Multivariate data visualization methods based on elemental analysis of wines by atomic absorption spectrometry

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Abstract: The contents of five metals (Cu, Mn, Fe, Cd, and Pb) in several red and white wines originating from different regions of Serbia were determined by flame and graphite furnace atomic absorption spectrometry. The data were processed using chemometric techniques. Principal component and factor analysis were applied in order to highlight the relations between the elements and, after data reduction, three main factors controlling variability were identified. Application of hierarchical cluster analysis to the studied wines indicated differentiation of the samples belonging to different origins. No discrimination between red and white wines was found.

Keywords: principal component analysis, factor analysis, cluster analysis, metals, wines, classification.

INTRODUCTION

A number of articles have been published involving the analysis of metals in wines.[1–15] The interest of studying minor and trace metals in wines is due to their potential toxicity, some undesired phenomena (precipitation, *etc.*) which can arise, and the use of mineral profiles to determine the authenticity of wines.[4] Due to the fact that grape pressing and the skin maceration time can substantially affect the final concentrations of minerals in wine, quantification of some typical elements can help in the improvement of the manufacturing process. Since metals are not metabolized during the vinification and storage, they can be considered as good indicators for the identification of the origin of a wine. The most frequently analyzed metals are: K, Na, Fe, Zn, Rb, Ca, Mg, Mn, Cu, Cr, Co, Sb, Cs, Br, Al, Ba, As, Li and Ag.[6–9] However, by selecting some elements as key features, it is possible to use a far smaller number of variables to classify wines.[10–15]

Recently, chemometric analysis has received increasing attention in the analysis of wines.[8–22] A variety of multivariate methods based on diverse chemical

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data were reported: principal component analysis (PCA), cluster analysis (CA) and discriminate analysis of the data from FAAS/FAES analysis,[8,12] proton and ^{13}C shifts measurements,[19] GC–MS,[20] ICP–OES,[11] ICP–MS[9,14] and SNIF–NMR results.[18,21] Furthermore, there were also reported PCA and CA from TXRF analysis,[13] K-nearest neighbors cluster analysis, canonical analysis, and soft independent modeling of class analogy (SIMCA) in GC and AAS analyses,[6,8,22] PCA and Kohonen artificial neural network (ANN) using SNIF–NMR and IRMS,[5,18] three-layer ANN using ICP–OES,[11] two-layer ANN using FAAS[12] and correlation between NIRS and AAS data by partial least squares regression (PLSR).

The objective of this study was to investigate the correlation among common trace metals in selected wine samples and to explore the possibility of wine classification by applying chemometrics.

EXPERIMENTAL

The samples of wines commonly found on the Serbian market: 1 – Kosovski cabernet (red), 2 – Kosovski riesling (white), 3 – Rubin burgundac (red), 4 – Rubin riesling (white), 5 – Džervin (red), 6 – Džervin riesling (white), 7 – Cabernet sauvignon (red) and 8 – Italian riesling (white), were supplied bottled. The origin of the grapes is as follows: southern Serbia (1 and 2), central Serbia (3 and 4), eastern Serbia (5 and 6) and northern Serbia (7 and 8).

A flame atomic absorption spectrometer (Perkin Elmer model 3100) was employed for the determination of Cu, Mn, and Fe, while Cd and Pb were determined by a graphite furnace atomic absorption spectrometer (Perkin Elmer model 4100zl). Analytical reagent grade chemicals, Merck standards (Darmstadt, Germany) and Milli-Q water were used. The metal concentrations were calculated using the standard addition method. The analytical procedures, described in detail elsewhere,[23-25] allowed the determination of the selected elements with no matrix effect of organic compounds. None of the wine samples analyzed in this work exceeded the EU's current limit value for heavy metals content of 100 ppm by weight.

The statistical analyses were performed by means of the Minitab 13.0 software package (Minitab Inc., USA).

RESULTS AND DISCUSSION

Multivariate analysis of wine was assessed without taking into account factors such as the type of wine. Some of the elements might be arise from the treatment (*i.e.*, Cu from the Bordeaux mixture), which will not be meaningful in the statistical evaluation unless the particular treatment is only used in one region. A data matrix was formed with 8 wine samples and 5 variables, the concentration of the several minor and trace metals. The average concentrations, standard deviations, minimum and maximum values of metals in the studied wines are presented in Table I. It can be seen that the examined metals are present in the following order of concentrations: Fe > Mn > Cu > Pb > Cd. The correlation matrix of the data on the minor and trace metals are given in Table II. The pairs Cu–Fe (0.786), Cd–Pb (0.696), and Mn–Pb (0.453) show the highest positive correlations. No significant correlations are observed between the other variables.

