The Analysis of the Residual Amount of Pesticides in Grapes and their Biochemical Indicators

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Abstract: The article examines the three grape varieties –Tabrizi, Cardinal and Italian Muscat from the grape sites of the Ganja-Gazakh region of Azerbaijan. The analyses of pesticides in these varieties carried out in the laboratory of the Chemistry department, of Azerbaijan State Agricultural University and Azerbaijan Institute of Food Safety. The qualitative determination of organic pesticides containing a phenyl and pyrimidine ring was performed on the GC-MS QP 2020 analyzer.

Keywords: grapes variety, pesticide, analyses, qualitative detection, biochemical indicators, gas chromatography, fungicide.

1. Introduction

Viticulture are one of the major industries in Azerbaijan. Industrial production of grapes is dangerous in terms of man-made impacts on the ecology [1]. The importance of winemaking and of the viticulture socioeconomic sector in Europe is largely acknowledged. The main winemaking regions in Europe commonly present very specific environmental characteristics, where climate often plays a central role. Furthermore, given the strong influence of the atmospheric factors on this crop, climate change can significantly affect yield and wine quality under next conditions. Trends recorded in the recent past on many cultural regions in Europe hint at an already pronounced increase in the growing-season mean temperatures [2]. The ecological and toxicological hazard of most pesticides is the prolongation of their decay to safe compounds and the formation of intermediate half-life products the toxicity of which may exceed the drug itself [3]. Pesticides sprayed in liquid form contaminate plants to a greater extent than preparations applied in powder form. The structure of the plant in question is also important because, for example, OCP insecticides accumulate in the waxy layer of the rind of many fruits, especially citrus fruits. It is therefore a matter of urgency that pesticide residues in fruit and vegetables are monitored, because they can put human health [4].Pesticides are widely applied to prevent unwanted pests from attacking crops and livestock which led to their access into the environment. Most of diseases (chronic obstructive pulmonary disease, cancer, birth defects, infertility) and more damages of human health are associated with the exposure of fungicides and insecticides. The maximum amount limits for pesticides have been regulated by the Codex Alimentarius Commission and European Union to protect human health. To date, many techniques have been developed for pesticide detection, from conventional analytical to advanced detection techniques. The conventional analytical methods are gas chromatography and high performance liquid chromatography coupled with various detectors and columns involved a sample preparation step prior to further analysis [5].The main methods to determine pesticides are based on sensors principles. Advanced methods offer several advantages including simple, rapid and low-cost operation, high sensitivity and selectivity, and on-site detection [5].

Currently, a method with modified dissolution conditions, such as ethyl acetate and acetonitrile, is used, which is more suitable for detection by gas chromatography and liquid chromatography. The approach to the QuEChERS method has surpassed significant changes. This method is often used due to its efficiency in extracting a wide range of analyses. The results obtained during the study show that this method is more effective compared to other methods [6].The berries of fresh grapes contain easily digestible sugars – monosaccharides ,such as glucose and fructose, organic acids - tartaric, malic, citric, succinic, etc., mineral salts of potassium, calcium, sodium, phosphorus, manganese, cobalt, iron, trace elements and phenolic substances [7]. Nowadays, enhance the agricultural productivity of vegetables and fruits, they are sprayed with excess pesticides. Traditional laboratory methods such as gas chromatography mass-spectroscopy, liquid chromatography and screening cards used to detection of pesticides. The Ganja-Gazakh zone is one of the main producers of grapes in Azerbaijan [8].

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 (Gazakh, Shamkir, and Ganja regions) against the background of ecological and toxicological monitoring. The objects of research are three grape varieties rkasitely, cardinal and bayanshire. 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 and in laboratory of Chemistry department, of Azerbaijan State Agricultural University. In the objects under study, the content of fungicide preparations containing a phenyl and pyridine residues using the example of kresoxim methyl, metalaxyl and azoxytrobin was determined by gas chromatography mass-spectroscopy GC-MS QP 2020.The active ingredients of these pesticides in the composition of azoxa- azoxytrobin in the composition of bio- strobi kresoxim- methyl and metalaxyl in the composition of ridomil gold. Due to the lack of a standard for the determination of mancozeb, metalaxyl, i.e. another active substance in grapes was determined.

