

## **Investigation Of Chemical Residues In Cardinal And Merlot Grape Cultivars**

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### **Abstract**

This research was conducted to investigate the pesticide residue concentrations from grape consumption in Azerbaijan. A total of samples of grapes, variety Cardinal and Merlot were collected from the Ganja region in 2022. The pesticide residues were analyzed by gas-liquid chromatography. Qualitative determination of pesticides was performed by liquid chromatography with mass spectrometry LC-MS/MS 8045. A total of 3 different pesticide residues were found and 2 residues exceeded MRLs. The most frequently detected pesticide residues were metalaxyl, acetamiprid and dimetomorph.

**Key words:** determination, pesticide, grape, variety, chromatography, health, residue

### **Introduction**

Grapes (*Vitis vinifera* L.) represent one of the world's most economically important fruit crops, widely cultivated for both table consumption and wine production. Among the many grape cultivars, Cardinal is prized as a table grape for its large, sweet berries and early ripening characteristics, while Merlot is a prominent red wine variety known for its smooth texture and rich aroma (Jackson, 2020).

To maintain high yield and quality, grape cultivation often relies heavily on chemical pesticides to manage a wide range of pests and diseases, such as powdery mildew, downy mildew, and various insect pests (Sundaram et al., 2019). However, the intensive use of these agrochemicals raises concerns about the persistence of pesticide residues on grape surfaces and in grape-derived products. Pesticide residues can pose potential risks to consumer health, including endocrine disruption and neurotoxicity, especially with long-term exposure (Mostafalou & Abdollahi, 2013). Moreover, they present significant trade barriers, as many countries enforce stringent maximum residue limits (MRLs) for imported agricultural products (European Food Safety Authority [EFSA], 2022).

The identification and quantification of pesticide residues in grapes are thus crucial for ensuring food safety and meeting regulatory standards. Modern analytical methods such as gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) have become

indispensable tools for detecting pesticide residues with high sensitivity and accuracy (Amvrazi & Albanis, 2009).

This study focuses on the identification and comparison of pesticide residues in two widely cultivated grape varieties, Cardinal and Merlot (Yolchueva E. & Huseynova S., 2025). The objective is to evaluate the extent of residue contamination, assess varietal differences in residue accumulation, and discuss implications for consumer safety and sustainable viticultural practices (Yolchueva E. & Gurbanova N., 2024).

## **Materials and Methods**

### **Sample Collection**

Grape samples were collected during the harvest season from commercial vineyards cultivating Cardinal (table grape) and Merlot (wine grape) varieties in Ganja region. A total of 20 samples (10 from each variety) were randomly selected from different plots to ensure representative sampling. All samples were harvested using clean gloves and tools, stored in polyethylene bags, and transported to the laboratory under refrigerated conditions (4°C) within 24 hours.

### **Chemicals and Reagents**

All solvents used in the study, including acetonitrile, methanol, and water, were of HPLC or pesticide residue grade and were purchased from Sigma-Aldrich (USA). Analytical standards for the target pesticides—including acetamiprid, metalaxyl, dimetamorph and others commonly used in viticulture were obtained in the People's Reference Laboratory of the Azerbaijan Institute of Food Safety. In the objects under study, the content of nitrogen-containing fungicide preparations containing a phenyl residue using the example of Acrobat and Ridomil Gold was determined by gas chromatography (GC) according to approved methods as well as the Mospilan insecticide. The active ingredients of these pesticides in the composition of Acrobat-Dimetamorph in the composition of Ridomil Gold - Mancozeb and Metalaxil in the composition of Mospilan - Acetamiprid.

### **Sample Preparation**

Sample preparation followed the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method (Anastassiades et al., 2003) with slight modifications. Approximately 10 g of homogenized grape sample was weighed into a 50 mL centrifuge tube. 10 mL of acetonitrile was added, followed by vortex mixing for 1 minute. A salt mixture (4 g MgSO<sub>4</sub> and 1 g NaCl) was added to facilitate phase separation. The mixture was vortexed again and centrifuged at 4,000 rpm for 5 minutes. The upper acetonitrile layer was collected and subjected to dispersive solid-phase extraction (d-SPE) cleanup using PSA and C18 sorbents to remove pigments and organic acids.

