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Detection of pesticide residues from the local grapes variety madrasa and tabrizi

Yolchuyeva E A, Nasibova G R, Gurbanova N T, Valiyeva L T, Rustamova A A
Department of Chemistry, Azerbaijan State Agricultural University, Ganja, Azerbaijan

Abstract
This study was conducted to investigate the pesticide residue concentrations from grape consumption in Arebaijan. A total of samples of grapes variety Madrasa and Tabriziwere collected from the Shamkir area in 2020. The pesticide residues were analyzed by gas-liquid chromatography. 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.

Keywords: Pesticide, grape, detection, analysis, pesticide, residue

Introduction

Pesticides are essential tools to increase agricultural productivity and cultivation convenience. However, pesticides inevitably remain in agricultural products and soil [1]. Excessive use of pesticides causes these chemicals and metabolites to remain in the environment and food, causing serious problems in the ecosystem and public health [2]. Chronic human exposure to unsafe levels of pesticides can cause a wide range of diseases affecting human health. Pesticides have potential adverse effects on human health such as carcinogenesis, immunotoxicity, birth defects, genetic changes, neurological toxicity and endocrine disruption. Fruits and vegetables are usually consumed directly without processing after washing, so they are the main cause of pesticide residue ingestion in humans [3]. Samples for analyse are grapes variety Madrasa and Tabrizi were collected from the Shamkir area. Grapes may contain toxic residual pesticides due to the use of pesticides during the production process of agricultural products.

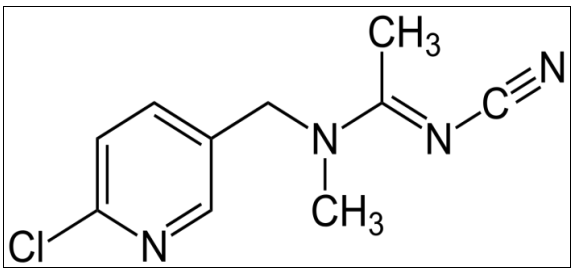
Pesticide residues in agricultural products are usually monitored with reference to maximum residue limits (MRLs), which represent the highest concentration of pesticide residues that is legally permitted or accepted in food commodities after the use of pesticides [4].

Data analysis and processing:

The objects of research are two grape varieties madrasa and tabrizi. Instrumental work to determine the residual amounts of pesticides in the specified material were performed 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 tthe composition of ridomil gold -mancozeb and metalaxil in the composition of mospilan - asetamiprid.

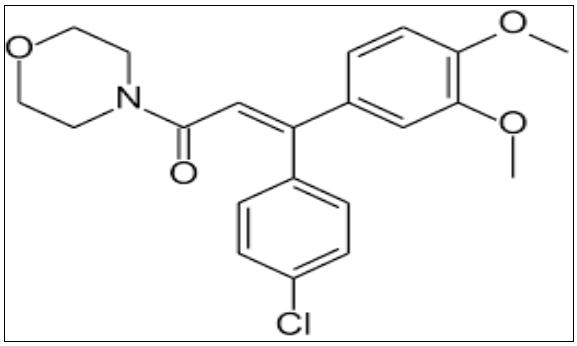
Acetamiprid is an organic compound with the chemical formula $C_{10}H_{11}ClN_4$. Acetamiprid is an insecticide belonging to the chloropyridiny lneonicotinoids, this family of insecticides was introduced in the early 1990s.This compound is an insecticide that is introduced for controlling pests, but also for domestic use to control fleas on cats and dogs. Acetamiprid is an α-chloro -N-heteroaromatic compound [5]. It is a neonicotinoid with a chloropyridinyl group and it is comparable to other neonicotinoids such as imidacloprid, nitenpyram and thiacloprid. These substances all have a 6-chloro-3-pyridine methyl group but differ in the nitroguanidine, nitromethylene, or cyanoamidine substituent on an acyclic or cyclic moiety [6].

Chemical structure of acetamiprid:



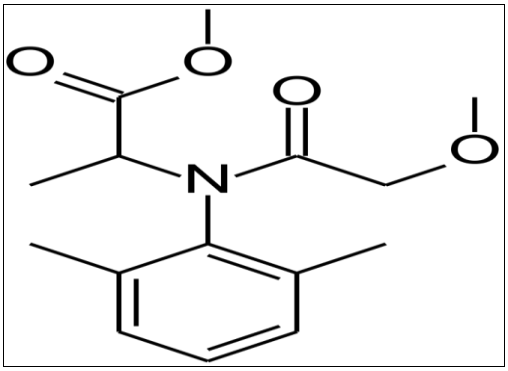
Dimethomorph -local systemic fungicide with good protective and antisporulation activity. Inhibits the formation of the oomycete cell wall.- 3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)-1-morpholin-4-ylprop-2-en-1-one.