Kresoxim-methyl [Methyl(E)-2-methoxyimino-[2-(2methylphenoxymethyl) phenyl] acetate] is the active ingredient of pesticides (fungicides). Metalaxyl is an acylalanine fungicide with systemic function. Azoxystrobin is a broad spectrum systemic fungicide widely used in agriculture to protect crops from fungal diseases. Azoxystrobin and other strobilurins inhibit mitochondrial respiration by blocking electron transport.In 2021 a qualitative analysis of rkasitely, cardinal and bayanshire varieties was carried out and by gas chromatography mass-spectroscopy.These analyzes were performed on GCMS QP 2020[8].

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 stir in a centrifuge for five minutes. Add 6 ml of an aliquot of acetonitrile 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 of the qualitative analyzes azoxytrobin and metalaxyl were found in the Tabrizi grape variety from the vineyard in the Gazakh region winery, azoxytrobin in the İtalian Muscat grape variety in the vineyards of the private territories of the Gazakh region and Kresoxym-methyl in Cardinal variety on the territory of the Shamkir winery. Below are the spectrumes and chromatograms for the detection of the listed compounds.

Table 1. Detected pesticides in grape varieties.

Varieties	Determined pesticides
Tabrizi	azoxytrobin ,metalaxyl
Cardinal	kresoxym-methyl
İtalian Muscat	azoxytrobin

Also, in the studied grape varieties the analysis of the physicochemical indicators carried out. Initially after peeling the grapes well all the spoiled berries were removed. After grinding, the juice was separated to determine the indicators. In winemaking they are guided not by the acid content in berry juice but by the pH value. The pH level indicates the concentration of active acids in grape juice and is determined in laboratory conditions using free hydrogen ions. A high pH indicates a low concentration of active acids a low pH indicates a high one. The pH level indicates the presence of palatable and non-volatile acids. The pH was measured with a pH meter. The hydrogen index for the Tabrizi variety was -3.38, for the Cardinal variety -3.39 and for İtalian Muscat -3.29. Total acidity shows the total content of titratable acids that is the content of all acids possible in bulk chemical analysis including volatile ones. To determine the total acidity 10 ml of grape juice and 6 drops of bromine thymol blue were added to the flask and titrated with 0.1 N NaOH solution. The used alkali solution was multiplied by a factor of 0.75 and the total acidity was determined from the table. For the Tabrizi variety the total acidity index is 4,8, for İtalian Muscat the total acidity index is 7.58 and for the Cardinal variety the total acidity index is 5,36. To determine the sugar content the grape must density was first determined by a hydrometer-sucrometer type AON with a range of 0-25%. The test sample was taken from bunches of grapes from different vines in order to obtain averaged data. The juice for measurement should be transparent let the juice settle for 1-2 hours. It was calibrating the hydrometer to a temperature of 200 C. If the temperature of the juice would be different then it would be necessary to make an amendment of 0.0002 for each degree of temperature. With a decrease in temperature the density increases and with an increase vice versa. Pour juice into the vessel so that the hydrometer can float freely in it without touching the bottom and at the same time the level of juice does not reach the top of the vessel. We carefully lower the hydrometer into it so that it does not touch the walls, and we take the hydrometer readings at the lower liquid level (lower meniscus) for the accuracy of the readings, the eye level should be at the height of the juice-air border. The extractives for the Tabrizi variety was 18,67, for the Cardinal variety 17,56 and for İtalian Muscat -19,20. The extractives were determined by refractometer RA 130 According to the density of the juice we determine its sugar content according to the corresponding table2.

Table 2. Physicochemical indicators of the grape varieties Tabrizi, Cardinal, İtalian Muscat

Physicochemical indicators of the grape varieties	Total acidity g/l	Sugar content, g/dm3	Density, g/dm3	pH	Extractives%
Tabrizi	4,8	229	1,098	3,38	18,67
Cardinal	5,36	239	1,2	3,39	17,56
İtalian Muscat	7.58	210	1,089	3,29	19,20

The density index for the Tabrizi variety is - 1.098 and accordingly this density the sugar content – 229, the density index for the İtalian Muscat variety is -1.089 and accordingly this density the sugar content is 210, for the Cardinal variety the sugar content is 1.2, the sugar content is 239.

The detection of azoxytrobin and metalaxyl in the Tabrizi variety, azoxytrobin in the İtalian Muscat, kresoxym-methyl in Cardinal does not negatively affect the physicochemical characteristics of these varieties (Table 2).

3. Conclusion

In the paper three grape varieties -Tabrizi, Cardinal and İtalian Muscat from the grape sites of the Ganja-Gazakh zone of Azerbaijan are studied, some pesticides are determined in the considered samples. Qualitative determinations of organic fungicides are made containing a phenyl and pyridine residue, using the example of azox , bio-strobi and gold ridomyl.

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