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Analyze of pesticides and physicochemical indicators in the composition of grape variety bayanshire

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Abstract
The paper deals with the grape variety –Bayanshirefrom the grape sites in the Gazakh province, of 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. Analyzes of quantitative determination of nitrogen-containing fungicides were performed by gas chromatography according to the approved methods, on the LCMS –MS 8045 analyzer.

Keywords: Analysis, fungicide, indicator, determination, grape variety, chromatography

Introduction

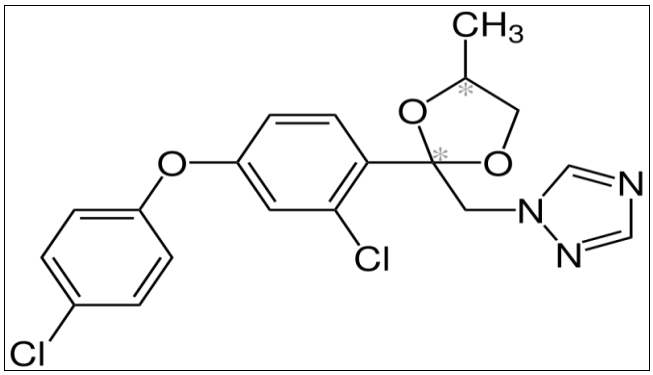
Grapes are among the most widely grown fruits worldwide, consumed both fresh and in the processed forms (wines, raisins). Approximately 50% of grapes are used in wine production [1]. In conventional production, various plant protection products (PPP), especially fungicides and insecticides, are widely used for protecting grapevine [2]. Winemaking and viticulture is one of the most important industries in Azerbaijan. Many local and foreign grape varieties are still grown in different regions of Azerbaijan. Grapes have been cultivated and wine made in these places since the ancient times [3]. The majority of methods for pesticides analysis are based on direct injection: an isotope-labelled standard and a buffer is added to the sample. The sample is then filtered and analysed by LC/MS technique. In the case of substances requiring a very low limit of detection or with compounds with love sensitivity, it is necessary to pre-concentrate the sample prior to analysis. However, they may contain toxic residual pesticides due to the use of pesticides during the production process of agricultural products [3]. 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 Pre-concentration steps can be performed manually, such as offline SPE, liquid-liquid extraction followed by evaporation of organic solvents, or by the QuEChERS technique. However modern instrumentation uses on-line concentration steps, such as on-line SPE or 2D chromatography. When needed, sample preparation includes a step for derivatisation. Certain types of compounds need to be treated with a derivatisation agent prior to analysis to make them more “suitable” for the selected instrumentation. Examples are compounds like glyphosate, AMPA, amitrole and gluphosinate [4]. Gas and liquid chromatography methods used in the work to identify toxic residues of the determined drugs and their metabolites allow obtaining complete and objective information on the sanitary and hygienic indicators of this material. A method for determining the pesticides (azoxystrobin, chlorpyrifos, cyprodinil, diazinon, dimethoate, metribuzin, penconazole, phosalone, pirimicarb, pirimiphos-methyl, prometryn, propargite, pyraclostrobin, pyrimethanil, triadimenol, triadimefon, fluazifop-P-butyl, malathiontrifloxystrobin) in grapes and tomatoes by high performance liquid chromatography with tandem quadrupole –time of flight mass spectrometry detector (HPLC-MS /TOF), using sample preparation QuEChERS [4]. The berries of fresh grapes contain easily digestible sugars - glucose and fructose, organic acids - malic, tartaric, citric, succinic, etc., mineral salts of potassium, calcium, sodium, phosphorus, manganese, cobalt, iron, trace elements and phenolic substances [5]. The Ganja-Gazakh zone is one of the main producers of grapes and its processed products in Azerbaijan.

