Research article

Authentication of selected white wines by geographical origin using ICP spectrometric and chemometric analysis

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ABSTRACT

An important aspect of assessing the authenticity of wines is its geographical origin. The aim of the work is to authenticate by geographical origin according to the data of the ICP-spectrometric and chemometric analysis of elemental "images" of wines produced from white grape varieties Chardonnay, Riesling and Muscat grown in four regions of the Krasnodar Territory, Russia. The difference in the contents of Al, Ba, Ca and Rb in wines was found depending on the variety, and Al, Ba, Rb, Fe, Li, Sr – depending on the region of grape growth. Different models of the experimental data processing were used for attribution of the produced varieties of wine to the area of the grape's growth. The criterion for the quality of the constructed models was the accuracy of the attribution of a wine variety to the area of the grape's growth (%). Analysis of the elemental analysis data of 153 wine samples showed that in terms of attribution accuracy, automated neural networks (100 %) are preferred among machine learning methods, followed by support vector machines (98.69 %) and general discriminant analysis (94.77 %). The applied mathematical models enabled the revealing of the cluster structure of the analyzed wine varieties and their attribution to the area of a grape growth with high accuracy. Sr, Li and Fe concentrations in wines were found as the dominating predictors in the constructed models for definition of the geographical origin of wines. The combination of ICP-spectrometric analysis data with the capabilities of statistical modeling of machine learning methods focused on large-dimensional data made it possible to successfully solve small-dimensional problems of the definition of the geographical origin of wines by their elemental composition and variety.

1. Introduction

The steady increase in the production and consumption of wine is accompanied by an increasing number of counterfeit and low-quality wine products. This is due to a number of factors, including the use of standardized parameters to measure the quality of wine [1–3].

The main way to evaluate the quality of wine is a sensory evaluation conducted by experts [4–6]. Sensory assessment is the main feature that determines consumer preferences [7,8]. When similarities in the organoleptic characteristics are found between wines made from different grape varieties, differentiation must be done using instrumental and chemometric methods, which allow

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recognition of a wine as a whole based on an analysis of its "image" [9–11].

The "image" of a wine consists of the component composition that determines its bouquet and flavor [12–16]. The quality of wines is established by methods of electrophoretic, chromatographic, and elemental analysis, followed by chemometric processing and comparison of the data obtained by the wine under study with its "image" [17–19]. This approach, due to the specifics of the established profiles, is widely used in assessing the quality of wines – processing the organoleptic properties of wines [17,20–22]; the influence of the chemical composition of wines and grapes on the taste and aromatic properties of the drink [23–26]; differentiation of wines by zones of grape cultivation [17,20–23,27–31], etc.

To control the authenticity of wine on a regional basis, it is first necessary to identify identifying criteria. The most significant among them will be parameters whose variability remains constant despite changes in external environmental factors. The mineral composition is a key indicator of the geographical attribution of wine, due to the consistency of the elemental composition of soil from grape-growing sites [32,33]. The relationships between the mineral content in the soil, grape, and wine make it possible to determine the varietal and geographical origins of wine, thanks to the consistency and specificity of the elemental makeup of the grape varieties grown on soil from specific areas [32–34].

The elemental composition of wine ideally should depend only on the mineral composition of the soil and the grapes, as well as the climatic conditions. It should not depend on the production technology, transportation, or storage [35]. The relationship between the soil, the grapes, and the wine in the formation of its elemental composition may be disrupted by technological methods used in wine production, such as stabilization and clarification using auxiliary materials to remove components that cause turbidity of different origins [34,36]. The variety of component compositions in wines is also determined by the maturity of the grapes [37]. It can be assumed that the ratio of mineral nutrients in finished wine has a complex relationship to the geological minerals found in the vineyard. Therefore, in order to determine the fact of adulteration and/or ascertain the regional origin of wine, many researchers use the mineral composition which is least affected by external influences in a specific geographical region [38,39].

Wine differentiation is carried out using statistical modeling methods - discriminant analysis, classification trees [40], principal component analysis [41], neural networks [40,42], machine learning, etc. [43–47]. To carry out calculations, statistical packages SPSS, STATISTICA, SAS, STATA, etc. are used, as well as modern data analysis tools, for example, the R programming environment [45, 48]. An analysis of the literature data on the use of chemometric classification methods shows that none of these publications analyzes the capabilities of discriminant analysis and various Data mining methods for identifying the varietal and regional affiliation of wines.

To determine significant indicators in assessing the quality and ownership of wines, a large amount of data on the elemental composition of the drink from different geo-graphical areas is required [49]. Currently, the elemental composition of wines is determined by methods that allow simultaneously determining the maximum list of elements in a wide range of their concentrations. For wines, the set of these elements is very wide. The content of elements in wines varies in the range: 10–1000 mg/L for macro-elements - Ca, K, Na, and Mg; 0.1–10 mg/L for minor elements - Al, Fe, Cu, Mn, Rb, Sr and Zn; 0.01–1000 μg/L for microelements - Ba, Cd, Co, Cr, Li, Ni, Pb, V and REE [50]. One of the main stages of multi-element analysis of wine is sample preparation. Traditional methods of "dry" and "wet" ashing do not fully meet the requirements of online multi-element analysis [51].

Modern requirements for elemental analysis are met by the methods such as atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) [52]. Instruments for ICP-AES and ICP-MS analysis allow analysis using element atomization systems with an inductively coupled plasma spectrometer [32,53]. The high temperature of the plasma discharge (7000–10000 K) ensures complete destruction of organic matter in wine samples, while the ability to adjust the amount of wine added to the sample ensures accurate results [54]. However, the addition of undiluted wine to the plasma results in the destabilization of the electrical discharge, the presence of matrix interferences from the sample, and an inevitable reduction in the analytical signals of the detected elements [55]. These issues were addressed by the authors [53,54], who proposed pre-diluting the wine with 1 M nitric acid. This acid solution does not have a negative impact on the analytical signals of the elements but does contribute to the destruction of the organic matrix in the wine.

The aim of the work is to authenticate by geographical origin according to the data of the ICP-spectrometric and chemometric analysis of elemental "images" of wines produced from white grape varieties Chardonnay, Riesling and Muscat grown in four regions of the Krasnodar Territory, Russia.

To achieve this goal, we have substantiated the optimal scheme for analyzing research objects, identified marker elements, and established the relationship between the elemental composition of wine and the soil in the region where it was grown. The data was obtained using ICP spectrometry and machine learning techniques, which made it possible to differentiate between regions with a high degree of confidence. After identifying the marker elements and understanding the relationship between wine, grape, and soil, we considered the possibility of establishing the varietal and regional origins of wines.

2. Materials and methods

2.1. Research objects

To determine the quality and regional affiliation, we studied 153 samples of dry white wines from the names Riesling (49), Chardonnay (56) and Muscat (48), produced on the territories of the main wineries in the geographical zones of the Krasnodar Territory: ZAO Zaporizhskoye, OOO Kuban-Vino, APF "Fanagoria", APK "Milstrim-Chernomorskie Vina", AF "Caucasus", "Abrau-Durso", APK "Gelendzhik", AF "Myskhako", "Sommelier Firm", AF "Sauk-Dere", "Soyuz-Vino". Wine producers belong to different geographical zones (subzones) of the Krasnodar Territory - South Foothill and Black Sea zones, Anapa and Taman subzones (Fig. 1).

