Review

FOURIER TRANSFORM INFRARED SPECTROSCOPY IN MONITORING THE WINE PRODUCTION

ESPECTROSCOPIA DE INFRAVERMELHO COM TRANSFORMADA DE FOURIER NA MONITORIZAÇÃO DA PRODUÇÃO DE VINHO

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SUMMARY

The complexity of the wine matrix makes monitoring of the winemaking process from the grapes to the final product crucial for the wine industry. In this context, analytical methodologies that can combine good accuracy, robustness, high sample throughput, "green character", and by preference real-time analysis, are on-demand to create high-quality vitivinicultural products. In the last years, Fourier-transform Infrared Spectroscopy (FTIR) combined with chemometric analysis has been evaluated in several studies as an effective analytical tool for the wine sector. Some applications of FTIR spectroscopy have been already accepted by the wine industry, mainly for the prediction of basic oenological parameters, using portable and non-portable instruments, but still many others are waiting to be thoroughly developed. This literature review aims to provide a critical synopsis of the most important studies assessing grape and wine quality and authenticity, and to identify possible gaps for further research, meeting the needs of the modern wine industry and the expectations of most demanding consumers. The FTIR studies were grouped according to the main sampling material used - 1) leaves, stems, and berries; 2) grape must and wine applications - along with a summary of the basic limitations and future perspectives of this analytical technique.

RESUMO

A complexidade da matriz do vinho torna a monitorização da sua produção, desde a maturação da uva até o produto final, fundamental para a indústria do vinho. Neste contexto, metodologias analíticas com boa exactidão, robustez, elevado rendimento de amostras, menos penalizadoras para o meio ambiente, e se possível capazes de fornecer resultados em tempo real, são muito importantes para a obtenção de produtos vitivinícolas de alta qualidade. Nos últimos anos, a Espectroscopia de Infravermelho com Transformada de Fourier (FTIR) combinada com a análise quimiométrica tem sido avaliada em diversos estudos por ser uma ferramenta analítica apropriada para o setor vitivinícola. Algumas aplicações de FTIR já foram adoptadas pela indústria do vinho, principalmente para a predição de parâmetros enológicos básicos, através de instrumentos portáteis e não portáteis, mas há ainda um enorme potencial de desenvolvimento a explorar. A presente revisão da literatura tem como objetivo fornecer uma sinopse crítica dos estudos mais importantes realizados para avaliação da qualidade e autenticidade do vinho e identificar possíveis lacunas para investigação futura, indo ao encontro das necessidades da indústria vinícola moderna e das expectativas dos consumidores mais exigentes. Os estudos sobre FTIR foram agrupados de acordo com o principal material de amostragem - 1) folhas, engaços e bagos; 2) mostos e vinhos - juntamente com informação sobre as limitações básicas e perspectivas futuras desta técnica analítica.

Keywords: FTIR spectroscopy, wine, winemaking monitoring, quality control, authenticity assessment.
Palavras-chave: Espectroscopia FTIR, vinho, monitorização da produção de vinho, controlo da qualidade, avaliação da autenticidade.

INTRODUCTION

Wine is considered the result of multiple biochemical and physicochemical reactions, which are responsible for its complex chemical composition. First of all, the grape composition at the harvest plays an important role in the future quality of the wine. Therefore, careful monitoring of specific grape quality parameters during ripening is essential for the wine industry. Monitoring of grape ripening by winemakers is mainly based on the measurement of total soluble solids (TSS), reducing sugars, pH, and titratable acidity. Generally, wine grapes with a high accumulation of sugars, phenolics (red grapes) and aromatic compounds,

intense colour (red grapes) and suitable acid content are the main goals. However, in some cases, these attributes are not sufficient to assess the wine quality. More assessments considering the maturation stage of grapes, the identification of the vineyard plots from which the grapes come, and the quality assessment of the grapes when they are delivered to the winery are needed (Dambergs *et al.*, 2015). Furthermore, considering that winemaking is based on several techniques and technologies to transform grapes into wine, there is a need for continuous quality control during these oenological procedures. The first important step of the quality control begins with the monitoring of the vinification (including alcoholic fermentation when glucose and fructose are converted mainly to ethanol and carbonic gas). It also includes other important transformations and chemical reactions due to the extraction and microbial metabolism of grape components. Moreover, malolactic fermentation (MLF), which can occur simultaneously with primary fermentation or sequentially, is another important step in the winemaking process for some wine styles. Furthermore, production techniques can be different according to the kind of grapes (white or red grapes) and the desired style of wine produced. For example, some fortified wines can be produced with the addition of wine spirit to stop alcoholic fermentation and enhance the final alcohol content. Finally, after the fermentation a series of important steps are also carried out, which include operations of clarification, stabilisation, maturation/ageing and packaging of the wine (Waterhouse *et al.,* 2016)

Nowadays, several analytical techniques and methods used in the wine industry are considered to be non-environmentally friendly as they are using hazardous chemical solvents, or time-consuming, consisting of many analytical steps. In this context, FTIR technique is applied in the wine industry due to various advantages that allow to overcome previous analytical limitations, namely practicability, of the traditional techniques. Each spectroscopic technique has different and limited frequency ranges. The Infrared (IR) region is between 50-14000/cm and is divided into three areas: near-infrared (NIR) (4000-14000/cm; 2500-715 nm), mid-infrared (MIR) (400-4000/cm; 25000-2500 nm), and far-infrared (FIR) (50-400/cm; 200000-25000 nm) (Ferreira, 2015). FTIR is a non-destructive, time- and cost-effective technique that does not use hazardous chemical reagents, is characterised by high degree of automation, and short preparation time. Most applications in the wine industry are based on MIR and NIR spectroscopy. More specifically, FTIR instrumentation in combination with state-of-the-art software, designed specifically for grape and wine analysis, has recently received much attention. For most FTIR measurements, the MIR region (400-

4000/cm) is investigated. FTIR can be used for qualitative and quantitative measurements, analysing at the same time several oenological parameters with a precision equal to the traditional techniques. Moreover, it is possible to combine portable and non-portable devices for monitoring the winemaking process in different locations (Ferreira, 2015).

Many applications based on IR spectroscopy of portable and non-portable devices are used to assess the maturation stage and to make decisions for the appropriate harvest time (Power *et al.*, 2019, Felix instruments, 2021). Furthermore, IR spectroscopy, and specifically FTIR, is already applied in routine analysis for quality control of wines by a high number of laboratories both from wine companies and control entities, such as a Portuguese one, IVDP (Instituto dos Vinhos do Douro e do Porto) under the accreditation of NP EN ISO/IEC 17025. Furthermore, this technique has been considered in an inter-laboratory essay (physicochemical and instrumental analysis) for laboratory performance assessment, involving a significant number of participants (Alabe-Associação dos Laboratórios de Enologia., 2021). However, to improve the technique, several validations and optimisation procedures took place along with the development of new databases for analytical calibration aims (Moreira *et al.*, 2002; Ferreira *et al.*, 2009; Brandão, 2019). Moreover, OIV has established specific guidelines on infrared analysers in the oenology sector, concerning the exploitation of the characteristic absorptions of the organic compounds in the IR region of wines and musts for quantification purposes (OIV, 2010)

In this context, this review aims to give a brief introduction to the basic concepts of IR spectroscopy chemometric tools, and recent applications of FTIR spectroscopy to monitor each step of wine production. For the literature search, some of the most recent references describing applications and developments were used. Moreover, some oldest scientific sources of great interest were analysed. Published articles on the web of science, science direct, and other credible sources were used, along with some books.

FTIR: BASIC CONCEPTS

Instrumentation

The principle of the IR technique relies on recording absorption changes of IR radiation by molecules after vibrational and rotational modes due to absorption of energy. Each molecule contains a quantity of different functional groups (for example a carbonyl group or an amide group). Each functional group imparts a characteristic IR absorption at a specific frequency range. The

functional groups will vibrate when they will be exposed to IR radiation (Stuart, 2004).

Specifically, FTIR spectroscopy is based on the interference of radiation between two beams that results in the creation of an interferogram. The interferogram is a signal produced according to the change of path length between the two beams. This generated signal from the interferometer can then be reconverted into the two domains of distance and frequency that form a signal, by the mathematical method of Fourier transformation. A typical FTIR spectrometer includes a source, sample cell, detector, amplifier, analog-to-digital (A/D) converter, and computer. Radiation derived from the sources passes through the interferometer before reaching the detector. An A/D converter and amplifier convert the signal into a digital form before being transferred to the computer where the Fourier transform is taking place (Titus *et al.,* 2019). The basic components of an FTIR spectrometer are shown in Figure 1.
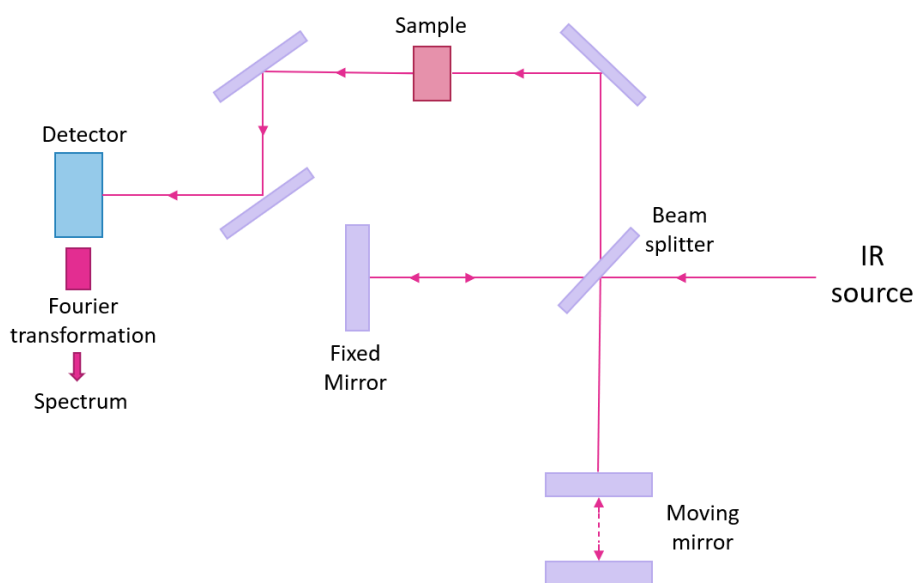

Figure 1. Schematic representation of FTIR equipment (adapted from Griffiths and De Haseth, 2007).

