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İdentification of Pesticide Residues in Grapes

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KEYWORDS

analysis, residues , insecticide, chromatography, quantity, fungicide, amount.

ABSTRACT:

Pesticides are control forms of plant and animal life considered to damage in agriculture and domestic life. Nowadays, to enhance the agricultural productivity of vegetables and fruits, they are sprayed with excess pesticides. Traditional laboratory methods such as liquid chromatography and screening cards used to detection of pesticides. The paper deals with the two grape varieties – merlot and savignon cabernet from the grape sites of the Ganja-Gazakh region of Azerbaijan. The determination of the residual amount of pesticides in these varieties carried out in the laboratory of the Azerbaijan Institute of Food Safety. The qualitative determination of fungicides containing heterocyclic compounds. Analyzes were performed on the GCMS QP 2020 analyzer.

1. Introduction

The agriculture sector is moving dynamically due to the high demand for food as the population increases. Pesticides are substances that kill pests that eat fruits and vegetables and decrease productivity. To grow quality fruits and vegetables, they must be provided with proper fertilizers and sprayed with pesticides. Viticulture and winemaking are one of the important industries in Azerbaijan. Industrial production of grapes is dangerous in terms of man-made impacts on the country's ecology (Abbasov et al., 2002). There are various pesticides such as fungicides , insecticides, herbicides, virusides and bactericides. Furthermore, pesticides are classified as organic and inorganic; organic pesticides are chemical-free, including organochlorines, organophosphates, carbamates, and pyrethroids. Inorganic pesticides contain copper, sulfur, ferrous sulfate, and copper sulfate (Kaur et al., 2019). In 2020 the study detection that the amount of pesticides consumed by the world would be around 3.5 million tones (Sharma et al., 2019).

Farmers sprayed the pesticides to achieve high agricultural productivity. But on the other hand, the high toxicity of chemicals used in pesticides was very harmful to human health (Hammoud et al., 2022). Fungicides are mainly used in the treatment of grapes diseases such as metalaxyl, azoxystrobin, carbendazim, cyprodinil, dichlofluanid, fenhexamid, folpet, fludioxonil, thiophanate methyl, penconazol, pyrimethanil, cymoxanil, procymidone, and vinclozolin (Cabras et al., 2000).

There are various ways by which pesticides are detected to avoid health issues, and high pesticide-concentrated layered fruits can be avoided by consumers. There are some available machine learning (ML) techniques and artificial intelligence (AI) that are effective (Wakchaure et al., 2023). Implementation of AI and ML techniques is rare due to the time required to teach and render the model with various possibilities. Also, the case of error is present (Thorat et al., 2023). Many researchers and scientists have studied and developed pesticide residue testing methods in agriculture. A quick, easy extraction technique was developed, followed by clean-up using SPE; as this technique was simple and consumed less solvent and less time, they termed it QuEChERS (Anastassiades et al., 2003). Further, a new modified QuEChERS method with a change in solvent conditions can be applied for pesticide detection such as organochlorine and organophosphate in gas chromatography (Collimore and Bent, 2020). After the successful completion of the process, there are three laboratory methods that we will be focusing on to detect

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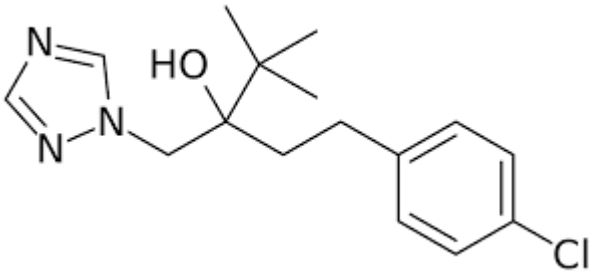
the pesticide, which include liquid chromatography, gas chromatography and screening cards.

Liquid chromatography (LC) is a technique in which the sample preparation is done by crushing the sample, spiking it with pesticide concentrate, adding chemicals, vortexing, centrifuging, etc..

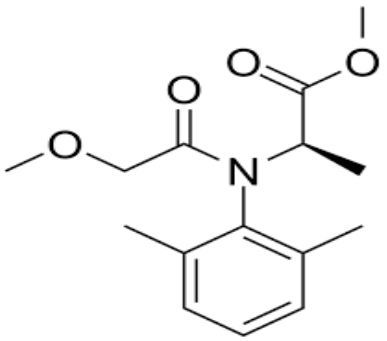
2. Data analysis and processing.

