

Detection of pesticide residues from the local grapes variety Merlo, cardinal and Cabernet sauvignon

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Abstract

This study was conducted to investigate the pesticide residue concentrations from the grape consumption in Azerbaijan. A total of samples of grapes variety Merlo, Cardina and Cabernet sauvignon were collected from the Ganja-Gazakh region of Azerbaijan. The pesticide residues were analyzed by liquid chromatography-mass-spectrometry. A total of 3 different pesticide residues were found. The most frequently detected pesticide residues were kresoxim methyl, metalaxyl and dimetomorph.

Keywords: Merlo, cardinal, sample, region, pesticide

Introduction

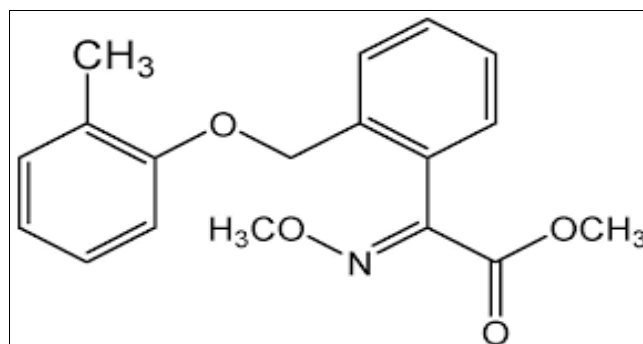
Pesticides are essential tools to increase agricultural productivity and cultivation. Pesticides are involved in a wide range of organic micro pollutants that have negative environmental effects. Several groups of pesticides have specific mechanism of contamination of living organisms, which is why generalization is difficult [1]. The use of pesticides in agriculture is a subcategory of the largest group of manufactured compounds used in the present world [2, 3]. The transfer of pesticides sourced from agricultural land may be harmful to terrestrial and aquatic ecosystems [3]. Samples for analyse are grapes variety Merlo and Cabernet sauvignon were collected from the 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 three grape varieties Merlo, Cardinal and Cabernet sauvignon. 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 liquid chromatography (LC) according to approved methods. The active ingredients of these pesticides in the composition of Acrobat-dimetomorph, in the composition of Ridomil Gold - mancozeb and metalaxil in the composition of Bio-Strobi- kresoxim-methyl [4]. Kresoxim-methyl is a broad-spectrum fungicide and a member of the strobilurin family, a class of biologically active compounds structurally related to strobilurin A, a natural product of the wooddecaying fungus *Strobilurus tenacellus*. It is intended for use as an agricultural spray in the control and treatment of fungal infections on crops and fruits. Strobilurins are known to bind bcl complex (complex III). Kresoxim-methyl was reviewed by the present.

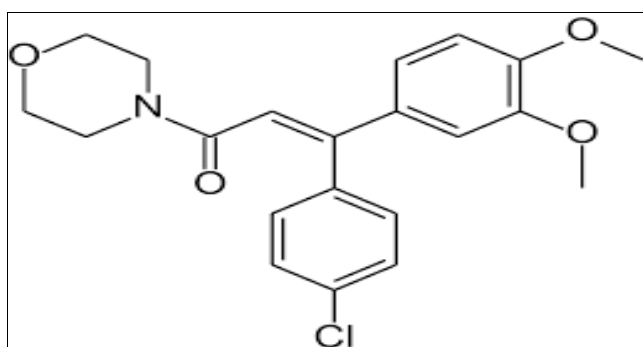
Newly submitted studies on acute toxicity, carcinogenicity in a different strain of rat, genotoxicity and neurotoxicity that were not made available to the 1998 Meeting were evaluated by the present Meeting. All critical studies contained statements of compliance with good laboratory practice (GLP) and were conducted in accordance with relevant national or international test guidelines, unless otherwise specified. No additional information from a literature search was identified that complemented the toxicological information submitted for the current assessment [5].

Chemical structure of kseroxim methyl:



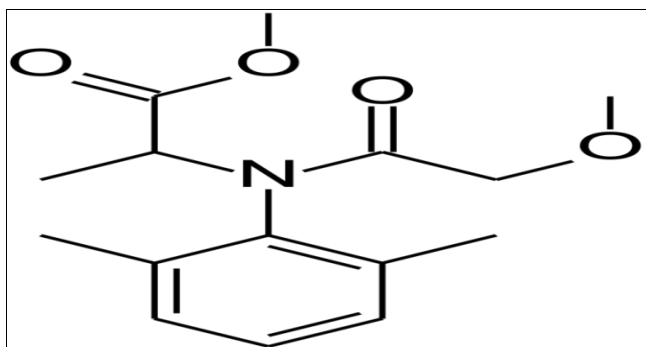
Dimetomorph, a cinnamic acid derivative, is a member of the morpholine group of fungicides and consists of a mixture of the Z and E isomers in approximately equal proportions. Its mode of action is through the disruption of fungal cell wall formation.