FTIR sampling methods

The most commonly used sampling techniques for Vibrational Spectroscopy are as follows: 1) Transmission (TR) or Reflectance; 2) Attenuated Total Reflection (ATR); 3) Diffuse Reflectance (DRIFT).

In TR spectroscopy, the sample is placed directly into the (IR) beam. As the IR beam passes through the sample, the transmitted energy is measured and a spectrum is generated. The transmission technique can be used alone or in conjunction with accessories such as microscopes, and liquid or gas cells to analyse. Typically, in the case of liquid samples, fixed-length transmission cells are used. In the case of solids, the most common preparation is either the nujol mull (paraffin oil) or alkali halide (KBr) pellets (Mendes and Duarte, 2021).

In ATR spectroscopy, measurement is based on the changes that occur in an internally reflected IR beam when it contacts with a sample. An IR beam is directed onto a high refractive index (high optical density) crystal at a certain angle. Most often this material is either diamond, Zinc selenide (ZnSe), or Germanium (Ge). This internal reflectance creates an evanescent wave that extends beyond the crystal's surface and penetrates the sample. In regions of the IR spectrum where the sample absorbs energy, the evanescent wave will be attenuated. The detector records the attenuated IR beam as an interferogram signal, which can then be used to generate an IR spectrum (Blum and John, 2012).

In DRIFT, the IR energy is directed into a sample cup filled with a mixture of the sample and an IR transparent matrix (such as KBr). The IR radiation interacts with the particles and then reflects off their surfaces, causing the light to diffuse, or scatter, as it moves throughout the sample. The output mirror then directs this scattered energy to the detector in the spectrometer. The detector records the altered IR beam as an interferogram signal, which can then be used to generate a spectrum (Olale *et al.,* 2017).

Multivariate statistical techniques

The FTIR measurements produce multivariate responses and, as a result, generate a large amount of data. Chemometrics combined with FTIR is used for calibration, validation, and comparison in order to facilitate the analysis of such complex matrix interactions. Chemometrics is a discipline that uses mathematical and statistical methods to extract, represent, and display maximum chemical information from a sample. The chemometric analysis involves three main methods: Mathematical pre-treatments; Classification methods; Regression methods (Jamwal *et al.,* 2021).

The Mathematical spectral pre-processing treatments are taking place in order to improve the acquired spectra, enhance the signal-to-noise ratio and reduce irrelevant spectra information. The most applied methods for this purpose can be divided into scatter correction methods and derivation methods. Scatter correction methods include Multiplicative Signal or Scatter Correction (MSC) (extended MSC, inverse MSC, inverse extended MSC and de-trending), Standard Normal Variate Scaling (SNV), normalisation, and baseline correction. The derivation methods include finite difference, Savitzky–Golay, and Norris–Williams (Rinnan *et al.,* 2009).

The multivariate classification methods can be unsupervised (exploratory data analysis) and supervised; the former is carried out with unknown data to identify the similarities and differences between samples by reducing the data dimensionality. The most widely used unsupervised methods are Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA). The supervised methods are mainly used for classification studies and the most widely known methods are Linear Discriminant Analysis (LDA), Soft Independent Modeling by Class Analogy (SIMCA), and Partial Least Squares Discriminant Analysis (PLS-DA) (Zhao and Liu, 2007; Jamwal *et al.,* 2021).

Finally, for quantification purposes, Regression methods are used. The most widely used regression models are Multiple Linear Regression (MLR), Principal Component Regression (PCR), Partial Least Squares Regression (PLS-R), and Orthogonal Partial Least Squares Regression (OPLS). All above are linear methods applicable to first-order data and suitable for Parallel Factor Analysis (PARAFAC). For second-order data N-way, Partial Least Squares Regression (N-PLS) is considered more effective (Guillen-Casla *et al.,* 2011; Mendes and Duarte, 2021). Non-linear methods can also be used, in which the variables show a non-linear relationship to the target characteristics (output variables). Artificial Neural Networks (ANN), Wavelet Neural Networks (WNN), and Support Vector Machines (SVM) are the most commonly used non-linear regression methods (Alexandidis and Zapranis, 2013; Moldes *et al.,* 2017; Costa *et al.,* 2019).

FTIR analytical calibration

The complexity and amount of the data obtained by FTIR make the development of analytical calibration procedures very important. The analytical methodologies based on FTIR measurements are not considered absolute methods of analysis, and therefore the obtained calibration models need to be validated in comparison with reference methods. The analytical calibration procedure consists of fitting the model to the data in order to obtain reliable estimations. Wine samples can differ extremely in the origin, vintage, cultivar, viticulture, winemaking procedures, and wine style, making important the selection of the calibration data to be considered representative (in terms of concentration ranges and sample matrix). Usually, to determine different chemical parameters, a selection process of specific spectral wavelengths is performed. Furthermore, the validation consists of examining the accuracy, precision, and prediction ability of the model for future samples deriving from the same population as the calibration samples. To estimate realistically the performance of the calibration model, an independent set of samples is required (Bauer *et al*., 2008; Ferreira, 2015).

FTIR APPLICATIONS IN WINE PRODUCTION

Analysis of grapes and leaves

Determination of basic oenological parameters

The first important step in the winemaking procedure, which is illustrated in Figures 2 and 3, is the collection of the grapes at the appropriate time, when they have reached the desired maturation stage according to the winemaking target. At this stage, the most usual evaluations, strongly correlated with the grape quality, are the determination of sugar content, acidity-related parameters, and phenolic content (red grapes). These parameters, which showed variations across the vineyard, making an easy, quick, and precise determination very important for the wine industry (Watson, 2003). In this context, some of the most interesting studies are summarised in Table I and analysed below.

Grape maturation control/harvest
- Sugars
- Total acidity
- pH

Transport/cooling/handling
- Sugars
- Total acidity
- pH
- Gluconic acid
- Laccase activity

Destemming/crushing

Pressing
- Conductivity

Must Clarification
- Turbidity

Alcoholic fermentation
- Sugars
- Total acidity
- pH
- Assimilable N
- Temperature
- Density

Racking/Clarification
- Alcoholic strength
- Total acidity
- pH
- Volatile acidity
- Total dry matter
- Density
- Glucose and fructose determination
- SO₂

Storage/Blending
- SO₂
- Volatile acidity
- pH
- Physical-chemical stability tests

Clarification/Fining
- SO₂
- Volatile acidity
- pH
- Turbidity

Tartrate stabilization
- SO₂
- Volatile acidity
- pH
- Filtration test

Membrane filtration
- SO₂
- Volatile acidity
- pH

Bottling/Labeling
- SO₂
- Volatile acidity
- pH
- General physical-chemical analysis

Figure 2. The most important steps of classical white winemaking with the identification of the most common analytical determinations.