The wine was supplied directly from the producers or purchased from retail chains. It was bottled in dark green bottles with cork

closures, and stored at temperatures up to 10 °C. According to the producers, the alcohol content of the wine ranged between 9 and 13 % by volume, and the acidity was between 4 and 7 g/L.

2.2. ICP-spectrometric analysis of wines

Elemental analysis of wine materials was determined by ICP-OES on an iCAP 7400 spectrometer (Thermo Scientific, Waltham, MA, USA) and ICP-MS on an iCAP RQ spectrometer (Thermo Scientific, Waltham, MA, USA). The use of two methods is due to the need to determine both medium concentrations of elements (ICP-OES) - Zn, Ni, Mn, Fe, Mg, Cu, Al, Sr, Ca, Ba, Na, K, Rb and low concentrations of elements (ICP-MS) - Li, Ti, V, Co, As, Mo, Cd и Pb [32,40,41,53]. Optimized analysis conditions and spectrometer operation parameters are summarized in Table 1.

2.3. Preparing wines for analysis

When choosing the method of sample preparation of wines for multi-element analysis, the methods of "dry", microwave acid mineralization, as well as dilution with nitric acid were used.

"Dry" mineralization was carried out taking into account the recommendations [56]. 25 mL of the analyzed wine sample was added to porcelain crucibles, which were placed in a muffle furnace and kept at 50 °C for 12 h. Wine samples were burned at 450 °C according to the program: temperature rise of 50 °C/h and holding at 450 °C for 18–24 h. The resulting white ash was dissolved with 5 % nitric acid to a volume of 25 mL.

Microwave acid mineralization was performed according to a multistage process: stage 1 – heating to 180 °C and 450W for 10 min, stage 2 – maintaining the reaction mixture at 180 °C and 1100W for an additional 20 min, and stage 3 – cooling to room temperature. Nitric acid was used as an oxidizing agent (2.5 mL of concentrated HNO_3 was added to 2.5 mL of wine sample) [57].

The preparation of wines for analysis by preliminary dilution by 15 times with 2 % nitric acid was carried out taking into account the data [51,53,54], as well as the capabilities of the measuring spectrometer used.

2.4. Data analysis

Predictive models for identifying the geographical origin of white wines were built using machine learning methods of the Data mining STATISTICA package: Decision trees, Machine learning procedures, automated neural networks (Automated neural networks). Decision trees are represented by General classification and regression trees (***C&RT***), Chi-square automatic interaction detection (***CHAID***), Boosted trees classifications and regression (***Boosted Trees***), Random Forest. Machine learning is represented by Support vector machine (***SVM***), k-nearest neighbor (***KNN***). Independent variables (predictors) of classification models were concentrations of 15 metals - Li, Na, Mg, Al, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Ba and wine grade. As a dependent (target) variable, the regions of grape sort represented by the subzone South Foothill and Black Sea, subzones Anapa and Taman were used. The accuracy of the classification models of machine learning methods was compared with the data of the traditional classification method General discriminant
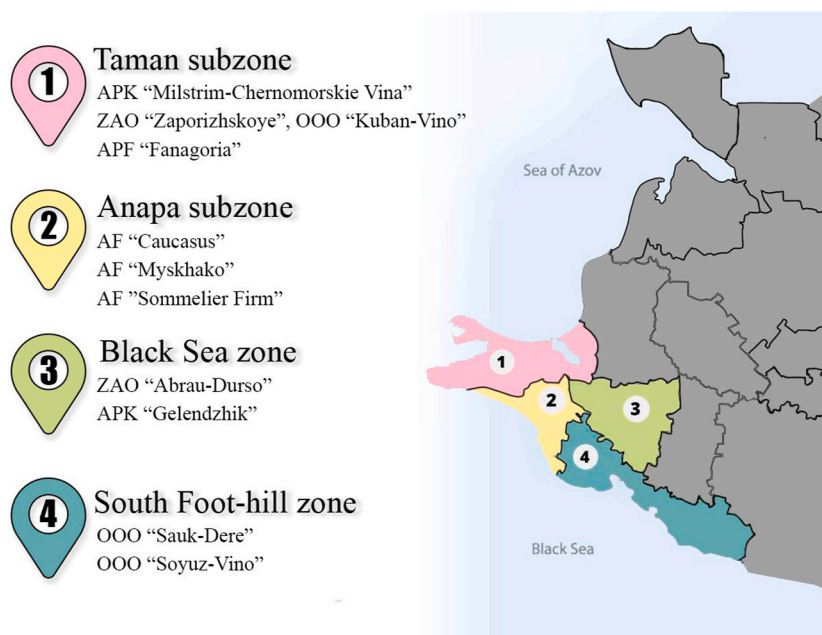

Fig. 1. Geographical zones for grape growing in the Krasnodar Region, Russia.

Table 1

Instruments operating parameters and elements limits of determination.

ICP-MS (iCAP RQ)		ICP-OES (iCAP 7400)	
Plasma gas flowrate, L/min	15.0	Plasma gas flowrate, L/min	12
Nebulizer gas flowrate, L/min	1.0	Nebulizer gas flowrate, L/min	0.5
Applied power, W	1550	Applied power, W	1200
Replicates	5	Replicates	5
Auxiliary gas flowrate, L/min	0.8	Auxiliary gas flowrate, L/min	0,5
Integration time, s	0.01		
Isotopes, (LOD, µg/L)		**Spectral lines, (LOD, µg/L)**	
^{7}Li, (0.001)	^{75}As, (0.015)	Zn 213.856 (I), (0.35)	Al 396.152 (I), (1.23)
^{49}Ti, (0.081)	^{98}Mo,(0.006)	Ni 231.604 (II), (0.26)	Sr 421.552 (II), (0.57)
^{51}V, (0.014)	^{111}Cd,(0.002)	Mn 257.610 (II), (0.15)	Ca 422.673 (I), (14)
^{59}Co,(0.008)	^{208}Pb, (0.009)	Fe 259.940 (II), (1.6)	Ba 455.403 (II), (0.41)
		Mg 280.270 (II), (8)	Na 588.995 (I), (2.4)
		Cu 324.754 (I), (0.11)	K 766.490 (I), (5)
			Rb 780.023 (I) (0.46)
		I – neutral atom,	
		II – singly ionized atom	

analysis (**GDA**), which allows the use of categorical variables and the use of a test sample to evaluate the predictive properties of the model.

3. Results and discussion

3.1. ICP-spectrometric analysis of wines

3.1.1. Optimization of sample preparation conditions for analysis

During the implementation of wine sample preparation and subsequent ICP-spectrometric analysis, special attention was paid to ensuring the completeness and accuracy of sample preparation. The established levels of analytes in wine, using sample preparation techniques such as "dry" ashing, microwave acid mineralization, and dilution with nitric acid, showed satisfactory agreement between the results within the limits of error of the measurement (Table 2).

