Usefulness of near infrared spectroscopy and chemometrics in screening of the quality of dessert wine Prošek

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Summary

NIRS has been applied for the analysis of dessert wine Prošek produced from dried grapes of Pošip and Plavac mali cv. in a semi-scaled fermentation. It is a fast and non-destructive analytical method that in association with chemometrics is becoming more frequently used technique. NIR spectra were measured and the relative density, alcohol content, dry extract, reducing sugars, pH, total acidity, volatile acidity, ash, free sulphur dioxide and total sulphur dioxide were determined. The range of NIRS used in this paper was 904–1699 nm (i.e. 11062–5886 cm^{-1}) because in this range vibrations of C–H, O–H, S–H and N–H bonds can mainly be observed.

Using the basic principles of multivariate analysis, principal component analysis (PCA), was used to reduce the input matrix in order to look for significant relationships between the NIR spectra and the observed characteristics of wine Prošek. Chemometrics applied here resulted in further discrimination between samples. The main features of the spectra are absorption bands at 1580 and 1670 nm, which are related to the first overtone of the C–H stretch. Absorption bands around 908 nm, present the stretches related to the 3rd C–H overtone and 2nd overtone of the O–H stretch of H_2O and ethanol. PC1 and PC2, the first two components, gave the highest level of classification (≈95 %) based on the grape used for wine production as well as on the added yeast.

The potential of NIRS, as a non-destructive method, is screening of basic parameters that are usually determined during the winemaking and ageing of wine. The results of investigations confirm that NIRS combined with chemometric analysis is a promising tool for quality control and for on-line application in the control of the final product, Prošek.

Keywords: dessert wine, quality parameters, NIRS, chemometrics

Introduction

Wine is an important component of the Mediterranean dietary tradition and is considered as an important health benefactor because it is rich in antioxidant compounds. Last harvest wines, commonly described as dessert wines, are generally characterized by being sweet. The most famous dessert wine in Croatia, traditionally produced in Dalmatia from dehydrated, overripe grapes, is Prošek. The high sugar content of Prošek derives from the partial alcoholic fermentation of dried grape pomace. This process preserves some of the natural sugars and produces a sweet alcoholic beverage with an attractive taste and flavour evoking honey, chocolate and vanilla, as well as fruit aroma like dried raisins and red berries (Budić-Leto et al., 2010). Over the recent years, consumers have become increasingly concerned with the effects of conventional agricultural food production practices on human health and environmental well-being (Forbes et al., 2009). Another consumers' interest is the authenticity of foods (Reid, et al. 2006) and, in particular, of wine, which has been extensively investigated because it is an easily adulterated product due to its strong chemical basis (high alcohol content, low pH) and its availability throughout the world (Moret et al., 1994). To ensure quality and safe product for the costumer as well as to confirm the authenticity of a food product, new techniques have been proposed. One of the techniques that have found new applications in the field of quality assurance is near infrared spectroscopy (NIRS) (Müller and Steinhart, 2007; Parpinello et al., 2009; Williams et al., 1988).

Near infrared region covers the range of electromagnetic spectrum between 780 and 2500 nm. The basic principle in NIRS is that the examined sample is irradiated with NIR radiation and the reflected or transmitted radiation is recorded in the form of a spectrum (Nicolaï et al., 2007). NIRS is a fast and non-destructive analytical method so it is of potential easy application in industrial setting.

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NIR spectroscopy is suitable for simple matrices such as yoghurt or beverages to determine the content of macronutrients (protein, fat, carbohydrates). It can be used to control according to specific production standards, so tedious reference methods need only be used if deviations from these quality standards occur during production (Azizian et al., 2004; Prevolnik et al., 2004).

This paper discusses the ability of NIRS in monitoring basic oenological characteristics in the production of dessert wine Prošek. In order to obtain the results that are based on multivariate analysis, this information needs to be as clear as possible. The inter-relationships between chemical properties and sensorial evaluation can provide reliable results (Urbano-Cuadrado et al., 2004; Williams et al., 1988; Bueno et al., 2010), which could be used in the production and market positioning of the wine (Parpinello et al., 2009; Charters & Pettigrew, 2007).

Materials and Methods

Wine samples

Samples of dessert wine Prošek produced from dried grapes of Pošip and Plavac mali cv. (harvest of 2008) by semi scaled fermentation were studied for NIRS (Table 1).

