Romanian Wines Quality and Authenticity Using FT-MIR Spectroscopy Coupled with Multivariate Data Analysis

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Abstract

Fourier Transform Mid-Infrared Spectroscopy (FT-MIR) combined with multivariate data analysis have been applied for the discrimination of 15 different Romanian wines (white, rosé and red wines), obtained from different origin-denominated cultivars. Principal component analysis and hierarchical cluster analysis was performed using different regions of FT-MIR spectra for all wines. The general fingerprint of wines was split in four characteristic regions, corresponding to phenolic derivatives, carbohydrates, amino acids and organic acids, which confer the wines quality and authenticity. By qualitative and quantitative evaluation of each component category, it was possible to discriminate each wine category, from red, to rosé and white colours, to dry, half-dry and half-sweet flavours. The multivariate data analysis based on absorption peaks from FT-MIR spectra demonstrated a very good, significant clustering of samples, based on the four main components: phenolics, carbohydrates, amino acids and organic acids. Therefore, the ATR-FT-MIR analysis proved to be a very fast, cheap and efficient tool to evaluate the quality and authenticity of wines, and to discriminate each wine category, based on their colour and sweetness, as consequence of their biological (cultivar) specificity.

Keywords: carbohydrates and acidity, Fourier Transform Mid-Infrared Spectroscopy, phenolics, Principal Component Analysis, red, rosé and white wines

Introduction

Grapes, grape juices and wines, consumed in moderate quantities, proved to contain a large number of phytochemicals with health benefits promoting effects (German and Walzem, 2000), from essential amino acids, minerals, organic acids, aromas, stilbenes (resveratrol), vitamins, and especially a large variety of pigments (flavonoids and anthocyanins) as well catechins, procyanidins and phenolic acid derivatives (Jackson, 2008). Therefore, the quality and authenticity of the varietal origin of grapes and wines is of great interest to both the wine industry and the consumer (Cozzolino et al., 2003; Cozzolino et al., 2009). The main secondary metabolites found in grapes, with important roles in plant resistance to pathogens, allelopathy, oxidative stress and plant growth regulation, are the phenolic derivatives (Ogbemudia and Thompson, 2014). These derivatives include monophenolic compounds (phenolic acids, as free or derivatized as esters or glucosides, e.g. benzoic and cinnamic acid derivatives), and especially polyphenolics (anthocyanins and flavonoids, catechins, procyanidins, and their derivatives) key-biomarkers of grapes and wines' quality, having antioxidant, antimutagenic, antiproliferative and antimicrobial properties (Guerrero et al., 2009). Phenolic acids are derived from benzoic and cinnamic acids and are found as free acids and esters, glycosides or bound complexes, which have also beneficial effects on human health (German and Walzem, 2000; Mateus et al., 2001; Socaciu, 2008).

The modern analytical methods to evaluate phenolic derivatives are usually based on reversed-phase high-performance liquid chromatography (HPLC), or another separation techniques such as gas chromatography or capillary electrophoresis, followed by ultraviolet (UV), electrochemical (EC), fluorescence (F) or mass spectrometric (MS) detection (Lorrain et al., 2013). Commonly, for wines direct analysis or solid-phase extraction followed by reversed phase HPLC-UV-VIS or HPLC-MS methods were used to analyze the phenolic...
fingerprint providing detailed information regarding individual phenolics and their quantity, enabling high resolution and accurate measurement of monomeric anthocyanins and catechins (Ginjom et al., 2011), but also the discrimination of cultivars (Muccillo et al., 2014), the influence of fermentation, vinification, maturation during storage, formation of oligomeric and polymeric pigments (García-Falcón et al., 2007; Ivanova et al., 2012). In spite of so many factors of influence, the differences in the overall quality of wines, their phenolic fingerprint still remains characteristic for each cultivar (Avar, 2007; Da Costa et al., 2000; Gruz et al., 2008).