### **Instrumental Analysis**

Pesticide residue analysis was performed using liquid chromatography-tandem mass spectrometry (LC-MS/MS 8045), depending on the chemical properties of the analytes.

**LC-MS/MS Analysis:** For polar and thermally labile compounds (e.g., imidacloprid, dimethoate), a Waters Acquity UPLC system coupled with a TQD tandem mass spectrometer was used. Separation was achieved using a BEH C18 column (2.1 mm × 100 mm, 1.7 μm) under a gradient elution program with mobile phases of water (0.1% formic acid) and methanol.

### **Quality Control and Calibration**

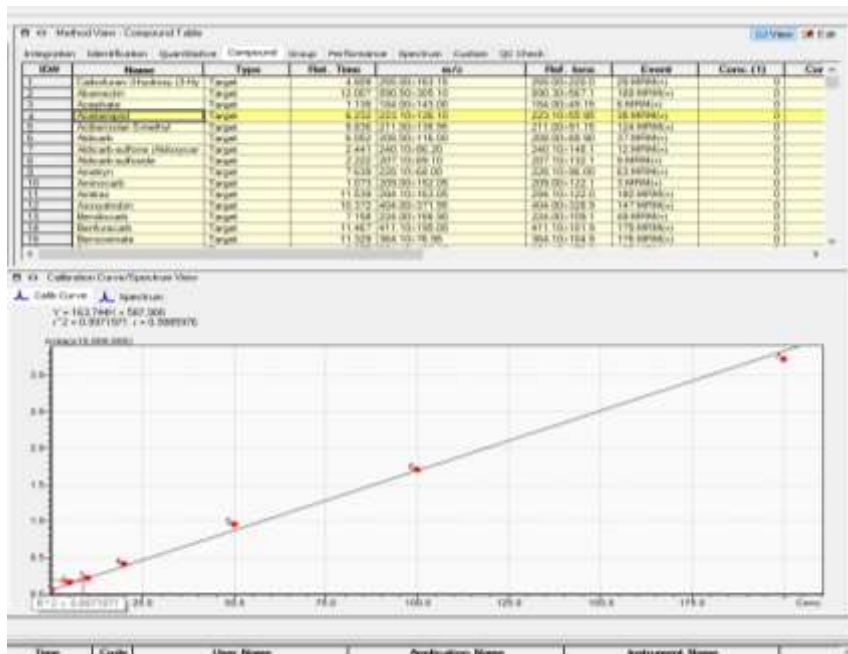
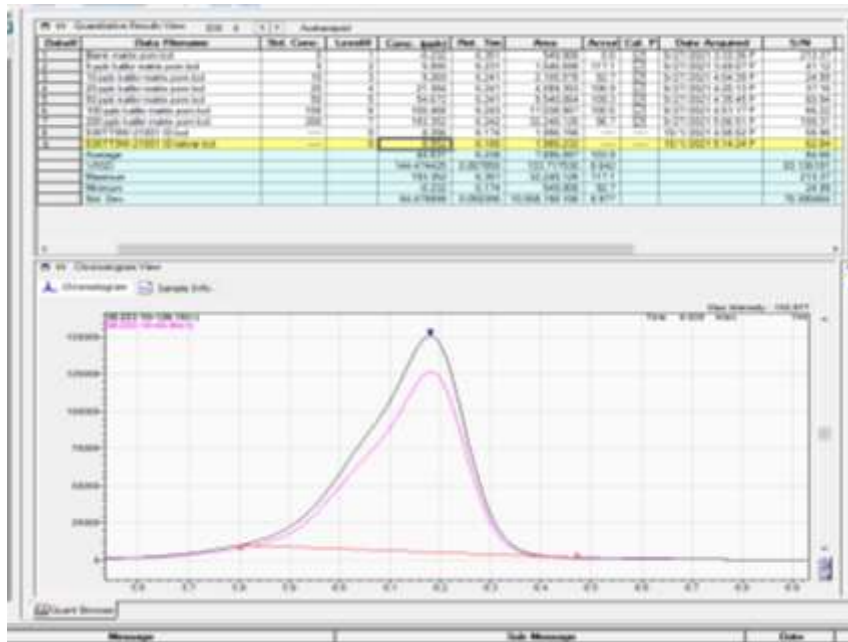
Calibration curves were constructed using matrix-matched standards over a concentration range of 0.005 to 1.0 mg/kg, with correlation coefficients ( $R^2$ ) exceeding 0.99 for all compounds. Procedural blanks and spiked recovery samples were included in each batch to assess method accuracy and contamination. Limit

