# Chemometric prediction of the geographical origin of Croatian wines through their elemental profiles

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**Summary**

The concentration of 16 selected elements in 140 wines from two wine producing regions in Croatia was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Multivariate statistical methods of cluster analysis and principal components analysis were used to evaluate data of these 16 elements in all wines. Differentiation of wines according to their colour and geographical origin on the basis of elements composition was achieved. White and red wines were clearly separated. Differentiation of Croatian white wines according to their origin was based on the following elements: Cd, Fe, Cr, K, Mg, Ca, Pb and Co (continental region) and Na, Sn, Ni, Zn Al, Cu and Zn (coastal region). In case of red wines, elements such as K, Ca, Mg, Na and Co turned out to be characteristic for wines originating from the continental region, while Cd, Ni, Cr, Zn, Al and As for wines originating from the coastal region of Croatia. The relationship between the concentrations of different considered elements could be an adequate tool in differentiating wines produced in different geographical areas in Croatia.

**Keywords**

elements; Croatian wines; geographical origin; inductively coupled plasma optical emission spectroscopy; cluster analysis; principal component analysis

The inorganic chemical pattern of wine is a reflection of regional soil geochemistry, climate and processing. Elements can be considered as good markers of the geographical origin of wine since they are neither metabolized nor modified during the wine making process [1]. Wine elements concentration depends on several factors such as: grape variety, area of production, soil characteristics, environmental conditions and climate. Their determination facilitates establishment of a “fingerprint” for each element [2], giving an opportunity to develop a link between wines and their geographical origin [3]. If properly developed, a chemically-based independent system of classification would support the “wine origin” identification that is used in all wine-producing countries with a main goal to prevent fraudulent practices in the wine industry [4].

Recently, several studies dealt with determination of geographical affiliation of wines based on their elements composition. It is assumed that the chemical composition of wine reflects the composition of the provenance soil, at least for certain elements [5]. Studies in different wine-producing European countries, such as Portugal [6], Italy [7, 8], Croatia [9–11], Czech Republic [12, 13], Spain [14, 15], Slovakia [16, 17], Romania [18–20], Macedonia [21], Cyprus [22], Slovenia [23, 24], Ukraine [25] or Turkey [26], provided data demonstrating the potential of fingerprinting techniques to identify the geographical origin of wines. On the basis of multivariate analysis of elements concentration in wines produced in countries of South America (Argentina, Brazil, Chile and Uruguay) it was stated that wines could be discriminated according to the country of origin, regardless of the type of grapes [27–31]. Multielement techniques applied in wine analysis are usually the first

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step in accessing problems associated with contamination, potential toxicity or quality control. Ražić and Onjia [32] showed that concentrations of individual elements seem to be suitable descriptors for classification of wines, since their concentration can be attributed to the site of grape growing and wine making, comprising both natural and other sources of influence. Today, there is an increasing volume of research exploring food traceability/authenticity, including wines, which uses chemometric techniques to establish relationships between products composition and geographic origin [33]. Robinson et al. [34] used discriminant analysis techniques to identify the underlying sensory and composition attributes of Cabernet Sauvignon wines from 19 geographic indications in Australia.

The aim of this study was to determine the concentration of 16 elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sn and Zn) by inductively coupled plasma optical emission spectrometry (ICP-OES) technique, in selected wines from two wine-producing regions of the Republic of Croatia, and to evaluate the data by multivariate statistical methods in order to establish the relationship between elements and geographical origin of the wines.

## MATERIALS AND METHODS

### Chemicals

All chemicals were of analytical grade. Multielement stock solution containing Al (495 $mg\cdot l^{-1}$), As (24.9 $mg\cdot l^{-1}$), Cd (99 $mg\cdot l^{-1}$), Co (101 $mg\cdot l^{-1}$), Cr (102 $mg\cdot l^{-1}$), Cu (100 $mg\cdot l^{-1}$), Fe (102 $mg\cdot l^{-1}$), Mn (101 $mg\cdot l^{-1}$), Ni (101 $mg\cdot l^{-1}$), Pb (101 $mg\cdot l^{-1}$) and Zn (99 $mg\cdot l^{-1}$), and stock solutions of Sn, K, Ca, Mg and Na at a concentration of 1 $g\cdot l^{-1}$ were obtained from Merck (Darmstadt, Germany). $HNO_3$ (60%) was obtained also from Merck. Ultrapure water from Easy pure RF (Barnstead, Dubuque, Iowa, USA) with conductivity of 18 $M\Omega\cdot cm^{-1}$ was used throughout the study. Working standard solutions were prepared by suitable dilution using 2% $HNO_3$ to cover the natural concentration range of each element in the wines. Solution of 2% $HNO_3$ was used as blank.