The material for analysis was selected in the vineyards of specialized farms of one of the main viticultural zones of the region (Shamkir, Gazakh and Ganja regions) against the background of ecological and toxicological monitoring. The objects of research are three grape varieties merlot and savignon cabernet .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 azox, captan and ridomil gold was determined by gas chromatography (GC). The active ingredients of these pesticides in the composition of Arbalet – tebuconazole, in the composition of Ridomil gold - metalaxil, in Captan-captan and in Azox-azoxytrobin

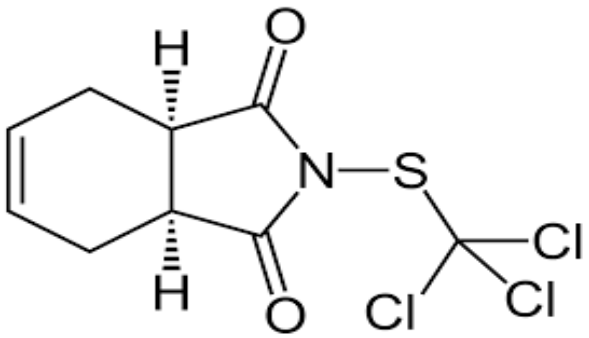
Tebuconazol**e (**(*RS*)-1-*p*-chlorophenyl-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)pentan-3-ol).is systemic fungicide with protective and eradicant action effective against various fungal diseases of cereals, vegetable, fruits and plantation. It is a triazole fungicide used agriculturally to treat plant pathogenic fungi. Structure of tebuconazole:



Metalaxyl [N- (2,6-dimethylphenyl) -N- (2-methoxyacetyl) alanine methyl ester] is a pesticide, systemic fungicide from the class of phenylamides, acylalanines, effective against pathogenic organisms belonging to the order Peronosporales. White or beige crystals of this substance are stable in acidic and neutral environments: at 20°C and pH = 1 50% hydrolysis occurs in 200 days at pH 9 - in 115, at pH> 10 - in 12 days. Decomposes at 300 ° C. Medium resistant to light. Soluble in most organic solvents. Volatility is negligible. Metalaxyl can exist as two isomers R and S that differ greatly in biological activity. The most active is the R isomer. Preparations based on it received the prefix "gold". Recently this isomer as an active ingredient has become known as mefenoxam. Structure of metalaxyl:



Captan is a general use pesticide (GUP) that belongs to the phthalimide class of fungicides. It is a white solid, although commercial samples appear yellow or brownish. Captan is often added as a component of other pesticide mixtures. It is used to control diseases on a number of fruits and vegetables as well as ornamental plants. It also improves the outward appearance of many fruits, making them brighter and healthier-looking. It is the product of the reaction trichloromethylsulfenyl chloride with sodium salt of tetrahydrophthalamide. Structure of captan:



Azoxystrobin is a new fungicide with a novel biochemical mode of action. İt is active compound

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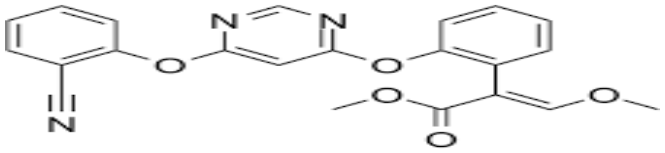
of Azox. Its synthesis was inspired by a group of natural products, the strobilurins, which are produced by several species of Basidiomycete fungi, which grow on decaying wood. The structures of azoxystrobin, Strobilurin A and the closely related Oudemansin A, another name -methyl ester of β-methoxyacrylic acid. Structure of azoxytrobin:



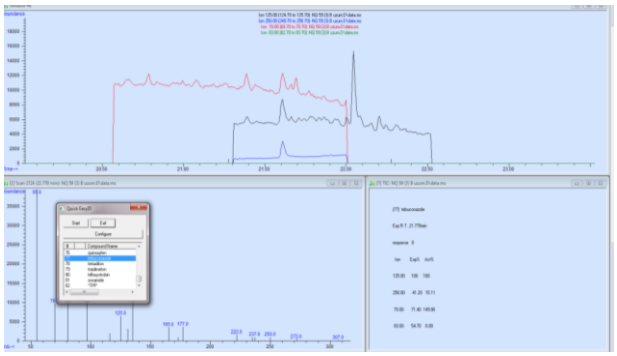


Figure 1. Chromatogram and mass spectrum of tebuconazole in the sample of the merlot variety from a vineyard on the territory of the Shamkir region