Table 1. Samples of dessert wine Prošek, from Pošip and Plavac mali cv., vintage 2008, with yeast inoculation

Sample	Yeast inoculation
Plavac mali-EC 1118	EC 1118
Plavac mali-EC 1118	EC 1118
Pošip-native	-
Pošip-native	-
Pošip-VIN 13	VIN 13
Pošip-VIN 13	VIN 13
Pošip-VIN 13	VIN 13
Pošip-EC 1118	EC 1118
Pošip-EC 1118	EC 1118
Pošip-EC 1118	EC 1118

The process of production of Prošek from Pošip cv.

A mass of 490 kg of grapes of Pošip cv. was picked from the vineyards of Korčula, Croatia, and put to dry in a glasshouse. Grapes were dried in the glasshouse for 5 days (10-15 September). Dried grapes were crushed, destemmed and sulphited with potassium metabisulphite (15 g/hL). After 4 hours of skin contact at 15 °C, the must was racked into a 25-litre glass container. The must was inoculated with selected yeast (Lalvin EC 1118, *Saccharomyces cerevisiae* var. *bayanus*, Danstar Ferment AG, Zug, Switzerland, and VIN 13, Anchor yeast) and two different alcoholic fermentations were done, each in triplicate. The third fermentation was done with native yeasts or native microflora. After one month Prošek was racked, sulphited and left to mature.

The process of production of Prošek from Plavac mali cv.

A mass of 400 kg of grapes of Plavac mali was harvested on Pelješac, Croatia.
Grapes were dried in a glasshouse for 18 days (10-29 October). Dried grapes were crushed and destemmed, after which the pectolitic enzyme Endozym cultivar (AEB S.p.A., Brescia, Italy, 30 g/100 kg) and potassium metabisulphite (15 g/hL) were added to the pomace. The pomace was divided into 3 equal parts and put into inox containers. Alcoholic fermentations were done in duplicate using comercial yeasts Lalvin EC 1118 (*Saccharomyces cerevisiae* var. *bayanus*, AEB S.p.A., Brescia, Italy) prepared according to the manufacturer's instructions. Maceration took 5 days and the pomace was punched down twice daily, after which it was pressed on the hydraulic press (pressure <2 bar). The must was put in 10-litre glass vials, where the alcoholic fermentation continued. Fermentation was controlled by measuring the temperature and determining the reducing sugars. Temperature during fermentation was between 22 and 24 °C. The first racking was done 29 days, and the second 184 days (6 months) after the beginning of fermentation. After the second racking, Prošek was bottled.

NIR analysis

The range of NIR spectra of 904–1699 nm (i.e. 11062–5886 cm^{-1}) was applied, which gives the

possibility to observe vibrations of C–H, O–H and N–H bonds, as can be seen from table 2. The spectra of the samples were measured by trans-reflectance and raw spectra and their second derivative were used. NIR spectroscopy is based on the electromagnetic absorption in the near-infrared region but the spectral analysis has to be assisted with

various chemometric techniques (Ding & Xu, 1999; Alishahi et al., 2010). NIR spectra of wine samples were collected in the range of 904–1699 nm using a Control Development, Inc., NIR-128-1.7-USB/6.25/50 μm, with the installed Control Development software Spec32.

Table 2. Chemical band-assignment in the NIR spectra

Frequency (cm^{-1})	Functional group assignment[*]
Near infrared region	
8600–8150	C–H 2nd overtone of –CH2, –CH3
7400–7000	C–H combination of –CH2, –CH3
6960	O–H 1st overtone of combination modes of OH
5950–5600	C–H 1st overtone of –CH3 and –CH CH–
5000–4500	N–H stretch and C O stretching and combinations of amide A/I and amide B/II

[*]summarised from Shiroma and Rodriguez-Saona, 2009

Oenological characteristics of desert wine Prošek

Basic oenological parameters of Prošek wine (see the Table 3) were determined in accordance with the official OIV practices (OIV 2005).

Modelling

NIR spectra were recorded in "dat" format and imported to STATISTICA v. 8. software for evaluation. The original spectra for data filtering were imported, (using Control Development software Spec32). The data were collected in a matrix **X** with samples placed in rows and NIR intensities are variables placed in columns. As Valinger and co-workers (2011) suggest, the modelling procedure is explained with equations 1–6. Each vector of the variables is auto-scaled with respect to the sample average wavelength (variable) and standard deviation:

$$\mathbf{X}_{i,j} \leftarrow \frac{X_{i,j} - \overline{X}_j}{\sigma_j(X_j)} \qquad [1]$$

Assuming normal distribution, for each variable sample statistics is calculated by:

$$\overline{\mathbf{X}}_j = \frac{1}{n} \cdot \sum_{i=1}^{n} X_{i,j} \qquad \sigma_j^2 = \frac{1}{n-1} \cdot \sum_{i=1}^{n} \left(X_{i,j} - \overline{\mathbf{X}}_j \right)^2 \qquad [2]$$