Chemical structure of dimetomorph:



Metalaxyl is an acylalanine fungicide with systemic function, chemical name is methyl N-(methoxyacetyl)-N-(2,6-xylyl)-DL- alaninate. It can be used to control *Pythium* in a number of fruits and vegetable crops, and *Phytophthora* in peas.

Chemical structure of metalaxyl:



Chemical and reagents

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. 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 ($RSD \leq 20\%$) was achieved at the fortification levels that were 0.5 to 2 times of European Union maximum residue limits (EU-MRLs) [4]. The validated method was successfully employed for the analysis of grapes variety Merlo and Cabernet sauvignon samples ($n = 20$) collected from Ganja region of Azerbaijan. The most frequently detected residues were dimetomorph,

metalaxyl and acetamiprid. The concentration of all the detected pesticides in real samples was below the EU-MRLs. The 400 pesticide standards used to detection 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 LCMS MS 8045. 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 $MgSO_4$, 1g of NaCl, 1 g of trinitrate citrate dihydrate, 0.5 g of disodium hydrocitrate sesquiguitrate 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 acetonitrile phase to the resulting solution [5]. 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 μ l of formic acid solution. Switch to avto sample mode and start chromatographic analysis. Chromatographic separation was performed on a Capcell Core C18 column (4.7 mm \times 100 mm, 2.7 μ m 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 μ L injection volume, 1.0 mL/min flow rate and 40 $^\circ$ C oven temperature. UV absorbance was monitored at 240 nm and 260 nm. The gradient program was as follows: initial (90% A/10% B), 0–12 min (10–80% B), 13–16 min (20% A), 16–16.3 min (20–90% A) and 16.2–20 min (90% A/10% B) [4].

As a result dimetamorph was found in the Merlo grape variety, metalaxyl was found in the Cabernet sauvignon, *kresoxim methyl* in the Cardinal grape variety from the vineyard of Ganja- Gazakh region of Azerbaijan. Below are the chromatograms for the detection of the listed compounds.

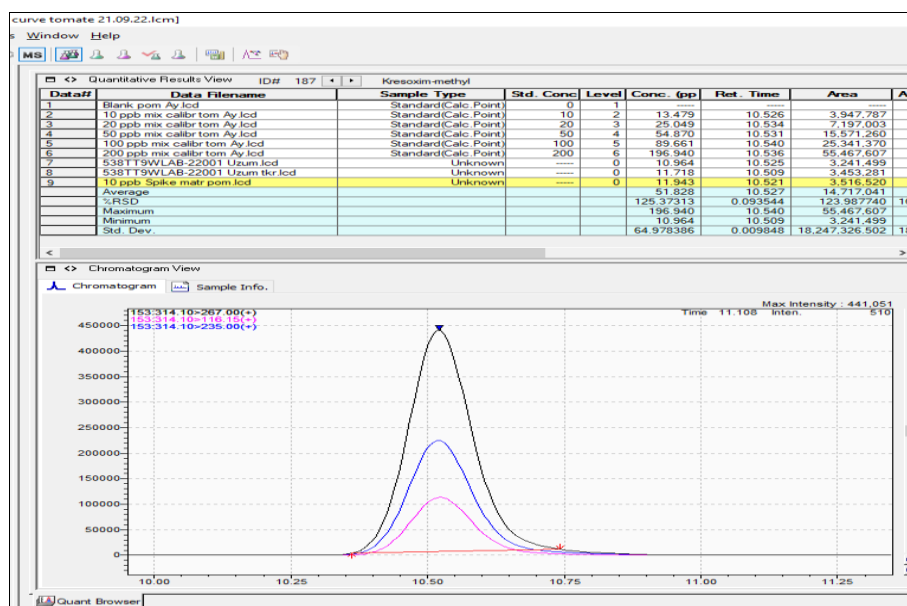


Fig 1: Chromatogram graph of *kresoxim methyl* in a sample of variety Cardinal by liquid chromatography-mass spectrometry