Chemical structure of dimetomorph:



Metalaxyl -systemic, phenylamide fungicide with protective and curative mode of action, acts by suppressing sporangial formation, mycelial growth and the establishment of new infections. Disrupts fungal nucleic acid synthesis - RNA ploymerase 1.

Chemical structure of metalaxyl:



The analysis of samples according to the presented methods allows for a qualitative analysis of these fungicides and a quantitative determination of the insecticide residue in the grapes [6]. A modified, efficient, and sensitive acetate-buffered QuEChERS extraction method was developed for the quantitative study of 3 commonly applied multiclass pesticides on grapes. Samples were extracted with acidified acetonitrile, buffered with acetate salt. To minimize the matrix interferences, clean-up of the rehydrated samples was optimized by comparison with different sorbents (alumina, silica gel, florisil, primary secondary amine (PSA), and chitosan). The method validation parameters were evaluated as per European Union (EU) guidelines (SANTE/12682/2019). For 3 pesticides, % recovery of 69 to 121.8% with an associated precision (RSD ≤ 20%) was achieved at the fortification levels that were 0.5 to 2 times of European Union maximum residue limits (EU-MRLs) [6]. The validated method was successfully employed for the analysis of grapes variety Madrasa and Tabrizi isamples ($n = 20$) collected from Shamkir region of Azerbaijan. The most frequently detected residues weredimetomorph, metalaxyl and acetamiprid. The concentration of all the detected pesticides in real samples was below the EU-MRLs [7].

The 400 pesticide standards used to analyze pesticide residues were purchased by Accustandard (New Haven, CT, USA). For the extraction of pesticide residues, acetonitrile, acetone, dichloromethane and *n*-hexane used in this experiment were purchase with HPLC grade reagents (Muskegon, MI, USA). These analyzes were performed on an Agilent 7820 A gas liquid chromatography instrument (USA). The sample is homogenized. After homogenization we add a part to the centrifuge tube. Due to the presence of 80% water in the composition, we do not add water. Add 10 ml of acetonitrile to the sample. Close the centrifuge and turn it on for one minute. 4g of MgSO4, 1g of NaCl, 1 g of trinitrate citrate dihydrate, 0.5 g of disodium hydrocitratesesguigitrate buffer-salt mixture were added to the resulting suspension. Vortex vigorously for one minute. After that stir in a centrifuge for five minutes. Add 6 ml of an aliquot of acetonitruleic phase to the resulting solution. We move it in the centrifuge. The solution is isolated and from the pure extract we take 1 ml. To increase the acidity add 10 µl of formic acid solution [8]. Switch to avto sample mode and start chromatographic analysis. The high performance liquid chromatography (HPLC) was carried out on Ultimate 3000 (Dionex, Sunnyvale, California, USA) with UV-VWD detector. Chromatographic separation was performed on a Capcell Core C18 column (4.6 mm × 100 mm, 2.7 µm particle size, Osaka Soda, Osaka, Japan). HPLC conditions consisted of mobile phase A (5% acetonitrile in water), mobile phase B (20% methanol/80% acetonitrile, v/v), 10 µL injection volume, 1.0 mL/min flow rate and 40 °C oven temperature [9]. UV absorbance was monitored at 220 nm and 250 nm. The gradient program was as follows: initial (90% A/10% B), 0–13 min (10–80% B), 13–16 min (20% A), 16–16.1 min (20–90% A) and 16.1–20 min (90% A/10% B) [10].

As a result dimetamorph and metalaxyl were found in the madrasa grape variety, acetamiprid and metalaxyl were found in the tabrizi grape variety from the vineyard in the Shamkir region. Below are the chromatograms for the detection of the listed compounds.

