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Wine discrimination based on chemometric analysis of untargeted markers using FT-Raman spectroscopy

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ABSTRACT

In this study, wine discrimination possibilities given by FT-Raman spectroscopy associated with chemometric methods, with respect to variety, vintage and geographical origin was discussed. As far as we know, the potential of Raman spectroscopy to include anti-Stokes range in the wine discrimination was explored here for the first time. The classification of 30 wines, from two sorts, known as Feteasca Regala and Sauvignon Blanc, produced in three Romanian viticulture regions, during five consecutive vintages was performed; an initial and cross-validation percent of 100% being obtained for all three classifications. A control sample set formed by four French samples (2 Sauvignon Blanc and 2 Chardonnay) was used for testing the efficiency of the proposed approach. By testing the control set, a discrimination of wine variety and geographical origin of 100% in both initial and cross-validation was obtained, while for vintage differentiation a percentage of 100% in initial and 94.1% cross-validation was reached.

1. Introduction

During the last years, considerable efforts were made in the development of accurate, rapid analytical techniques, which require either no sample preparation process or an easy one. In this regard, a special attention is given nowadays to the use of vibrational techniques for food and beverages authenticity control due to their fast, automated, cost-effective, non-destructive and environmental-friendly character. Beside this, the recorded progresses made in the field of data mining (chemometric methods) increased the versatility of vibrational techniques in food industry. The main techniques which are applied for detection of molecular vibrational motions are infrared spectroscopy (which may be near, mid or far depending on the infrared spectral region) and Raman spectroscopy (Teixeira dos Santos, Pascoa, & Joao, 2017). Infrared spectroscopy (IR) is nowadays extensively used for different purposes in wine industry, but its main disadvantage is represented by its limitation for the water-rich samples assessment, due to the strong absorption bands of water (Wang, Li, Ma, & Si, 2015). In contrast, Raman spectroscopy appears more suitable for the vibrational assessment of water containing samples, due to the relatively weak water bending mode in the vibrational spectroscopy fingerprint range (Numata, Iida, & Tanaka, 2011).

Raman spectroscopy, based on the inelastic light scattering on molecules, is gaining an increasingly wider area of applications. The inelastic scattered light by the molecule provides rich information on the vibrational modes of them, thus being characteristic to each molecular structure. Although a small amount of the incident light is inelastically scattered (Raman effect is an inherently weak effect), the weak counterpart of the incident light energy is modulated by the molecular vibrations of the scattering sample, thus, the observed vibrational modes provide information on the chemical composition and dynamics of the sample. Measuring the Raman spectra of complex samples in situ became accessible once the high resolution portable instruments with optimised detection capability were released on the market. Compared to other analytical techniques, Raman spectroscopy presents advantages in terms of: accessibility for in situ analyses, relatively low cost, high sensitivity and specificity (Popp & Kiefer, 2006).

Raman scattering effect was prospected in wine samples in several studies, with different purposes like: i) identification and/or determination of some wine compounds (anthocyanidins, total phenolic content, phenolic acids (Martin et al., 2017; Martin et al., 2015; Wu et al., 2016; Zaffino, Russo, & Bruni, 2015); ii) quality control of fermentation process (Wang et al., 2015; Wu et al., 2015);

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iii) wines discrimination studies (Mandrile, Zeppa, Giovannozzi, & Rossi, 2016) and the potential of the technique is increasingly explored for wines analysis. However, the specificity of wines related to their chemical content and provenance is wider, while little is still understood on their characteristic Raman scattering signal under different excitation energy. Certain wines components could be resonantly excited either in UV or in visible range, thus, combined Raman techniques to characterize varieties is still needed. Additionally, non-resonant excitation provided by the FT-Raman technique could be probed either in the Stokes or anti-Stokes range. To the best of our knowledge, the anti-Stokes range of the Raman spectra was not employed for wines analysis. Anti-Stokes range is known to exhibit much lower intensity of the Raman bands due to the normal distribution (Boltzmann) of few molecules on vibrational excited state (also known as the population of the excited vibrational state) when Raman excitation occurs. Thus, certain molecular species from the sample being in vibrational excited state prior to the Raman scattering may provide characteristic anti-Stokes signal, whose intensity is decreasing with increasing distance (cm^{-1}) from the Rayleigh line.

This work presents the first exploratory prospect on the potential of the FT-Raman spectroscopy with 1064 nm line and particularly of anti-Stokes spectral range of the Raman spectra for wines discrimination. To achieve this goal, a set of 30 Romanian white wines samples with respect to their variety, vintage and geographical origin were taken under study. Furthermore, four samples (2 Sauvignon and 2 Chardonnay), having a different origin country (France), were considered to test the extinction possibilities of the proposed discrimination methodology.

