Differentiation between commercial wine samples using fluorescence spectroscopy and multivariate analysis

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Abstract: Steady state fluorescence spectroscopy in combination with Multivariate Curve Resolution – Alternating Least Squares (MCR-ALS) for spectral analysis was used to differentiate between commercial samples of wines available on the market. Wine trade marks from two Serbian producers that contain only one wine type were chosen, since such an approach is a starting step for further analyses of more complex samples containing different wine types. We also studied changes in the emission spectra of these samples over a period of seven days after opening the wine bottle. The emission spectra were recorded in the wavelength range 275 - 500 nm, after excitation in the 255 - 300 nm range. The spectra of the wine samples obtained from the same producer are very similar, i.e. they contain the same components at similar ratios. The changes in spectral components at 315 nm and 430 nm were the basis for differentiation between the wine samples obtained from the two producers, as well as for estimation of wine stability over time after the bottle.

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opening. The results indicate that this may be a useful approach to fingerprinting wines from various producers, as well as to screening the stability of wine.

**Key words:** wine types, riesling, emission spectra, Multivariate Curve Resolution, phenolic compounds.

### Introduction

Fluorescence is a non-destructive, sensitive and fast method for the analysis of fluorescent compounds present in very low amounts (nanomolar concentrations) in samples. It can be used for structural or concentration studies, for analytical or diagnostic purposes (Valeur 2001). We have been developing methods for the measurement and analysis of emission spectra of compounds of various complexity in mixtures (Kalauzi et al. 2007) or as macromolecules composed of different kinds of monomers, such as proteins or polyphenols (Djikanović et al. 2012, Radotić et al. 2006, Savić et al. 2013).

The advantage of fluorescence measurement is that it does not require sample pretreatment or physical separation of sample components, as in the case of HPLC.

The most fluorescent molecules in wines are of phenolic nature, such as phenolic acids, stilbenes, anthocyanins, flavanols and tannins. The nature and amounts of these molecules differ from one grape variety to another, and depend on wine processing and ageing. Moreover, wines contain some other emitters, such as proteins (Sádecká and Tóthová 2007).

Fluorescence spectra, in combination with appropriate statistical methods, may provide useful fingerprints in food analysis (Sádecká and Tóthová 2007). During the last few years, the application of chemometrics and developments of spectrofluorometers have boosted the potential of using fluorescence in food research. Food products contain numerous intrinsic fluorophores and thus are appropriate for fluorescence spectroscopy investigations (Dion et al. 2008). This method in combination with chemometrics has been used to differentiate brandies from wine distillates (Sádecká et al. 2009) or identity of wines from a geographic region (Yin et al. 2009). Quantification of certain ingredients in wines may also be achieved by fluorescence spectroscopy (Molina-Garcia et al. 2011, Sádecká and Tóthová 2012, Vidal-Carou et al. 1989).

The aim of this paper was to assess whether steady state fluorescence spectroscopy, in combination with multivariate statistical methods, can be used as a quick and non-destructive screening method to distinguish between
commercial samples of wines available on the market. We chose wine trade
marks that contain only one wine type, since such an approach is a starting step
for further analyses of more complex samples containing different wine types.
We used wine trade marks that contain riesling wine samples from two trade
marks, originating from two wine producers in Serbia and purchased in
supermarkets. We chose one of the most popular white wine types from two
renowned wine producers in Serbia. We also studied changes in the emission
spectra of these samples over a period of seven days after opening the wine
bottle. We intended to see whether it is possible to distinguish between wine
samples on the basis of the above designations.

Materials and methods

_Samples._ The study was performed on 4 wines from two different regions of
Serbia. All samples were white wines obtained from grape cv. “Riesling”, 2012
vintage, and purchased from local supermarkets. Two wines were from the region
of Vojvodina – the “Vršački Vinogradi” producer (Italijanski Riesling, Banatski
Riesling) and two from Central Serbia - the “Vino Župa” producer (Riesling,
Graševina).

All measurements were made immediately after bottle opening and two and
seven days afterwards. The samples were stored in the dark at room temperature
until analysis, diluted with water (1:49 v/v) and measured.

_Fluorescence spectroscopy._ Fluorescence spectra were recorded using a
Fluorolog-3 spectrofluorimeter (Jobin Yvon Horiba, Paris, France) equipped with
a 450 W xenon lamp and a photomultiplier tube. The slits for the excitation and
emission beams were fixed at 4 nm and 2 nm, respectively. The samples were
placed in 10 mm (optical path) quartz cell (volume 1.5 ml).

Fluorescence emission spectra were recorded from 275 nm to 500 nm, for
excitation wavelengths ranging from 255 - 300 nm, with a 5 nm step. Fluorescence measurements were done in triplicate for each sample.

_Statistical analysis of data._ The intensities of the emission spectra were
normalized to the 0 – 1 scale. We used 12 matrices (4 wine types x 3 time points)
that corresponded to the wine samples. Each matrix was analyzed by MCR-
ALS\(^\text{10}\) which extracted a number of components, as well as their emission and
excitation profiles.

