Authentication of Geographic Origin of Wine by using EDXRF and Multivariate Statistics

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Abstract: The controlled geographic origin of wine is value added and therefore of great interest to both consumers and manufacturers. It is widely accepted that soil is important component of a wine region terroir, but the reflection of the soil characteristics into the wine, and especially soil elemental composition which is very specific for each vineyard location, is not yet fully understood. By assuming that link between elemental composition of soil and wine exists, the discrimination technique Between Group - Principle Component Analysis (BG-PCA) was used on $\log(c_{soil})/\log(c_{wine})$ ratios of elements Ca, Mn, Fe, Cu, Zn, Rb and Sr to find and evaluate differences between wine regions. The results have been shown for 16 wine samples of Graševina (variety of grapevine Riesling), which can be grouped in 5 viniculture regions of the continental part of the Republic of Croatia. Wine samples pre-concentrated by freeze drying and corresponding soil samples were analyzed by the EDXRF technique.

Keywords: EDXRF, BGO-PCA, geographic origin of wine, Croatia, Riesling, Graševina.

1. INTRODUCTION

Wine Graševina is planted in vineyards across southeastern parts of Europe, however it is believed to show the best results in the continental Croatia, in wine regions of Slavonija and Podunavlje. Graševina is the most planted grape variety in Croatia and can be found almost everywhere in its continental part. Every fifth wine bottle in Croatia goes to Graševina. The same wine in Slovenia is known by the name Laški Rizling, in Hungary it is known as Alaszrizling, while in Vojvodina (part of Serbia) is called simply Rizling. In vine growing areas of the Northern Italy it is known by the name Riesling Italico, while in Austria, Czech Republic, Slovakia and Southern Germany as Welschriesling. In France, assumed as the country of origin, Graševina is cultivated in the northern parts together with other white cultivars. It is known that specific pedological and climate conditions characteristic to each wine region have important influence on wine aroma. Therefore, it is quite common to control the geographic origin of wine and to mark it following the vine sort, e.g. Graševina from Slavonija, Graševina from Erdut, Graševina from Đakovo, etc.

Over the centuries, European winemakers have determined which types of soil are best suited for breeding various grape varieties and how to harmonize them [1]. Some soils can produce a better vine than others, and various grape varieties give the best results on the certain types of soil. This relationship between wine and soil is a fundamental part of the concept of terroir, a complete natural environment in which certain wine is produced, including factors such as soil, topography and climate. The concept and role of the terroir in viniculture is well known, but fundamental science is only beginning to understand it. Determining the geographical origin of wine is of great importance for producers and consumers, as this can be a decisive criterion that guarantees the quality [2]. Several factors such as environmental pollution, agricultural technology, climate change and vinification processes can drastically change the multielemental composition of the wine and jeopardize the relationship between the chemical composition of the wine and the soil of the vineyard. Currently, the authentication of food, and therefore wine, is of great interest to modern society, which is increasingly promoting healthy and quality nutrition. In the last ten years, many studies have been conducted in the world that has sought to develop different methods for determining the traceability of the geographical origin of the wine [3-10].

2. METHODS

2.1. Wine and Soil Sampling

The 16 samples of the Graševina wine were collected from winemakers representing the following viniculture sub-regions of the continental Croatia, as defined by the Croatian regulation on viniculture geographical regions (Official Gazette 74/12) [11]:

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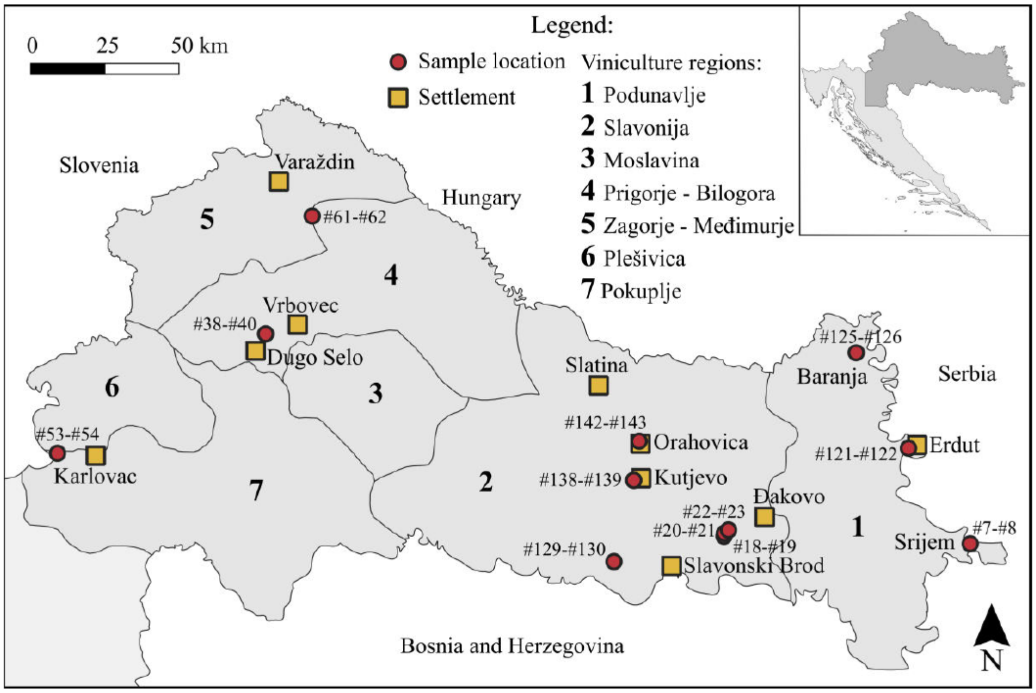

Figure 1: The wine and soil sampling locations presented on the map of the continental Croatia main viniculture regions.

Srijem, Đakovo, Dugo Selo-Vrbovec, Karlovac, Varaždin, Erdut, Baranja, Slavonski Brod, Kutijevo, Orahovica-Slatina, Međimurje and Prigorje-Bilogora. These viniculture's sub-regions can be grouped in 5 of 7 major viniculture regions of the continental Croatia [12] as presented in Figure **1**, which shows the sampling locations. Wine was collected in bottles of 1 liter. Two soil samples of approximately 1 kg from the wine's corresponding vineyard were collected from the depth of 20 cm. GPS coordinates of the vineyards' locations and identification of the corresponding wine samples and wineries are given in Table **1**.

2.2. Wine and Soil Analysis

Two samples of each wine were prepared by pouring 50 mL of wine into plastic containers dimensions of 58x58x40 mm. 10 μg of Se was added as internal standard. Samples were afterwards frozen in liquid nitrogen and lyophilized for about 40 hours in a "Labconco – FreeZone 2.5 L " lyophilizer at -80°C and pressure of 0.015 mbar. Approximately 1 g of freeze dried sample was subsequently transferred into a plastic holder with a bottom covered by 3 μm thick mylar film. Samples were weighed and covered with mylar foil to prevent outpouring. Energy Dispersive X-ray Fluorescence (EDXRF) method was used to analyze the elemental composition of freeze dried samples of wine and associated soil samples. There is consensus in literature, that none of the drying procedures can be *a priori* considered free of losses. In other to validate the results obtained for elemental concentrations in wine by lyophilization in combination with EDXRF, the comparison was made with the Total Reflection X-ray Fluorescence (TXRF) method on the sample of Welschriesling wine from Austria (TXRF measurement done at Atominstitut TU Wien). It was found that acceptable agreement exist for the following chemical elements: Ca, Mn, Fe, Cu, Zn, Rb and Sr. Consequently those were the elements selected for the further evaluation.

Soil samples were dried at 105°C, sieved (Φ = 2 mm), homogenized, crushed in mortar and sieved again (Φ = 45 μm) in order to prepare tablets of 2.5 cm in diameter weighing about 2 g.

Excitation source for EDXRF was Philips x-ray tube with W anode and Mo secondary target in rectangular geometry. Characteristic x-rays were detected by SiLi detector with 3 mm thickness, 30 mm^2 active area and 0.025 mm Be window thickness, having resolution of 170 eV (FWHM) at 5.9 keV. X-ray tube operated at 35 kV and 35 mA. Soil samples were measured at pressure of 10^0 bar. Wines were measured in air in order to prevent degassing of volatile elements. Measurement time for each spectrum was 1000 s. QXAS package program was used to determine the intensity and concentrations of the characteristic x-rays of elements Ca, Mn, Fe, Cu, Zn, Rb and Sr. Direct

Table 1: GPS Coordinates of the Vineyards Locations and Identification of the Corresponding Wine Samples, Wineries and Viniculture Regions

