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Analytical Methods

Raman spectroscopy of white wines

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ABSTRACT

The feasibility of exploiting Raman scattering to analyze white wines has been investigated using 3 different wavelengths of the incoming laser radiation in the near-UV (325 nm), visible (532 nm) and near infrared (785 nm). To help in the interpretation of the Raman spectra, the absorption properties in the UV–visible range of two wine samples as well as their laser induced fluorescence have also been investigated. Thanks to the strong intensity enhancement of the Raman scattered light due to electronic resonance with 325 nm laser excitation, hydroxycinnamic acids may be detected and analyzed selectively. Fructose and glucose may also be easily detected below *ca.* 1000 cm^{-1}. This feasibility study demonstrates the potential of the Raman spectroscopic technique for the analysis of white wines.

1. Introduction

Analytical methods are essential tools for wine quality control and authentication. Among all spectroscopy techniques currently used in this context, often complementary, there is a great need for low cost analytical tools that are small and light enough to be handled for field analysis. Optical methods based on the phenomenon of light absorption have experienced significant developments in recent years for the characterization of wines. These methods encompass absorption spectroscopy in the mid-infrared (MIR) and the near-infrared (NIR) for studying fundamental molecular vibrations and their harmonics (Bauer et al., 2008; Cozzolino, Dambergs, Janik, Cynkar, & Gishen, 2006; Cozzolino, McCarthy, & Bartowsky, 2012), absorption spectroscopy in the ultra-violet and visible (UV–vis) for probing electronic transitions (Acevedo, Jiménez, Maldonado, Domínguez, & Narváez, 2007; García-Jares & Médina, 1995; Harbertson & Spayd, 2006; Roig & Thomas, 2003; Urbano, Luque de Castro, Pérez, García-Olmo, & Gómez-Nieto, 2006). These techniques are well suited in an industrial context due to their ease of use, their measurement quickness, their relatively low financial cost and also because they can be small enough (miniaturized in a near future) for in situ operation.

Surprisingly there has been very little research carried out on wines by means of spectroscopic techniques analyzing the emission of light. Indeed for wavelengths of light in the 260–1100 nm range, several phenomena will take place involving the electronic polarization of the molecules. Let us consider the interaction of a monochromatic electromagnetic radiation (laser) with molecules. If there is no absorption of the incoming radiation, elastic (Rayleigh) and inelastic (Raman) scattering of photons will occur. The spectral analysis of the Raman scattering provides information on molecular vibrations (Raman scattering effect is fully described in many books, see for instance (Dietzek, Cialla, Schmitt, & Popp, 2010)). If now the molecule absorbs the exciting radiation, two phenomena involving different mechanisms may take place if we exclude phosphorescence. The first one is fluorescence (Lakowicz, 2006) and the second is resonance Raman scattering (Dietzek et al., 2010). The resonance Raman spectrum will display maxima at the same positions to that of normal Raman scattering, but the vibrations coupled to the absorbing functional groups may be strongly intensified.

To the best of our knowledge, only one paper has been published so far about Raman scattering of white wines (Meneghini et al., 2008) and none about resonance Raman scattering. A very few studies based on front face fluorescence spectroscopy for direct and global analyzes of wines have already been published (Airado-Rodríguez, Durán-Merás, Galeano-Díaz, & Wold, 2011; Dufour, Letort, Laguet, Lebecque, & Serra, 2006; Le Moigne et al.,

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2008). However, fluorescence detection coupled to HPLC system have been extensively used to quantify flavanols (*e.g.* catechin, epicatechin...) and procyanidin dimer (*e.g.* procyanidin (Gómez-Alonso, García-Romero, & Hermosín-Gutiérrez, 2007; Silva, Ky, Jourdes, & Teissedre, 2012)).

Molecular vibrations may be analyzed either in the MIR–NIR regions by probing the absorption of light by molecules, or by Raman and resonance Raman scattering of light in the visible range. Because the mechanisms of light-matter interaction are not the same for absorption and scattering, MIR–NIR and Raman spectroscopic techniques are complementary with distinct vibration selection rules. We will show that, for this reason, Raman spectroscopy possesses advantages for wine analysis. Also very small amount of sample is required (several μm^3) as a Raman spectrometer may be coupled to a confocal microscope (a quite large majority of commercial Raman spectrometers combine Raman spectroscopy to optical microscopy). This method is a very effective tool in chemical analysis because it is non-destructive and usually does not require special preparation of the sample. Finally Raman spectrometers may be very compact and equipped with optical fibers allowing in situ measurements. For example mobile Raman spectrometers are efficient tools in the domains of arts and archeology (Colomban, 2012).