In a chemometric exploratory analysis, Fourier Transformed Mid-infrared spectroscopy (FT-MIR) was applied to a grape must sample from South Africa (Swanepoel *et al.,* 2007). The purpose of the study was the simultaneous quantification of total soluble solids (TSS, measured as °Brix), pH, and titratable acidity (TA, expressed as g tartaric acid/L) using PCA and PLS. The spectra region used for the calibrations was 1474-2685/cm. The results obtained were satisfactory for qualification analysis, but the analytical accuracies were not good enough to quantify these oenological parameters. This fact was ascribed to an insufficient fit of the South African grape samples to the global FT-MIR WineScan calibrations (Swanepoel *et al.,* 2007). In a similar study, FT-MIR in combination with PCA analysis was used to monitor the evolution of red berries from veraison to harvest. The most important wavenumbers associated with these evolutions were linked with carbohydrates. Also, discrimination of the geographical origin was also achieved for the two areas under study (Touraine and Anjou, France). Generally, good estimations values were obtained for titratable acidity and sugars concentration. However, the parameters´ prediction was improved when only the data from one location were considered. These observations suggest the need for global calibration models applicable to a wider range of samples from different origins (Piqué *et al.,* 2010). FT-NIR and ATR FT-MIR spectroscopy in combination with chemometrics were used to qualitatively and quantitatively analyse 'Sauvignon Blanc' grape berries at five distinct developmental stages: green, pre-véraison, véraison, post-véraison and ripe (harvest). MIR spectra provided more reliable discrimination between the berry samples from the different developmental stages than NIR spectra. ATR FT-MIR spectra from fresh homogenised berry samples were more discriminatory than with the frozen homogenised berry samples. The key to discrimination in between-stage variation was the sugar-organic acid absorption band, underlining the role of organic acid and sugars concentration as berry growth biomarkers. However, the discrimination of the last two stages of berry maturity faced more difficulties indicating the need for additional information deriving from the identification of other important compounds such as terpenoids (e.g., monoterpenes, sesquiterpenes, and carotenoids) or phenolics (e.g., flavonols, anthocyanins, and tannins) (Musingarabwi *et al.,* 2016).
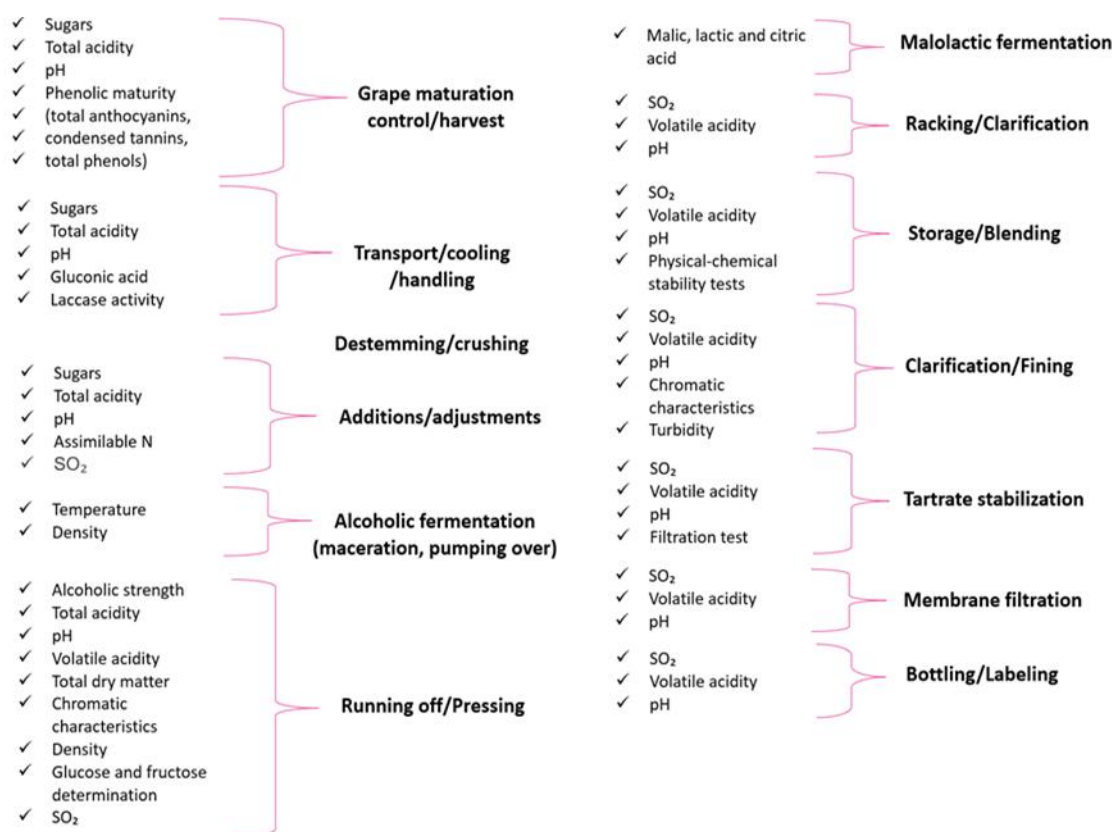
Left column:

- ✓ Sugars
- ✓ Total acidity
- ✓ pH
- ✓ Phenolic maturity (total anthocyanins, condensed tannins, total phenols)

→ **Grape maturation control/harvest**

- ✓ Sugars
- ✓ Total acidity
- ✓ pH
- ✓ Gluconic acid
- ✓ Laccase activity

→ **Transport/cooling /handling**

Destemming/crushing

- ✓ Sugars
- ✓ Total acidity
- ✓ pH
- ✓ Assimilable N
- ✓ SO₂

→ **Additions/adjustments**

- ✓ Temperature
- ✓ Density

→ **Alcoholic fermentation (maceration, pumping over)**

- ✓ Alcoholic strength
- ✓ Total acidity
- ✓ pH
- ✓ Volatile acidity
- ✓ Total dry matter
- ✓ Chromatic characteristics
- ✓ Density
- ✓ Glucose and fructose determination
- ✓ SO₂

→ **Running off/Pressing**

Right column:

- ✓ Malic, lactic and citric acid

→ **Malolactic fermentation**

- ✓ SO₂
- ✓ Volatile acidity
- ✓ pH

→ **Racking/Clarification**

- ✓ SO₂
- ✓ Volatile acidity
- ✓ pH
- ✓ Physical-chemical stability tests

→ **Storage/Blending**

- ✓ SO₂
- ✓ Volatile acidity
- ✓ pH
- ✓ Chromatic characteristics
- ✓ Turbidity

→ **Clarification/Fining**

- ✓ SO₂
- ✓ Volatile acidity
- ✓ pH
- ✓ Filtration test

→ **Tartrate stabilization**

- ✓ SO₂
- ✓ Volatile acidity
- ✓ pH

→ **Membrane filtration**

- ✓ SO₂
- ✓ Volatile acidity
- ✓ pH

→ **Bottling/Labeling**

Figure 3: The important steps of classical red winemaking with the identification of the most commons analytical determinations.

A classification study took place using ATR FT-IR and ANN. Specifically, spectra derived from grape skins and leaves were used for the classification of the samples according to their variety and ripeness degree. Pectin (associated with a peak at 825/cm) present in grapes influenced that classification for both variety and ripeness identification, while fructose content was associated with the ripeness degree. Polyphenols did not contribute to a great extent to the samples' classification (Murru *et al.,* 2019).

Determination of phenolic compounds

In order to enhance the spectra response, grape extracts were enriched with distinct phenolic compounds of different chemical structures (Fragoso *et al.*, 2011). In this way, FT-MIR spectroscopy combined with PLS regression was able to quantify phenolic compounds for monitoring the ripening process in red grapes during the harvest period (Fragoso *et al.*, 2011. Indeed, this method allowed evaluating total phenolic compounds, total anthocyanins, and condensed tannins simultaneously. Moreover, in this study, an attempt of developing models for individual varieties was quite promising. These results suggest the possible application of FT-MIR by each winery to design specific models for the varieties they are using. In each case, more samples are needed to cover a wider range of values (Fragoso *et al.*, 2011).

The phenolic content of the wines depends on the extraction of phenolic compounds from the grapes. It is known that when the sugar content (degree of ripening) increases, the cell wall material decreases, affecting the phenolic compounds' extractability (Ortega-Regules *et al.*, 2008). For this reason, ATR-FTIR and Raman spectra of grape skin have been recorded and linked to the extractability of phenolic compounds (anthocyanins, flavanols, and total phenolics) of the inner grape skin surface. Concerning the ATR-FTIR data, the spectra peaks showed a significant influence of the number of polysaccharides and the degree of methyl esterification of pectins on the phenolic extractability levels of grape skin tissue, which were found mainly at 3324, 1732, 1018/cm. However, these correlations were only possible using the spectra of the inner skin surface of the grapes. The result was assigned to possible low amounts of phenolic compounds on the external skin surface (Nogales-Bueno *et al.*, 2017).

Table I

Representative examples of FTIR analysis of grapes, and leaves

Aim of the analysis	Type of sample/ Preparation mode	Wavenumber range (/cm)	Spectral pre-treatment	Statistical method	Reference
Optimisation of the quantification of total soluble solids, pH and titratable acidity	Fresh homogenates of berries	964-1542 1717-2969	NM	PCA, PLS	Swanepoel et al. (2007)
Assessment of grape maturity	Fresh homogenates of berries	926-5012	1st derivative (Savitzky-Golay)	PCA, PLS, PLS-DA	Piqué et al. (2010)
Estimation of mDPs of grape seeds procyanidins	Grape seeds powder	700-1800	SNV	PCT-PLS, O-PLS	Passos et al, (2010)
Quantification of phenolic compounds	Fresh homogenates of berries	1168-1457	NM	PCA, PLS	Fragoso et al. (2011)
Determination of assimilable nitrogen	Frozen, crushed, centrifugated berries	1480-1800	NM	PLS	Skoutelas et al. (2011)
Monitoring nitrogen and starch grapevine reserves	Wood and root grape tissue	374–7496	MSC, 2nd Der, MC, SNV, PLS	PLS, SVR	Schmidtke et al. (2012)
Quantification of Botrytis bunch rot	Frozen homogenates of berries	3717-12500 388-3984	1st derivative (Savitzky-Golay)	PLS	Hill et al. (2013)
Measurement of the concentration of nutrients in grapevine petioles	Dried grape leaves petioles	375–7500	SNV	PCA, PLS	Smith et al. (2014)
Analysis and discrimination of grape spoilage via volatiles	Whole berries	600–4000	Baseline correction, low pass filtering and smoothing	PCA, SIMCA	Dong et al. (2014)
Quantification of Tannin mDPs and %G in Grape Seeds	Freeze dried and ground grape seeds	400-4000	2nd derivative	PLS	Pappas et al. (2015)
Quantification of total phenolics and condensed tannins in grape seeds	Freeze dried and ground grape seeds	400-4000	2nd derivative	PLS	Kyraleou et al. (2015)
Qualitative and quantitative evaluation of grape berries at various stages of maturity	Fresh and frozen homogenates of berries	900-3800 5000-12000	NM	MVDA, PCA OPLS-DA, PLS	Musingarabwi et al. (2016)
Determination of phenolic extractability	Whole berries, frozen berry skin layers	600-4000	MSC, Baseline correction	PCA	Nogales-Bueno et al. (2017)
Differentiation according to ripeness degree and grape variety	Berry skin layer, leaves	600-4000	NM	ANNs	Murru et al. (2019)
Discrimination of Aspergillus spp., Botrytis cinerea, and Penicillium expansum	Frozen homogenates of berries	375-1850	SNV, Mean centred data	PCA, SIMCA, SVR KNN, RFM	Schmidtke et al. (2019)
Discrimination of geographical origin and year of harvest, prediction of oenological parameters	Grape homogenates, grape skins	400-4000	Normalization, 1st derivative	PLS-DA, PLS	Lemos et al. (2020)
Determination of yeast assimilable nitrogen content	Grape juice	4000-12500 600-4000 929-4000 4000-5011	1st derivative, constant offset elimination	PLS	Petrovic et al. (2020)
Qualitative analysis of grape seeds	Freeze dried grape seeds	500-4000	NM	PCA	Lucarini et al. (2020)
Characterisation of red grapes skin extracts	Hydroalcoholic extracts of berry skin	800-4000 400-1700	NM	PCA, LDA, PC-LDA	Alecu et al. (2020)

NM=Not mentioned; PCA=Principal Component Analysis; PLS=Partial Least Squares Regression; PLS-DA=Partial Least Squares-Discriminant Analysis; PCT-PLS=Principal Components Transform-Partial Least Squares Regression; O-PLS=Orthogonal Partial Least Squares; SNV=Standard Normal Variate; SVR=Support Vector Regression; MSC=Multiple Scatter Correction; MC=Mean Centering; SIMCA=Soft Independent Modeling by Class Analogy; MVDA=Multivariate Data Analysis; ANN=Artificial Neural Networks; OPLS-DA=Orthogonal Projections to Latent Structures Discriminant Analysis; KNN=k-Nearest Neighbors; RFM=Recency, Frequency, and Monetary value; PC-LDA=Principal Components-Linear Discriminant Analysis; LDA=Linear Discriminant Analysis.