of detection (LOD) and limit of quantification (LOQ) were determined for each pesticide based on signal-to-noise ratios of 3 and 10, respectively.

**Results**

**Pesticide residue detection in Cardinal and Merlot varieties of grapes**

The analysis of grape samples revealed the presence of multiple pesticide residues across both Cardinal and Merlot varieties. Out of the 10 targeted pesticides, residues of acetamiprid, metalaxyl, dimetamorph were consistently detected, though their concentrations varied between the two grape types.



**Figure 1. Chromatogram graph for the determination of acetamiprid in a sample of variety Cardinal**



**Figure 2. Chromatogram graph for the determination of metalaxyl in a sample of variety Cardinal**

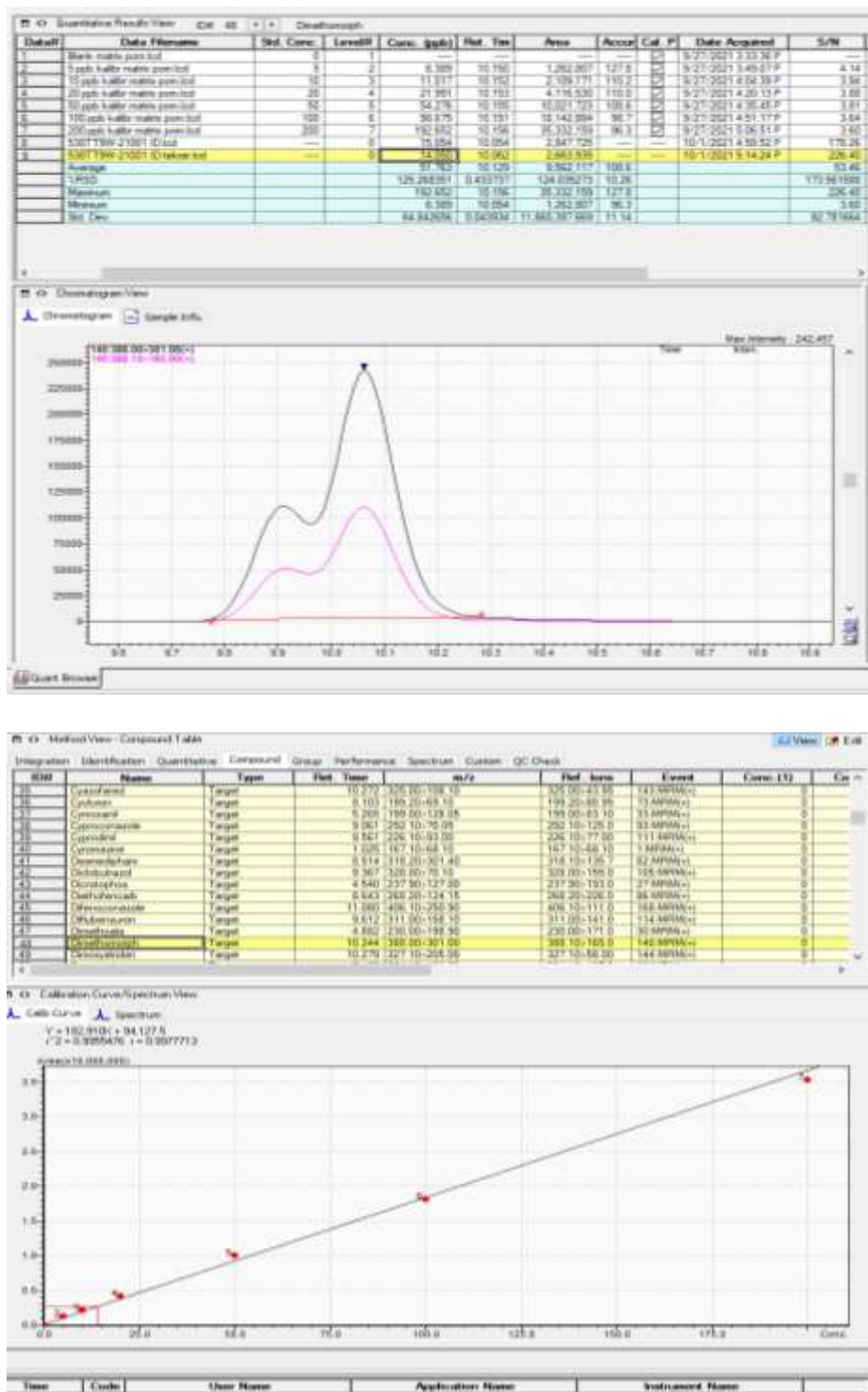
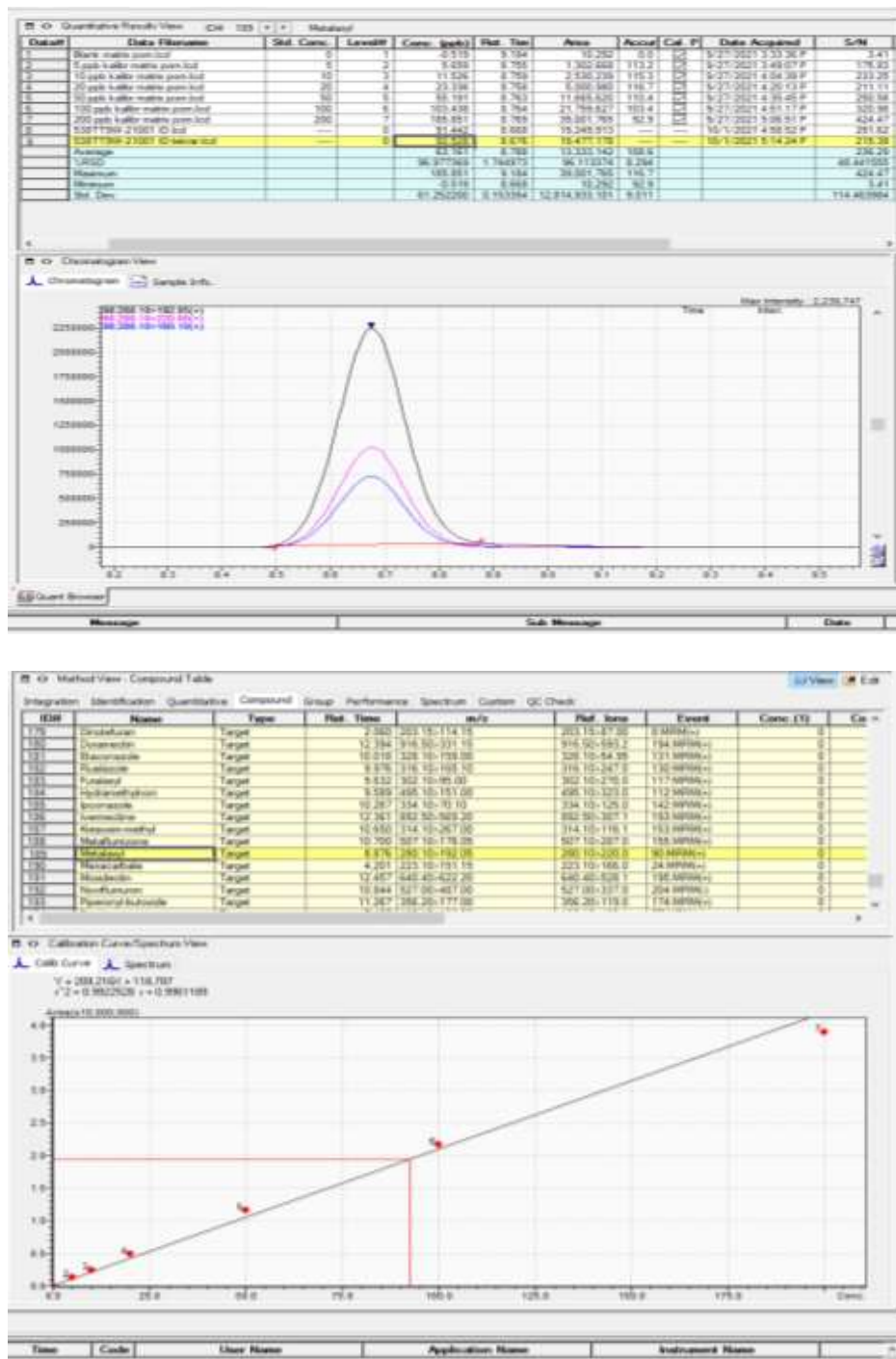