Data on the ICP determination of metals in wines are given for three parallel measurements for each method. The measurement accuracy level was monitored using the introduced-found method. The ANalysis Of VAriance (ANOVA) analysis shows that the difference in the metal content after opening the same samples by all the above methods was within the measurement error.

The difference between the methods of mineralization of samples was in the time factor. The differences in the methods of mineralization of samples were in the timing factor. The time it takes to open wines by "dry" ashing is more than 30 h. Microwave mineralization of wine using the oxidizing agents HNO_3 and HCl is taking around 1.5–2 h. Preliminary dilution of wine with 2 % nitric acid 15 times was found to be the fastest and least labor-intensive method, with a simultaneous preparation time of 30–35 min for ten samples.

3.1.2. Effect of metal concentrations on wine quality

The influence of the mineral composition on the quality of wines was assessed considering the regulatory restrictions on the content of metals in them, as well as the recommendations of researchers when assessing their consumer properties. The International Organization of Viticulture and Winemaking (OIV) [58] has established the maximum permissible concentrations of the following elements in wines: As - 0.20 mg/L; Cd - 0.01 mg/L; Cu - 1.00 mg/L; Pb - 0.15 mg/L and Zn - 5.00 mg/L [58]. In the EU countries, the concentration of Na is also standardized, and should not exceed 60 mg/L, because its high content impairs the harmony of taste - the wine acquires "soapy tones" [59].

Mineral components, interacting with amino acids and phenolic compounds, determine mainly the taste properties of wines [7]. The content of Al above 5 mg/L in wine leads to the appearance of a metallic taste and the smell of hydrogen sulfide, and the concentration of Zn above 5 mg/L gives an unpleasant odor, rough, astringent-bitter taste [59,60]. Cu and Fe concentrations of more than 1 and 7 mg/L, in addition to a bitter metallic taste, affect the aroma of wine [7]. Elevated concentrations of Al, Fe and Zn (more than 5 mg/L), Cu and Ni (more than 1 mg/L) can cause the formation of metal-cass and colloidal opacities [7].

Data from ICP-spectrometric analysis of the wines under study indicates that in all samples, the content of regulated elements by the OIV is below the established maximum limit (Table 3).

The established ranges of metal content in wine samples of various groups depended on the variety and region of grape cultivation. The average metal content in wines from different grape varieties differed significantly by group. Thus, in the Taman subzone for Riesling and Chardonnay wines, the content of all elements turned out to be higher than in other regions. For Muscat wine, the maximum content of elements was observed in the Black Sea zone. The highest content of Li, Mg, Ni and Rb in Chardonnay wines was found in the Taman subzone, in the Black Sea zone - Al, Ba, Ca, K, Ti and Zn; in the Southern foothill zone there are Cu, Fe and Sr, and in the Anapa subzone Mn and Na. Riesling wines from the Taman subzone had the highest concentrations of Ca, Cu, Li, Mg, Mn, Na, Ni,

Table 2

The results of the determination of metals in wines after various methods of sample preparation.

Element	"Dry" mineralization				Microwave acid mineralization				Dilution 1:15			
	Measured, mg/L	Added, mg/L	Found, mg/L	Rec., %	Measured, mg/L	Added, mg/L	Found, mg/L	Rec., %	Measured, mg/L	Added, mg/L	Found, mg/L	Rec., %
Al	0.800	1.0	1.733	92 %	0.733	1.0	1.751	103 %	0.746	1.0	1.728	98 %
Ba	0.090	0.10	0.176	84 %	0.077	0.10	0.177	100 %	0.077	0.10	0.177	100 %
Ca	80	100	174	93 %	74	100	176	102 %	75	100	174	99 %
Cu	0.540	0.50	0.992	91 %	0.534	0.50	0.986	91 %	0.489	0.50	1.015	105 %
Fe	7.280	7.0	13.6	91 %	6.659	7.0	13.6	99 %	6.599	7.0	13.7	101 %
K	630	500	1105	96 %	605	500	1100	99 %	599	500	1104	101 %
Li	0.015	0.02	0.031	71 %	0.014	0.02	0.031	79 %	0.012	0.02	0.032	100 %
Mg	55	50	102	95 %	52	50	102	100 %	53	50	102	100 %
Mn	0.620	0.50	1.093	96 %	0.608	0.50	1.090	97 %	0.587	0.50	1.105	103 %
Na	35	50	80.3	87 %	33	50	81.1	94 %	31	50	83.7	106 %
Ni	0.024	0.02	0.045	103 %	0.023	0.02	0.044	108 %	0.025	0.02	0.043	93 %
Rb	0.220	0.20	0.387	85 %	0.178	0.20	0.359	90 %	0.162	0.20	0.365	102 %
Sr	1.310	1.0	2.242	95 %	1.228	1.0	2.222	100 %	1.221	1.0	2.227	101 %
Ti	0.020	0.02	0.039	96 %	0.019	0.02	0.039	100 %	0.019	0.02	0.039	100 %
Zn	0.410	0.50	0.877	92 %	0.390	0.50	0.881	98 %	0.383	0.50	0.893	102 %

Content As, Cd, Co, Mo, Pb and V < LOD.

Table 3
Ranges of elements in wines by grape varieties and regions of origin, mg/L (except Ca, K, Mg, Na – g/L).

