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Towards on-line monitoring of phenolic content in red wine grapes: A feasibility study

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ABSTRACT

Spectroscopy techniques to efficiently measure phenolic composition in grape berries may be a suitable analytical practice, provided that robust calibrations are established. A contactless FT-NIR instrument was used for on-line spectral data collection from grapes transported on a conveyor belt system. Spectral data was also collected on static samples using the same NIR instrument. Spectral measurements of crushed berries captured from the conveyor belt system and the use of the homogenate extraction protocol as reference method provided the most accurate prediction models. Values obtained for errors in prediction (RMSEP%) and RPD were 12% and 2.37, 12.3% and 3.37, 7.8% and 3.2, 16.7% and 2.84 for tannins (mg/g) and anthocyanins (mg/g) on a fresh weight basis, total phenols and colour density (AU), respectively. The results observed in this study show the ability of NIR spectroscopy to monitor the phenolic composition of grape berries transported on a conveyor belt system online.

1. Introduction

The biosynthesis and accumulation of phenolic substances in grapes take place throughout the ripening season. Anthocyanins and flavan-3-ol polymers, the so called proanthocyanidins, are the major flavonoids found in the inner thick-walled layers of the grape berry skin tissue (Adams, 2006). Additionally, proanthocyanidins are also found in large concentrations in the soft parenchyma of the grape seed coat tissue (Adams, 2006). Flavan-3-ols and their polymeric forms, proanthocyanidins, start accumulating in the berry from blooming, reaching a maximum at véraison with a subsequent decrease during the last stages of the ripening period (Teixeira, Eiras-Dias, Castellarin, & Gerós, 2013). In contrast to the flavan-3-ol phenolics, anthocyanins start accumulating in the skin tissue from véraison and reach a maximum during the late stages of ripening, when the synthesis stops (Teixeira et al., 2013). The strong influence of phenolic substances on wine quality is due to its importance in the colour and mouthfeel attributes. Anthocyanins in their different forms and structures are mainly responsible for red wine colour (He et al., 2012), while flavan-3-ols and proanthocyanidins play a major role in wine bitterness and astringency (McRae & Kennedy, 2011).

It is still very common to harvest wine grapes taking only the sugar to acid ratio into account. Often, only sugar concentration is used as a harvesting parameter, as tartaric acid additions during winemaking can be used to adjust this ratio if allowed. It is also not common to take other wine components, such as phenolic compounds, into account when deciding on the optimum harvesting date, for benchmarking purposes or for decision-making practices prior to the fermentation process (Nogales-Bueno, Hernández-Hierro, Rodríguez-Pulido, & Heredia, 2014). The measurement of phenolics in grape berries is a lengthy process, as the phenolic compounds first need to be extracted from the berry material before analysis. Despite recent advances in the field with the inclusion of hand-held devices, analytical techniques for fast and easy-to-operate methods for the quantification of phenolic levels in grape berries are still not readily available in the wine industry (Dambergs, Gishen, & Cozzolino, 2015). To overcome this, the use of spectroscopy with chemometrics tools may provide a suitable solution (Dambergs et al., 2015). Spectroscopy applications combine chemical information obtained from the emission of light (UV–Vis, IR and Raman, among others) with the measurement of the compounds or parameters of interest following established reference methods. This information is then correlated, in most cases using regression techniques, with the final goal to obtain prediction algorithms that are used to estimate phenolic levels in new samples using only spectral information (Aleixandre-Tudo, Buica, Nieuwoudt, Aleixandre, & Du Toit, 2017). A substantial reduction in the analysis time is thus achieved, with this

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being the most relevant feature of spectroscopy applications (Dambergs et al., 2015).

A number of attempts to shorten this analytical process have recently been investigated. The application of spectroscopy techniques to assess grape extracts and homogenates has been reported previously (Aleixandre-Tudo, Nieuwoudt, Olivieri, Aleixandre, & du Toit, 2018; Cozzolino, Cynkar, Dambergs, Mercurio, & Smith, 2008; Ferrer-Gallego, Hernández-Hierro, Rivas-Gonzalo, & Escribano-Bailón, 2011; Fragoso, Aceña, Guasch, Busto, & Mestres, 2011). Vis-near infrared (Vis-NIR) was used to predict dry matter and tannin content from a large dataset of grape homogenates (Cozzolino et al., 2008). The use of ultraviolet visible (UV–Vis) spectroscopy to predict the grape extract phenolic composition obtained following two different extraction protocols showed accurate calibrations for anthocyanins, tannins, total phenols and colour density phenolic parameters (Aleixandre-Tudo et al., 2018). Accurate predictions were obtained for the main phenolic subclasses (anthocyanins, flavanols, flavonols and phenolic acids) and for the total phenolic content using NIR and HPLC reference data (Ferrer-Gallego et al., 2011). Mid-infrared spectroscopy (MIR) was also used to evaluate the phenolic ripeness of red grape extracts through robust models for anthocyanin, tannin and total phenol calibrations (Fragoso et al., 2011). NIR was also able to accurately predict anthocyanin content in Canaiolo grape berry homogenates (Muganu et al., 2013), and total phenols and potential and extractable anthocyanins in Nebbiolo grapes (Guidetti, Beghi, & Bodria, 2008). FT-NIR was also used to quantify extractable phenolic compounds from seed samples with models, with varying accuracy being reported (Rolle et al., 2012; Torchio, Río Segade, Giacosa, Gerbi, & Rolle, 2013). Calibration data using cross-validation also showed the potential of Fourier transform infrared spectroscopy (FT-IR) to predict the mean degree of tannin polymerisation (mdP). Finally, calibrations for total phenol and tannin contents in seeds were also reported (Kyraleou et al., 2015). However, these studies of grape extracts/homogenates (or seed tissue) accounted only for the realisation of the reference analytical methods, without addressing the tedious sampling and extraction/homogenisation steps.