In contrast to chromatography, spectroscopic techniques (UV-Vis, IR), when applied to mixtures, are less selective but may contain information about the complete phenolic composition of the wines under investigation (Gorinstein et al., 1992). UV-Vis spectrometry coupled with infrared spectroscopy, proved to be a cheap and rapid analytical method to be used for wine composition, quality and authenticity evaluation (Linskens and Jackson, 1988; Somers and Verètère, 1988).

The use of infrared (IR) spectroscopy for routine analysis of wine began with near infrared spectroscopy (NIRS) as preferred method in the early 1980’s (Hashimoto and Kameoka, 2008; Ough and Amerine, 1988). Since that time, the focus for quantitative analysis of grapes and wine has moved towards Fourier transform infrared (FT-IR) technology in the mid-infrared region, since it offers better accuracy in determination and more constituents and properties can be quantified compared to NIRS (Dubernet and Dubernet, 2000; Eichinger et al., 2004; Patz et al., 2004; Soriano et al., 2007). Modern infrared spectroscopic instrumentation is fitted with chemometric software packages that facilitate the establishment of calibration models which can be used to quantify many components simultaneously, thereby reducing the analysis time and cost (Eichinger et al., 2004). FT-IR spectroscopy technology and chemometric techniques for analysis of grapes and wine were implemented in South Africa in the early 2000’s (Bauer et al., 2008) and several qualitative and quantitative applications were developed in the last few years.

Near-infrared (NIR), as well as mid-infrared (MIR) spectroscopic techniques combined with multivariate data analysis, proved to be very promising for their good reproducibility in routine analysis (Irudayaraj and Tewari, 2003; Schulz and Baranska, 2007). While NIR absorptions reflect only overtones and combination bands of fundamental transitions, less distinct, the mid-infrared (MIR) absorption bands are related to defined vibrational transitions and are better resolved. The significant improvements in the IR instruments design and auxiliary optics have made modern MIR spectrometers robust for routine applications for liquids, MIR spectra being conveniently recorded using the attenuated total reflection (ATR) technique (Wilson and Tapp, 1999).

The Fourier Transform Infrared Spectroscopy (FT-IR) technique, in combination with chemometrics, is a fast and reproducible technique for identifying the authenticity and adulteration of different food and beverage products (Da Costa et al., 2004). The FT-IR is increasingly used for the authentication of alcoholic beverages (Gallignani et al., 2005; Kupina and Shrikhande, 2003) or to verify the authenticity of different fruit juices (Leopold et al., 2011).

During the last two decades, extended studies on grapes and wines were reported, using NIR and FT-IR coupled with biostatistical tools, either to evidentiate saccharides, alcohols or other quality parameters, or their authenticity and traceability, related to origin (cultivar or region) (Cheda et al., 2010; Coimbra et al., 2002; Da Costa et al., 2004; Edelmann et al., 2001; Edenharder et al., 2001; Orbán et al., 2006; Peña-Neira et al., 2000). Using the FT-IR spectra of the wine polysaccharide (1200 and 800 cm⁻¹) of the dry extracts coupled with PCA and CCA chemometric methods, it was possible to discriminate extracts based on the polysaccharide composition. Based on the bands from 1600 cm⁻¹, the polyphenolic content was also evaluated (Gorinstein et al., 1992).

Mid-infrared spectroscopy and UV-Vis spectroscopy combined with multivariate data analysis have been applied also for the discrimination of different red wine cultivars (‘Cabernet Sauvignon’, ‘Merlot’, ‘Pinot Noir’, ‘Blaufrankisch’, ‘St. Laurent’, and ‘Zweigelt’). Both authentic wines and their phenolic extracts were investigated by ATR-MIR spectroscopy and UV-Vis spectroscopy (Edelmann et al., 2001). The main components (sugar and organic acids) failed to offer satisfactory classification of wines, but by using phenolic extracts, a complete discrimination of all cultivars investigated was achieved.