Viniculture major regions	Viniculture sub-regions	Winery	Soil sampling coordinates		Soil	Wine
Podunavlje	Srijem	Srijemska kapljica	45°13,769′	19°17,167′	#7, #8	V2
	Erdut	Erdutski vinogradi	45°30,918′	19°01,367′	#121, #122	V65, V66
	Baranja	Podrumi Kusic	45°47,970′	18°47,991′	#125, #126	V69, V70
Prigorje-Bilogora	Dugo selo-Vrbovec	OPG vinarija Sesan	45°51,400′	16°16,832′	#38	V13
	Dugo selo-Vrbovec	OPG vinarija Sesan	45°51,402′	16°16,814′	#39	V13
	Dugo selo-Vrbovec	OPG vinarija Sesan	45°51,386′	16°16,805′	#40	V13
Slavonija	Slavonski Brod	OPG Grozdanovic	45°10,560′	17°45,969′	#129, #130	V73, V74
	Kutjevo	Obrt Adzic	45°25,179′	17°51,030′	#138, #139	V78, V79
	Orahovica-Slatina	OG Vinkovic	45°32,172′	17°52,399′	#142, #143	V80, V81
	Đakovo	Apostol	45°15,140′	18°14,139′	#18, #19	V7
	Đakovo	Apostol	45°15,681′	18°14,245′	#20,#21	V7
	Đakovo	Apostol	45°16,248′	18°15,284′	#22,#23	V7
Zagorje-Međimurje	Varaždin	OPG Josip i Anton Pokos	46°12,244′	16°28,717′	#61,#62	V28
Pokuplje	Karlovac	OPG Krešimir Mlikan	45°30,003′	15°23,511′	#53,#54	V20,V23

comparison with the reference materials IAEA Soil-7 was used for quantification of elements in soils. Standard reference solutions of 1000 mg/L of Fluka TraceCERT manufacturer were used to prepare calibration lines and a sensitivity curve for quantification of elements concentrations in wine [13]. Relative errors and MDLs for the soil and wine analysis were shown in Tables **2** and **3** respectively. Figures **2** and **3** show typical soil and wine spectra.

2.3. Statistical Analysis

Multivariate statistical method BG-PCA was performed using the open source software Ade4 [14] on $\log(c_{soil})/\log(c_{wine})$ ratios of elements Ca, Mn, Fe, Cu, Zn, Rb and Sr. Samples were classified into predefined groups according to the Croatian viniculture geographic regions. Multivariate discrimination and classification technique was used in order to allocate an unknown wine sample to a predefined group.

3. RESULTS AND DISCUSSION

Results obtained for analyzed wine and soils have been shown in Tables **4** and **5**, respectively. In order to link the concentrations of the elements measured in wine and corresponding soil, the mathematical quantity defined by the equation (1) was introduced:

$$x_{ji} = \frac{log\left(\frac{c_{soil}}{ppm}\right)}{log\left(\frac{c_{wine}}{ppb}\right)}, \quad (1)$$

Table 2: Relative Errors and MDLs. for the Soil Analysis

	Ca	Mn	Fe	Cu	Zn	Rb	Sr
Relative errors (%)	5.2	3.7	2.1	22	5.75	8.8	5.1
MDL (mg/kg)	270	20	13	2	3	2	1.5

Table 3: Relative Errors and MDLs. for the Wine Analysis

	Ca	Mn	Fe	Cu	Zn	Rb	Sr
Relative errors (%)	12.9	3.8	14.6	5.6	8.1	13.1	2.1
MDL (μg/L)	331000	11	7	6	1.3	0.5	0.5

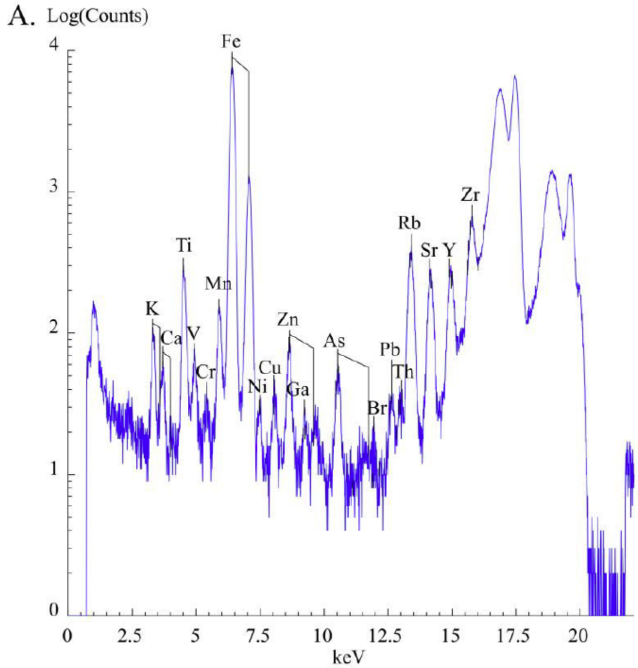

Figure 2: The x-ray spectrum of #53 soil sample.