The scaled data matrix **X** is approximated by the projections into the subspace of principal components **P**:

$$\mathbf{T} = \mathbf{X} \cdot \mathbf{P} \qquad [3]$$

The principal components form the loading matrix **P** and all the scores are collected in the target matrix **T**. The principal component model reconstructs the original data by the relation:

$$\mathbf{X} = \mathbf{T} \cdot \mathbf{P}^T + \mathbf{E} \qquad [4]$$

In Eq. 4, **E** is the error matrix of the residuals between the experimental data and the principal component projections. Components of the error matrix are assumed to be a result of all random factors included in the experiment, such as instrument error, sample treatment and laboratory conditions. Due to high colinearity between the data of the spectra, very significant reduction in the dimension is obtained. The principal component vectors are determined by sequential maximization of the variance of the projected data with the assumption of the sample-based covariance. The principal components are eigenvectors of the sample covariance, while the corresponding eigenvalues are the variances:

$$\mathbf{X}^T \cdot \mathbf{X} \cdot \mathbf{P}_i = \lambda_i \cdot \mathbf{P}_i \qquad [5]$$

Variance of the data matrix is given by the sum:

$$\sigma^2(\mathbf{X}) = \sum_{i=1}^{m} \lambda_i^2 \qquad [6]$$

The method enables extraction of the essential deterministic information from large sets of spectra, using only the first *r* significant principal components (**P**$_1$, **P**$_2$ ···**P**$_r$) allowing data reduction.

The method enables extraction of the essential deterministic information from large sets of spectra correlated data by reduction of the dimension by only the first r significant principal components ($\mathbf{P}_1$, $\mathbf{P}_2 \cdots \mathbf{P}_r$).

In this work, the main purpose of the principal component analysis (PCA) as a chemometric tool is to apply cluster analysis in the plane of the first two principal components for discrimination of sample origin and detection of possible product adulteration. Simplified, this means that PCA was used in order to identify patterns in the experimental data and to express the data based on their similarities and differences.

Results and Discussion

The names of samples in the first column in Table 1 are used in the following data presentation and multivariate modelling process. Using NIR process analyzer, each spectrum of different Prošek wine from Pošip and Plavac mali cv. was recorded. Each sample was recorded in triplicate and the mean value was calculated. Fig. 1 shows mean values of NIR spectra (absorbance units) of samples, which are original records of the samples. As it can be seen in the Fig. 1, it is impossible to distinguish a sample based only on the recorded NIR spectra, and in this case it is recommended to show the first derivatives of the curves (Fig. 2). This display indicates the parts of the spectrum that could be important for the observed wine.
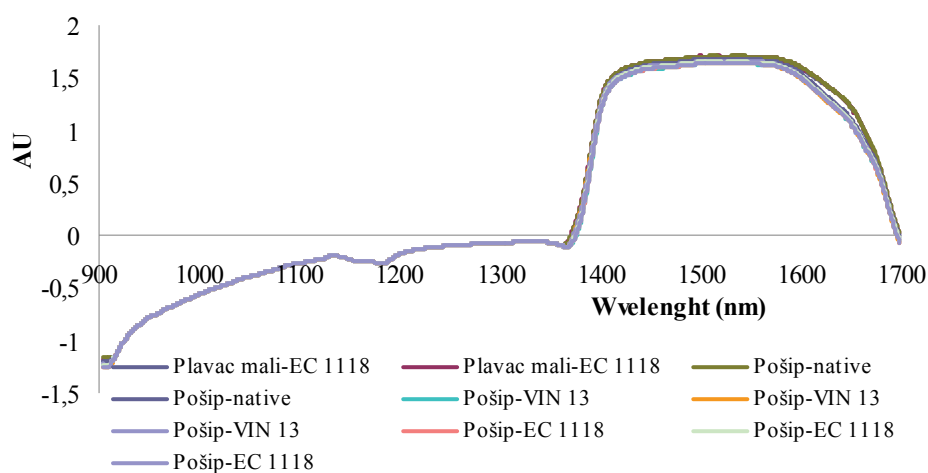