Principal component analysis (PCA) is a well-established multivariate technique in which data reduction is performed by transforming the data into ortho-

gonal components which are linear combinations of the original variables. The application of PCA to the data matrix of the wine analysis revealed that a total of three PCs accounted for 94 % of the total variance (Fig. 1).

TABLE I. Average content (mg l^{-1}, except for Cd µg l^{-1}) of minor and trace metals in the examined wine samples

Metal	Mean value	Standard deviation, SD	Minimum value	Maximun value
Cu	0.58	0.78	0.09	2.30
Mn	1.61	1.02	0.40	3.65
Fe	4.55	2.78	1.93	10.7
Cd	12.0	3.62	8.60	17.7
Pb	0.14	0.05	0.10	0.23

TABLE II. Correlation coefficients for the total samples (Pearson correlation)

	Cu	Mn	Fe	Cd
Mn	0.081 0.879[a]			
Fe	0.786 0.064[a]	0.172 0.745[a]		
Cd	−0.168 0.750[a]	−0.107 0.840[a]	0.045 0.933[a]	
Pb	−0.053 0.921[a]	0.453 0.367[a]	−0.094 0.860[a]	0.696 0.125[a]

[a]The significance level (P value)

Fig. 2 shows that Cd and Pb load highly into the first component whereas Cu and Fe are high in the second. A different behavior is noticed for Mn, for which both components are significant. The loading plot is related to the variables and shows their association with respect to the models. In this case, discrimination between the minor metals (Cu, Fe) and trace metals (Cd, Pb) is obvious.
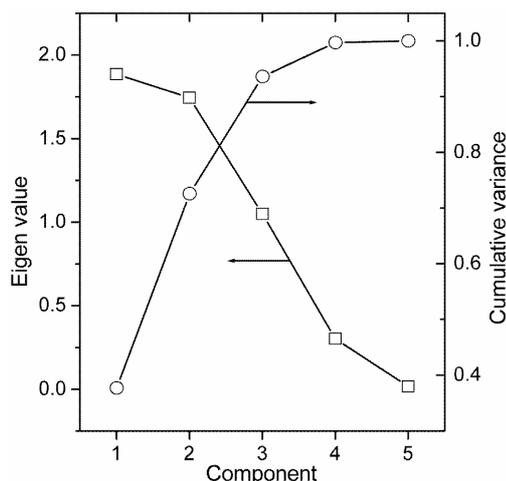

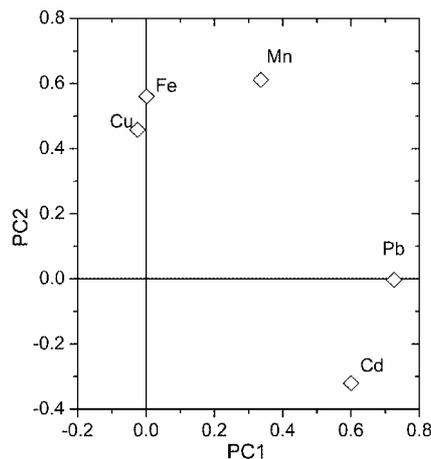Fig. 1. Eigen analysis of the correlation matrix.

Fig. 2. Plot of the first two component weights of the variables.

In order to identify interrelated variables and make easier the visualization, the data were compressed to a few dimensions using factor analysis (FA). The number of significant factors was selected on the basis of the Kaiser criterion (eigenvalue > 1).[26] Three significant factors were extracted and varimax orthogonal rotation (Table III) enabled a better visualization of the latent structure of the database. Factor 1 has a high loading of Cu and Fe, while Pb and Cd contribute to Factor 2. Mn dominantly contributes to Factor 3. It can be supposed that Factor 1 is related to the influence of the wine making process on minor metals, while Factor 2 can be related to trace metal pollution. However, the fate of Mn in wines is defined by Factor 3, which indicates a different input of Mn.