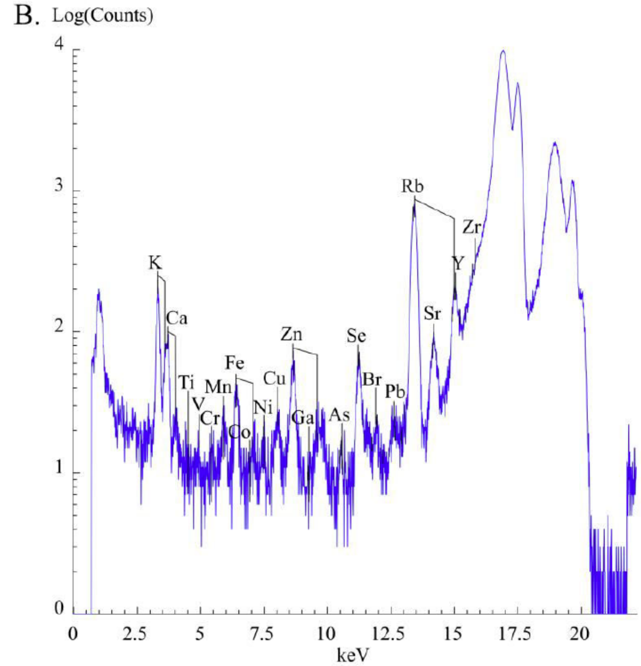

Figure 3: The x-ray spectrum of V20 wine sample.

where c_{soil} and c_{wine} are concentrations of analyzed elements in soil (ppm) and wine (ppb), *j* is a row and *i* is a column of the Table **6**. All combinations of measured concentrations were taken into account, e.g. two samples of wine from Karlovac region V20 and V23 and corresponding two soil samples #53, #54 have produced four rows in Table **6**.

3.1. BG-PCA

Between-group analyses are methods to separate groups of samples, given a set of variables for observations. In the case of measurements on observations, the between-group method is the analysis of the table of group means. Between-group

Table 4: Concentration of Elements Measured in Wine Samples

ID vine	Ca ppb	Mn ppb	Fe ppb	Cu ppb	Zn ppb	Rb ppb	Sr ppb
V2	41970	931	1542	228	207	846	240
V65	53800	1017	2058	277	1036	1143	232
V66	60660	1239	2489	690	955	1000	336
V69	81820	1245	619	219	453	605	174
V70	31710	841	1051	217	352	1033	131
V13	53680	1338	914	213	628	1223	153
V73	45920	682	538	313	856	769	172
V74	21020	627	276	225	640	1203	144
V78	24820	711	408	320	438	1082	133
V79	65980	1190	778	309	615	1067	218
V80	32250	888	266	242	529	1243	171
V81	41220	847	629	276	688	1243	174
V7	58570	619	613	544	486	619	148
V28	48620	545	896	329	1128	321	84
V23	56030	1162	1046	160	571	1670	113
V20	53950	907	959	180	375	1528	104

Table 5: Concentration of Elements Measured in Soil Samples of the Respective Vineyards

ID soil	Ca ppm	Mn ppm	Fe ppm	Cu ppm	Zn ppm	Rb ppm	Sr ppm
#8	11000	921	39120	85	108	122	127
#7	7500	1011	41640	64	111	141	133
#121	26300	897	42880	50	125	123	151
#122	13900	922	43770	41	128	126	140
#125	67400	608	28230	17	116	92	182
#126	75800	678	28570	16	110	87	188
#38	3600	647	73750	21	67	142	83
#39	3600	493	52640	21	107	130	138
#40	3700	412	36130	16	80	111	133
#129	5200	782	45870	78	146	135	118
#130	8300	922	51230	57	121	138	122
#138	4800	926	50290	31	116	127	140
#139	4300	968	59590	50	137	143	125
#142	3600	774	53190	35	120	130	133
#143	4000	755	50910	41	181	129	130
#20	4900	763	44490	37	103	128	141
#21	5400	755	42400	41	111	128	143
#22	6900	632	47940	61	122	137	121
#23	13500	666	45140	77	152	132	127
#19	4500	654	36760	33	101	129	150
#18	4600	712	38740	23	97	127	145
#61	239800	958	29880	64	145	92	294
#62	213300	958	31370	62	124	90	241
#54	3100	1381	55270	27	140	200	116
#53	3100	1428	58310	31	143	186	102

