic profile, whereas the four pear extracts display a simpler pattern dominated by a narrow signal at approximately 6.2 min. A smaller preceding signal at approximately 4.7 min and several weak later signals are also visible in the pear extracts. The dominant peak is approximately 9 × 10^4 counts in the fortified extract and approximately 5 × 10^4 counts in the four pear extracts. These are visual estimates of signal height, not calculated residue concentrations. The common dominant feature indicates a signal shared by the displayed runs. Its identity cannot be established from a total-ion representation: it could correspond to a target compound, the internal standard, or another monitored contribution. Assignment requires the relevant precursor/product-ion transitions and comparison with reference standards.

The similarity of the four displayed profiles is consistent with comparable chromatographic behavior, but does not demonstrate equal residue concentrations. The fortified and pear-extract panels use different vertical ranges, although both are labeled in counts × 10^4. Peak height is not a substitute for integrated response relative to the internal standard. The number of visible peaks also cannot be equated with the number of pesticides detected: individual compounds may contribute multiple transitions, peaks may overlap, and weak responses may not be apparent at the displayed scale. Consequently, neither the presence of all seven pesticides nor their absence can be concluded from this figure alone.

A defensible confirmation would compare analyte-specific traces in the fortified matrix, procedural blank, and each sample, using the laboratory's retention-time and ion-ratio criteria. The existing figure is useful as an overview of the chromatographic profiles. It cannot

establish baseline separation for all analytes, quantify matrix effects, or prove acceptable recovery. These are separate questions requiring transition-level data and validation experiments. The qualitative interpretation therefore complements the reported method-performance summary without replacing the underlying analytical measurements.

Residue findings in the context of pear production

According to the experimental summary, all detected residues were below the MRLs used in the original assessment. This is encouraging for the sampled fruit, but the absence of numerical concentrations prevents comparison of residue burdens among samples or calculation of concentration-to-MRL ratios. It also prevents evaluation of how close individual results were to a legal threshold. The four chromatograms do not indicate the detection frequency of individual pesticides across a defined sampling population. For publication, a sample-by-analyte table should distinguish quantified residues from results below the LOQ and from analytes not included in a particular determination.

Residue decline cannot be inferred from the labels 1–4 because no sampling chronology is provided. Repeated measurements over known intervals after treatment are needed to estimate dissipation and determine how application-to-harvest timing influences residues. The three-year pear study of SCHUSTEROVA et al. (2024) provides a directly relevant longitudinal comparison, whereas the present chromatograms represent an endpoint-style analytical illustration. Field conditions and application history must be documented before differences between independent studies can be interpreted as evidence of faster degradation or superior residue management.

The sampled fruit fraction is another important source of variation. Under identical phytosanitary treatments and growing conditions, BARROS et al. (2026) found that pesticide distribution differed among pear tissues and compounds. Peel was the principal residue reservoir in most cultivars, while some compounds were also detected in seeds. This evidence reinforces the need to state whether the analytical portion was whole fruit, peeled fruit, pulp, or another defined fraction. The present 10 g extraction portion describes laboratory subsampling but does not resolve which fruit tissues entered the homogenate.

MRL compliance and dietary safety should be discussed separately. An MRL is a regulatory residue limit, whereas dietary risk assessment incorporates residue concentration, food consumption, body weight, and toxicological reference values. CHMIELEWSKI et al. (2026) used monitoring and consumption data to calculate chronic exposure in adults and children, illustrating the additional information required beyond a chromatographic result. Their findings cannot establish the risk associated with the present samples. Without individual concentrations and an exposure assessment, the current results should not be described as proof of unrestricted health safety or absence of cumulative risk.

Residue definitions also matter when an active substance has relevant metabolites, isomers, or component compounds. An analytical result for a parent substance may not represent the complete regulated residue. The applicable definitions for spirotetramat, spinetoram, abamectin, and the other targets must therefore be checked against the method scope and the legislation used for the original comparison (European Commission, 2026). No numerical MRL has been inserted here because the experimental year, destination market, and exact analyte coverage were not supplied. Historical use in this study should likewise not be interpreted as a statement of current product authorization.

Implications for integrated pear psyllid management

The agronomic value of residue testing is greatest when laboratory results can be linked to a documented protection program. A dataset that combines pest-stage counts, treatment records, harvest timing, and residue concentrations can help evaluate whether acceptable crop protection was obtained with proportionate chemical inputs. The present analysis addresses the residue component; it does not establish which treatment was most effective against *C. pyri* or which management program minimized residues. Biological control, selective chemistry, and preventive measures remain complementary approaches, but their success requires orchard-level evidence.

The reported analytical sensitivity provides a practical basis for this combined evaluation. Once the missing laboratory and field records are added, the same workflow could support comparison of monitored protection programs without changing the original experiment. Future sampling should preserve the distinction between biological field replication and repeated laboratory analysis. This would allow uncertainty in fruit residues to be evaluated at the appropriate level and prevent visual similarity among chromatograms from being mistaken for statistical equivalence among treatments.

CONCLUSIONS

The supplied QuEChERS–LC–MS/MS workflow was reported to determine seven insecticides in pears with recoveries of 70–120%, $R^2 > 0.99$, and an LOQ of 0.01 mg/kg. The comparative chromatograms show similar overall profiles in four pear extracts, but do not independently identify or quantify individual residues. Reported concentrations below the applied MRLs are consistent with a favorable residue outcome for the sampled fruit; confirmation requires the individual results and applicable residue definitions. Integrating validated residue measurements with documented *C. pyri* management can strengthen evaluation of pear-protection programs. Complete field and analytical records are required before this draft can support a reproducible compliance assessment.

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