The FT-IR spectra were also used for the differentiation and classification of wines and brandies during their ageing process, as well as for the characterization and differentiation of distilled drinks from several countries (Palma and Barroso, 2002), good linear regression coefficients (0.995) between the ageing scale and the FT-IR data being obtained (Eichinger et al., 2004).

The oenological wine parameters (alcoholic degree, volumic mass, total acidity, glycerol, total polyphenol index, lactic acid and total sulphur dioxide) were investigated by infrared spectroscopy (Edelmann et al., 2001). The main components (sugar and organic acids) failed to offer satisfactory classification of wines, but the use of both methods improved the determination of glycerol and total sulphur dioxide. The validation sets used for developing general equations were built with samples from different “appellation d’origine” (Urbano Cuadrado et al., 2005).

A fast and accurate study was reported on 22 Romanian red wines of ‘Cabernet Sauvignon’, ‘Merlot’, ‘Fetească Neagră’, ‘Pinot Noir’ and ‘Burgund’ varieties, comparing 1H-NMR with the IR spectroscopy (Todasca et al., 2007). By IR spectroscopy, characteristic bands for amino acids (1604 cm⁻¹) and organic acids (1719 cm⁻¹) were investigated, but the method could not provide good differentiations. Meanwhile, the NMR method is considered to be more accurate, but much more expensive.

This study aims to investigate the use of mid-infrared (MIR) and multivariate data analysis techniques to classify Romanian wines produced from autochthonous cultivars. In this respect, the Fourier Transform mid-infrared (FT-MIR) spectroscopy was applied to characterize 15 different Romanian wines (white, rosé and red wines), obtained from different authentic, origin-denominated cultivars, found in different Romanian regions. The wines were investigated by
attenuated total reflectance (ATR) and the most important components (phenolics, carbohydrates, amino acids and organic acids) were localized in specific fingerprint regions of the spectra. Based on the differences between the FT-MIR spectra, by multivariate data analysis (Principal component analysis), were identified the specific discrimination factors useful to authenticate the biological (cultivar) and regional origin, as well their sweetness index.

Materials and methods

Wine samples

Fifteen Romanian wines, including white (n=4), rosé (n=2) and red (n=9), of different sweetness indexes (5 samples dry, 7 samples half-dry and 3 samples half-sweet) were investigated. These wines originated from different cultivars and were produced in ten different wineries from Romania, namely Jidvei, Coteşti, Panciu, Huşi, Recaş, Ceptura, Tohani, Sarica-Niculiţel, Murfatlar, and Sadova Corabia. The wines, packed in glass bottles and produced in the vintage years 2008-2012, were purchased from local supermarkets and stored at room temperature until analyzed. Tab. 1 includes data from each wine sample, the specific cultivar, the year of production and the denomination (as dry, half-dry, half-sweet) and their region of origin. All wine samples were centrifuged at 3000 rot/min for 15 min, then used directly for recording the FT-MIR spectra.

Tab. 1. Numbering of wine samples: white (1-4), rosé (5-6), red (7-15) with references to the sweetness index (dry, half-dry, half-sweet) and the production year