**Tab. 1.** Origin of wine samples.

| Origin | Number of samples | |
|---|---|---|
| | White wines | Red wines |
| Subregion of the continental region of Croatia | | |
| Podunavlje | 9 | – |
| Slavonia | 24 | 8 |
| Prigorje-Bilogora | 4 | – |
| Zagorje-Međimurje | 6 | – |
| Plešivica | – | 19 |
| Subregion of the coastal region of Croatia | | |
| Istria | 18 | 1 |
| Croatian Coast | 6 | – |
| Central and South Dalmatia | 4 | 35 |
| Northern Dalmatia | – | 6 |

### Wine samples

A total of 140 wines (71 white and 69 red) were analysed, 70 wines of them originated from continental and 70 wines from coastal wine-producing region of Croatia. This study was performed on wines that were undergoing the procedure of placing on the market. The wine samples represented 12 white and 8 red wine grape varieties. Details about origin of wines, including regions and sub-regions are given in Tab. 1.

### Sample preparation for ICP-OES

Wine samples were prepared by adding of 4 ml of 60% $HNO_3$ to 50 ml of wine. This solution was evaporated in a water bath at 90–95 °C to reduce the volume to approximately 30 ml by removing ethanol, in order to minimize matrix interference during analysis and to diminish plasma instability caused by introduction of organics into the plasma. The sample residue was than quantitatively transferred to a volumetric flask and the volume was set to 50 ml with 2% $HNO_3$. Each sample was analysed in triplicate.

### Instrumentation

Multielement determinations were carried out by PerkinElmer Optima 2000 DV inductively coupled plasma optical emission spectrometer (PerkinElmer, Shelton, Conncecticut, USA), equipped with a Meinhard spray chamber (Meinhard, Golden, Colorado, USA), nebulizer and a peristaltic sample delivery system. The instrument was controlled by ICP WinLab 1.35 software (PerkinElmer). The flow conditions for plasma gas, auxiliary gas and nebulizer gas were 15.0 $l\cdot min^{-1}$, 0.2 $l\cdot min^{-1}$ and 0.8 $l\cdot min^{-1}$, respectively. Power was set at 1300 W. Wines were analysed by the direct calibration curve method. Operating conditions were as published previously [35].

### Statistical analysis

Analysis of variance (ANOVA) was used to find significant differences between concentrations of selected elements in wine samples from different regions of origin. In this analysis, the difference was taken as significant at $p \leq 0.05$ for 95% confidence level. The elements concentration was evaluated by descriptive statistical analysis. Multivariate analysis, comprising cluster analysis (CA) and principal component analysis (PCA), was employed in wine differentiation and classification according to the geographical origin. Statistical calculations were done using software package Statistics (version 8.0; Statsoft, Tulsa, Oklahoma, USA).

## RESULTS AND DISCUSSION

Concentration of elements in wines was determined and, using these as chemical descriptors, statistical methods were applied to establish criteria for wine classification and differentiation according to geographical origin. Concentration of elements in a set of 140 Croatian wines is presented in Tab. 2. Elements can be divided into macro-elements ($c$ > 10 mg·l$^{-1}$), micro-elements ($c$ > 10 $\mu$g·l$^{-1}$) and trace elements (c < 10 $\mu$g·l$^{-1}$) [36]. The most abundant macro-elements were K, Mg, Ca and Na, most abundant micro-elements were Fe, Mn, Al, Cu, Zn, Sn, Pb, Ni, Cr, and most abundant trace elements were Co, As and Cd.

If the wines were observed as red and white, then it can be said that red wines contained significantly higher concentrations of Cu, Fe, Pb, Sn, K and Mg, white wines contained significantly higher concentrations of Al, Co, Ni, Zn and Na, while the concentrations of As, Cd, Cr, Mn and Ca were not significantly different in wines of the two colours. These results are in accordance with the results of Vinković Vrček et al. [10] with the exception of Ni concentration, which was similar in both groups of wines, while Zn concentration was significantly higher in red wines. In white wines originating from the continental region, significantly higher concentrations of As, Cd, Cu, Fe, Ni, Zn, Ca and Mg were recorded, while in white wines from the coastal region, higher concentrations of Co and Na were recorded. In red wines from the continental region, there was a significantly higher concentration of Co and K, while in red wines from the coastal region, significantly higher concentrations of Al, Cd, Cr, Cu, Zn, Mg and Na were found. The significantly higher concentration of Na occurred in white and red wines from coastal region, which was expected and could be explained by proximity of sea. Pb concentrations were in all investigated wines lower than those allowed by the International Organization of Vine and Wine. Pb concentration for all white