The aim of this work is to investigate the potential of Raman spectroscopy for analyzing commercial wines. This preliminary study focuses on two samples of white wines (one dry and one medium) for establishing the potential of the technique. This study focus on white wines as their chemical composition is less complex than red wine one's. Because the mechanisms at the origin of light emission depend on the absorption of the exciting radiation, we will first investigate the absorption of light in the UV–visible for the two samples of white wines. Then the emission spectra recorded using three wavelengths from the near-UV to the NIR for the laser excitation will be analyzed. As mentioned above, spectra where fluorescence emission and resonance Raman or normal Raman scattering take place are expected.

2. Materials and methods

2.1. Samples

The white wines, one dry and one medium, that were investigated in this work originate from south-west of France. These two wines were chosen as visually their yellow color looked very similar and because their chemical composition must be significantly different. The first sample (sample #1) is a Bordeaux dry wine AOC "entre deux mers" vintage 2013 and the second (sample #2) sample is a medium wine AOC "côtes de Bergerac" vintage 2012. To help in the interpretation of the wine's spectra, those of pure phenolic compounds or sugars dissolved in a wine model solution have been recorded. The used wine model solution was a hydroalcoholic solution (*e.g.* 12% ethanol) acidified with 5 g l^{-1} of tartaric acid with the pH adjusted at 3.5 (*e.g.* 3.5 is considered as the average wine acidity (Ribéreau-Gayon, Dubourdieu, et al., 2012; Ribéreau-Gayon, Glories, et al., 2012)) with a solution of NaOH (1 M). Phenolic acids and sugars with purity >99% were obtained commercially from Sigma–Aldrich.

2.2. Absorption spectroscopy

UV–visible spectroscopy measurements were performed using a Lambda-650 UV–vis spectrophotometer (Perkin Elmer). Wine samples taken from freshly opened bottles were scanned in transmission mode (200–900 nm). Samples of white wines were placed in quartz cells of thickness 1 mm.

2.3. Emission spectroscopy

All phenomena involving emission of light such as fluorescence, Raman scattering and resonance Raman scattering were recorded in the backscattering geometry by means of Raman spectrometers coupled to optical microscopes. Experiments using the 325 nm excitation wavelength of a He–Cd Laser were performed on the Raman spectrometer Labram-UV HR800 (Horiba Jobin Yvon) using a 4× UV-lens, experiments at 532 (frequency doubled Nd:YAG laser) and 785 nm (diode) were performed on the Xplora instrument (Horiba Jobin Yvon) using a 10× objective. The laser power at sample was 2 mW for 325 nm excitation wavelength, 13 mW for 532 nm and 50 mW for 785 nm. To analyze the emission of light at 325 nm excitation over a broad range of wavelengths, *i.e.* to analyze fluorescence, a 150 lines mm^{-1} diffraction grating was used. For Raman scattering a better spectral resolution in the range 2–5 cm^{-1} was needed and gratings with 2400 lines mm^{-1} for a 325 nm excitation wavelength, 1800 lines mm^{-1} at 532 nm and 1200 lines mm^{-1} at 785 nm were used. Samples of white wines and model solutions were placed in NMR glass tubes with overall diameter 4.97 mm and internal diameter 4.20 mm. The emission spectra were corrected for detector efficiency and could be therefore qualitatively compared to each other. However quantitative information on the absolute intensities of the emitted light cannot be provided in this study.

3. Results and discussion

A difficulty to be overcome is related to the chemical nature of the wines with composition of about 12% of ethanol and 84% water. The other molecules include carboxylic acids (for example tartaric acid), sugars, glycerol and also polyphenols that represent a very small proportion of the total composition. As emphasized in the introduction of this paper, optical spectroscopy has been widely exploited for the analysis of wines and it is obvious that the obtained spectra will result from the superposition of all the optical responses of different molecules that make up the medium. A very large number of molecular species have been identified in wines, and two of these species alone represent about 96% of the total number of molecules. One may therefore easily understand that Raman signals are expected to be dominated by those of water and ethanol.

3.1. UV–visible absorption spectra

In wines, mainly polyphenols will absorb light at wavelengths between 250 and 900 nm. The absorption features of these species are now well identified (Cerovic et al., 2002; Jurd, 1957). The UV–visible absorption spectra between 250 and 500 nm of the two samples of white wines are shown in Fig. 1a. There is no significant absorption around 500 nm, as expected for a white wine that does not contain anthocyanins known to have absorbance features at 267–275 and 475–545 nm. Hydroxycinnamic acids have absorbance maxima at 227–245 and 310–332 nm; benzoic acids show a single absorbance in the region of 235–305 nm and flavanols typically have maxima in the 250–270 and 350–390 nm regions. As white wines do not contain significant amounts of flavanols, the peaks around 263 nm may be therefore assigned mainly to the phenolic acids that are present in the white wines and the peak around 326 nm mainly to hydroxycinnamic acids. Of course these peaks are broad and overlap around 300 nm. Interestingly the two white wines have quite similar absorptions for wavelengths above 300 nm and the very weak tails of the spectra above 400 nm are responsible for their similar yellow color. In contrast,