In addition, due to an increasing interest in the full exploitation of the oenological by-products, determination of the quality parameters of grape seeds is important. Phenolic compounds are located in all the grape cluster: stems and berries (skins, seeds, pulp) (Sun et al., 1999). The extraction of phenolic compounds from the skins is faster for phenolic acids and anthocyanins, but for flavanols it requires more time. Moreover, when more extended maceration (red winemaking) is taking place, the process is more complex (Sun et al., 1999). In this case, the phenolic composition of the grape seeds is of great interest for the winemakers. The quantification of total phenolic and condensed tannins contents of grape seeds was possible with the application of a chemometric analysis of FTIR spectra of grape seeds samples. The samples were lyophilised before analysis and as for the quantification of the phenolic content, the second derivative of the spectral region 1170-1560/cm was examined (Kyraleou et al., 2015). In the same context, seeds of different grapevine cultivars were analysed by FTIR and chemometrics to be discriminated according to their fatty acid and phenolic composition. For this purpose, lyophilised seed samples of three different Italian cultivars grown in an experimental vineyard (Lazio) were used. The reference values for the method

validation were obtained by conventional analysis HPLC/DAD/MS and GC/MS. The method allowed differentiating successfully the grape seeds from the different grapevine cultivars (Lucarini *et al.*, 2020).

Another specific factor correlated in the long term with wine quality is the type of proanthocyanidins´ structures. Proanthocyanidins with a different mean degree of polymerisation (mDP; the average number of units in the polymer) and different degree of galloylation (% G; percentage of subunits containing gallic acid esters) correlate to different organoleptic properties (Vidal *et al.*, 2003). The average degree of polymerisation of procyanidins (DPn) derived from red and white grape seeds was examined by FTIR and PLS regression. Before analysis, the samples underwent an extraction pre-treatment process and then a fractionation step was carried out using methanol/chloroform. Thiolysis was used as pre-treatment followed by HPLC-UV and MS detection to obtain reference values. The method allowed to correlate the increase of the absorbance peaks at 1203-1099/cm with an increase of DPn, and this was ascribed to the greater substitution in the aromatic ring of the polymerised procyanidin molecules (Passos *et al.*, 2010). DRIFT spectra were combined with the PLS regression in a quantification study of tannin mean degree of polymerisation and percentage of galloylation in grape seeds. For this purpose, seed samples from two different vintages, two different Greek grapevine varieties ('Maurotragano' and 'Xinomauro') were used after freeze-drying. The developed models were compared with reference values from samples treated by phloroglucinolysis followed by HPLC-UV and LC-MS analyses. The second derivative of 1832-1416/cm and 918-739/cm spectral regions were used (values varied from 1.57 to 11.77) for quantification of mDP, while the second derivative of the spectral area 1813-607/cm (values ranges of %G from 2.98 to 15.85) was examined for %G quantification (Pappas *et al.,* 2015).

Determination of other quality parameters

Usually at the reception of the grapes in the wineries, the basic grapes' quality indicators (TSS, acidity-related parameters) are insufficient for a comprehensive quality control. In addition, phytosanitary status of the grapes influences their quality. Some types of fungi developing in grapes can lead to the formation of undesirable metabolites (e.g., 1-octen-3-ol and 1-octen-3-one), mycotoxins dangerous for human health, and wine oxidation through the production of laccase (Dewey *et al.*, 2008). As a result, it is of great importance to identify infected grapes in the winery's receiving line.

In this context, a differentiation study of four types of fungal mycelia in samples of 'Chardonnay' grapes using FTIR spectroscopy and a series of

modelling approaches was performed. Support vector modelling was chosen as the best chemometric prediction modelling technique for pathogen and control samples (Schmidtke *et al.*, 2019). However, the developed method needs to be applied in samples where the pathogens have occurred naturally and consider a larger sample set (Schmidtke *et al.*, 2019). A study of *Botrytis* bunch rot in white grapes was focused on the suitability of FT-NIR and MIR spectroscopy combined with PLS regression for quantification purposes. Interesting results were attained, highlighting the importance of 7299-7937/cm region for the identification of important compounds produced by *Botrytis cinerea*. However, the method did not give sufficiently accurate results concerning the ranges that are relevant for quality control in the wineries. More wide sampling for validating similar methods deriving from different regions and varieties is required (Hill *et al.*, 2013). Furthermore, it is known that specific volatile compounds, such as carbon dioxide, ethanol, and esters, are released from grapes during spoilage and their concentration can gradually change over storage time. A long optical path FTIR and sensor arrays (carbon dioxide and ethanol sensors) along with chemometric tools were investigated as possible ways of determining grape spoilage. The method was evaluated positively as a tool for the identification of different grape spoilage stages based on their volatile status. In addition, sensor arrays allowed to discriminate between healthy and decayed grapes as well (Dong *et al.*, 2014).

Yeast assimilable nitrogen (YAN) content, including the nitrogen sources [free amino nitrogen (FAN) and ammonia] available in the grape juice matrix for the yeasts, is another crucial parameter strongly correlated with the healthy evolution of the fermentation process. Some amino acids (branched-chain and aromatic) are considered precursors of specific volatile compounds, influencing the quality of the final product Bell and Henschke, 2005). FT-MIR combined with PLS regression was applied to determine assimilable nitrogen in grape juice derived from red and white grapevine varieties. The method showed good accuracy and precision, and the results were confirmed using the formol titration as reference method, highlighting its feasibility for quantification purposes in the wineries (Skoutelas *et al.*, 2011). Contextual information derived from the quantification of YAN content in grape juice was investigated using FT-IR, FT-NIR, and ATR-MIR and chemometrics. The best results were attained through FT-IR. The study considered a large and variable data set, and the developed models were evaluated by an independent data set. The developed method allowed predicting the YAN status of samples from a new vintage, highlighting the feasibility of this technology for industrial scale usage, providing quick and useful information for

nutrient supplementation decisions by the winemakers (Petrovic *et al.*, 2020).

The nutritional status of the grapevine, correlated with mineral nutrient deficiency or toxicity, is of relevance for winemaking (Robinson, 1992). ATR-FTIR spectra with chemometric tools was applied in order to determine the nutrient status of petioles. The method was successful in determining the macronutrients in grapevine petiole tissue with good accuracy, but not adequate for certain micronutrients (Smith *et al.*, 2014).

The nitrogen and starch contents in the perennial parts of the grapevine are correlated with the yield, the sugar accumulation, and the secondary metabolite production at the stage of berry ripening (Holzapfel *et al.,* 2010). ATR-FTIR, and PLS or SV regression were applied to grapevine tissues to assess starch and nitrogen reserves. The results showed sufficient precision and accuracy, with support vector SV regression giving the best prediction values. The method could give useful information about the vine growth cycle and development (Schmidtke *et al.,* 2012).

Discrimination studies

In addition, bearing in mind the influence of different spectral pre-treatments and sample preparation in many studies, 'Tempranillo' grape clones were analysed by ATR FT-MIR combined with multivariate analysis, resorting to different spectral pre-treatments (first derivative; normalised; normalised plus first derivative) to discriminate them in terms of geographical origin and year of harvest. At the same time, it was possible the prediction of the basic oenological parameters of interest, TSS, pH, and titratable acidity (Lemos *et al.,* 2020). According to the authors, ATR FT-MIR combined with PLS-DA gave the most satisfactory results for the aforementioned discrimination. The better classification was obtained using the normalised spectra for the grape homogenates, and the normalised plus 1st derivative spectra for the skins (Lemos *et al.,* 2020). Moreover, specific intervals were chosen to eliminate spectral interferences. Regarding the spectra regions, 750-1900/cm and 2650-3850/cm were selected for the homogenates, while those of 450-1900/cm and 2600-3700/cm were selected for the skins, corresponding to the fundamental vibrational modes of interest of the compounds under study (Lemos *et al.,* 2020). In another discrimination study, based on a chemometric analysis (PC-LDA) of FTIR and Raman spectra, hydroalcoholic skin extracts from four different red grapevine varieties and two different types of vineyards (conventional and organic) were used. According to the chemometric analysis of the spectra, the method was able to discriminate between vineyards, but not the antioxidant activity levels and total phenolics content (Alecu *et al.*, 2020).