**Tab. 2.** Concentration of elements in white and red wines from continental and coastal regions of Croatia.

| Element | White wine | | | Red wine | | |
|---|---|---|---|---|---|---|
| | A | B | C | D | E | F |
| Al | $0.96 \pm 0.39^{a}$ | $0.99 \pm 0.39^{c}$ | $0.94 \pm 0.38^{c}$ | $0.77 \pm 0.49^{b}$ | $0.36 \pm 0.16^{e}$ | $1.04 \pm 0.45^{f}$ |
| As | $0.004 \pm 0.007^{a}$ | $0.005 \pm 0.007^{c}$ | $0.001 \pm 0.002^{d}$ | $0.002 \pm 0.004^{a}$ | $0.001 \pm 0.003^{e}$ | $0.003 \pm 0.005^{e}$ |
| Cd | $0.0003 \pm 0.0007^{a}$ | $0.0004 \pm 0.0009^{c}$ | $0.0002 \pm 0.0004^{d}$ | $0.0006 \pm 0.0011^{a}$ | $0.0004 \pm 0.0005^{e}$ | $0.0008 \pm 0.0013^{f}$ |
| Co | $0.004 \pm 0.002^{a}$ | $0.003 \pm 0.002^{c}$ | $0.004 \pm 0.002^{d}$ | $0.002 \pm 0.002^{b}$ | $0.003 \pm 0.002^{e}$ | $0.002 \pm 0.002^{f}$ |
| Cr | $0.015 \pm 0.006^{a}$ | $0.015 \pm 0.005^{c}$ | $0.015 \pm 0.006^{c}$ | $0.016 \pm 0.007^{a}$ | $0.012 \pm 0.006^{e}$ | $0.018 \pm 0.006^{f}$ |
| Cu | $0.14 \pm 0.15^{a}$ | $0.18 \pm 0.12^{c}$ | $0.09 \pm 0.18^{d}$ | $0.24 \pm 0.27^{b}$ | $0.14 \pm 0.18^{e}$ | $0.31 \pm 0.30^{f}$ |
| Fe | $2.31 \pm 1.75^{a}$ | $2.68 \pm 1.95^{c}$ | $1.76 \pm 1.23^{d}$ | $3.76 \pm 2.33^{b}$ | $3.24 \pm 2.47^{e}$ | $4.09 \pm 2.20^{e}$ |
| Mn | $1.1 \pm 0.56^{a}$ | $1.25 \pm 0.65^{c}$ | $1.08 \pm 0.37^{c}$ | $1.03 \pm 0.61^{a}$ | $1.15 \pm 0.91^{e}$ | $0.94 \pm 0.27^{e}$ |
| Ni | $0.04 \pm 0.029^{a}$ | $0.05 \pm 0.031^{c}$ | $0.03 \pm 0.022^{d}$ | $0.02 \pm 0.026^{b}$ | $0.02 \pm 0.025^{e}$ | $0.02 \pm 0.026^{e}$ |
| Pb | $0.049 \pm 0.03^{a}$ | $0.046 \pm 0.03^{c}$ | $0.054 \pm 0.02^{c}$ | $0.078 \pm 0.07^{b}$ | $0.079 \pm 0.11^{e}$ | $0.080 \pm 0.03^{e}$ |
| Sn | $0.08 \pm 0.07^{a}$ | $0.07 \pm 0.09^{c}$ | $0.09 \pm 0.04^{c}$ | $0.17 \pm 0.19^{b}$ | $0.21 \pm 0.17^{e}$ | $0.14 \pm 0.19^{e}$ |
| Zn | $0.67 \pm 0.55^{a}$ | $0.77 \pm 0.65^{c}$ | $0.51 \pm 0.26^{d}$ | $0.37 \pm 0.26^{b}$ | $0.26 \pm 0.28^{e}$ | $0.44 \pm 0.22^{f}$ |
| K | $683 \pm 224^{a}$ | $656 \pm 242^{c}$ | $716 \pm 197^{c}$ | $1160 \pm 296^{b}$ | $1284 \pm 313^{e}$ | $1062 \pm 243^{f}$ |
| Ca | $83.9 \pm 18.7^{a}$ | $88.8 \pm 16.2^{c}$ | $77.9 \pm 19.9^{d}$ | $80.8 \pm 13.5^{a}$ | $80.8 \pm 12.3^{e}$ | $80.8 \pm 14.7^{e}$ |
| Mg | $83.9 \pm 14.0^{a}$ | $91.8 \pm 10.7^{c}$ | $74.3 \pm 11.3^{d}$ | $93.5 \pm 18.2^{b}$ | $83.1 \pm 17.0^{e}$ | $101.7 \pm 14.6^{f}$ |
| Na | $17.4 \pm 10.1^{a}$ | $14.9 \pm 8.9^{c}$ | $20.5 \pm 10.9^{d}$ | $12.3 \pm 6.3^{b}$ | $10.1 \pm 7.0^{e}$ | $14.1 \pm 5.2^{f}$ |