2. Materials and methods

2.1. Sample collection

For this work, 30 white wines from two varieties, Feteasca Regala and Sauvignon Blanc, produced during five consecutive years (from 2011 to 2015), among three different Romanian regions (Transylvania, Banat and Moldova) were investigated by mean of FT-Raman spectroscopy. From all above mentioned vintages, one sample of Feteasca Regala and another one of Sauvignon Blanc, belonging to each geographical area, were collected. Beside these samples, a control set formed by four authentic, laboratory made wines, 2 Sauvignon Blanc, coming from Bordeaux area and other 2 Chardonnay samples from Val de Loire and Puy de Dôme, from 2015 vintage were used for this study.

Ultrapure water (electrical resistivity 18.2 M Ω cm), ethanol of analytical grade (Sigma-Aldrich) and a solution of water-ethanol (15% ethanol) have been also analyzed.

2.2. Instrumentation

FT-Raman spectra of the wine samples have been recorded in capped quartz cuvette of 2 ml using an Equinox 55 (Bruker) FT-IR spectrometer with an integrated FRA106S Raman module. A Nd:Yag operating at 1064 nm was employed for excitation with an output power of 350 mW. Detection was achieved with a Ge detector operating at liquid nitrogen temperature. Spectra were acquired in the range, from −1000 to 3600 cm^{-1}, to comprise both the Stokes and anti-Stokes regions and 500 scans were co-added. Opus 2.0 and Origin 6.1 software were used for acquisition and data processing, respectively.

2.3. Chemometric data analysis

Chemometric interpretation of spectral data was made using SPSS Software, version 24 (IBM, USA). Generally, results obtained from Raman spectra consist in large number of variables (wavenumbers), which characterize the analyzed matrices. For optimizing the results interpretation, supervised chemometric techniques, such stepwise linear discriminant analysis (SLDA), are usually applied. The main purpose of SLDA is to investigate the differences among predefined groups and to provide a classification model, which should be able to maximize the ratio between groups variance and to minimize the ratio within group variance, meaning that cases belonging to the same group have similar properties. The success of the discriminant model is evaluated through the percent of correctly classified samples. The cross-validation procedure consists of extracting one sample each time, and tested as a new one (“leave-one out cross validation”) (Dias, Peres, Veloso, & Machado, 2009).

Based on FT-Raman measurements performed on 30 wine samples, three classifications were made in this study using SLDA, as function of wine variety (Feteasca and Sauvignon), geographical origin (Transylvania, Moldova and Banat) and vintages (five consecutive years). Additionally, the limitations and possibilities of the proposed models extinction were tested using an external sample set formed by four samples (2 Sauvignon and 2 Chardonnay) produced in France during 2015 vintage.

3. Results and discussion

FT-Raman spectra of all wine samples are showed in Fig. 1A for both: Stokes and anti-Stokes range, from - 1000 cm^{-1} to 3600 cm^{-1}. As easily observed, the main characteristic bands of the wines are associated with the main compounds of ethanol (bands at 877, 1047, 1095, 1276, 1454, 2717, 2882, 2933, 2980 cm^{-1}) and water (stretching modes above 3200 cm^{-1} and bending mode at 1636 cm^{-1}). The spectral variability which reflects the wine differences is prominent either in the Stokes range (50-850 cm^{-1}, 1600-1750 cm^{-1}) or in the anti-Stokes (Fig. 1 B).

From Fig. 1A and B, small differences among FT-Raman spectra of wines could be observed. These appear due to distinct concentrations of wine constituents and also, to the discrete bands shifts. As the main contribution to the wine Raman spectra are given by ethanol and water, a subtraction of these signals would allow the observation of differences that appear among samples, given by the minor compounds, some of them having a contribution in wine discrimination. On the other hand, in order to better emphasize the discreet differences, in terms of Raman shifts of ethanol peaks, which appear from a sample to another, the Raman spectrum of ethanol having analytical purity and of a water-ethanol solution (15% ethanol) measured in similar quartz cuvette were recorded and shown in Fig. 1. A detail of the main ethanol bands are shown in Fig. 1C and D emphasizing an important shift between the ethanol signals from wines as compared with the bands given by the pure ethanol. As could be seen, this displacement is more subtle in the case of water-ethanol solution (15%) due to the ethanol-water hydrogen-bonding. As a consequence, the wine ethanol signals also present some small shifts among samples, explained by their differences in terms of different composition i.e. alcoholic strength (Fig. 1). Taking into account these subtle ethanol bands displacements, a rigorous subtraction of these contributions (water and ethanol) to highlight the minor compounds, which could be responsible for wines classifications, cannot be made.

However, starting from these considerations and just for highlight the differences among wine samples, two comparisons among wines from different vintages and also, between the two wine sorts (Feteasca Regala and Sauvignon) are illustrated in Fig. 2. Although not rigorously set as exact concentration value in wines, a solution of water-ethanol (15% ethanol) has been used to record a reference