Data analysis and processing

The material for analysis was selected in the vineyards of specialized farms of one of the main viti cultural zones of the region Ganja-Gazakh against the background of ecological and toxicological monitoring. The objects for research is grape variety: Bayanshire. Bayan Shirey is a high-quality local grape variety native to Azerbaijan. Named after the village of Bayan, Dashkesan region of Azerbaijan. Bunches weigh 180-190 grams. Vegetation period is 160-165 days. Bayan Shirey is also the name for a white wine made from the Bayan Shirey grape variety grown in some areas of Azerbaijan. 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 chlorine residue using the example of Amistar Gold contains 125q/l azoxytrobin and 125 q/l difenoconazole, the active ingredients of these pesticides in the composition of Acrobat- dimetamorph were determined by gas chromatography- LCMS –MS 8045 analyzer. The active ingredients of these pesticides in the composition of Amistar Gold – difenoconazole. Acrobat is a systemic fungicide containing Dimethomorph. It is used for treating downy mildew and Late blight caused by organisms such as Pythium and Phytophthora species. Difenoconazole is a systemic fungicide that controls a broad spectrum of foliar, seed and soil-borne diseases caused by Ascomycetes,

Basidiomycetes and Deuteromycetes in cereals, soya, rice, grapes, pome fruit, stone fruit, potatoes, sugar beet and several vegetable and ornamental crops. Difenoconazole is a member of the class of dioxolanes that is 1,3-dioxolane substituted at position 2 by 2-chloro-4-(4- chlorophenoxy) phenyl and 1,2,4-triazol-1-ylmethyl groups. A broad spectrum fungicide with novel broad-range activity used as a spray or seed treatment. It is moderately toxic to humans, mammals, birds and most aquatic organisms. It has a role as an environmental contaminant, a xenobiotic, an EC 1.14.13.70 (sterol 14alpha-demethylase) inhibitor and an antifungal agrochemical. It is an aromatic ether, a dioxolane, a member of triazoles, a cyclic ketal, a conazole fungicide and a triazole fungicide. Difenoconazole has known environmental transformation products that include CGA 205375, CGA 205374, CGA 189138, and 1,2,4 triazole. Mechanism of action of difenoconazoleis applied by foliar spray or seed treatment and acts by interference with the synthesis of ergosterol in the target fungi by inhibition of the 14alpha-demethylation of sterols, which leads to morphological and functional changes in the fungal cell membrane [6].

Structure of difenoconazole



Below chromatogram and calibration graph of difenoconazole sample in the grape variety Bayanshire:

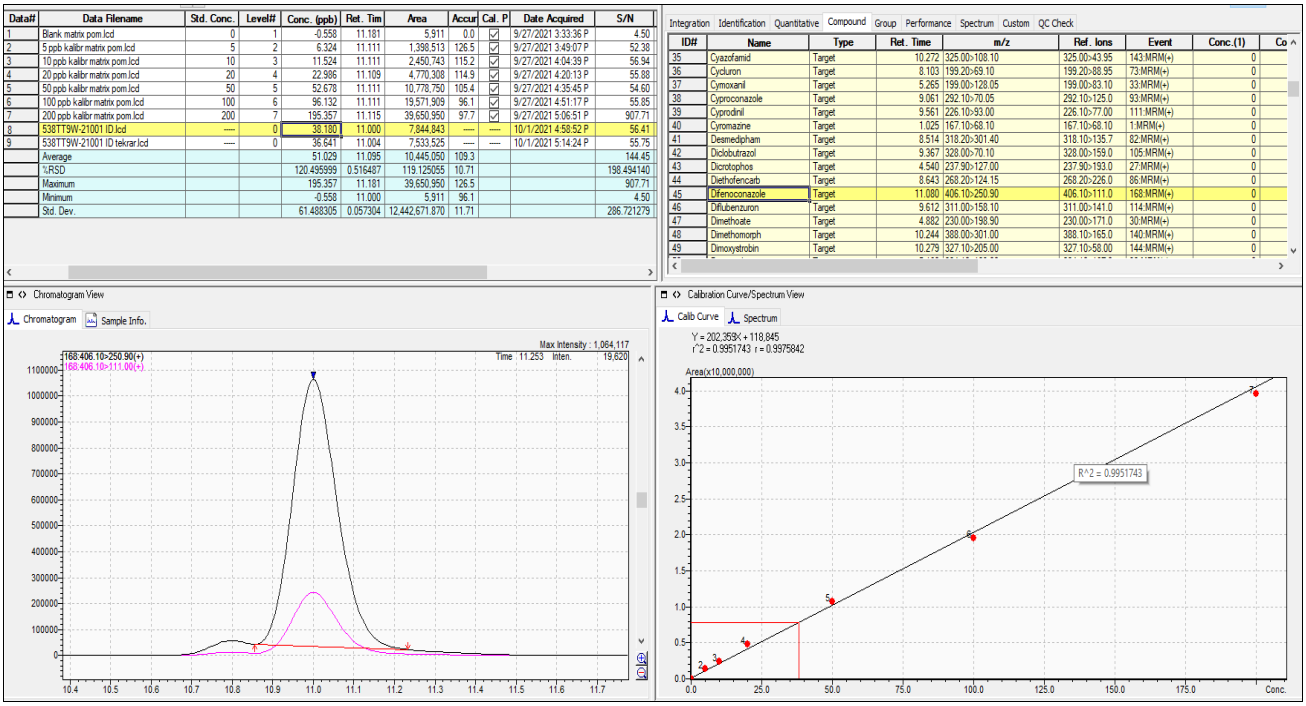
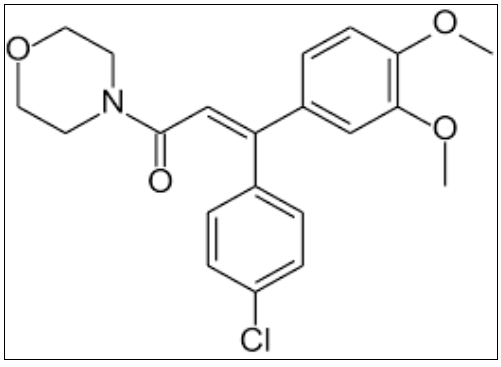