A, D – both regions; B, E – continental Croatia; C, F – coastal Croatia.
Concentration is given in milligrams per litre. All values are average ± standard deviation. Different small letters in a row indicate significant differences ($p$ < 0.05); a, b – all wines of both regions; c, d – white wines from continental and coastal regions; e, f – red wines from continental and coastal regions.

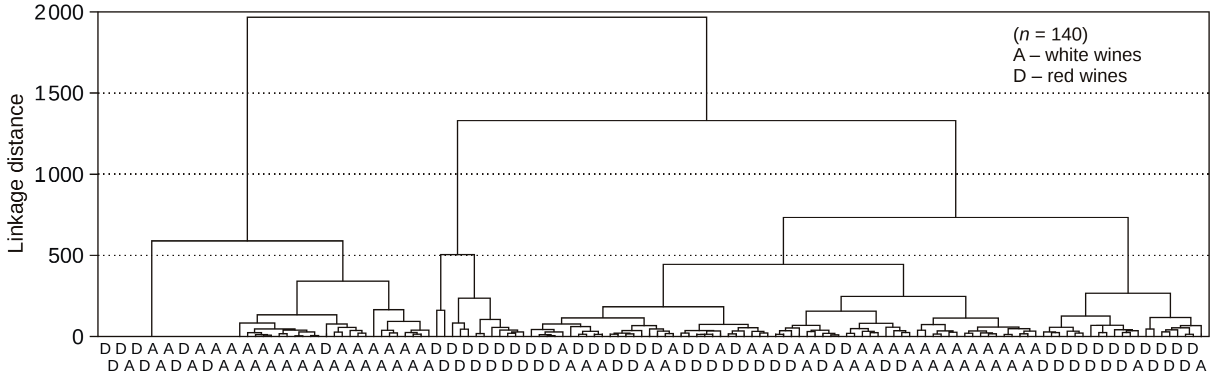


**Fig. 1.** Dendrogram of cluster analysis of all wines.

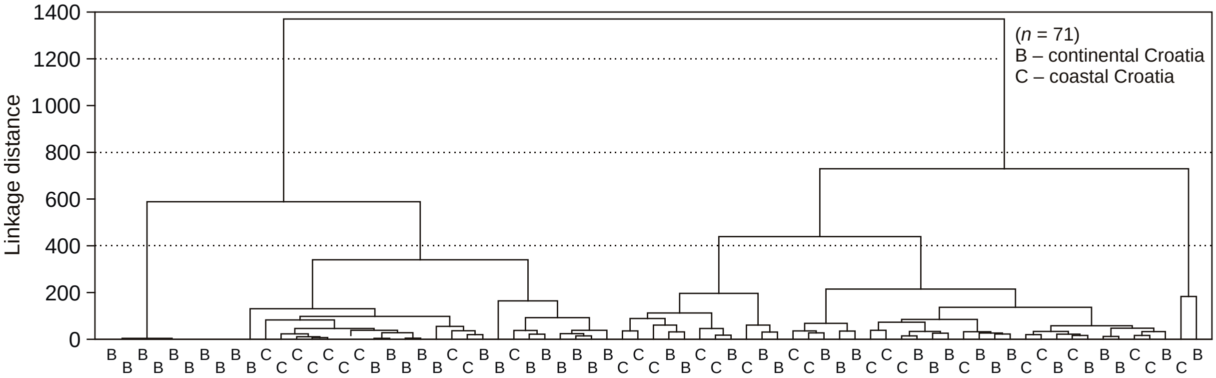


**Fig. 2.** Dendrogram of cluster analysis of white wines.

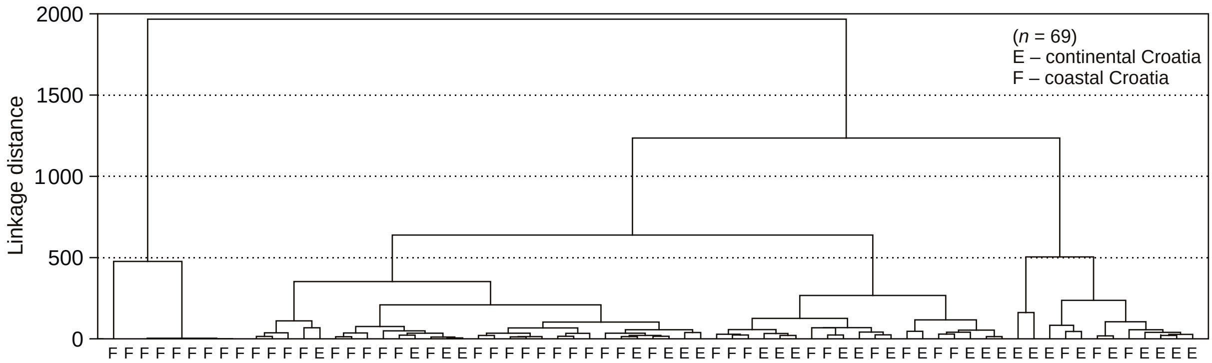


**Fig. 3.** Dendrogram of cluster analysis of red wines.

wines was 0.049 mg·l$^{-1}$ ± 0.03 mg·l$^{-1}$ and for all red wines was 0.078 mg·l$^{-1}$ ± 0.07 mg·l$^{-1}$, which was below the upper limit value given by the International Organization of Vine and Wine of 0.15 mg·l$^{-1}$ [37]. Alkis et al. found that the values of element concentrations may be found in a wide variety of ranges for different wines even if they were produced from the same type of grapes because there are many variables in wine production, such as region, vineyard, soil and climate [38]. Results of this study on various wines with regard to above mentioned influence factors also show differences in the element concentration profile.

A study of the data structure by virtue of cluster analysis and principal component analysis was carried out to establish whether white and red wines, white wines from different wine producing regions and red wines from different wine producing regions constitute distinctive, well-defined groups. Cluster analysis is frequently used as an unsupervised classification procedure, which involves measurement of either the distance or the similarity between objects in a cluster. Cluster analysis that includes all of the investigated elements (16 variables) in form of columns, describes the overall nearness of the wines (140, 71 and 69, respectively) in the form of rows.

Euclidean distance was used as the similarity measure. The results obtained are shown in Fig. 1, Fig. 2 and Fig. 3 in the form of dendrograms.