<table>
<thead>
<tr>
<th>No.</th>
<th>Cultivar (Variety)</th>
<th>Vineyard</th>
<th>Year</th>
<th>Wine type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fetească Alba</td>
<td>Cotesti</td>
<td>2011</td>
<td>Half-dry</td>
</tr>
<tr>
<td>2</td>
<td>Fetească Alba</td>
<td>Jidvei</td>
<td>2011</td>
<td>Dry</td>
</tr>
<tr>
<td>3</td>
<td>Fetească Regala</td>
<td>Jidvei</td>
<td>2011</td>
<td>Half-dry</td>
</tr>
<tr>
<td>4</td>
<td>Fetească Regala</td>
<td>Recas</td>
<td>2012</td>
<td>Half-dry</td>
</tr>
<tr>
<td>5</td>
<td>Babească Rose</td>
<td>Panciu</td>
<td>2012</td>
<td>Half-dry</td>
</tr>
<tr>
<td>6</td>
<td>Busuiocasa de Bohotin</td>
<td>Husi</td>
<td>2011</td>
<td>Half-sweet</td>
</tr>
<tr>
<td>7</td>
<td>Babească Neagra</td>
<td>Panciu</td>
<td>2012</td>
<td>Half-dry</td>
</tr>
<tr>
<td>8</td>
<td>Babească Neagra</td>
<td>Husi</td>
<td>2009</td>
<td>Dry</td>
</tr>
<tr>
<td>9</td>
<td>Babească Neagra</td>
<td>Sarica-Niculiţel</td>
<td>2011</td>
<td>Dry</td>
</tr>
<tr>
<td>10</td>
<td>Babească Neagra</td>
<td>Sadova Corabia</td>
<td>2010</td>
<td>Dry</td>
</tr>
<tr>
<td>11</td>
<td>Fetească Neagra</td>
<td>Cotesti</td>
<td>2008</td>
<td>Half-sweet</td>
</tr>
<tr>
<td>12</td>
<td>Fetească Neagra</td>
<td>Panciu</td>
<td>2011</td>
<td>Half-dry</td>
</tr>
<tr>
<td>13</td>
<td>Fetească Neagra</td>
<td>Ceptura</td>
<td>2012</td>
<td>Dry</td>
</tr>
<tr>
<td>14</td>
<td>Fetească Neagra</td>
<td>Tohani</td>
<td>2010</td>
<td>Half-dry</td>
</tr>
<tr>
<td>15</td>
<td>Fetească Neagra</td>
<td>Murfatlar</td>
<td>2011</td>
<td>Half-sweet</td>
</tr>
</tbody>
</table>

Table 2 includes the specific wave numbers and fingerprint regions used to identify the stretching and bending vibrations, depending on the functional groups, as reported in literature (Coimbra et al., 2002; Gorinstein et al., 1992; Todasca et al., 2007). Such data were useful in the interpretation of the FT-MIR absorption peaks obtained in red wines.

Tab. 2. Characteristic IR wave numbers (cm\(^{-1}\)) for stretching and bending vibrations in wines, according to literature reports (Coimbra et al., 2002; Gorinstein et al., 1992; Todasca et al., 2007)

<table>
<thead>
<tr>
<th>Fingerprint regions (cm(^{-1}))</th>
<th>Characteristic frequencies (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 1000</td>
<td>690, 745, 961, 964</td>
<td>Phosphates, Phenolics, Mono-substituted phenyl derivatives, Unsaturated lipids, incl. carotenoids</td>
</tr>
<tr>
<td>970-1100</td>
<td>976, 1030, 1060, 1065, 1079</td>
<td>Glucose, Oligo- and polysaccharides, incl. metoxylated derivatives, Alcohols (ethanol)</td>
</tr>
<tr>
<td>1500-1716</td>
<td>1566, 1574, 1650, 1665, 1665, 1700</td>
<td>Organic acid stretching vibrations at 1700 cm(^{-1})</td>
</tr>
<tr>
<td>2800-2935</td>
<td>2854, 2920, 2934</td>
<td>Aromatic ring stretching at 1600 cm(^{-1})</td>
</tr>
<tr>
<td>3300-3500</td>
<td></td>
<td>Stretching vibrations of Amino acids and their derivatives at 1530-1600 cm(^{-1})</td>
</tr>
</tbody>
</table>

Multivariate data analysis

Advanced chemometrics was applied to discriminate between different wine samples, based on their colour, content of phenolic derivatives, amino acids and organic acids, as well as carbohydrates. Therefore, the discrimination was performed using the whole FT-MIR spectra (600-3500 cm\(^{-1}\)) as well as the regions identified (1-4) at frequencies of 600-940 cm\(^{-1}\) (1), 970-1100 cm\(^{-1}\) (2), 1600-1716 cm\(^{-1}\) (3) and 2800-3000 cm\(^{-1}\) (4). To discriminate among these samples and regions, the principal component analysis (PCA) was applied on the peak areas corresponding to each region, using Unscrambler X 10.1 Software, version 10.1. The correlation factors were calculated using Origin software (OriginLab, version 8.0).