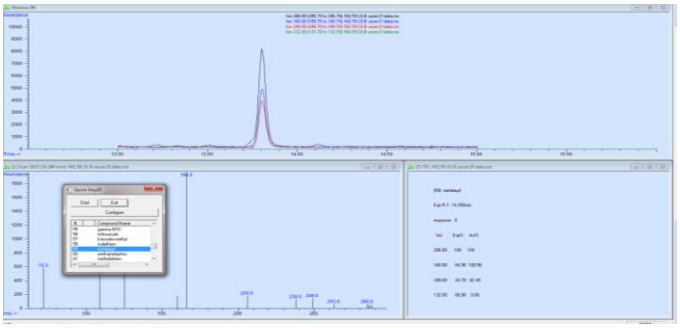


Figure 2. Chromatogram and mass spectrum of metalaxyl in the sample of the merlot variety from a vineyard on the territory of a winery in Shamkir region

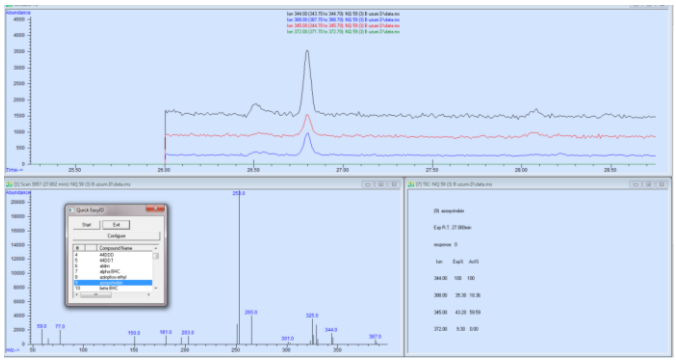


Figure 3. Chromatogram and mass spectrum of azoxytrobin in the sample of the savignon cabernet variety from a vineyard on the territory of the Shamkir region

Journal of Chemical Health Risks

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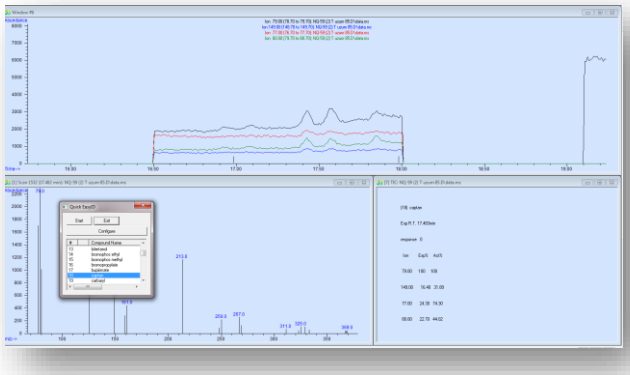

Figure 4. Chromatogram and mass spectrum of captan in the sample of the savignon cabernet variety from a vineyard on the territory of the Shamkir region

The analysis of samples according to the presented methods allows for a qualitative analysis of these fungicides in the grapes (Fantke et al., 2012). In 2021 a qualitative analysis of Merlot and Savignon Caberne varieties was carried out by gas chromatography mass-spectroscopy. These analyzes were performed on GCMS QP 2020 .

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 hydrocitrate sesguigitrate buffer-salt mixture were added to the resulting suspension. Vortex vigorously for one minute,after that 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. Switch to avto sample mode and start chromatographic analysis.

As a result tebuconazole and metalaxyl were found in the merlot grape variety, the captan and azoxytrobin in the sauvignon cabernet grape variety from the vineyard in the Shamkir region on the territory of the Ganja-Gazakh winery. Below are the chromatograms for the detection of the listed compounds.

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

Varieties	**Detected pesticides**
Merlot	tebuconazole, metalaxyl
Savignon cabernet	captan,azoxytrobin

As a result of the qualitative analyzes tebuconazole and metalaxyl were found in the composition of the merlot grape variety the presence of captan and azoxytrobin in the savignon cabernet variety.

3. Conclusion

In the paper two grape varieties – merlot and savignon cabernet from the grape sites of the Ganja-Gazakh zone of Azerbaijan are studied, some pesticides are determined in the considered samples. For qualitative determinations of nitrogen-containing fungicides are made containing a phenyl residue, using the example of azox , captan ,arbalet and gold ridomyl. The detection of these pesticides in grapes does not negatively affect the physicochemical characteristics of these varieties .

Journal of Chemical Health Risks

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