Element	Taman subzones			Anapa subzones		South Foothill zones			Black Sea zones		
	Chardonnay	Riesling	Muscat	Chardonnay	Muscat	Chardonnay	Riesling	Muscat	Chardonnay	Riesling	Muscat
Al	0.167–1.238	0.755–2.683	0.376–1.562	0.468–0.566	0.616–2.026	1.040–1.718	1.692–2.261	1.056–1.956	0.347–1.250	0.661–2.618	1.941–8.735
Ba	0.041–0.183	0.119–0.246	0.053–0.290	0.054–0.111	0.087–0.121	0.093–0.284	0.129–0.460	0.089–0.186	0.059–0.200	0.085–0.177	0.076–0.157
Ca	0.019–0.082	0.073–0.100	0.058–0.111	0.034–0.039	0.065–0.095	0.040–0.066	0.068–0.099	0.069–0.083	0.037–0.080	0.066–0.091	0.075–0.088
Cu	0.003–0.910	0.008–0.059	0.026–0.196	0.029–0.035	0.533–0.669	0.022–0.040	0.026–0.073	0.029–0.062	0.044–0.065	0.029–0.463	0.284–1.049
Fe	0.468–7.928	1.073–6.393	0.964–7.081	2.377–3.153	7.254–8.974	4.594–5.758	3.489–5.696	3.255–4.697	0.681–3.087	0.514–6.550	5.250–6.331
K	0.490–1.055	0.301–0.950	0.395–1.249	0.687–0.784	0.580–0.717	0.355–0.964	0.548–1.079	0.749–0.888	0.490–0.999	0.195–0.552	0.555–0.125
Li	0.013–0.065	0.015–0.035	0.020–0.039	0.008–0.015	0.014–0.017	0.009–0.013	0.011–0.015	0.013–0.023	0.006–0.037	0.003–0.038	0.010–0.032
Mg	0.025–0.173	0.045–0.214	0.055–0.153	0.051–0.055	0.050–0.064	0.041–0.065	0.059–0.086	0.066–0.091	0.045–0.056	0.037–0.074	0.061–0.093
Mn	0.094–2.811	0.775–3.006	0.828–1.782	0.758–0.815	0.581–0.735	0.511–1.110	0.366–0.650	0.787–1.127	0.646–1.981	0.580–1.691	0.778–1.599
Na	0.021–0.082	0.021–0.134	0.022–0.104	0.021–0.025	0.032–0.040	0.048–0.065	0.021–0.065	0.041–0.053	0.023–0.057	0.015–0.106	0.066–0.076
Ni	0.007–0.132	0.005–0.076	0.019–0.053	0.007–0.016	0.012–0.045	0.016–0.041	0.017–0.052	0.028–0.045	0.029–0.058	0.009–0.126	0.026–0.184
Rb	0.109–6.088	0.293–1.296	0.431–0.847	0.580–0.647	0.176–0.293	0.204–0.810	0.494–0.700	0.507–0.764	0.865–2.352	0.462–0.737	0.278–0.839
Sr	0.411–1.284	0.665–1.744	0.541–1.040	0.865–0.907	1.270–1.441	0.381–0.596	0.577–0.712	0.611–0.998	0.508–1.469	0.489–1.193	0.762–1.093
Ti	0.005–0.028	0.009–0.035	0.007–0.028	0.011–0.017	0.003–0.043	0.017–0.026	0.018–0.047	0.015–0.018	0.018–0.026	0.013–0.051	0.021–0.032
Zn	<LOD-1.439	<LOD-1.492	0.241–0.546	0.338–0.404	0.329–0.707	0.278–0.666	0.213–0.939	0.513–0.759	0.543–0.849	0.289–1.457	0.291–1.182

Content As, Cd, Co, Mo, Pb and V < LOD.

Table 4

Content of elements in white wines produced in different regions.

№	Manufacturer country	Average element content, mg/L															References
		Al	Ba	Ca	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Rb	Sr	Ti	Zn	
1	Italy	0.56	0.07	84	0.08	0.87	786	0.004	73	0.67	18	0.02	0.71	0.31	0.004	0.84	[61]
2	Argentine	–	0.06	–	0.21	–	–	0.67	–	1.50	–	0.22	0.75	0.85	–	–	[62]
3	Portugal	0.07	–	77	0.004	0.12	716	0.001	57	0.08	32	0.001	0.14	0.03	–	0.03	[63]
4	China	0.39	0.10	69	0.20	4.68	1506	0.03	212	0.67	17	0.08	1.23	1.42	–	0.67	[42]
5	Spain	0.07	0.04	55	0.10	0.38	568	–	92	0.65	17	0.01	–	1.29	–	0.31	[64]
6	South Africa	0.27	0.13	45	0.33	0.71	–	0.01	168	1.07	14	0.02	1.36	0.53	0.02	1.65	[65]
7	Germany	–	–	107	–	1.98	–	0.01	77	1.00	–	–	0.40	0.38	–	0.93	[66]
8	Croatia	–	0.02	49	0.15	0.86	441	–	–	0.64	–	0.01	1.12	0.15	–	0.58	[67]
9	Russia	1.34	0.13	70	0.20	3.62	602	0.02	71	0.99	54	0.07	0.89	0.82	0.02	0.55	This work

Rb, Sr and Zn, and Al, Ba, Fe and Ti in the Southern Foothill subzone. For the Muscat variety, the highest average contents of Li, Mg, Mn, Na and Rb were typical in wine from the Taman subzone; Al, Ni and Zn – from the Black Sea subzone; Ba, Ca, Cu, K and Ti – from the Southern Foothill zone, and Fe and Sr – from the Anapa subzone. The contents of Li, Mg and Rb in all the studied varieties of wines from the Taman subzone turned out to be the highest compared to others.

A significant difference was observed in the concentrations of Al, Ba, Ca and Rb was observed between different wine varieties, and Al, Ba, Rb, Fe and Li – between growing regions. At the same time, the concentrations of metals varied in different groups of wines, with the magnitude of these variations relative to the average. For some elements, these deviations were small, with standard deviations less than half the average, such as Ba, Ca, K, etc. Others were high, such as Al, Cu, Ni, etc. The similarity of the average concentrations in different groups indicated their internal homogeneity. This allowed modern chemometric techniques to establish the geographical origin of wine by its authenticity.

According to various authors [42,61–67], we tried to conduct a comparative analysis of the average element contents in white wines produced in different regions of grape growth and production (Table 4). Unfortunately, the publications did not fully indicate information about the climate, the chemical composition of the soils on which grapes were cultivated, the forming elemental composition of berries and wine, the technology of processing wine materials, and the timing of harvest. From these data, we can state that, depending on the region of origin, the average concentration of Al in white wines varies depending on the region of production from 0.07 to 1.34, Ba – from 0.02 to 0.13, Cu – from 0.004 to 0.33, Fe – from 0.12 to 4.68, Na – from 14 to 54, Sr - from 0.03 to 1.42 mg/L, which can significantly affect their consumer properties [7,59,60].

3.2. General discriminant analysis (GDA)

The classification of wines is determined by a cluster structure describing its indicators, depending on their uniformity within and heterogeneity between classes, represented by the distances between them as points of multidimensional space in the coordinate system. We visualized classes by transferring objects into a lower-dimensional space while maintaining the order of distances using discriminant analysis and constructing scatterplots of canonical values.

For the studied wine samples, the scatter diagram of the canonical values is presented in Fig. 2 in the coordinate system with the canonical roots Root 1, Root 2. The concentrations of 15 metals were used as predictors in the discrimination model, and the grape growing region was the target grouping variable. Samples of wines from the same group (class) are depicted with identical geometric figures – squares, diamonds, rectangles and triangles of different colors. From the diagram we can see that the samples of each region are mainly localized in "their" specific part of the plane, forming groups of similar objects - clusters. Samples of the Taman and Anapa subzones are located in lower right and left parts of the plane, and those from the South Foothill and Black Sea zones were localized above and below the central part of the plane. It can be assumed that the studied wine samples, based on the content of 15 metals, have a cluster structure relative to the region where the grapes grow, which allows for the construction of models for establishing their geographical origin.