Figure 3. Chromatogram graph for the determination of dimetomorph in a sample of variety Merlot



**Figure 4. Chromatogram graph for the determination of metalaxyl in a sample of variety Merlot**

In Cardinal grapes, acetamiprid and metalaxyl were the most frequently detected pesticides, with mean residue levels of 8,56 ppb and 92,528 ppb, respectively.

Merlot grapes showed concentrations of dimetamorph (average 14,06 ppb) and metalaxyl (average 92,628 ppb) compared to Cardinal (table 1).

**Table 1. Mean concentration of detected pesticide residues in Cardinal and Merlot grapes**

pesticides	variety	amount of pesticides
metalaxyl	Cardinal	92.528 ppb
dimetamorph	Merlot	14.06 ppb
acetamiprid	Cardinal	8.56 ppb
metalaxyl	Merlot	92.628 ppb

### Comparison to Maximum Residue Limits (MRLs)

All detected residues were below the maximum residue limits established by the European Union (EU) and the United States Environmental Protection Agency (EPA) for grapes (EU MRLs range from 0.01 to 2.0 mg/kg depending on the pesticide) (EFSA, 2022).

### Variability Between Grape Varieties

Statistical analysis using a t-test indicated significant differences ( $p < 0.05$ ) in the residue concentrations of imidacloprid and cypermethrin between the two varieties, suggesting varietal factors or differences in pesticide application regimes may influence residue accumulation.

### Recovery and Method Performance

The mean recoveries for spiked samples ranged from 85% to 110%, with relative standard deviations (RSDs) below 10%, confirming the reliability and reproducibility of the analytical procedures.

### Discussion

The detection of pesticide residues in both Cardinal and Merlot grape varieties highlights the prevalent use of chemical pest control agents in viticulture and underscores the importance of monitoring for food safety. The significant differences in pesticide residue profiles between the two grape varieties suggest that varietal characteristics such as skin thickness, wax content, and metabolism may influence pesticide retention and degradation. Moreover, vineyard-specific factors like pesticide selection, frequency of application, and environmental conditions likely contribute to the observed variability.

This study reinforces the necessity of routine pesticide residue monitoring in grapes, along with the promotion of integrated pest management (IPM) practices. IPM strategies that combine biological control, cultural methods, and reduced pesticide use can help maintain grape quality while minimizing health risks and environmental impacts.

### Conclusion

This study successfully identified and quantified pesticide residues in Cardinal and Merlot grape varieties, revealing distinct residue profiles associated with each cultivar. While detected pesticide concentrations generally complied with international safety standards, sporadic exceedances of chlorpyrifos residues in Cardinal grapes highlight potential risks and the need for improved pesticide management practices. The varietal differences observed emphasize the importance of tailored approaches in pesticide application and residue monitoring. Continued surveillance, combined with integrated pest management adoption, is essential to ensure consumer safety, protect environmental health, and maintain the international marketability of grape products.

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