The dendrogram (Fig. 1) sets out the results obtained for all wines. Six main clusters can be recognized (from left to right): red wines are aggregated in one cluster (on the left), at a linkage distance of around 340 a cluster of white wines is positioned, at a linkage distance of approx. 180–240 are two clusters of red wines, two small clusters at approx. 150 combine at 250 linkage distance giving one cluster of white wine and, finally, at approx. 250 (on the right) a cluster of red wines can be observed. The cluster composition indicates that pertinent data of wine elements can confer the information that might aid to distinguish the white and red wines.

In Fig. 2, results obtained for white wines according to wine producing regions are presented. Several small clusters were observed and two were especially noticeable on the left side: one for white wines from continental Croatia and the second for white wines from the coastal region. Sub-clusters that follow are constituted of wines from both regions.

The results obtained for red wines according to wine producing regions are presented in Fig. 3. On the left side of the dendrogram at a linkage distance of approx. 470, there is the first cluster of red wines from coastal Croatia. On the right side of the dendrogram at a linkage distance of approx. 500, there is a cluster of red wines from continental Croatia. Between them, at a linkage distance of approx. 600, there is a cluster made of wines from both regions, for which interpretation was not possible. However, the results of the cluster analysis revealed that wine elements concentrations (variables) had sufficient explanatory power to distinguish white from red wines, and wine producing regions for both white and red wines.

Cluster analysis of wines element composition was employed in several studies to achieve classification of wines from different regions. Sen and Tokatli [38] found that hierarchical cluster analysis was successful in showing differences between some Turkish red and white wines. González et al. [15] found cluster analysis as a good tool for discrimination between Spanish wines from Utiel-Requena, and Jumilla (PDO, protected designation of origin), while wines from Valencia and Yecla (PDO) were not differentiated, which was explained by heterogenity of Valencia PDO.