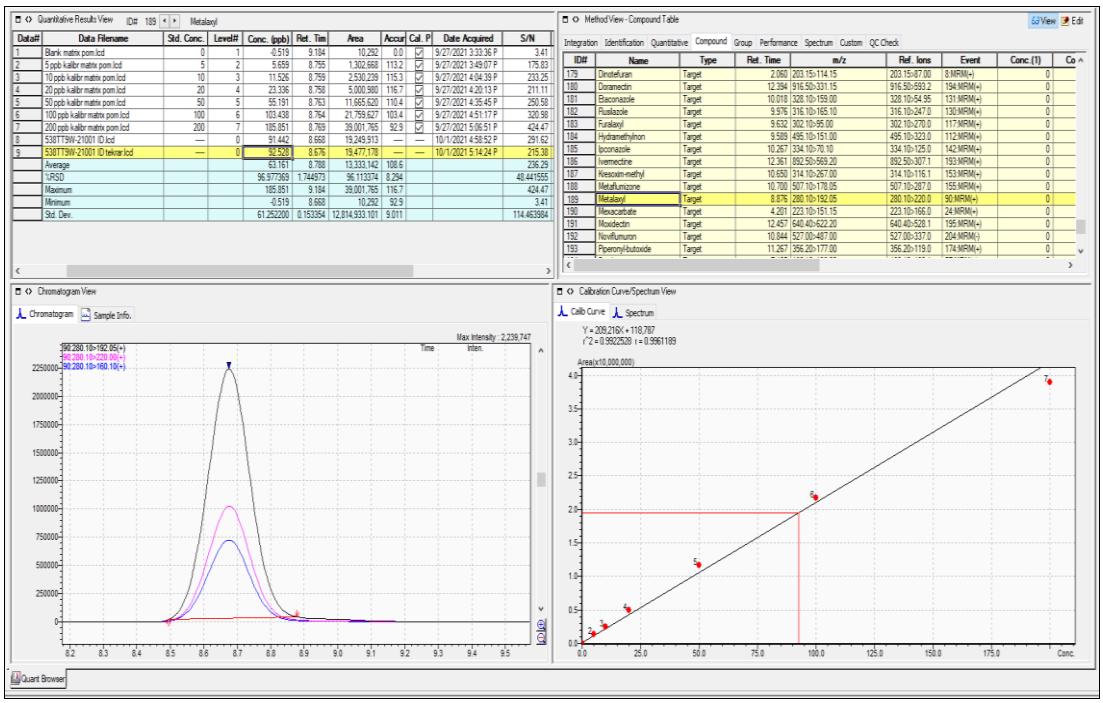


Fig 1: Chromatogram graph for the determination of metalaxyl in a sample of variety tabrizi from a vineyard on the territory of Shamkir by gas-liquid chromatography

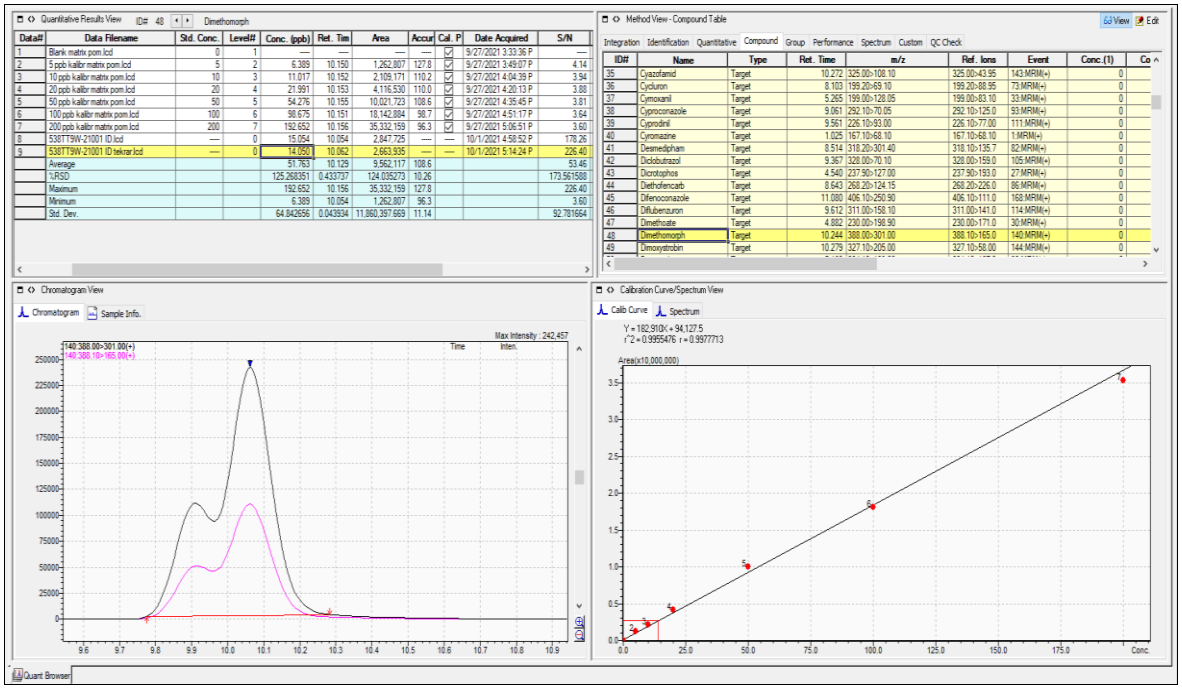


Fig 2: Chromatogram graph for the determination of dimetomorph in a sample of variety madrasa from a vineyard on the territory of Shamkir by gas-liquid chromatography