Results and discussion

FT-MIR spectral fingerprinting of individual wine samples

Fig. 1 exhibits the general FT-MIR spectra of all wine samples, from white (samples no. 1-4), to rosé (samples no. 5, 6) and red wines (samples no. 7-15), according to their list in Tab. 1 in the whole IR region range, from 600 to 3500 cm\(^{-1}\). In all samples, similar spectral features were generally obtained, but with specific quantitative modifications in the fingerprint region (1800-600 cm\(^{-1}\)). Comparing the shapes of spectra, there were identified four different regions (1-4) which can show specific differences, related to the colour of wines (white, rosé and red wines), and to the sweetness (dry vs half-dry and half-sweet).

Tab. 2 includes the specific wave numbers and fingerprint regions used to identify the stretching and bending vibrations, depending on the functional groups, as reported in literature (Coimbra et al., 2002; Gorinstein et al., 1992; Todasca et al., 2007). Such data were useful in the interpretation of the FT-MIR absorption peaks obtained in red wines.
Fig. 1. Individual FT-MIR spectra registered for all 15 wine samples, in the region 600-3500 cm$^{-1}$
all wine spectra. The region 750-900 cm\(^{-1}\) corresponds to absorptions of phenyl/aromatic derivatives, including phenolics. Aromatic derivatives have also O-H stretching bands between 1200-1250 cm\(^{-1}\). The region 1030-1100 cm\(^{-1}\) is specific to absorptions of C-OH groups found in carbohydrates, e.g. 1030 cm\(^{-1}\) for glucose and 1060 cm\(^{-1}\) for fructose (Leopold et al., 2009). Amino acids like proline, alanine, arginine, glutamic acid, \(\gamma\)-aminobuteric acid absorb at 1608 cm\(^{-1}\) and simple phenolics like gallic acid and catechins absorb around 1600 cm\(^{-1}\). The absorption band at 1716 cm\(^{-1}\) is characteristic to organic acids found in wines (tartaric, acetic, lactic, citric, malic acids). The absorption band at 2938 cm\(^{-1}\) is usually related to polyols, like glycerol and other compounds like flavours. Generally, wines contain water, alcohols, glycerol, sorbitol, mannitol, amino acids, esters, minerals, sulfites, phenols, sugars, organic acids such as tartaric, malic and citric acids, aldehydes, as well as volatile acids as common ingredients (Cerdán et al., 2004). Similarity of the most important components gave rise to similar peak positions in the FT-IR spectra of the studied Romanian wines.

**Identification of specific functional groups and molecules in wines, depending on their colour and sweetness.**

According to Fig. 2, representing a generic FT-MIR spectra of wines, it was possible to consider 4 specific regions which can be useful for wines’ characterization: region 600-940 cm\(^{-1}\) (1) corresponds to phenolics derivatives (including esters), region 2 (970-1100 cm\(^{-1}\)) to carbohydrates (glucose, fructose and oligosaccharides, mainly saccharose), region 3 (1600-1716 cm\(^{-1}\)) to free amino acids, peptides and organic acids and region 4 (2800-3000 cm\(^{-1}\)) for polyols (mainly glycerol). Tab. 3 includes the FT-MIR absorption wave numbers, specific to the 4 regions of each wine fingerprinting: 600-940 cm\(^{-1}\) (1), 970-1100 cm\(^{-1}\) (2), 1600-1700 cm\(^{-1}\) (3). In the 4th region (2800-3000 cm\(^{-1}\)), all wines absorbed at the same wave numbers, 2887 and 2931 cm\(^{-1}\). Generally, the range 600-1800 cm\(^{-1}\) was considered as “fingerprint region”, useful to differentiate wines according to their sweetness index (dry to half-dry and half-sweet). One can notice that in region 1, the absorptions are determined mainly by the polyphenols, region 2 was specific to carbohydrates, mainly glucose (1033 cm\(^{-1}\)), but also fructose and sucrose (1100 cm\(^{-1}\)); region 3 was specific to amino acids (1602-1608 cm\(^{-1}\)) and organic acids (1700 cm\(^{-1}\)).