Fig 1: Chromatogram and calibration graph of difenoconazole sample in the Bayanshire

Dimethomorph is a fungicide with high activity against Peronosporomycetes plant pathogens. The present study showed that dimethomorph is effective on controlling the oomycete fungal pathogen *Pseudoperonospora cubensis* causing downy mildew on cucumber. The fungicide did not affect zoospores discharge from sporangia of *P. cubensis*, but it strongly inhibited mycelial growth and sporangial production *in vitro* and increased lysis of zoospores. The biocharacteristics of dimethomorph make it well suitable for integration of a control programme against downy mildew disease on cucumber and as a component to delay other peronosporomycetes fungicide-resistance development. 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



Below chromatogram and calibration graph of dimetomorph sample in the grape variety Bayanshire:

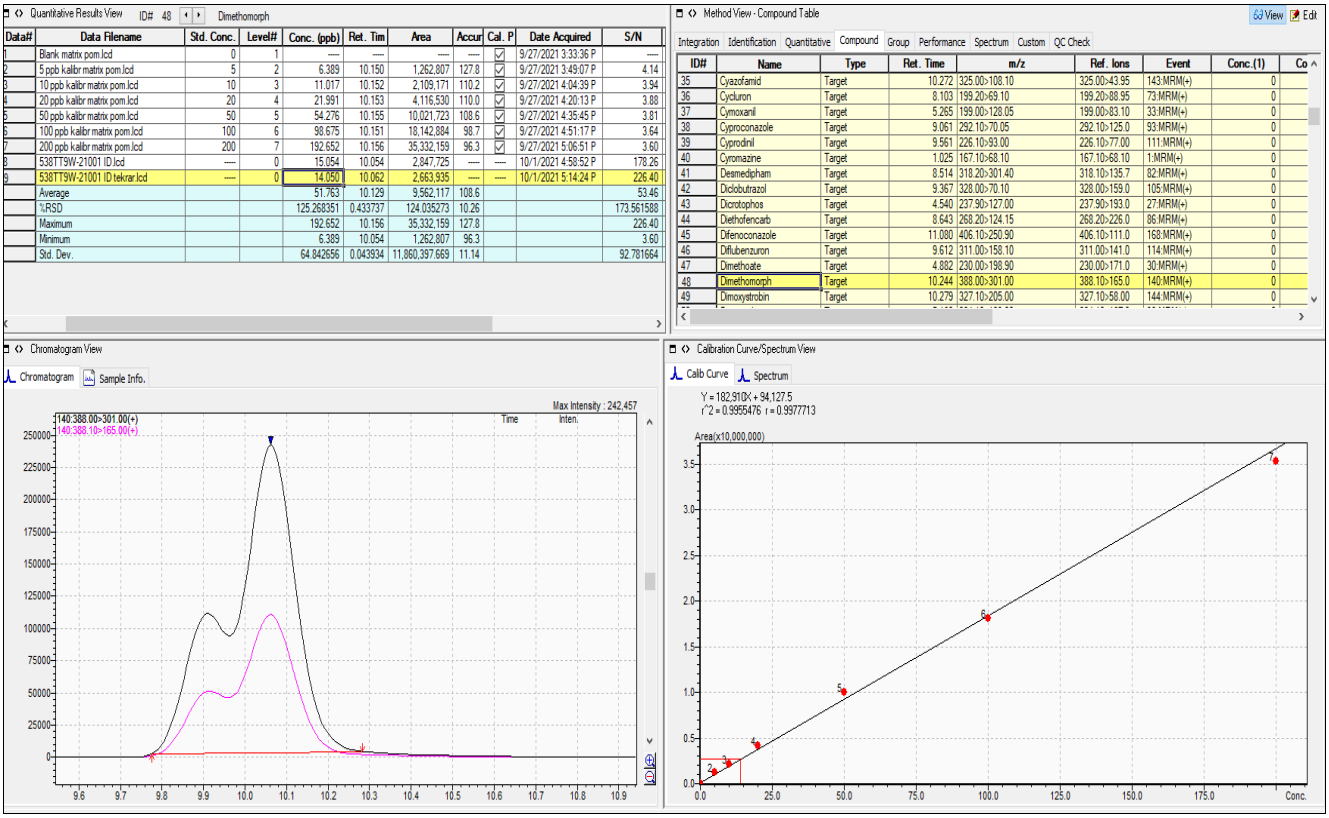


Fig 2: Chromatogram and calibration graph of dimetomorph sample in the Bayanshire

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 [7]. These analyzes were performed on LCMS –MS 8045 analyzer, using sample preparation QuEChERS. 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. Switch to avto sample mode and start chromatographic analysis. The amount of dimetomorf-14,050 ppb, the amount of difenoconazole-38,180 ppbwere found in the composition of the Bayanshire. Also in the studied grape varieties the analysis of the physicochemical indicators carried out. At first the work was obtained from the grapes of the studied varieties. 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 Bayanshire variety with difenoconazole was -3.37, with dimetomorph-3.39. 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 5 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 grapes with difenoconazole the total acidity index is 5.34, with dimetomorph is 5.35. 