An important difference between machine learning methods and other methods for constructing predictive models is their ability to learn in the course of solving the given problems. The classification model allows us to identify all objects in the source data although
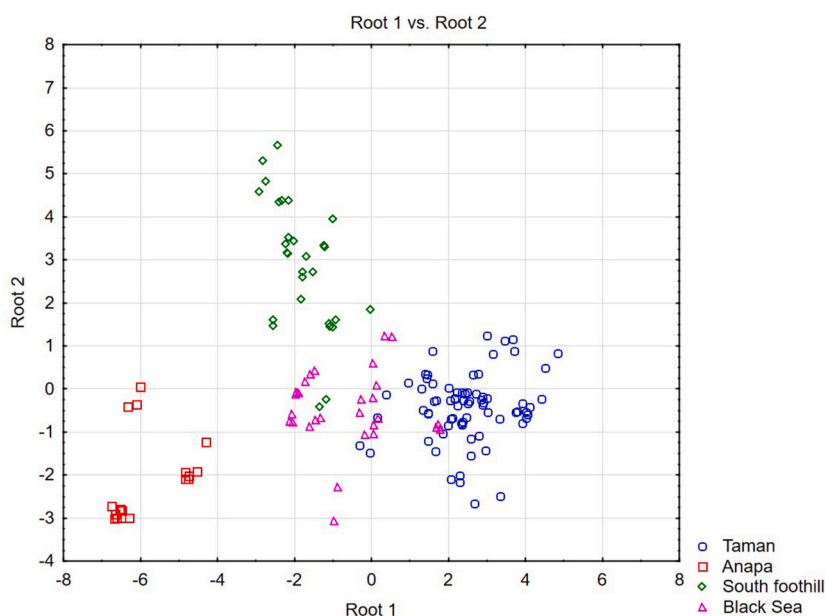
Fig. 2. Scatterplot of canonical values.

for other objects its prognostic abilities are limited. An effective way to prevent the overfitting of the model is to divide the data into training and test sets. The model is trained on the first set, and its predictive properties are checked (tested) on the second. We divided the wine samples using a random number sensor into training and test sets of 111 (73 %) and 42 (27 %) samples, respectively. The regional and varietal structures of the training and test sets are presented in Table 5. All the considered methods, when solving the classification problem, allow us to use along with continuous predictors, the categorical predictors. Classification models were built using 15 continuous predictors—concentrations of 15 metals-and a categorical predictor-wine variety.

The **GDA** provides 6 different procedures for building a classification model - « *All effects*», «*Forward stepwise*», «*Backward stepwise*», «*Forward entry*», «*Backward removal*», «*Best subsets*». The « *All effects* » procedure involves including all predictors in the discrimination model under construction. The next 4 procedures are based on step-by-step inclusion/exclusion of predictors into the model depending on the values of the Fisher criterion parameters – F to enter, F to remove. The Best subsets procedure selects the subset with the best predictive properties among all valid predictor subsets. Using step-by-step discrimination procedures, we obtained identical classification accuracies on the training (93.69 %) and testing (92.86 %) sets. The « *All effects*» and «*Best subsets* » procedures showed a higher quality of classification - the accuracies on the training and test sets reached 94.59 and 95.24 %, respectively. Next, we considered the classification model of the «*All effects* » procedure, which uses all predictors when constructing the model.

The model was built with the prior probabilities of classifications parameter Estimated and enabled Cross-validation. The following training set contained 6 erroneous classifications out of 111. The program classified two samples from the South Foothill zone as samples from the Black Sea zone, and 4 samples from the Black Sea zone as ones from the Taman subzone (Table 6). There were 2 erroneous classifications in the test set (Table 6) - the sample from the Black Sea zone was defined as a sample from the Taman subzone, and the sample from the South Foothill zone was assigned to the Black Sea zone. Classification accuracies, determined by the ratio between the number of correct classifications and the total number of samples, were 94.6 and 95.24 % on the training and test sets, with the overall accuracy of the entire set of samples being 94.77 %.

The **GDA** provides an assessment of the statistical significance and importance of predictors in the classification model (Table 7). At a significance level p of the Fisher test less than 0.05, the predictor in the classification model is considered statistically significant. Ba, Ti, Rb and Na will be statistically insignificant according to this criterion. With a smaller Wilks statistic and a larger F value of the Fisher test, the contribution (importance) of the predictor to the classification model becomes greater. The most important contribution to the model is made by Li, then Sr, Fe, Mg, …, less important by – Na.

3.3. Data mining machine learning methods

3.3.1. Decision trees

The **C&RT** method includes various algorithms for growth and pruning of trees. A wine classification tree with the best predictive properties was built using the following parameters: Misclassification costs – equal, agreement criterion – Gini measure; Prior probabilities – estimated; stopping rule – Fact style direct stopping; stopping parameter – Minimum n of cases = 1; Fractional of objects 0.01; v-fold cross validation enabled at v = 10. The constructed tree (Fig. 3) contains 21 vertices, of which 11 are terminal (have no branches), and has good predictive properties. In the training set (Table 8) there were 2 erroneous classifications - 2 samples of the Taman subzone were assigned to the Black Sea zone. There were also 2 erroneous classifications in the test set (Table 8) - one sample from the South Foothill zone was assigned to the Taman and Anapa subzones. The classification accuracies on the training and test sets were 98.2 % and 95.24 %, the overall accuracy was 97.39 %.

In some decision tree methods, it is possible to assess the importance of predictors in determining whether objects belong to given classes. Fig. 4 shows a diagram illustrating the significance of predictors in the classification model using the **C&RT** method. Analysis of the graph shows that the most important of the predictors in the model is Sr, followed by Al, Na, Fe, …, the least important are Rb and the categorical predictor Sort.

The idea behind the **CHAID** algorithm is to select combinations of predictors that define the dependent variable in such a way that some nodes can have more than two branches. The tree with the best predictive properties was built with the following parameters: Minimum n = 1, Prob. for splitting = 0.3; Prob. for merging = 0.3; Bonferroni correction is disabled, v-fold cross validation is enabled.

Table 5

Frequency distribution of wine samples by varietal and regional affiliation for test and training samples.

Identifier	Sort	Region Taman	Region Anapa	Region South Foothill	Region Black Sea	Row Totals
Summary Frequency Table (White wines) Marked cells have counts >10						
(Marginal summaries are not marked)						
test	Chardonnay	7	2	5	4	18
test	Riesling	5	0	4	2	11
test	Muscat	7	4	1	1	13
Total		19	6	10	7	42
training	Chardonnay	22	4	8	4	38
training	Riesling	14	0	8	16	38
training	Muscat	18	8	4	5	35
Total		54	12	20	25	111
Column **Total**		73	18	30	32	153

Table 6

Classification of the training and test sample by GDA method.

Class	Classification Matrix (White wines) Rows: Observed classifications Columns: Predicted classifications)				
	Percent Correct Training Sample	Taman p = 0.496	Anapa p = 0.111	South Foothill p = 0.185	Black Sea p = 0.207
Taman	100.00	54	0	0	0
Anapa	100.00	0	12	0	0
South Foothill	90.00	0	0	18	2
Black Sea	84.00	4	0	0	21
Total	94.60	58	12	18	23
	Test Sample				
Taman	100.00	19	0	0	0
Anapa	100.00	0	6	0	0
South Foothill	90.00	0	0	0	1
Black Sea	85.71	1	0	9	6
Total	95.24	20	6	9	7

Table 7

Multivariate tests of significance.