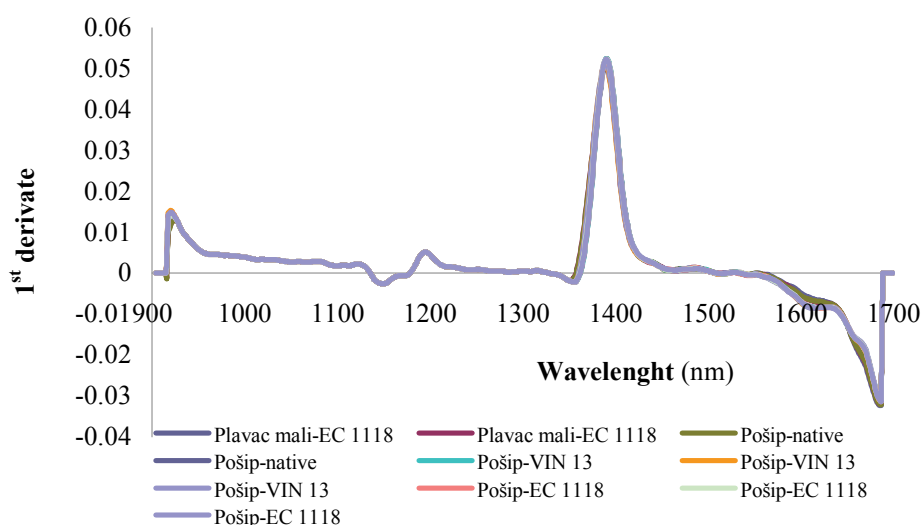**Fig. 1.** Average absorbance spectra of dessert wine Prošek (Pošip and Plavac mali cv.) – absorbance units, AU

Fig. 2. Average absorbance spectra of dessert wine Prošek (Pošip and Plavac mali cv.) – 1st derivative

Analyzing the presented spectra in Figs. 1 and 2, it seems that all records are very similar with an exception in the range of 1550-1700 nm, where the curves show slight differences. Presented results are in accordance with the study conducted by Cozzolino et al. (2010). The range of the used NIR instrument is significantly narrower than the instruments usually used (with a range from 400 to 2500 nm), but to ensure the data differentiation between the samples for further analysis, the values of oenological parameters of each sample were assigned to the set of spectrum data (Table 2). This observation justifies the use of chemometrics in order to detect differences between the observed samples. In order to detect if the data reduction can be made, factor analysis was used (Table 3).

Table 3. Range and mean values, and factor loading of physicochemical properties of dessert wine Prošek, from Pošip and Plavac mali cv., vintage 2008, and the best correlations with NIRS, based on chemometric modelling

Sample	Range	Mean	Factor 2 loading	Factor 3 loading	Factor 4 loading
Relative density (20/20ºC)	1.0038-1.0303	1.0088	**-0.9391**	0.0332	-0.2919
Real alcohol (vol %)	15.06-16.62	16.18	0.4316	-0.0681	**0.8465**
Total extract (g/L)	64.20-129.80	75.84	**-0.9485**	-0.0115	-0.2206
Reducing sugars (g/L)	26.8-87.22	37.65	**-0.9407**	0.0379	-0.2881
pH	3.68-4.32	4.19	0.5147	0.0345	**0.7848**
Total acidity (g/L)	4.32-6.37	5.07	**-0.7164**	-0.2663	-0.4273
Volatile acidity (g/L)	0.68-0.92	0.75	**-0.9261**	0.1397	0.1476
Ash (g/L)	3.14-5.69	4.85	0.4200	0.4920	0.6334
Free sulphur dioxide (mg/L)	3-15	7.30	**-0.7035**	0.3139	-0.5843
Total sulphur dioxide (mg/L)	112-247	205	**0.9170**	0.2706	-0.0566

According to the factor loadings, the data screening can be made (Factor 1 loading are NIR spectrums, and the oenological properties are divided in loading Factors 2 to 4). The variable "Ash" was not included in any factor, so this is the third variable that can be excluded from the data set in further analysis.

Table 4. Eigenvalues of the covariance matrix of the complete data set

Extraction of eigenvalues: Principal components				
Factor	**Eigenvalue**	**% Total variance**	**Cumulative Eigenvalue**	**Cumulative %**
1	119.2522	91.03220	119.2522	91.03220
2	7.5258	5.74492	126.7780	96.77713
3	2.1392	1.63300	128.9173	98.41013
4	1.4259	1.08846	130.3432	99.49859