TABLE III. Varimax rotated factor loadings

Variable	Factor 1	Factor 2	Factor 3
Cu	0.964	–0.099	0.011
Mn	0.075	0.035	0.997
Fe	0.916	0.031	0.103
Cd	–0.033	0.975	–0.137
Pb	–0.051	0.833	0.427

The provenance and authenticity of wines can be recognized on the basis of typical mineral and trace elements patterns by means of chemometric methods. The Cu and Fe content of wines originate from the grapes. It has been reported that up to 90 % of the Cu and up to 70 % of the Fe initially present in grape juice is eliminated during fermentation, mainly by yeast assimilation.[27] However, an excessive content of Cu and Fe in wines is the result of careless contact of wine, after fermentation and during aging or processing, with steel or Cu alloy surfaces. The wines containing an excess of 0.5 mg l^{-1} Cu or 10 mg l^{-1} Fe my be susceptible to clouding or sedimentation as well as flavor deterioration by the strong catalytic and oxidative properties of these cations. As wines with a Pb content of above 100 µg l^{-1} are considered to have been polluted by the material during the wine making process or storage,[17] for most of the studied wines a proximity to a busy road or a city was implied. In spite of Cd being generally associated to oil or fossil fuel combustion, the high value for Pb reveals that traffic exhaust gases were a more relevant source of Cd. The levels of Mn are of special interest, the great differences in the concentration for this metal in wines can be an indicator for the geographical classification of the samples.[10−12,15]

A hierarchical cluster analysis of the standardized variables using the Ward method[28] as an amalgamation rule and the squared Euclidean distance as a measure of the proximity between the samples was carried out. The dendrogram presenting the clustering of wines is shown in Fig. 3. A good separation of the Džervin wines from the Rubin ones and that originating from other regions was found,

while, on the other hand, the grouping of the Kosovo wines was not satisfactory. However, there seems to be no discernible differences among white and red wines.
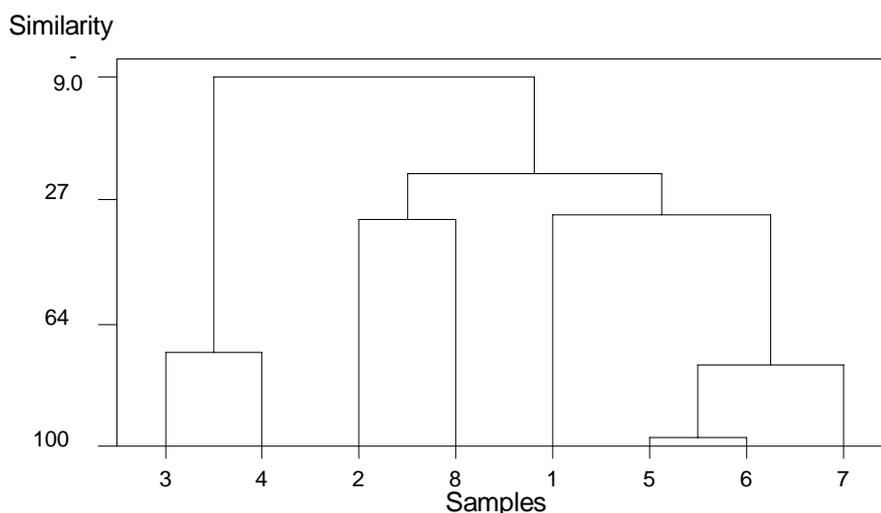

Fig. 3. Dendrogram of cluster analysis of wines.

CONCLUSION

The application of flame atomic absorption spectroscopy and graphite furnace atomic absorption spectrometry in conjunction with multivariate statistics gave good results in the characterization of wines. Principal component analysis reduced the dimensionality of the descriptor space to a total of three PCs. A differentiation between trace metals was obtained by means of factor analysis. Cadmium and Pb load highly into the first component, whereas Cu and Fe are high in the second. A different behavior was noticed for Mn, for which both components are significant. Hierarchical cluster analysis applied to study the results of the analysis of metals in wines seems to discriminate between samples belonging to different origins.

И З В О Д

МЕТОДЕ МУЛТИВАРИЈАНТНЕ ВИЗУАЛИЗАЦИЈЕ ПОДАТАКА БАЗИРАНЕ НА ЕЛЕМЕНТАЛНОЈ АНАЛИЗИ ВИНА АТОМСКОМ АПСОРПЦИОНОМ СПЕКТРОМЕТРИЈОМ

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Применом метода пламене атомске апсорпционе спектрометрије, као и атомске апсорпционе спектрометрије са електротермалном атомизацијом, одређиван је садржај пет метала (Cu, Mn, Fe, Cd и Pb) у узорцима неколико црвених и белих вина, из раличитих региона Србије. Резултати су обрађивани хемометријским методама. Примењена је анализа главних

компоненти, као и факторска анализа, у циљу разјашњавања односа између елемената. На-кон редукције података идентификована су три главна фактора који утичу на варијабилност. Кластерска анализа узорака вина наглашава диференцијацију узорака различитог порекла али не и раздвајање између црвених и белих вина.

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