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 calibrate 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 [8]. 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 [9]. According to the density of the juice we determine its sugar content according to the corresponding table. The density index for the grapes with difenoconazale variety is -1.4, with dimetomorph is - 1.2, sugar content for the grape with difenoconazale variety is-238, with dimetomorph is-239.

Table 1: Physicochemical indicators of the grape variety Bayanshire

Pesticides	Total acidity g/l	Sugar content g/dm3	Density, g/dm3	pH
Dimetomorph	5.34	239	1.2	3.39
Difenoconazole	5.35	238	1.4	3.37

As can be seen from the table, the amount of total acidity, sugar content, density and pH are average due to excessive uses of nitrogen containing pesticidess.

In the study of the physical and chemical composition of the must and wine materials were determined: 1) sugar in grapes according to GOST 27198-87;2) total acidity, density, pH - respectively, according to GOST 13192, GOST R 51621, GOST R 51653, GOST R 51654.A chemical analysis of grape samples was carried out on analyzer Wine Scan [10].The detection of difenoconazole and dimetomorf in the Bayanshire variety, does not negatively affect the physicochemical characteristics of these grapes (Table 1).

Conclusion

In the paper one grape variety – Bayanshire from the grape sites of the Ganja-Gazakh zone of Azerbaijan are studied. Some pesticides are determined in the considered samples and the detection of difenoconazole in this variety of grape, does not negatively affect the physicochemical characteristics of these variety of grape. Qualitative determinations of nitrogen-containing fungicides are made containing a chlorine residue, using the example of Amistar Gold and Acrobat.

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