Table 6: Viniculture Main Regions, Groups and Ratios of Logarithms of Concentrations of Elements in Soil and Wine

Viniculture main region	Group	Ca	Mn	Fe	Cu	Zn	Rb	Sr
1.Podunavlje	1a. Srijem	0.87	0.10	1.44	0.82	0.88	0.71	0.88
	1a. Srijem	0.84	1.01	1.45	0.77	0.88	0.73	0.89
	1b. Erdut	0.93	0.98	1.40	0.695	0.695	0.68	0.92
	1b. Erdut	0.875	0.985	1.40	0.66	0.70	0.69	0.91
	1b. Erdut	0.92	0.95	1.36	0.60	0.70	0.70	0.86
	1b. Erdut	0.87	0.96	1.37	0.57	0.71	0.70	0.85
	1c. Baranja	0.98	0.90	1.59	0.52	0.78	0.71	1.01
	1c. Baranja	0.99	0.915	1.60	0.52	0.77	0.70	1.015
	1c. Baranja	1.07	0.95	1.47	0.52	0.81	0.65	1.07
	1c.. Baranja	1.08	0.97	1.475	0.52	0.80	0.64	1.07

(Table 6). Continued.

Viniculture main region	Group	Ca	Mn	Fe	Cu	Zn	Rb	Sr
4.Prigorje-Bilogora	4. D.Selo	0.75	0.90	1.64	0.565	0.65	0.70	0.88
	4. D.Selo	0.75	0.86	1.59	0.56	0.72	0.68	0.98
	4. D.Selo	0.75	0.84	1.54	0.51	0.68	0.66	0.97
2.Slavonija	2a. S.Brod	0.80	1.02	1.71	0.76	0.74	0.74	0.925
	2a. S.Brod	0.84	1.05	1.72	0.70	0.71	0.74	0.93
	2a. S.Brod	0.86	1.03	1.91	0.80	0.77	0.69	0.96
	2a. S.Brod	0.91	1.06	1.93	0.74	0.74	0.69	0.97
	2b. Kutina	0.84	1.04	1.80	0.59	0.78	0.69	1.01
	2b. Kutina	0.83	1.05	1.83	0.68	0.81	0.71	0.99
	2b. Kutina	0.76	0.965	1.63	0.60	0.74	0.69	0.92
	2b. Kutina	0.75	0.97	1.65	0.68	0.77	0.71	0.90
	2c. Orahovica	0.79	0.98	1.95	0.645	0.76	0.68	0.95
	2c. Orahovica	0.80	0.98	1.94	0.68	0.83	0.68	0.945
	2c. Orahovica	0.77	0.99	1.69	0.63	0.73	0.68	0.95
	2c. Orahovica	0.78	0.98	1.68	0.66	0.795	0.68	0.94
	2d. Đakovo	0.77	1.03	1.67	0.57	0.75	0.755	0.99
	2d. Đakovo	0.78	1.03	1.66	0.59	0.76	0.755	0.99
	2d. Đakovo	0.805	1.00	1.68	0.65	0.78	0.765	0.96
	2d. Đakovo	0.87	1.01	1.67	0.69	0.81	0.76	0.97
	2d. Đakovo	0.77	1.01	1.64	0.56	0.745	0.755	1.00
	2d. Đakovo	0.77	1.02	1.65	0.50	0.74	0.75	1.00
5.Zagorje-Međimurje	5. Varaždin	1.15	1.09	1.515	0.72	0.71	0.78	1.28
	5. Varaždin	1.14	1.09	1.52	0.71	0.69	0.78	1.24
7.Pokuplje	7. Karlovac	0.735	1.02	1.57	0.65	0.78	0.71	1.005
	7. Karlovac	0.74	1.06	1.59	0.64	0.83	0.72	1.02
	7. Karlovac	0.74	1.07	1.60	0.66	0.84	0.71	1.00
	7. Karlovac	0.735	1.03	1.58	0.68	0.78	0.70	0.98

analyses and discriminant analyses highlight differences between groups of observations but are not based on the same constraints for combinations of initial variables. Between-group analyses do not require special numbers of samples compared to the number of variables, and it is not sensitive to correlated variables, as it is the case in linear discriminant analysis [14]. It is always possible to run it for any number of variables, groups or individuals by group.