Analysis of grape must under alcoholic fermentation

Determination of basic oenological parameters

Wine production is based on the biochemical process called alcoholic fermentation. This process includes the transformation of sugars (glucose and fructose) into ethanol and carbon dioxide, and usually is carried out by yeasts of the *Saccharomyces* genus. During winemaking, the parameters that are routinely measured daily to monitor the healthy evolution of the fermentation are sugars, total acidity, assimilable N, temperature, density, and pH (Ribereau-Gayon *et al.*, 2021). Many studies have been focused on the determination of these parameters simultaneously using FTIR spectroscopy in combination with chemometrics, as shown in Table II.

FT-NIR coupled with chemometrics was applied for the determination of sugars, (FAN), malic acid, lactic acid, and ethyl carbamate content. The prediction values were very good for the sugars´ concentration but were not satisfactory for the remaining parameters. However, must samples with different FAN levels and wine samples with different organic acid and ethyl carbamate content could be classified when the discriminatory SIMCA method was applied to the spectra (Manley *et al.,* 2001). FTIR with chemometric tools was used to quantify the volatile acidity, glycerol, ethanol, reducing sugars, and glucose content in fermented natural and model musts deriving from small-scale fermentations. The obtained results showed that the method can be considered effective in the simultaneous determination of these parameters. The prediction values for the volatile acidity showed the highest accuracy (Nieuwoudt *et al.,* 2006). FTIR modelled with two-dimensional correlation techniques was proven to be an efficient tool for monitoring physicochemical changes occurring during red wine fermentation (chemical reactions and their dynamics). The method allowed to show that the conversion reaction rate of glucose to alcohol was more rapid than the one of fructose (Wynne *et al.,* 2007). FT-NIR and FTIR spectroscopy was applied for more detailed monitoring of a maceration/fermentation classical red winemaking process. The results after different chemometric treatments were quite promising. The method made it possible to simultaneously determine sugars, ethanol, glycerol, and phenolic content, and the samples could be classified according to their stage of fermentation (Di Egidio *et al.,* 2010). These results were confirmed by a similar study in which FTIR and FT-NIR spectroscopy were applied again to identify molecular changes involved in wine fermentation. In addition, to combine more information for taste and aroma profiles of the samples, electronic tongue and electronic nose were used. Furthermore, the

chemometric analysis of the spectral, electronic nose and electronic tongue data was able to underline specific critical points during the

fermentation process, which is useful for quality control of the final product (Buratti *et al.,* 2011).

Table II

Representative examples of FTIR analysis in musts

Aim of the analysis	Type of sample/ Preparation mode	Wavenumber range (/cm)	Spectral pre-treatment	Statistical method	Reference
Determination of analytical parameters	Musts	4000-10000	MSC	PLS, SIMCA	Manley *et al.* (2001)
Authentication of white grape musts	Musts	800-4000	GA	PLS-DA, FDA	Roussel *et al.* (2003)
Monitoring of wine fermentation	Frozen fermentation musts	13514-50000 351-7407	1st or 2nd derivative	MLR, PLS	Urtubia *et al.* (2004)
Determination of compositional dynamics of wine fermentation	Frozen musts	900-4000	NM	Two-dimensional correlation	Wynne *et al.* (2007)
Monitoring of red fermentation	Centrifugated musts	3600-12500 700-4000	SNV, MSC, 1st and 2nd derivative	PCA, LDA, One-way ANOVA	Di Edigio *et al.,* (2010)
Monitoring of alcoholic fermentation	Centrifugated musts	3600-12500 700-4000	SNV, 1st derivative (Savitzky–Golay)	PCA	Buratti *et al.* (2011)
Surface measurement of mannoproteins and β-glucans of yeast cell walls during wine fermentation	Powdered natural and synthetic musts	650-4000	baseline correction	PCA, OPLS-DA, ANOVA	Moore *et al.* (2015)
Monitoring *Saccharomyces cerevisiae* grape must fermentation	Centrifugated musts	800-4000	Mean centered, 2nd derivative	PCA, SIMCA	Puxeu *et al.* (2015)
Determination of anthocyanins	Digested, blended, squeezed musts	926-5012	NM	PCA, PLS-R	Rasines-Perea *et al.* (2015)
Strain typing of yeasts	Musts	400-4000	NM	HCA	Gerhards *et al.* (2015)
Study of inter-and intraspecific biodiversity of cultivable non-*Saccharomyces* yeasts	Musts	400-4000	NM	HCA	Grangeteau *et al.* (2016)
Monitoring of wine process and prediction of its parameters	Frozen musts and wines	650-4000	WCS, WOSC, OSCW, 1st and 2nd derivative	PCA, PLS	Canal and Ozen, (2017)
Determination of calcium	Filtered musts	4348-9091	SNV, MSC, 1st derivative (Savitzky-Golay)	PLSR	Véstia *et al.* (2019)
Early detection of undesirable deviations in must fermentation	Diluted musts	649-3999	Smoothing and normalization	PCA, PLSR, PLS-DA	Cavaglia *et al.* (2019)
Monitoring wine fermentation deviations	Homogenized, centrifugated musts	650-4000	1st and 2nd derivative, (Savitzky-Golay) smoothing, SNV	PCA, PLSR, PLS-DA, SPC	Cavaglia *et al.* (2020a)

NM=Not mentioned; MSC=Multiple Scatter Correction; PLS=Partial Least Squares Regression; SIMCA=Soft Independent Modeling by Class Analogy; GA=Genetic Algorithms; PLS-DA=Partial Least Squares-Discriminant Analysis; FDA=Functional Data Analysis; MLR=Multiple Linear Regression; SNV=Standard Normal Variate; MSC=Multiple Scatter Correction; PCA=Principal Component Analysis; LDA=Linear Discriminant Analysis; ANOVA=Analysis of Variance; OPLS-DA=Orthogonal Projections to Latent Structures Discriminant Analysis; PLS-R=Partial-Least-Squares Regression; HCA=Hierarchical Cluster Analysis; WCS=Wavelet Compression of Spectra; WOSC=Orthogonal Signal Correction; OSCW=Orthogonal Signal Correction in Combination with Wavelet; PLSR=Partial-Least-Squares Regression; MSPC=Multivariate Statistical Process Control.

However, when deviations occur implying sluggish or stuck fermentations or other unwanted contaminations by microorganisms, distinct time-consuming chemical analyses are required. As a result, there is a growing need for real-time information delivered by methods, such as vibrational spectroscopy, for the appropriate readjustments to take place in a timely manner before the process ends. IR spectroscopy was used as an analytical tool to distinguish between normal and problematic fermentation. The developed calibration models showed sufficient accuracy for the determination of glucose, fructose, glycerol, ethanol, and most of the organic acids (tartaric, succinic, lactic, acetic, and citric) during

fermentation of 'Cabernet Sauvignon' musts. The only exception was malic acid, for which the developed calibration was not good enough to distinguish between normal and problematic behaviour. When the calibration models were applied to the other varieties under study, the results were not so adequate for any of the parameters (Urtubia *et al.,* 2004). ATR-FTIR spectra derived from a portable device were used to discriminate between normal fermentation and problematic in terms of accumulative yeast nitrogen deficiencies. Several models have been developed to monitor the evolution of fermentation and, at the same time, discriminate between normal and problematic fermentations. The outcomes showed that the

method could be applied in the wine industry for monitoring the sugar content and identifying nutrient deficiencies early (Cavaglia *et al.,* 2019). Spectra coming from a portable ATR-MIR device and multivariate analysis were used to control the alcoholic fermentation process and detect wine fermentation problems. Generally, the method succeeded to predict density and pH in fermenting must samples. The spectra recorded during fermentations with LAB (*Lactobacillus*)-inoculations (ICF) were performed showed only minor changes than in normal fermentation conditions (NFC). This fact was assigned to the small concentration changes involved in the malolactic fermentation process. In most samples, the deviations in L-malic acid were between 0.7 to 0.8 g/L concentrations resulting in a small pH increase. The novelty of this ATR FT-MIR method was the detection of no NFC before the end of malolactic fermentation (Cavaglia *et al.,* 2020b). In a different chemometric approach, detection of lactic bacteria spoilage during fermentation took place with the use of a portable ATR FT-MIR instrument and Multivariate Statistical Process Control charts (MSPC). For this purpose, samples from alcoholic fermentation in normal conditions (NOC) and alcoholic fermentation with the addition of lactic bacteria (MLF). MSPC charts based on Q residuals and Hoteling's T2 statistics proved to be efficient in detecting lactic bacteria spoilage before the end of the alcoholic fermentation (Cavaglia *et al.,* 2020a). The analysis of the cell wall composition of yeasts is an indirect approach for monitoring the fermentation. ATR FT-MIR and chemometrics was used to evaluate the cell wall composition during fermentation. Different yeast strains were investigated, including *Saccharomyces* (laboratory and industrial) and non-*Saccharomyces* strains. PCA analysis was able to differentiate *Saccharomyces* strains from the non-*Saccharomyces* ones, and industrial wine yeast strains from laboratory ones. The fingerprint region (1768-770/cm) was associated with lipid, protein (including CHO and amide groups), mannans, nucleotide, phospholipid, and glucan functional groups. Mannoproteins were more abundant in industrial strains, whereas mannan and glucan polymers were more plentiful in laboratory strains (Moore *et al.*, 2015). In the same context, ATR-FTIR coupled with SIMCA was applied in fermented 'Grenache Blanc' and 'Chardonnay' musts to determine the physiological state (exponential and stationary) of three commercial strains of *Saccharomyces cerevisiae* (ES454, E491, and ES181). The different physiological states were possible to be identified based on the different cell wall components of the strains. At the exponential phase mainly glucans, mannoproteins, and lipids were identified, while at the stationary phase glucans and mannans were observed (Puxeu *et al.*, 2015).