FT-IR spectra of wines showed absorption bands at different frequencies and these bands can be attributed to the various functional groups. IR spectral peaks are related to the bonds in the compounds, thus they could be assigned to the composition of the specific food sample such as its phenol, alcohol, aldehyde, higher alcohol, polyol, acid, sugar, volatile acid and amino acid content (Lee et al., 2009).

Tab. 4 shows detailed information regarding the values of peak intensities at 1033, 1100, 1600, 1700 cm\(^{-1}\), which can be used as quantitative markers of differences between the individual wines and wine types (based on colour and sweetness index). The ratios 1033/1100 cm\(^{-1}\) and 1600/1700 cm\(^{-1}\) were also used to characterize quantitatively the sweetness claimed on the label of these wines (dry, half-dry and half-sweet). Fig. 3 represents the differences between mean values registered from peak intensities corresponding to glucose (G), fructose+ sucrose (F+S), amino acids (AA) and organic acids (OA). Characteristic absorbance peaks of sugar components (970-1100 cm\(^{-1}\)) as well as amino acids and organic acids (1600-1700 cm\(^{-1}\)).

[Fig. 2. The FT-MIR spectra of a wine sample: 1 - spectral region 600-940 cm\(^{-1}\); 2 - spectral region 970-1100 cm\(^{-1}\); 3 - spectral region 1600-1716 cm\(^{-1}\); 4 - spectral region 2800-3000 cm\(^{-1}\).]

<table>
<thead>
<tr>
<th>Wine no.</th>
<th>1 (600-940 cm(^{-1}))</th>
<th>2 (970-1100 cm(^{-1}))</th>
<th>3 (1600-1700 cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>630, 777, 817, 864, 920</td>
<td>1033</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>2</td>
<td>775, 817, 854, 921</td>
<td>1033</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>3</td>
<td>605, 667, 777, 817, 862, 920</td>
<td>1031</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>4</td>
<td>630, 779, 817, 864, 921</td>
<td>1033</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>5</td>
<td>603, 775, 817, 860, 920</td>
<td>1031</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>6</td>
<td>630, 775, 815, 864, 898, 898</td>
<td>1028</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>7</td>
<td>603, 630, 775, 817, 862, 920</td>
<td>1033</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>8</td>
<td>605, 630, 775, 817, 923</td>
<td>1033</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>9</td>
<td>771, 854, 923, 995</td>
<td>1033</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>10</td>
<td>771, 854, 923</td>
<td>1033</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>11</td>
<td>775, 815, 862, 920</td>
<td>1033</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>12</td>
<td>603, 775, 815, 862, 921</td>
<td>1033</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>13</td>
<td>607, 630, 775, 854, 921</td>
<td>1033</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>14</td>
<td>605, 775, 817, 862, 921</td>
<td>1033</td>
<td>1602, 1716</td>
</tr>
<tr>
<td>15</td>
<td>603, 775, 817, 862, 920</td>
<td>1033</td>
<td>1602, 1716</td>
</tr>
</tbody>
</table>
1716 cm\(^{-1}\)) appeared and the intensity of these peaks increased with the increase of sugar and acid content. Thus, according to the characteristic peaks in the infrared spectra in the range of 970-1100 cm\(^{-1}\) and 1600-1716 cm\(^{-1}\), dry, half-dry and half-sweet wines can be divided according to the amount of sugar, amino acids and organic acids, that can be evaluated in accordance with such spectra. Tarantilis et al. (2008) also reported differentiation between wine samples based on small differences between spectra of their phenolic extracts, the spectral region between 1800-900 cm\(^{-1}\) being chosen for wine fingerprinting. Also, Chen et al. (2009) have achieved discrimination between dry and sweet red wine samples using 2D correlation spectroscopy and MIR.