Results and Discussion

Fig. 1. presents overlaid emission spectra obtained for various excitation
wavelengths, of the two different riesling samples, Riesling and Graševina
produced by Vino Župa, and Italijanski Riesling and Banatski Riesling produced
by Vršački Vinogradi. Fig. 2. shows the emission spectra of pure components
obtained by the MCR-ALS method used in the analysis of the series of emission spectra from Fig. 1. The three components with the peaks at 315 nm, 370 nm and 430 nm were found in all samples. The shape of these components was the same for all 12 matrices (samples). It is obvious that the spectra of the wine samples obtained from the same producer are very similar, i.e. they contain the same components at similar ratios (Fig. 1). This is confirmed by the MCR-ALS analysis (Fig. 2). The corresponding loadings (excitation profiles) of the components from Fig. 2, are shown in Fig. 3. The loadings of the individual components for the samples from the same producer change in a similar way with changing excitation wavelength. This additionally confirms high similarity of the riesling wines from the two trade marks produced by the same producer. However, there is a difference between the wine samples from the trade marks produced by different producers (Figs. 1, 3), although the position of the spectral components is the same as for the other producer (Fig. 2). The 315 nm component is significantly higher in the wine spectra of both Riesling and Graševina from Vino Župa, in comparison to both the Banatski Riesling and Italijanski Riesling samples from Vršački Vinogradi (Fig. 1). This peak is more expressed in the case of Riesling wine. This difference is related to the higher content of the compound(s) emitting at 315 nm in the Vino Župa riesling wines than in the Vršački Vinogradi riesling wines. The corresponding loading of the 315 nm component (Fig. 2, 3) changes in a different way with the excitation wavelengths in the samples of these two producers, attaining maximum more abruptly for the Riesling wine than for the others. Also, the 430 nm maximum is higher for both wine samples from the Vršački Vinogradi producer than for the samples from Vino Župa. This is also obvious through the change of the corresponding loading of this component (Fig. 3), which increases more abruptly and attains higher maximum (3.3. rel. u.) for the Vršački Vinogradi producer, while its rise is slower and maximum is lower (1.5 rel. u.) for the Vino Župa. This is due to a higher amount of the corresponding phenolic compounds emitting in this spectral region, with a maximum at 430 nm (Fernández et al. 2000, Lang et al. 1991).
Figure 1. Emission spectra of riesling wine samples from four trade marks, viz. Riesling and Graševina produced by Vino Župa, and Italijanski Riesling and Banatski Riesling produced by Vršački Vinogradi, from top to bottom, respectively. For each sample the emission spectra were recorded for the excitation wavelengths in the 255 - 300 nm range in steps of 5 nm.

Figure 2. Emission spectra of the pure components obtained by the MCR-ALS method used in the analysis of the emission spectra of the riesling wine samples from Figure 1. The components have the same maxima positions and the same shape for all 12 samples.

For both wine producers, no changes were observed in the spectral parameters after two days of opening of the wine bottle for all trade marks (Fig. 1). However, in the case of the Vino Župa producer, for the Riesling trade mark, there is a decrease in the 430 nm spectral component after seven days of bottle opening.
opening, and its loading changed accordingly (Fig. 3), at a lower rate of increase and attaining a lower maximum (1.5 rel. u.) than for the sample after two days of bottle opening (2 rel. u.). Also, there was an increase in the same component for the Graševina wine after the same time period, and a corresponding change of its loading occurred, being more abrupt and with a higher maximum (2 rel. u.) than for the sample two days after bottle opening (1.5 rel. u). These changes indicate that certain phenolic structures emitting at 430 nm changed possibly by oxidation processes after the bottle opening. The wine producers add certain additives that have a preserving role, such as sulfuric compounds (Plaza et al. 2013). The spectral changes recorded over time after bottle opening may be an indicator of the presence of higher concentrations of preserving additives in wine.

Figure 3. The excitation spectra profiles (loadings) corresponding to the spectral components from Figure 2, obtained by the MCR-ALS method. The curves marked with the symbols (□), (○), (△) correspond to the components in Figure 2 with the maxima at 315 nm, 370 nm and 430 nm, respectively. From top to bottom: the four trade marks, Riesling and Graševina from the Vino Župa producer, and Italijanski Riesling and Banatski Riesling from the Vršački Vinogradi producer.

The 315 nm peak may be related to the flavonoid type of compounds of the catechin type (Shumow and Bodor 2011). The 370 nm maximum may originate from certain types of phenolic compounds such as gallic acid or syringic acid (Sikorska et al. 2012). The 430 nm maximum is related to the phenolic compounds of the type of chlorogenic acid, caffeic acid, coumarins, stilbenes (Fernández et al. 2000, Lang et al. 1991).

The type of analysis presented has the potential to screen many wine samples, from different producers, since it may give quick results, without detailed
analysis of the content of the corresponding wines. This may provide a very useful approach to fingerprinting wines from various producers, as well as to screening the compositional stability of wine.

Conclusion

These results show that the fluorescence method in combination with the appropriate statistical analysis may be a tool that has the potential to differentiate between the samples of the trade marks containing the same wine type, but originating from different producers. The results also show that this method may be used for simple and quick tracking of changes in wine composition, caused by the oxidation processes over time after the bottle opening.

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References


RAZLIKOVANJE KOMERCIJALNIH UZORAKA VINA KORIŠĆENJEM FLUORESCENTNE SPEKTROSKOPIJE I MULTIVARIJACIONE ANALIZE

- originalni naučni rad -

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Rezime


Ključne reči: tipovi vina, rizling, emisioni spektar, multivariaciona rezolucija krivih, fenolne komponente.