Principal component analysis (PCA) is commonly used to aid interpretation of the experimental data and modelling of relationships established between the data sets. PCA was performed for all wines and variables (elements) to determine

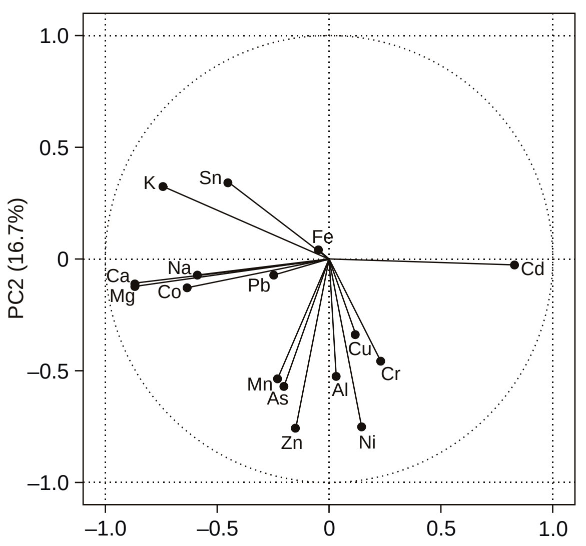


**Fig. 4.** Projection of the elements on the factor plane for all wines.

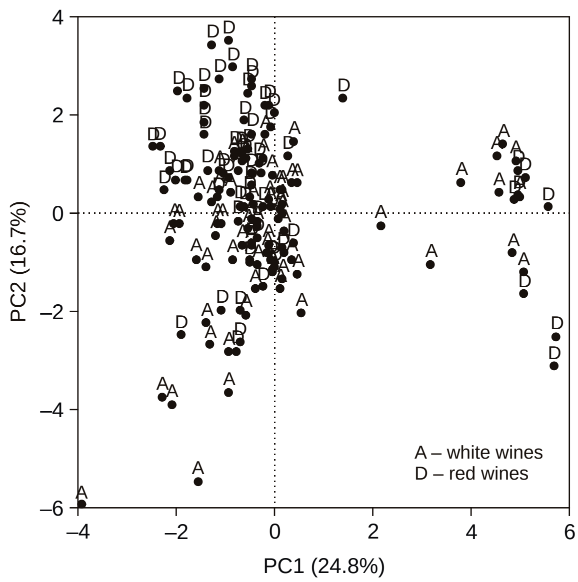


**Fig. 5.** Projection of all wines on the factor plane.

whether different wines (white and red) and different regions of origin (continental and coastal) influenced the elements profile. In this context, 16 elements posed as the investigated variables, while wines posed as the cases under investigation. The results of PCA came out in the form of 6 graphs (projections of variables, loading plots and cases, score plots), but the interpretation comprised also the eigenvalues of the correlation matrix, factor-variable correlations (factor loadings) and case contributions, which are only briefly discussed herein.

The first two factors (PC1 and PC2) represented 41.5% of the initial data variability (Fig. 4). This was a satisfactory result, even though some information might be hidden behind the next four factors (the third factor, PC3, 11.6%; the fourth factor, PC4, 9.8%; the fifth factor 8.0% and the sixth factor 7.0%), despite of the fact that the eigenvalues of the first six factors were greater than 1.

In Fig. 5 the difference between white and red wines can be seen. Most of wines were positioned on the positive side of PC1. Difference was obtained on PC3 vs PC4, where white wines still remained on the negative side of PC3, while red wines were positioned on the positive side of PC3.

Element Cd strongly positively correlated with PC1, but it could characterize both white and red wines. Elements such as Mg, Ca, K, Co and Na showed a strong negative correlation with PC1. Elements K and Sn positively correlated with PC2, while all others were in a negative correlation in particular with Zn, Ni, As, Mn and Al. The other factors were not shown in the figures, although they accounted cumulatively for 75.8% of the initial data variability. Elements Fe, Cr, Sn, Cu, Al and Pb revealed a strong positive correlation with PC3, and could be linked to red wines. Elements Ni, Co, Zn and Na had negative correlation with PC3 and, together with Mg and Ca, could be linked to white wines.