**Multivariate Data Analysis by Principal Component Analysis**

PCA was performed on the MIR spectra, to examine qualitative differences within the set of red, rosé and white wines. Figs. 4-7 present the results of PCA analysis and scoring, to discriminate between wine types, based on the general FT-IR fingerprint (Fig. 4, from 600 to 1800 cm\(^{-1}\)) considering as well the three regions of IR absorption specific to phenolic derivatives (Fig. 5, 750-940 cm\(^{-1}\)), carbohydrate derivatives (Fig. 6, 970-1100 cm\(^{-1}\)) and amino acids and organic acids (Fig. 7, 1600-1716 cm\(^{-1}\)).

As presented in Fig. 4, for the whole fingerprint region, the first principal component (PC1) explained 68% of the variability and the second principal component (PC2) explained 22% of the variability; while together PC1 and PC2 explained 90% of the whole variability of wine samples and showed a good similarity for white wines (grouped in the positive quadrant), also for rosé wines (close in the inferior quadrant). Red wines were more heterogeneous in the composition and were spread, not clustered in a specific group. Nevertheless, the red, half-sweet wines (11 and 15) were close to the rosé wines, which proved to be superior in sweetness.

As presented in Fig. 5, for the region 750-940 cm\(^{-1}\), specific to phenolic derivatives, the first two components have achieved discrimination between dry and sweet red wine samples using 2D correlation spectroscopy and MIR.
(PC1 and PC2) together, explained 98% of the whole variability of wine samples. Although the variance explained was high (98%), a weaker clustering of wines based on their different colours was obtained. In this case, the wines were discriminated along the axis PC2, depending on the type of wine to which they belong (white, rosé or red), the three groups being partially overlapped with each other. Such overlaps are due to the closer relationship between some of the wines which come from the same vineyard (eg, sample no. 1 overlapped red wines, close to the sample no. 11) or the same manufacturer (eg, sample no. 5 overlapped red wines, close to the samples no. 7 and 12). A weaker clustering of wines can also be explained by the fact that PCA is sensitive to the number of samples in the data set and it requires relative equality in group sizes to adequately discriminate between groups with very similar characteristics (Bevin et al., 2008).

Fig. 5. The PCA scoring to discriminate between wine types, based on the FTIR fingerprint region specific to phenolic derivatives (750-940 cm⁻¹). Sample numbering as in Tab. 1

Fig. 6. representing the scores for the region 970-1100 cm⁻¹, specific to carbohydrates derivatives, revealed an excellent clustering of wines, not only based on colour, but especially considering their sweetness index, excepting wine no. 9. The first principal component (PC1) explained 90% of the variability and the second principal component (PC2) explained 7% of the variability; together, PC1 and PC2 explained 97% of the whole variability of wine samples.

Fig. 7. The PCA scoring to discriminate between wine types, based on the FTIR fingerprint region specific to amino acids and organic acids derivatives (1600-1716 cm⁻¹). Sample numbering as in Tab. 1
Conclusion

This study has demonstrated that mid-infrared spectroscopy, coupled with principal component analysis represents a very powerful tool for distinguishing groups that have very similar properties, but have consistent overall differences, and might be used as a technique for the discrimination between different red, rosé and white wine varieties.

The results suggested that mid-infrared spectroscopy is an overall and effective method that offers the possibility to evaluate the authenticity of wines, without the need for costly and laborious chemical analysis.

The use of this fast technique can offer benefits for the wine industry by being a robust rapid screening tool for the discrimination of different types of wine, based on their colour and sweetness, and also being capable of measuring wine quality and assuring consumers of the quality of the final product to be enjoyed.

References