Effect	Multivariate Tests of Significance (White wines). Sigma-restricted parameterization. Effective hypothesis decomposition					
	Test	Value	F	Effect df	Error df	p-level
Li	Wilks	0.278	78.747	3	91	0.000
Sr		0.329	61.917	3	91	0.000
Fe		0.583	21.663	3	91	0.000
Mg		0.620	18.582	3	91	0.000
Ca		0.682	14.142	3	91	0.000
Intercept		0.706	12.657	3	91	0.000
Cu		0.717	11.987	3	91	0.000
Al		0.732	11.085	3	91	0.000
Sort		0.776	4.111	6	182	0.001
K		0.800	7.597	3	91	0.000
Ni		0.872	4.457	3	91	0.006
Zn		0.883	4.031	3	91	0.010
Mn		0.886	3.909	3	91	0.011
Ba		0.949	1.634	3	91	0.187
Ti		0.951	1.558	3	91	0.205
Rb		0.956	1.385	3	91	0.252
Na		0.987	0.397	3	91	0.756

The constructed tree has 34 vertices, of which 22 are terminal (Fig. 5). There are no misclassifications in the training set. There are 3 erroneous classifications in the test set - one sample of the Taman subzone is identified as a sample of the Black Sea zone; one sample of the South Foothill zone is assigned to samples of the Taman subzone and another one to the Black Sea zone. The classification accuracies of the training and test sets were 100 % and 95.24 %, the overall accuracy was 98.69 %. A disadvantage of the **CHAID** method is the lack of ability to assess the importance of predictors in the classification model.

Boosted Trees is a data mining method that uses the boosting technique and involves constructing a sequence of "simple" trees, in which each subsequent one is formed by taking into account the errors of the previous one, trying to reduce them. We built an optimized wine classification model with high predictive properties with the following parameters: Subsample proportion = 0.5; Learning rate = 0.12; Number of additive terms = 200; Minimum n of cases = 5; Maximum n of levels = 12, Minimum n in child node = 1; Maximum n of nodes = 3. As a result, 118 simple trees were built by the model, which together cannot be graphically depicted. There are no erroneous classifications on the training set. There were 2 erroneous classifications on the test set - one sample from the South Foothill and Black Sea zones were classified as samples from the Taman subzone. The classification accuracies on the training and test sets reached 100 % and 95.24 %, the overall accuracy was 98.69 %. The most significant predictors of the classification model were Li, followed by K, Al, Fe, …, Sort.

Random Forest as **Boosted Trees** uses a technique that involves building simple independent models and choosing a solution by voting. The main feature of the method is that the solution of each tree depends on a random set of predictor values, chosen independently and with the same distribution for all trees in the forest, which is a subset of the predictor values of the original data set. The basic principle of constructing trees using a random forest lies in the complete independence of the obtained models from each other. An acceptable classification forest of 70 random trees with the best predictive properties was built with the following parameters: Number of predictors = 5; Number of trees = 70; Subsample proportion = 0.5; Minimum n of cases = 2; Maximum n of levels = 10; Minimum n in child node = 1; Maximum n of nodes = 100. There were no erroneous classifications on the training set. In the test sample, one sample from the Taman subzone was erroneously identified as a sample from the South Foothill and one as a sample from
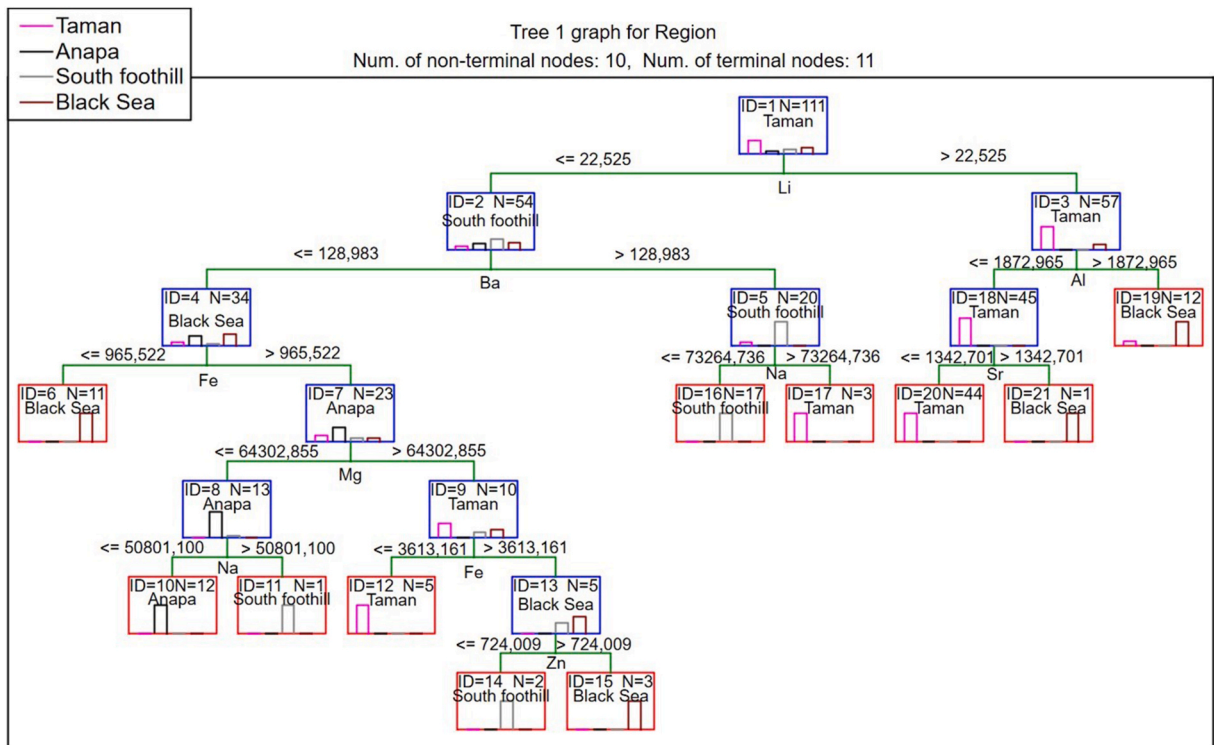
Fig. 3. Decision Tree Graph constructed by the C&RT method.

Table 8

Classification of the Training and Test Sample by the C&RT method.

	Classification matrix 1 (White wines) Dependent variable: Region Options: Categorical response, Tree number 1, Test sample			
	Observed Taman	Observed Anapa	Observed South Foothill	Observed Black Sea
Training Sample				
Predicted Taman	52	0	0	0
Predicted Anapa	0	12	0	0
Predicted South Foothill	0	0	20	0
Predicted Black Sea	2	0	0	25
Test Sample				
Predicted Taman	19	0	1	0
Predicted Anapa	0	6	1	0
Predicted South Foothill	0	0	8	0
Predicted Black Sea	0	0	0	7

the Black Sea zones. The classification accuracies on the training and test sets were 100 % and 95.24 %, the overall accuracy was 98.69 %. The most important predictor in the classification model is Sr, followed by Li, Al, Rb, …, Sort.