Figure **4** shows the BG-PCA results indicating that elements Fe, Sr, Cu and Ca are the best discriminating variables which can differentiate 16 samples of Graševina wine into 5 viniculture regions: Podunavlje Srijem, Podunavlje Erdut, Podunavlje Baranja, Slavonija – Prigorje/Bilogora – Pokuplje and Zagorje-Međimurje. These 5 groups could be further grouped into 3 main viniculture regions of Graševina in the continental Croatia– the Eastern (Podunavlje), the Middle (Slavonija, Prigorje-Bilogora and Plešivica) and the Northern (Zagorje-Međimurje). Since soil characteristics under different agriculture practices can be changed in time and viniculture practices can influence the final composition of wine, it would be necessary to investigate over longer period of time the impact of these aspects on geographic authentication of wine based on elemental composition analysis.

3.2. Multivariate Discrimination and Classification

In the following it is assumed that we have in total "g" different groups which was proven by using the BG-

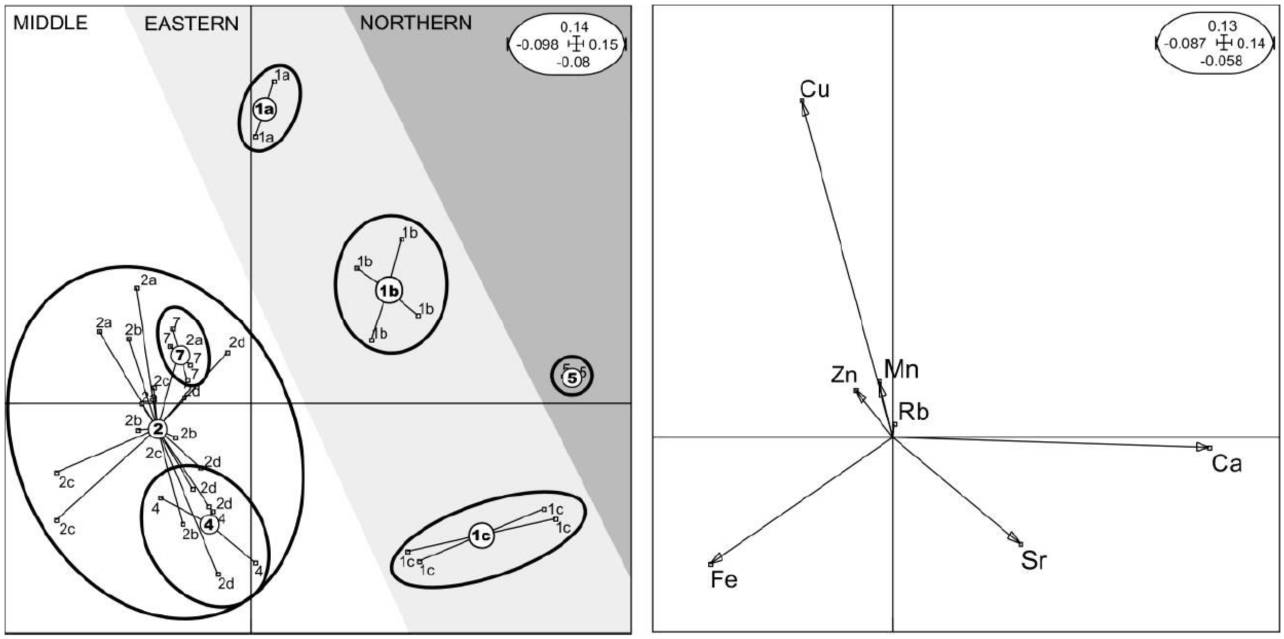

Figure 4: Left: BG-PCA for wines classified into groups according to the vinuculture regions (groups) of the continental Croatia (2. Slavonija- 4. Prigorje/Bilogora-7. Pokuplje; 1a. Srijem; 1b. Erdut; 1c. Baranja; and 5. Zagorje-Međimurje. These 5 groups could be further classified into 3 main viniculture regions of Graševina - the Eastern (Podunavlje), the Middle (Slavonija, Prigorje-Bilogora and Pokuplje) and the Northern continental Croatia (Zagorje-Međimurje). Right:. The graphical presentation of variables contribution to discrimination of the groups. The length of the vector determine the element contribution to discrimination of the groups.