In order to determine which elements showed the best characterization of white wines with regard to producing regions (continental and coastal), another PCA was done. The first two factors, PC1 and PC2 (Fig. 6 and Fig. 7), represented 47.4% of the initial data variability. Most of elements had strong negative correlation with PC1, while only Cd had strong positive correlation. Elements Na, Co and Sn revealed a positive correlation with PC2, while elements Ni, Cu, Zn, Cr, As and Fe had strong negative correlation (Fig. 6). Other factors (the third factor, PC3, 10.7%; the fourth factor, PC4, 7.9% and the fifth factor, 6.8%) are not shown in the figures, but were responsible cumulatively for 72.8% of the initial data variability. Elements Al, Fe, Cr, Cd and Sn negatively correlated with PC3, while Cu and Ni had a weak positive correlation. Thus, elements such as Cd, Fe, Cr, K, Mg, Ca, Pb and Co could be clearly linked to white wines originating from continental Croatia (Fig. 7). Likewise, elements Na, Sn, Ni, Al, Cu and Zn could be attributed to white wines originating from coastal Croatia.

In order to determine which elements showed

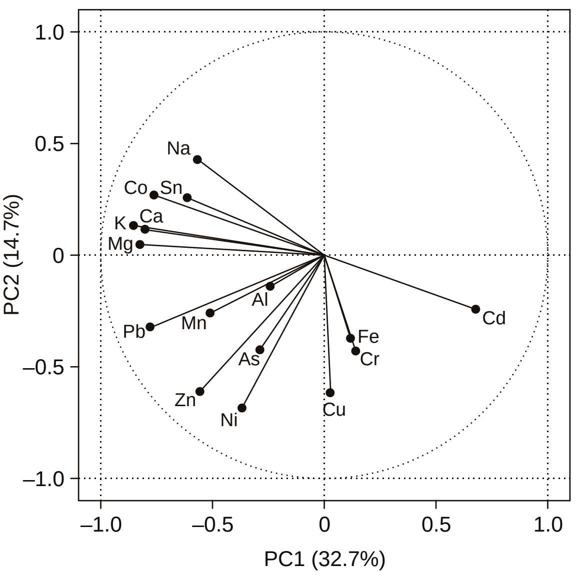


**Fig. 6.** Projection of the elements on the factor plane for white wines.

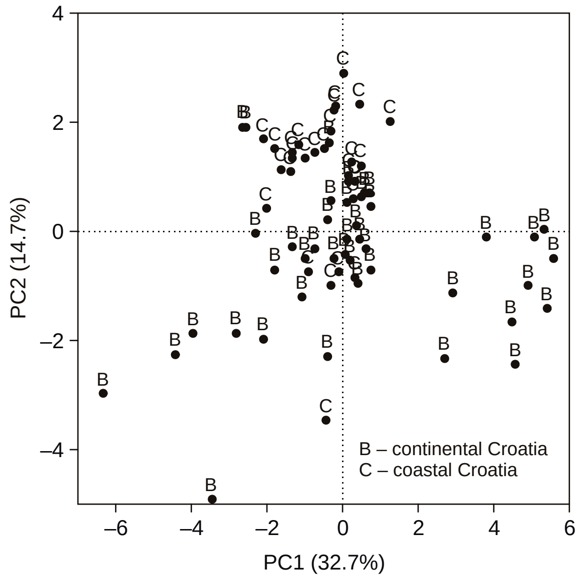


**Fig. 7.** Projection of white wines on the factor plane.

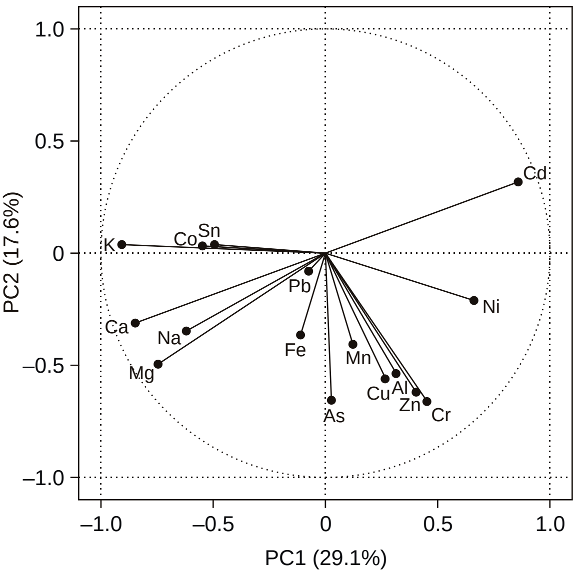


**Fig. 8.** Projection of the elements on the factor plane for red wines.

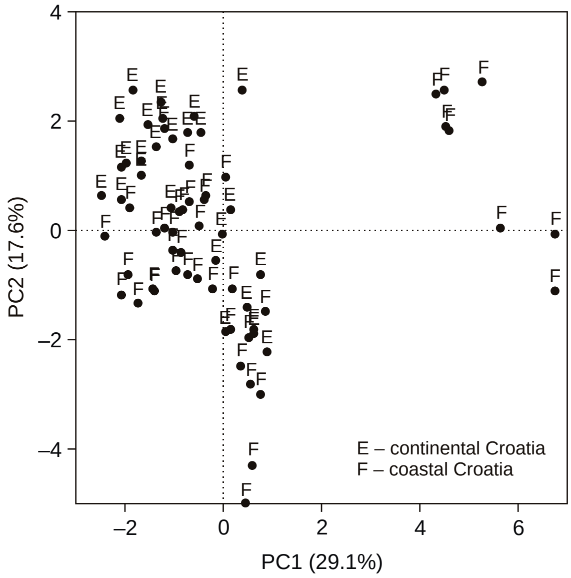


**Fig. 9.** Projection of red wines on the factor plane.

the best characterization of red wines with regard to viticulture regions, a separate PCA was done as well. On Fig. 8 and Fig. 9, the first two factors (PC1 and PC2) accounted for as much as 46.7% of the initial data variability. Elements K, Ca, Mg, Na, Co and Sn revealed a strong negative correlation with PC1, while elements Cd, Ni, Cr, Zn and Al revealed a strong positive correlation with PC1. The elements Cr, As, Zn, Cu, Al and Mg strongly negatively correlated with PC2 (Fig. 8). Elements K, Ca, Mg, Na and Co turned out to be characteristic for red wines originating from the continental region of Croatia, while Cd, Ni, Cr, Zn, Al and As turned out to be representative of the red wines originating from the coastal region of Croatia (Fig. 9). The eigenvalues attributable to the first five factors should also be deemed important for further discussion, although not shown in the figures, as they were cumulatively responsible for 75.2% of the initial data variability. The high negative correlation with PC3 had Fe, Sn and Al, while Mn and Ni positively correlated with PC3. They could be linked to red wines from the coastal region except for Fe and Mn, which could be related to red wines from continental Croatia. The results of other studies showed that the first three principal components explained around 40% and first six PC values explained around 80% of the total variability, which was similar to results obtained by this research [31, 39].