3.3.2. Machine learning methods

For building classification models with high predictive properties machine learning methods provide v-fold cross validation, in which the set is randomly divided into v parts, after which the model is trained v times and the resulting solutions are averaged. In this case, training is carried out on the v-1 part, and control is carried out on one part of the data. The importance of predictors is not assessed in Machine learning classification models.

The **SVM** method is based on the concept of hyperplanes, which define the boundaries of hypersurfaces separating a set of objects from different classes. At the same time most classification problems are not that simple, and often require more complex structures than hyperplanes for optimal separation. The main idea of **SVM** is to reorder objects with sets of mathematical functions such that the objects become linearly separable. The STATISTICA package provides such kernel transformation functions as linear, polynomial, exponential (RBF radial basis function) and sigmoid. The best classifier, consisting of 74 vectors, was built with the following
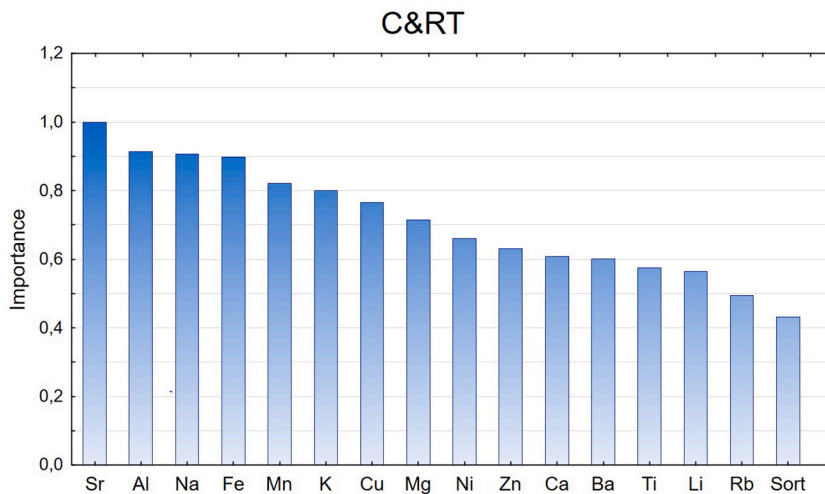
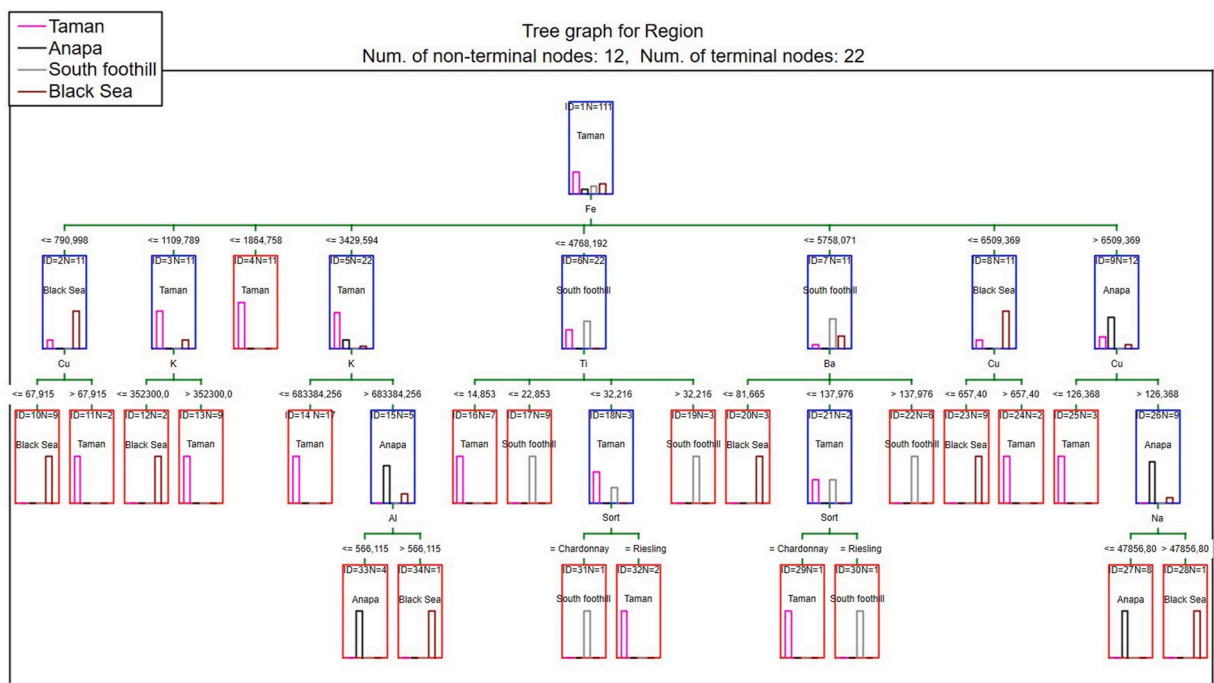**Fig. 4.** Diagram showing the importance of predictors using C&RT method.

Fig. 5. Decision Tree Graph constructed by the CHAID Method.

parameters: classification error function - Classification *SVM*, Type 1; Capacity = 10; RBF kernel transformation function; Gamma = 1.5; Cross-validation enabled; other parameters are accepted by default. There are no erroneous classifications on the training set. There were 2 erroneous classifications on the test set - 2 samples of the Taman zone were identified as samples of the South Foothill zone. The classification accuracy on the training set was 100 %, on the test set – 95.24 %, overall accuracy – 98.69 %.

Estimating the similarity between objects using distances is the basis of the *KNN* method. The object being classified belongs to the same class as the closest to it objects in the training set Therefore, the classification accuracy on the training set is not assessed, since it is used to select the nearest neighbors when classifying objects in the test set. This method is quite simple to implement; the key parameter is the number of nearest neighbors, the optimal value of which k = 1 was found by cross-validation when changing k values in the range from 1 to 10. There are no erroneous classifications on the training set. There were 2 erroneous classifications on the test set - 2 samples from the South Foothill zone were classified as samples from the Black Sea zone. The classification accuracy on the test sample is 95.24 %.

3.4. Automated neural networks (ANN)

The **ANN** method is intuitively appealing and humanly understandable because many of its principles are based on crude and low-level models of biological information processing systems. The input signals of a neural network (NN) are converted into weighted output signals through a mathematical activation function. The ability to learn from training samples is one of the features of NN, which allows the user to set rules governing the underlying relationships between various data attributes. A collection of singular artificial neural systems NN allows you to model complex functions and non-linear relationships of variables, extracting patterns in the form of knowledge, rules and trends from the data. Such patterns are difficult, and often impossible, to model using analytical or parametric methods. The problem of overfitting, as in other machine learning methods, is one of the main problems of NN. When a network is fitted to the training data in a way that reproduces even the random noise in a particular data set, it is difficult for the network to make accurate predictions using the new data. Therefore, to solve such problem, we used the Identifier variable to divide the data into training and test sets. We built networks using the Automated Neural Networks method with the following parameter settings: neural network type – multilayer perceptron (MLP), Min. hidden units = 5; Max. hidden units = 16; Networks to train = 20; Network to retain = 5. The training algorithm, the number of iterations during training, error functions, activation of hidden and output neurons were selected by the program automatically. The program built 200 neural networks, from which the MLP 18-9-4 network was selected with the best predictive properties - network performance on both samples, i.e. classification accuracy on the training and test sets was 100 %.