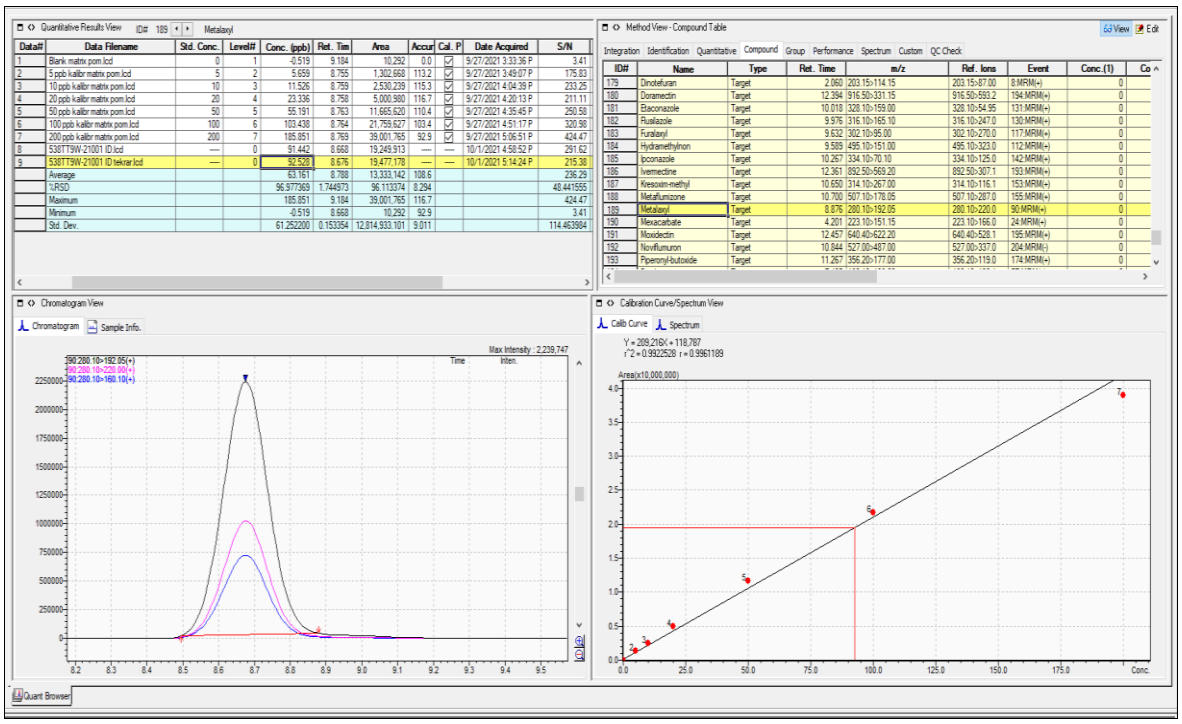


Fig 3: Chromatogram graph for the determination of metalaxyl in a sample of variety madrasa from a vineyard on the territory of Shamkir by gas-liquid chromatography

The amount of acetamiprid was 8.55 ppb, the amount ofmetalaxyl was 92.528 ppb in tabrizi variety using quantitative analysis. The amount of dimetomorph in the madrasa variety by quantitative analysis is 14.05 ppb, the amount of metalaxyl was 92.628 ppb.

Below is a list of grape samples that should be used to determine pesticides:

Pesticides	Variety	Amount Of Pesticides
Metalaxyl	Tabrizi	92.528 ppb
Dimetamorph	Madrasa	14.05 ppb
Acetamiprid	Tabrizi	8.55 ppb
Metalaxyl	Madrasa	92.628 ppb

Conclusion

In the paper two grape varieties - madrasa, and tabrizi from the grape sites of the Ganja-Gazakh zone of Azerbaijan are studied, some pesticides: acetamiprid, metalaxyl and dimetomorph are determined in the considered samples. Analysis of the quantitative determination of pesticides are carried out in the considered samples.

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