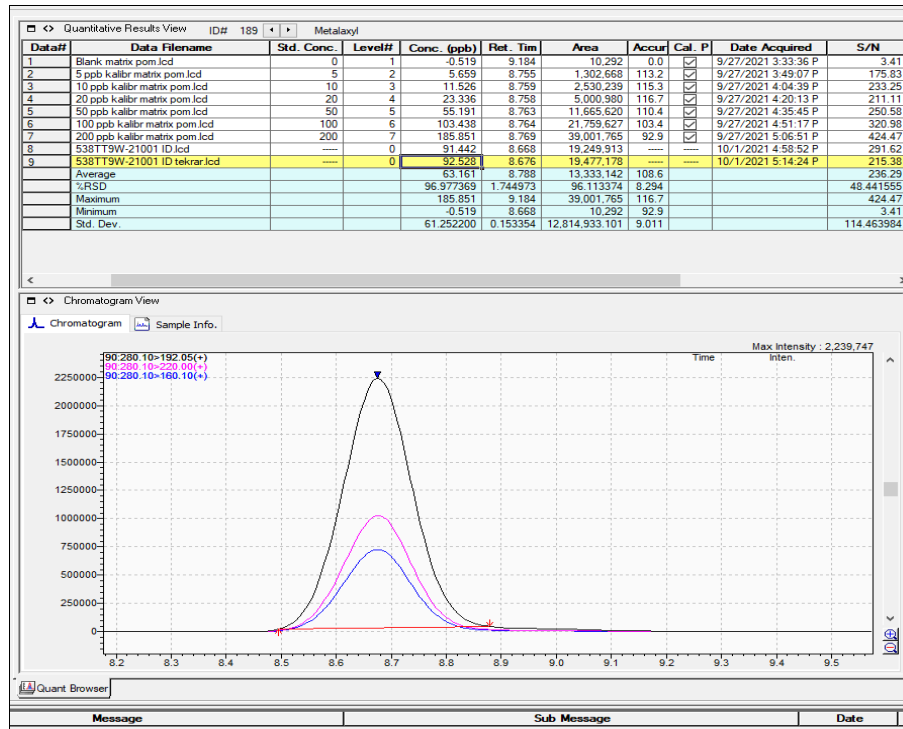


Fig 2: Chromatogram graph of metalaxyl in a sample of variety Cabernet sauvignon by liquid chromatography-mass spectroscopy

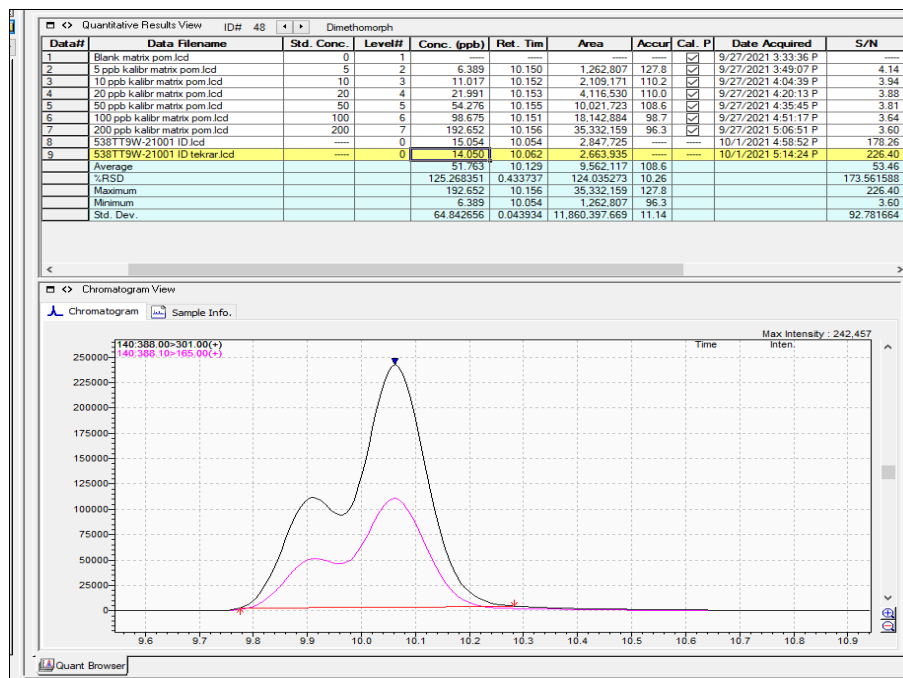


Fig 3: Chromatogram graph of dimetomorph in a sample of variety Merlo by liquid chromatography-mass spectroscopy

The amount of kresoxim methyl was 11.543 ppb, the amount of metalaxyl was 92.538 ppb and the amount of dimetomorph is 14.03 ppb using quantitative analysis. Below is a list of grape samples that should be used to determine pesticides:

pesticides	variety	Amount of pesticides
metalaxyl	Cabernet sauvignon	92.538 ppb
dimetamorph	Merlo	14.03 ppb
kresoxim methyl	Cardinal	11.543 ppb

Conclusion

In the paper three grape varieties- Merlo, Cardinal and Cabernet sauvignon from the grape sites of the Ganja-

Gazakh zone of Azerbaijan are studied, some pesticides are determined by liquid chromatography- mass-spectroscopy in the considered samples.

References

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