In the MLP 18-9-4 network, the abbreviation MLP stands for multilayer perceptron, 18 is the number of input neurons, which is equal to the sum of the number for continuous predictors (15) and the number of values for the categorical independent variable Sort (3); 9 – number of hidden neurons, 4 – number of output neurons, determined by the number of regions. During training, we used an iterative algorithm for numerical optimization of weights - BFGS with a number of iterations equal to 49, error function - SOS (Sum of squares), activation functions for hidden and output neurons - Tanh and Identity. Fig. 6 shows the architecture of the MLP 18-9-4 neural network.

The importance of predictors in a neural network classification model is determined by the sensitivity coefficient. The ordered sequence of model predictors in descending order of their sensitivity coefficients is as follows: Sort, K, Sr, Li, Fe, Mg, Mn, Ca, Na, Al, Ba, Ti, Cu, Rb, Zn and Ni.

The results of the comparative analysis of the implemented methods are given in Table 9. The **ANN** method achieved the maximum possible accuracy of 100 % on the test and training sample. The other methods, including **GDA**, obtained the same result on the test sample, the accuracy is 95.24, which corresponds to 2 erroneous classifications out of 42 samples. The **C&RT**, **CHAID**, **Boosted Trees, Random Forest, SVM** methods achieved 100 % accuracy on the training sample; the classification accuracy of the **C&RT** and **GDA** methods are 98.2 % and 94.6 %, which corresponds to 2 and 6 classification errors out of 111 wine samples. According to the general classification accuracy, **ANN** took the first place (100 %), the second place was shared by 4 **C&RT**, **CHAID**, **Boosted Trees, Random Forest** (98.69), the third place by **C&RT** (97.39 %) and the last fourth place by **GDA** (94.77 %). When predicting the geographical origin of wines, the concentrations of Sr, Li, Fe, and Al dominated in importance in the constructed models.

4. Conclusion

Elemental composition of 153 samples of Chardonnay, Riesling and Muscat white wines grown and produced in four regions of Krasnodar Territory were measured by ICP-OES and ICP-MS techniques. Correlations between the elemental composition of the soils, grapes and wines were found which allowed to distinguish the areas of the grapes growth and wine varieties with high accuracy. Inspite of the close location of the regions the found mean elemental concentrations in different wine varieties varied significantly. Concentrations of all elements in Risling and Chardonnay wines produced in Taman region were higher comparing to other regions. The highest element concentrations were measured in Muscat wines produced in Black Sea zone. It was found that Al, Ba, Ca and Rb are
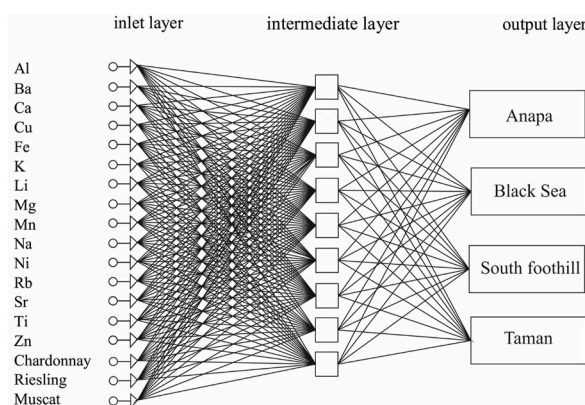

Fig. 6. Neural network architecture.

Table 9

Results of comparative analysis of implemented methods.

Samples	Decision trees				Machine learning		ANN	Multivariate Techniques
	C&RT	CHAID	Boosted Trees	Random Forest	SVM	KNN		GDA
Classification accuracy, %								
Train	98.2	100	100	100	100	–	100	94.6
Test	95.24	95.24	95.24	95.24	95.24	95.24	100	95.24
Total	97.39	98.69	98.69	98.69	98.69	–	100	94.77
Assessing the importance of model predictors								
	Sr, Al, Na, Fe, Mn	the possibility of evaluation is not provided	Li, K, Al, Fe, Mg	Sr, Li, Al, Rb, K	the possibility of evaluation is not provided		K, Sr, Li, Fe, Sort	Li, Sr, Fe, Mg, Ca

good precursors of the white wines variety, while concentrations of Al, Ba, Rb, Fe and Li define the area of the grape growth.

Similarity of the average values of metal concentrations in different groups of wines indicates homogeneity within the groups, while the cluster structure established by discriminant analysis made it possible to construct predictive models for the of white wines by geographic origin. Data mining machine learning methods and General discriminant analysis were tested for data processing. The predictors of the classification models were metal concentrations and wine variety.

The quality of the constructed predictive models was determined by the accuracy of classification – the percentage of correctly identified wine samples. The neural network method has achieved the highest classification accuracy on test and training samples. The rest of the used machine learning methods in the test sample gave similar results with a classification accuracy of 95.24 %. The C&RT, CHAID, Boosted Trees, Random Forest, and SVM methods achieved 100 % accuracy on the training sample; C&RT (98.2 %) and GDA (94.6 %) provided slightly lower accuracy. ANN (100 %) had the highest classification accuracy for the entire set of 153 wine samples, followed by CHAID, Boosted Trees, Random Forest, SVM (98.69), C&RT (97.39 %) and GDA (94.77 %).

The significance of the predictors in the neural network classification model is determined by the value of the sensitivity coefficient. The descending sequence ordered of the element sensitivity coefficients is as follows: Variety, K, Sr, Li, Fe, Mg, Mn, Ca, Na, Al, Ba, Ti, Cu, Rb, Zn and Ni. In predicting the geographical origin of wines, the significance of metal concentrations in the constructed models was mainly dominated by metals Sr, Li, Fe, Al.

It should be noted that Data Mining machine learning methods focused on large-dimensional data, in combination with ICP spectrometric analysis, successfully solved small-dimensional problems of the definition of the authenticity of wines by their geographical origin, component composition and variety.

Data availability statement

Data included in article/supp. material/referenced in article. The following are available online at https://doi.org/10.17632/nxnm4r5ck7.2, https://doi.org/10.17632/nxnm4r5ck7.1 Table S1. Elemental composition of various varieties of wines.

CRediT authorship contribution statement

Zaual Temerdashev: Methodology, Project administration, Writing – original draft, Writing – review & editing. **Alexan Khalafyan:** Software, Writing – original draft, Formal analysis, Methodology, Validation. **Aleksey Abakumov:** Validation, Writing – original draft, Writing – review & editing. **Mikhail Bolshov:** Writing – review & editing. **Vera Akin'shina:** Formal analysis, Software, Validation, Writing – original draft. **Anastasia Kaunova:** Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e29607.

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