Determination of other quality parameters

Moreover, during the fermentation process, other important quality parameters need to be determined. The prediction of calcium is of great importance for the winemakers, and especially for the sparkling wine industry, due to the risk of aggregation with alginate capsules when this technique is used. Usually, the calcium content is determined by atomic absorption spectrometry (AAS). In a different approach, FT-NIR was applied in combination with chemometrics for the prediction of calcium content in base wine samples and musts. AAS was used as a reference method, after pre-treatment of the samples by dry ashing. High concentrations of of calcium were observed.. FT-NIR–PLSR models could be used in real-time industrial monitoring for quantitative analysis of calcium in wines (Véstia *et al.,* 2019). Another pivotal quality parameter is the anthocyanins content. FT-MIR in combination with PLS-R evaluated the prediction of 12 anthocyanins (five non-acylated, three acetylated, three *p*-coumaroylated and one caffeoylated 3-O-glucosides) in red grapes musts. Internal and external validation sample sets were used to confirm the obtained results. Unfortunately, when must samples from a new harvest were used the results were not satisfactory. However, when the model was built from samples derived from all the different consideredharvests, the prediction values were improved. This fact demonstrates the potential of the method for a quick semi-quantitative determination of anthocyanin content in the wineries but more studies are needed to improve the prediction values (Rasines-Perea *et al.,* 2015).

The final quality of the product is known to be influenced by the 'terroir', including soil, climate, grapevine plant, and viticultural and oenological practices (OIV, 2010).

However, there is a need for information about site-specific differences of vineyard yeasts and how they can influence fermentation. This topic was investigated by analysing spontaneous fermentations from six different vineyards. FTIR spectra were acquired from randomly isolated yeasts to discriminate at the strain level. The yeasts coming up from the vineyard were discriminated from those winery related. The latter showed the biggest influence on the spontaneous fermentation, without following a constant pattern (Gerhards *et al.,* 2015). Similar results were attained by FT-IR spectra in an inter- and intra-biodiversity study of non-*Saccharomyces* yeasts. The pyrosequencing method was used as a reference to compare the obtained results. In terms of global diversity, the method identified efficiently seven different genera (*Aureobasidium*, *Candida*, *Cryptococcus*, *Hanseniaspora*, *Issatchenkia*, *Metschnikowia* and *Pichia*). Concerning the intraspecific analysis, 19

different strains from 58 isolates were identified. The FT-IR spectroscopy proved to be an effective tool for yeast strain characterisation and monitoring of yeast starter strains (*Saccharomyces* and/or non-*Saccharomyces*) during fermentation (Grangeteau *et al.,* 2016).

Authentication studies

Bearing in mind a continuous need for authenticity confirmation of the products of the wine industry, an authentication study in terms of varietal classification of musts was made using FTIR, ultraviolet spectrophotometry, and analysis by electronic nose. Genetic Algorithms were used as a pre-processing technique to improve the interpretation of the data. FTIR spectroscopy matched with multivariate chemometric techniques proved to be superior in comparison to ultraviolet spectrophotometry, and analysis by electronic nose (Roussel *et al.,* 2003).

FT-MIR spectra combined with multivariate analysis were used for the determination of chemical (ethanol, glycerol, organic acids, titratable acidity, ^{o}Brix, sugars, total phenolics, and anthocyanins content) and microbiological parameters of red, rose and white wines during the whole winemaking process. Regarding the pre-treatment of the spectra, the second derivative seemed to be the most appropriate option for the determination of most of these chemical parameters, except for ethanol. The results were satisfactory for the prediction of almost all the chemical parameters (except pH and organic acids). On the other hand, the prediction of microbiological parameters was not accurate enough. In addition, the method was able to differentiate the beginning of the fermentation process from the remaining winemaking steps (Canal and Ozen, 2017).

Analysis of wines and wine spirits

Determination of basic oenological parameters

Monitoring of winemaking process is a dynamic task that examines continuously the wine quality after the fermentation, from the ageing stage to the bottling. The basic routine analysis includes determination of alcoholic strength, sulphur dioxide (SO_2), volatile acidity, and pH. Some representative examples of the literature are presented in Table III.

Optimisation of a FTIR method applied for general analysis of wine samples from red, white, rose, and sparkling Portuguese wines was performed (Moreira *et al.,* 2002). Global calibrations were built for the simultaneous determination of various oenological parameters (density, dry extract, total acidity, volatile acidity, total SO_2); total sugars were determined through an independent calibration. The outcomes revealed good precision for most of the parameters in comparison with the reference

methods, except for total SO_2. Comparing the accuracy of the global calibration and the specific calibration for the total sugars, in the second case the results were more satisfactory (Moreira *et al.,* 2002). A series of changes in the oenological parameters of white wines packed in bag-in-box (BIB) were monitored by chemometric-based FTIR analysis. The developed calibration models, based on a PLS algorithm, successfully predicted the colour, free and total SO_2 contents, total phenolics and aldehydes contents, and the storage time in bag in box. However, a potential optimisation of the method's accuracy requires the use of a larger range of samples (Fu *et al.,* 2009). FT-MIR spectroscopy in combination with chemometrics was used for determination of several quality parameters (pH, total phenolic content, anthocyanin content, titratable acidity, sugar content, electrical conductivity, and some colour parameters) of alcoholic beverages made of twice-distilled grapes and anise (Raki) and wine. The developed PLS models for wines showed good prediction values for total phenolics, anthocyanin contents, pH, ^{o}Brix, and colour intensity. Concerning the Raki samples,, total phenolics, sugar content, and pH, were predicted successfully (Ozturk *et al.,* 2012). The ATR-FTIR wine spectra provided contextual information. Some common parameters of wine were predicted (alcoholic content, sugars, total acids), while the determination of others did not provide satisfactory results (SO_2 and volatile acidity) (He *et al.,* 2013). In a similar study in grape-derived spirits, FTIR–ATR combined with chemometrics was applied for the determination of their alcoholic strength, methanol, acetaldehyde, and fusel alcohols content. Most of the parameters were predicted with good accuracy, except for 2-butanol (Anjos *et al.,* 2016). In this context, one of the most recent studies evaluated the feasibility of FTIR combined with Network analysis in an Eigenspace layout for wine analysis. A network can be defined as a collection of nodes connected through links. Each sample is represented by each node in the network. Each edge (formed by the links) represents the difference between the two connected nodes (dissimilarity weight). The FTIR data sets derived from different wine samples, lead to the creation of a networking in the Eigenspace layout, giving specific chemical significance to the positioning nodes. The method allowed to identify compositional differences among the samples, classifying them into two groups, and assessing their inter- and intra-group homogeneity. The wines were separated into two groups based on the differences found in the spectra region 970-1100/cm, suggesting different levels of ethanol, phenolics, phosphates, phenyl derivatives, unsaturated lipids and saccharides (Kumar *et al.,* 2021).

Table III

Representative examples of FTIR analysis in wines and wine spirits

Aim of the analysis	Type of sample/Preparation mode	Wavenumber range (/cm)	Spectral pre-treatment	Statistical method	Reference
Optimisation of wine analysis	Degassed wines	926-5012	NM	NM	Moreira *et al.* (2002)
Analysis of wine polysaccharides	White wine polysaccharide extracts	800-1200	Autoscaling (Mean centred, standardized) centring of the data set by column	PCA, CCA, PLS	Coimbra *et al.* (2002)
Analysis of organic acids	Wines	929-5011		PLS	Moreira and Santos (2005)
Quantitative analysis of red wine tannins	Wines purified by SPE	650-4000	Mean-centring, 1st and 2nd derivatives	PLS	Fernández and Agosin (2007)
Analysis of wine polysaccharides	Red wine polysaccharide extracts	950-1850	Linear standardization	PLS	Boulet *et al.* (2007)
Identification of spectral regions for the quantification of red wine tannins	Wines	926-5012	NM	PLS	Jensen *et al.* (2008)
Differentiation of Greek red wines based on the grapevine variety	Phenolic extracts of red wines	900-1800	2nd derivative (Savitzky-Golay)	Match value	Tarantilis *et al.* (2008)
Determination of oenological parameters	Wines	600-4000	Mean centre and baseline corrections	PLS	Fu *et al.* (2009)
Prediction of total antioxidant capacity of red wine	Wines	600-4400	Mean-centring	PLS	Versari *et al.* (2010)
Discrimination of oenological tannins	Solution of oenological tannins	950-1500	NM	NM	Laghi *et al.* (2010)
Authentication of Cypriot sweet wine "Commandaria"	Freeze-dried and concentrated wines under nitrogen flow	400-4000	NM	PCA, CA, LDA, CART, RDA	Ioannou-Papayianni *et al.* (2011)
Determination of anthocyanins content	Degassed wines	4000-12500	1st first and 2nd derivatives, Detrend, smoothing, MSC, SNV, mean centring	PCA, PLS-DA, WILMA-D	Ferrari *et al.* (2011)
Direct determination of organic acids	Filtered wines and wine derived-products	1000-7895	NM	PLS	Regmi *et al.* (2012)
Determination of anthocyanins in wine	Filtered and thermostated wines	926-5012	NM	PCA, PLS	Romera-Fernández *et al.* (2012)
Measuring of wine routine parameters	Wines	400-4000	NM	PCA, PLS	He *et al.* (2013)
Discrimination between subzones inside a controlled Designation of Origin	Heated Wines	4000-52632	SNV, 2nd derivative (Savitzky-Golay)	PCA, LDA, SIMCA, SVM	Martelo-Vidal *et al.* (2013)
Prediction of total phenolics and flavonoid contents and antioxidant capacity	Wines	650-4000	NM	PLS	Silva *et al.* (2014)
Quality control of grape-derived spirits	Grape derived spirits	400-4000	MSC, VecNor, MinMax, SLS, 1st and 2nd derivatives	PCA, PLS	Anjos *et al.* (2016)
Determination of chloride and sulphate	Filtered and degassed wines	1000-3050	NM	PCA, PLS	Teixeira dos Santos *et al.* (2016)
Analysis of ash in wine	NM	NM	1st derivative, centred average	Multivariate analysis	Jug *et al.* (2017)
Characterisation of Marsala wines and ageing monitoring	Incubated wines	350-4000	Baseline correction	ANOVA, PCA, LDA	Condurso *et al.* (2018)
Discrimination of Romanian wines	Centrifugated wines	400-4000	2nd derivative (Savitzky-Golay)	PCA	Topala and Tataru, (2018)
Discrimination of sweet wines	NM	400-4000	2nd derivative (Savitzky-Golay)	PCA	Topala and Tataru, (2019)
Analysis of ellagitannins	Wines	950-1820	Smoothing and baseline correction (Savitzky–Golay polynomial filter)	PLS	Basalekou *et al.* (2019)