The other studies also indicated that elements in wine are suitable parameters for wine differentiation and classification according to the geographical origin. Paneque et al. [40] using PCA (the first two principal components, that accounted for 74.8% of the total variance) and CA methodology showed that wine samples originating from Andalusian province of Córdoba (southern Spain) could be roughly grouped in accordance with their geographical origin. The recently used fingerprinting methodology based on multi-element data and multivariate statistical analysis provided promising modus operandi for classification of South African wines at estate level in a single wine district in South Africa [4].

It should be emphasized that the studied wines were produced under different conditions. The expected variability of macro- and micro-element composition was due to the different vineyards, harvest year, or grape varieties, and might also be affected by the different production practices. Despite these various sources of variations, wines of different geographical origins could be separated.

## CONCLUSIONS

Chemometric analysis of data on elemental composition was undertaken with the aims of classification and discrimination between red and white wines from two wine-producing regions in Croatia. The results of the cluster analysis and principal component analysis revealed that concentrations of elements in wines were sufficient to facilitate discrimination of white wines from red wines, and white and red wines from two wine-producing regions. The best characterization of wine-producing regions of white wines was achieved by elements Cd, Fe, Cr, K, Mg, Ca, Pb and Co, and it could be clearly linked to white wines originating from continental Croatia. Likewise, elements Na, Sn, Ni, Al, Cu and Zn could be linked to white wines originating from coastal Croatia. On the other side, elements such as K, Ca, Mg, Na and Co turned out to be characteristic for red wines originating from the continental region of Croatia, while Cd, Ni, Cr, Zn, Al and As turned out to be representative of red wines originating from the coastal region of Croatia. The relationship between concentrations of different elements could be also a good tool to differentiate these wines from those produced in different geographical areas, and in establishing criteria of genuineness to assure the origin of the wines produced in Croatian regions.

**Acknowledgements**

The authors would like to thank to the wine producers for the support of this study.

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Received 4 December 2014; revised 11 March 2015; accepted 16 March 2015; published online 4 May 2015.