PCA (in our graševina case g=5). Assuming that a soil and wine data base exists, the aim of the geographic wine authentication is to prove that a wine subjected to analysis belongs to a particular geographical group of wines as declared by a producer. The observations in data base were separated or classified on the basis of measurements of seven associated random variables $x'=[x_1,x_2,\dots,x_7]$ (row in Table **6**), where the prime denotes the operation that transposes a column to a row. The discrimination and classification procedure assumes that observations in each group are normaly distributed according to the Eq.2.:

$$f_i(x) = \frac{1}{(2\pi)^5|\Sigma_i|^{1/2}} exp\left[-\frac{1}{2}(x-\mu_i)'\Sigma_i^{-1}(x-\mu_i)\right]$$

(2), i=1,2,...,g; g....number of groups (g=5), (2)

where μ_i is a mean vector and Σ_i is a covariance matrix. The normal distribution is acchived by using the logarithm of concentrations, as was definied in (1). In practice, the μ_i and Σ_i are unknown, but a good estimate is to take $\mu_i = \overline{x^i}$ and $\Sigma_i = S_i$, where $\overline{x^i}$ and S_i are the sample mean vector and the sample covariance matrix, respectively, as defined in Eq.3 and 4.

$$\overline{x^i_k} = \frac{1}{n_1}\sum_{j=1}^{n_i} x^i_{jk} \quad , \quad \overline{x^i}' = \left[\overline{x^i_1} \quad \dots \quad \overline{x^i_7}\right];$$

n_i...number of observations in group *i* (3).

$$S_i = \begin{bmatrix} s^i_{11} & \cdots & s^i_{17} \\ \vdots & \ddots & \vdots \\ s^i_{17} & \cdots & s^i_{77} \end{bmatrix} = \left\{ s^i_{lk} = \frac{1}{n_i-1}\sum_{j=1}^{n_i}\left(x^i_{jl}-\overline{x^i_l}\right)\left(x^i_{jk}-\overline{x^i_k}\right)\right\}$$

(4).

A simplification is possible if the population covariance matrices are equal to $\Sigma_i=\Sigma$, and the pooled estimate of Σ is given by Eq.5.

$$S_{pooled} = \frac{(n_1-1)\boldsymbol{S_1}+(n_2-1)\boldsymbol{S_2}+\cdots+(n_g-1)\boldsymbol{S_g}}{n_1+n_2+\cdots+n_g-g} \quad (5).$$

The linear discriminant score is defined as:

$$d^i(x) = \overline{x^i}'S^{-1}_{pooled}x - \frac{1}{2}\overline{x^i}'S^{-1}_{pooled}\overline{x^i} + ln p_i \text{ for i=1, 2, ..., g}$$

(6),

where p_i is a prior probability, if it is unknown than $p_i=1/g$. "*x*" is a new observation which has to be allocated to one of the groups. According to the estimated minimum total probability of misclassification rule for equal covariance normal populations [15], *x* has to be allocated to group π_k for which Eq. 7 is satisfied.

$$d^k(x) = Max[d^1(x), d^2(x), \dots, d^g(x)] \quad (7).$$

Generaly $n_1+n_2+\cdots+n_g-g-p>0$ must hold (*p* is a number of variables).

4. CONCLUSION

It was found by using the BG-PCA that Graševina wines and associated soils collected from different vineyards in continental Croatia could be classified in 3 main viniculture regions: the Eastern (Podunavlje), the Middle (Slavonija, Prigorje-Bilogora and Pokuplje) and the Northern (Zagorje-Međimurje). The best discriminating variables were Fe, Sr, Cu and Ca.

The authentication process of the geographic origin of wine is proposed to be done as follows:

1. Determine the concentration of chemical elements Ca, Mn, Fe, Cu, Zn, Rb and Sr in a wine sample of interest.

2. The sample has to be classified in the predetermined group "i" which soil elemental composition is registered in a data base.

3. The $\log(c_{soil})/\log(c_{wine})$ ratios should be calculated.

4. If the linear discriminant score of the evaluated sample is found to be the highest for the predetermined group *i* – i.e. to the corresponding viniculture region, the authenticity of the origin is confirmed.

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