NM= Not mentioned; PCA=Principal Component Analysis; CCA=Canonical-Correlation Analysis; PLS=Partial Least Squares Regression; CA=Correspondence Analysis; LDA=Linear Discriminant Analysis; CART=Classification and Regression Tree Analysis; RDA=Redundancy Analysis; PLS-DA=Partial Least Squares-Discriminant Analysis; WILMA-D=A Novel Algorithm based on the Fast Wavelet Transform (FWT); MSC=Multiple Scatter Correction; SNV=Standard Normal Variate; SIMCA=Soft Independent Modeling by Class Analogy; SVM=Support Vector Machine; ANOVA=Analysis of Variance.

Table III (continuation)

Representative examples of FTIR analysis in wines and wine spirits

Aim of the analysis	Type of sample/Preparation Mode	Wavenumber Range (/cm)	Spectral Pre-treatment	Statistical Method	Reference
Varietal and vintage year discrimination	Filtered wines	500-4000	SNV, 2nd derivative (Savitzky-Golay)	PCA, LDA	Geană et al. (2019)
Discrimination of aging technologies	Wine spirits	450-4000	NM	ANOVA, FDA, FANOVA	Anjos et al. (2020)
Determination of phenolic content and colour parameters	Wines	400-4000	NM	PCA, PLS	Garcia-Hernandez, et al. (2020)
Quantification of polyphenols in red wine	Wines	925-5011	NM	PCA, PLS	Miramont et al. (2020)
Characterisation of the medium infrared spectra of polyphenols of red and white wines	Wines purified by SPE, dealcoholized and centrifugated	600-4400	NM	SIMCA-P, Heat map of Pearson correlation matrix	Scano (2021)
Characterisation of sparkling wines	Filtered wines	1285-4000	NM	PCA, HCA, PLS-DA, ANOVA	Izquierdo Llopart and Saurina (2021)
General wine analysis	Filtered wines	926-5012	Normalisation	PCA	Kumar et al. (2021)
Direct authentication and composition quantitation of red wines	Wines	650-4000	Normalisation, 2nd derivative (Savitzky-Golay polynomial fitting), SNV	PCA, PLS	Wang et al. (2022)

NM=Not mentioned; PCA=Principal Component Analysis; CCA=Canonical-Correlation Analysis; PLS=Partial Least Squares Regression; CA=Correspondence Analysis; LDA=Linear Discriminant Analysis; CART=Classification and Regression Tree Analysis; RDA=Redundancy Analysis; PLS-DA=Partial Least Squares-Discriminant Analysis; WILMA-D=A Novel Algorithm based on the Fast Wavelet Transform (FWT); MSC=Multiple Scatter Correction; SNV=Standard Normal Variate; SIMCA=Soft Independent Modeling by Class Analogy; SVM=Support Vector Machine; ANOVA=Analysis of Variance.

As shown above, most of the studies were focused on the simultaneous assessment of several wine parameters, but often the results are not enough satisfactory for the prediction of all of them. Due to spectral interferences, the analytical calibration of compounds that are found in low concentrations in the wine matrix, in comparison with other abundant components like ethanol and organic acids, is facing difficulties. Independent studies have been performed on the determination of organic acids to achieve better performances. For this reason, FTIR measurements took place in samples spiked with known organic acid concentrations (tartaric, malic, lactic, acetic, and citric acids). The obtained recoveries for the total acidity and the individual organic acid concentrations (for the same spiked additions) were compared. Nevertheless, validation procedures should not be forgotten and should be fully performed. The estimations for total acidity recovery were good, but for the individual organic acid concentrations the recovery results revealed a lack of accuracy. This fact was assigned to spectral similarities between the organic acids (Moreira and Santos, 2005). In another chemometric approach, FTIR combined with PLS regression was used to build calibration models for tartaric acid, malic acid, lactic acid, succinic acid, citric acid, and acetic acid in wines, vinegars, and spirits. HPLC was used as a reference method for the validation of the obtained results. Excellent performance was observed for the determination of tartaric acid, malic acid, succinic acid, and lactic acid at high concentrations, except for tartaric acid in vinegar samples. The method was also efficient for the assessment of malic and citric acid at low concentrations and acetic acid in red and white wine and brandy samples. This fact was considered to be correlated with the predicting performance of the reference method and the composition of the data set. Moreover, it was not possible to obtain a global calibration due to the different nature of the samples under study (Regmi et al., 2012). White wines obtained from different maceration and pectic enzyme clarification procedures were used to obtain polysaccharide extracts in order to develop a method for monitoring polysaccharide composition. The samples resulting from wine concentration, dialysis and lyophilisation were fractionated by graded ethanol precipitation. Through chemometric analysis of the FTIR spectra, the wine extracts were differentiated according to their polysaccharide content and correlated with the different winemaking processes addressed. Moreover, a calibration model was developed successfully for the quantification of mannose (Coimbra et al., 2002). Contextual information was obtained in chemometric investigation of red wine polysaccharides with FTIR application. The samples were obtained from the purification of red wine. The information extracted from the spectral region 950-1850/cm, allowed to identify the different polysaccharide families (mannoproteins, arabinogalactan-proteins, RG-I, and RG-II) (Boulet et al., 2007).

Determination of phenolic compounds

In addition to the basic monitoring analysis, other relevant chemical markers are needed to ensure the quality of the final product, such as the phenolic content, chloride and sulphate content, antioxidant capacity, and chemical age of the wine. However, the quantification of red wine tannins faces specific difficulties due to spectral interferences from other components of the wine matrix. To overcome these difficulties, some wines were purified by a Solid-Phase extraction column before analysis. Furthermore, six different predictive models were evaluated in combination with spectral pre-processing procedures to develop a quantification method for tannins with the use of FT-MIR. Besides, two different reference methods, protein precipitation, and phloroglucinolysis were examined as well. The best combination for tannin quantification and prediction of the mean degree of polymerisation was the one using PLS regression of the spectrum full range (650-4000/cm), the second derivative of the spectra, and phloroglucinolysis as the reference method. The samples used were from 'Carménère' grapevine cultivar and resulting from two different vintages and different Chilian wineries (Fernández and Agosin, 2007). In another similar study, four different variable selection tools were evaluated to identify the specific FT-MIR spectra area for tannin quantification in order to avoid the time-consuming pre-treatment extraction. The two regions selected and identified by all the tools under examination were 1485-1425/cm and 1060-995/cm. Based on these regions, a successful calibration model was developed using a large data set (128 commercial red wines from different vintages, grapevine varieties, and production countries) for the quantification of red wine tannins (Jensen *et al.*, 2008).

ATR-FTIR was compared with electronic tongue in terms of their discrimination capability of phenolic content. PLS-1 was applied to the data set derived from both techniques and led to good estimations for simultaneous determination of Total Phenolics Index (TPI), CIELab, and Glories parameters. Both techniques were considered robust enough to be applied for a quick and efficient assessment of phenolic composition but electronic tongue showed better prediction values (higher coefficients of correlations and lower residual errors) (Garcia-Hernandez *et al.*, 2020). Determinations of twelve anthocyanins and three different groups of anthocyanins were examined with the application of FT-IR combined with PLS-R, and HPLC-DAD was used as a reference method. One hundred fifty-three Rioja wines (young wines of 2004 and 2005, "Crianza", and "Reserva" wines) were analysed for the calibration model, which was evaluated by internal and external data sets. Unfortunately, only the anthocyanin content of young wines was able to be predicted with a low error. These results were assigned to the higher concentration level of anthocyanins in young wines than in the aged ones (Romera-Fernández *et al.*, 2012). In another work, ATR-FTIR was used for the prediction of total phenolic and flavonoid contents and antioxidant activities (DPPH and FRAP assays) in 'Moscatel' dessert wines. Through chemometric analysis of the spectral region 900-1800/cm, a good determination capability for total phenolic and flavonoid composition was observed, but the results were not enough satisfactory regarding the determination of antioxidant activities. This fact was attributed to the poor specificity of the DPPH and FRAP methods and the possible influence of interferent molecules, not included in the study (for example polysaccharides) (Silva *et al.*, 2014). Another research was focused more specifically on the determination of the total antioxidant capacity of red wines. FTIR matched with PLS regression was applied in the fingerprint region 965-1543/cm and the obtained results showed promising estimation values. However, more studies in extended data sets are needed for the validation of the method and its application in the industry (Versari *et al.*, 2010). The use of FTIR spectra from samples of 'Cabernet Sauvignon' Mexican wines in combination with multivariable statistical analysis led to the creation of an optimised chemometric model for the determination of total bioactive phenolic compounds and antioxidant capacities (ABTS and DPPH assays). The spectral area used was 824-1550/cm (Grijalva-Verdugo *et al.*, 2018). In a comparison study between FTIR and UV-vis spectroscopy, FTIR showed more accurate results for the prediction of tannin concentration, while UV-vis stood out for the prediction of anthocyanins. However, the analysis of some wavelengths in the visible region in combination with FTIR spectrum contributed to a better determination of anthocyanin content (Miramont *et al.*, 2020). The quantification of hydrolysable tannins is of great importance for the wine industry because they are responsible for very important modifications in the wine's organoleptic characteristics (Michel *et al.*, 2011). The determination capability of FTIR spectroscopy in combination with chemometrics was investigated by analysing the spectral region 950-1821/cm deriving for wine samples aged in different wooden barrels. The method was an effective tool for the prediction of total ellagitannins concentration in samples aged in different French and American oak barrels or being in contact with oak sticks of different types of oak. However, the estimations for samples aged in chestnut barrels were not good enough. This observation could be related to the existence of ellagic acid derivatives (Basalekou *et al.*, 2019). In a more detailed study considering different samples derived from all the winemaking stages, ATR-FTIR and UV–Vis were combined to investigate the fingerprint region of polyphenols (900-1800/c[1]). For this purpose, the wine samples of

red and white varieties underwent a solid-phase extraction. Both spectra derived from ATR-FTIR and UV–Vis were analysed by a Heat Map to establish correlations between the spectra. The method was able to identify peaks correlated with anthocyanins and flavanols for the red wines, non-flavonoids and flavonoidsfor the white wines, and glycosylated phenolics for both wines (Scano, 2021).