According to the performed PCA analysis, the wine parameters as real alcohols and pH fall in the fourth loading factor show agreement with the NIR spectrum (PC2=1.43 %). As expected reducing sugar is a part of the factor loading 2, what implies a significant correlation with the NIR spectrums, but as a part of enological parameters that are in the a part of "factor loading 2". The reason why reducing sugars can not be directly in correlation with NIR spectrum is that the monitoring of carbohydrates and their relationship with the NIR spectrum lie in the range of 1200-900 cm^{-1} (Urbano-Cuadrado et al., 2004; Cozzolino et al., 2010), which is outside the range of NIR instrument used for measurements.
From this data matrix, variables such as "pH" and "real alcohol" were excluded, which are classified in the fourth factor loading that contributes to the total variance with 1 % (Table 4).
The modelling should allow further discrimination between samples according to the used grape for the production of Prošek. The chemometric procedure was applied on the NIRS and physicochemical data to accomplish the principal component (PC) scores. The differentiation of the observed samples based on chemometry is presented in Fig. 3. The main features of the spectra are absorption bands at 1580 and 1670 nm, which are related to the first overtone of the CH stretch (Moret et al., 1994; Müller and Steinhart, 2007; Nicolaï et al., 2007), and 917 nm, which are related to the 3rd CH overtone and 2nd overtone of the OH stretch of H_2O and a combination of stretch and determination of the OH group in H_2O and ethanol (Alishahi et al., 2010; Charters and Pettigrew, 2007).
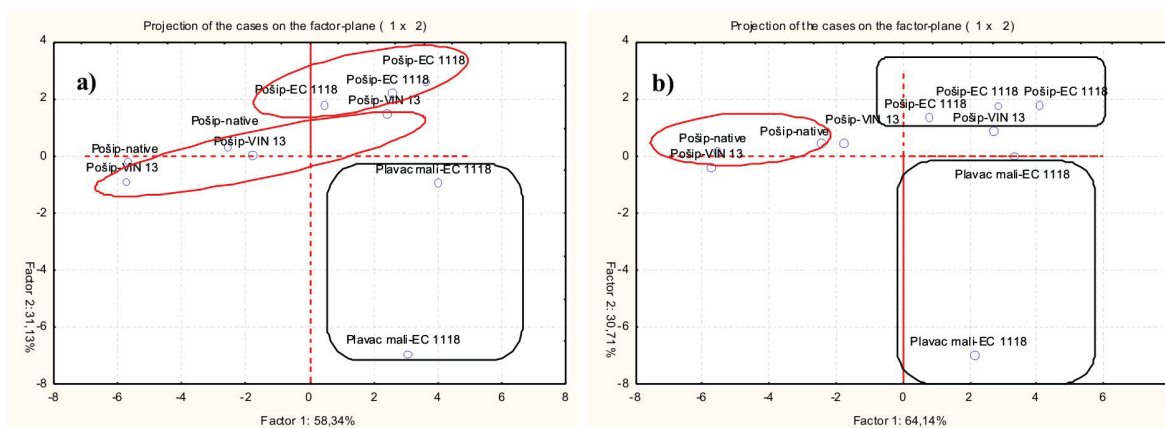
Fig. 3. PCA scores used in: a) the differentiation of the basic grape and type of yeast inoculation, and
b) the differentiation of the basic grape and type of yeast inoculation based on reduced matrix (according to Table 3)

From the results presented in Fig. 3a, it can be concluded that the chemometric approach that uses principal component analysis (PCA) is effective because the data have grouped toward grape used in the wine production (Pošip and Plavac mali cv.) as well as according to the added yeasts (VIN 13 and EC 1118). The first two factors (PC1+PC2) gave a high level of product classification (≈90 %) with the emphasis on the added yeasts and the grape. Excluding the data that are not representative for the complete data set (according to the results presented in tables 3 and 4), the classification can explain almost 95 % of interactions of the observed variables (Fig. 3b). This paper confirms the recommendation for the use of NIR for on-line monitoring of product quality and selection (Alishahi et al., 2010; Nicolaï et al., 2007). It has also demonstrated the potential of NIR spectroscopy for detection of the added yeast as well as the starting material (grape) used in Prošek wine.

Conclusions

The applicability of near infrared spectroscopy for the evaluation of 10 oenological parameters of Prošek wine was studied in this work. The results showed that NIRS is a rapid, non-destructive method that can be used in detection of the product material (grapes of Pošip cv. and Plavac mali cv.) used for the production of Prošek as well as determination of the added yeasts.
Adding the oenological parameters to the NIRS data, the chemometric approach showed the potential for separation of dessert wine Prošek based on its NIR spectra with a special indication of the wavelength around 908 and the range of 1580-1670 nm. This paper

presented that NIRS in combination with chemometric analysis is a useful tool for quality control and for on-line applications. NIRS can be used qualitatively to detect, identify, and qualify raw materials and to control the final product, dessert wine Prošek.

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