Determination of other quality parameters

Another important analysis for certified wines to enter the market is the assessment of the wine ash. FTIR matched with multivariate analysis with different spectral pre-treatments was evaluated for its applicability in the prediction of ash content in wines. The use of four wavelengths and a centred average proved to be the most efficient solution. The validation of the method provided good estimations values and, according to the authors, after enlargement of the data set the method could be applied on an industrial scale (Jug *et al*., 2017). In addition, several other chemical elements, like chloride and sulphate anions, are considered important quality markers of the wine. FTIR spectroscopy combined with chemometrics was used successfully for the determination of chloride and sulphate in a wide range of Portuguese wine types. The calibration models were able to achieve quantification of the sulphate and semi-quantification of the chloride (Teixeira-dos Santos *et al*., 2016).

Authentication studies

Moreover, due to the globalisation of the wine market and due to many cases of mislabelling and adulterations, a series of authentication studies have been carried out to guarantee the quality and authenticity of the final product. The related studies have resorted to chemical compounds that are considered as authentication "markers" and are characteristic and unique for each parameter or comparisons with known and authentic samples (Basalekou *et al*., 2020).

A chemometric approach took place comparing the performance of FT-NIR and ^{1}H NMR in differentiating adulterated wine samples. The adulterated samples derived from a blend with wine very rich in anthocyanins (called "Rossissimo") or from the addition of anthocyanins extracted fromblack rice. The results achieved by NIR spectroscopy gave less satisfactory results than NMR, but still, a relationship with the anthocyanins content and the NIR spectra was noticeable. These results were ascribed to the low sensitivity of the method in determining low concentrations levels and to the possible matrix effect (Ferrari *et al*., 2011). FTIR-ATR combined with the multivariate analysis was used for the discrimination of "Marsala" wine from Sicily (Italy) based on the

grapevine cultivar, production technology, and ageing. The samples were differentiated according to their sugar concentration, and a clear discrimination between the high-quality samples (Virgin) and the remaining ones was found. Moreover, "Marsala" wine samples with different ageing times were discriminated successfully using the spectral area 1058-1076/cm (Condurso *et al*., 2018). Successful differentiation of Greek red wines was performed using FT-MIR spectroscopy and specific software. For this purpose, extracts of wine phenolic components were obtained by solid-phase extraction with C-18 columns and elution by methanol. The study allowed to discriminate different grapevine cultivars based on the absorption characteristics in the fingerprint spectral region of 900-1800/cm, leading to the creation of libraries for each cultivar. The characterisation of a new unknown sample took place using the spectra bank data set (Tarantilis *et al*., 2008). FTIR Spectroscopy and chemometrics were used in order to distinguish between sweet wines in terms of sugar content, acidity, and total polyphenol content. Through PCA analysis of MIR spectra derived from some Romania wine samples, it was possible to discriminate the red from the white samples and the dry and the half-dry ones (Topala and Tataru, 2018). In a similar study, Romanian sweet wines and Canadian ice wines were differentiated according to their MIR spectra correlated with their different chemical composition. The chemometric approach underlined the biggest differences in terms of sugar content due to the very high sugar concentration of the ice wines, while they did not express significant differences in terms of antiradical activity (Topala and Tataru, 2019). An identification study of oenological tannins took place using different analytical techniques. Among them, FTIR was applied and was able to identify five of the six samples of oenological tannins (three of them condensed tannins and two mixtures of hydrolysable tannins). The difficulties of identifying and quantifying the tannins under analysis were assigned to the different botanical origin and to the extraction/purification processes, and could be overcome with the enlargement of the database (Laghi *et al*., 2010). In the same context, two different analytical approaches were examined for red wine authentication in terms of varietal and vintage year identification. Through chemometric analysis of the data, UV-Vis spectroscopy was considered more appropriate for varietal discrimination and FTIR spectroscopy for vintage year discrimination. However, both multiparametric techniques allowed to identify red wine samples aged for more than six years, correlating spectral differences with the formation of new compounds during ageing (Geană *et al*., 2019). Moreover, successful differentiation of wine spirit samples aged through different technologies was possible with the use of FTIR (Anjos *et al*., 2020). The

functional data analysis (FDA) was applied to ATR-FTIR spectra, and was proven efficient in discriminating the studied wine spirits. The observed results were confirmed with the parallel determination of various analytical parameters, including chromatic characteristics (CIELab method), total phenolic index, concentrations of furfural, ellagic acid, vanillin, and coniferaldehyde, and total content of low molecular weight phenolic compounds (HPLC). In this context, another discrimination study was performed using NIR spectra combined with UV-Vis spectra, and chemometrics. Samples from different subzones of the same Protected Designation of Origin (PDO) were differentiated and also samples that did not belong to this PDO were identified (Martelo-Vidal *et al.*, 2013). The discrimination capacity of FTIR was evaluated in terms of authentication of sweet wines from Cyprus, ("Commandaria") through chemometric analysis of FTIR spectra of 65 sweet wines. Differentiation of several types of Commandaria wine (non-fortified, fortified and homemade) from Cyprus and other countries was also made (Ioannou-Papayianni *et al.*, 2011). A series of different analytical approaches were used in combination with chemometrics for the characterisation of sparkling wines (cava wines) from different grapevine cultivars, wine blends, and wine-making stages. FTIR spectroscopy was applied for the analysis of total reducing sugars, pH, acetic acid, total acidity, malic acid, lactic acid, and alcoholic strength. The models were established mainly depending on the polyphenol and organic acid content. Rosé wine samples and 'Chardonnay' wines samples showed the highest levels of phenolic acids. Concerning the samples underwent malolactic fermentation, the discrimination was mainly based on malic acid and lactic acid contents (Izquierdo-Llopart and Saurina, 2021). Tri-step IR spectroscopy in combination with electronic nose was applied for an authentication study of 'Cabernet Sauvignon' wines. Through chemometric analysis of the fingerprint region of ethanol and sugar dry wines (DW), semi-dry wines (SD), semi-sweet wines (SS), and sweet wines (SW), were discriminated Furthermore, it was possible a quantitative determination of ethanol and total sugar levels based on PLS regression (Wang *et al.*, 2022).

CONCLUDING REMARKS

Several studies found in the literature have been focused on the applicability of FTIR in monitoring the wine production from the grapes to the final product. The wine industry demands constant product monitoring and requires process control from the grape ripening until bottling. IR spectroscopy is already being applied in the wine industry from the vineyard, assessing the grape maturation, during the winemaking process, in real-time analysis of the general chemical parameters in musts and wines, until bottling. The measurements have been performed with portable and non-portable instrumentation coupled with calibration models already built by the manufacturer. However, other IR applications combined with chemometric approaches could also be considered a promising tool for the determination of more specific parameters and applied widely in all the winemaking stages. Methodologies that depend on IR analysis demand minimal or zero sample preparation, are environmentally friendly, easy to use, fast, and more economical than the traditional techniques. As a result of all these advantages, FTIR measurements are already applied in the wine sector, but many challenges still remain. The most important limitations and critical aspects of the studies that were mentioned in the present work are summarised below.

First of all, it was noticeable that the different preparation modes can influence the spectra and the determination of the desired oenological parameters. Therefore, careful consideration of the appropriate mode for each factor should be taken. Moreover, most of the developed methodologies found in the literature depend on feasibility studies using a limited number of samples (less than 100 in most cases) and the validation of the methods took place with the cross-validation tests. External validation using independent sets of samples is needed. Besides, developed models were not applied to different grapevine cultivars, harvests, and types of wines, and led to a poor representativity of the samples. Furthermore, many developed methods were focused on a specific oenological parameter or chemical compound or they have been applied to a specific stage of the winemaking process. In fact, the simultaneous determination of a large number of parameters was more challenging in most cases. Moreover, compounds with a concentration higher than 1 g/L are easier to be determined by FTIR due to their ability of engaging absorption phenomena.

Finally, the complexity of the wine matrix and the chemical similarity of the compounds under study makes the interpretation of the spectra very difficult. In addition, the presence of water and ethanol leads to interference in the IR spectra due to their large absorption band.

In the context of all these critical points, it is of great importance that the initial commercial analytical calibration be updated by each winery, using samples representative of those under study. Most applications in the wine industry consider the use of techniques based on FTIR for the evaluation of the basic chemical composition. In the future, more applications evaluating more specific factors (for example aroma compounds or tannins) or for

authenticity purposes would be of great interest to the contemporary wine industry.

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