To overcome the phenolic extraction from grape berries, a Vis-NIR portable device was used in the vineyard to investigate prediction models for total phenols, and potential and extractable anthocyanins in intact grape berries (with errors < 20%) (Guidetti et al., 2008). Vis-NIR calibrations for total phenols and anthocyanins were also reported for intact berries measured in the laboratory (Fadock, Brown, & Reynolds, 2016). Calibrations to predict individual monomeric anthocyanin components were investigated for Sangiovese red grapes during the ripening season (Ribera-Fonseca, Noferini, Jorquera-Fontena, & Rombolà, 2016). A similar Vis-NIR device was tested to predict extractable and potential anthocyanins and tannins with cross-validation errors of 17.00, 14.16 and 21.10% respectively (Giovenzana et al., 2013). A portable NIR device in reflectance mode was evaluated for the prediction of anthocyanin content in the field. The authors concluded that the lack of an accurate reference method for the determination of anthocyanin content in individual berries might have influenced the performance (error in validation = 0.302 mg/g) of the predictions (Larraín, Guesalaga, & Agosin, 2008).

Another technique that is gaining attention is the use of hyperspectral imaging directly on grape berries. A NIR hyperspectral imaging system was employed to generate spectral data and calibrations for some of the most common phenolic parameters (Nogales-Bueno, Rodríguez-Pulido, Heredia, & Hernández-Hierro, 2015; Zhang et al., 2017). However, hyperspectral imaging is not the most accessible spectroscopy technique due to the complex chemometric analysis required during the feature-extraction step that, together with the cost of the instrument, makes its use almost exclusive to research applications.

In addition, some authors suggest that light penetration depth can be as deep as 10 mm in NIR applications, depending on the sample tissue under evaluation (Roberts, Motin, Swain, & Cozzolino, 2017). The ability of light to be absorbed or scattered has been widely used to investigate the internal properties of fruits, reporting varying penetration depths depending on the tissue under study (Magwaza et al., 2012). Light penetration is dependent on several aspects such as the geometry of the infrared device, the wavelength, the light scattering and the sample characteristics (Magwaza et al., 2012; Roberts et al., 2017). As mentioned, phenolic compounds are located mainly in the skin and seed berry tissues. Focusing only on the skin tissue has the danger of excluding a big part of the tannin chemical information due to the large proportion of seed vs skin tannins present in wines (Casassa & Harbertson, 2014).

Furthermore, the number of applications of NIR spectroscopy in an on-line scenario is still very limited in the wine industry. Due to the intrinsic characteristics of the technique (low running costs, absence of sample preparation (non-destructive), environmentally friendly and time-efficient), the future implementation of non-destructive, on-line applications for process control and monitoring purposes is thus foreseen. NIR spectrometers integrated into the receiving lines of two wineries provided spectral data that were successfully correlated with a number of oenological measurements (Porep, Mrugala, Pour Nikfardjam, & Carle, 2015). In this study we therefore present the evaluation of a NIR contactless system to predict the phenolic composition of two different sample formats, namely intact and crushed berries that are transported on a moving conveyor belt. Using the penetration ability of the NIR light, we hypothesise that, in the case of intact berries, the chemical information contained in the seeds may also be captured and therefore included in the process of PLS model optimisation. In the case of crushed berries, it is speculated that the light penetration is of minor importance, as at least part of the seeds became visible in the light beam.

2. Materials and methods

2.1. Samples

One hundred batches of grape samples from different blocks were collected from three different commercial wineries covering several geographical locations, which included Stellenbosch, Paarl, Malmesbury, Swartland and Elgin (all in the Western Cape province of South Africa). Fifteen kilograms of grapes were collected per grape sample batch. Approximately 500 berries were randomly sub-sampled from every grape batch. A number of cultivars were represented in the samples set, including Cabernet Sauvignon (24), Cabernet Franc (2), Cinsault (3), Grenache noir (2), Malbec (5), Merlot (11), Mourvedre (2), Petit Shiraz or Durif (1), Petit Verdot (6), Pinotage (1), Red Muscadel (1), Roobernet (1), Shiraz (38), Tannat (1), and two unknown samples. Grapes were collected on the harvest date as decided by the commercial cellars. Brix, titratable acidity and pH were measure for each batch, and are reported in Supplementary material S1.

2.2. Phenolic extraction from the grape berries

Two extraction protocols were tested, with the aim of investigating different extraction conditions. The first method, reported by Iland, Ewart, Sitters, Markides, and Bruer (2000), is based on a blended/homogenised grape phenolic extract, using high solvent concentrations during a short extraction time (one hour). The method provides an estimation of the potential phenolic content in a grape sample. The second method, reported by Bindon et al. (2014) (also known as wine-like protocol), simulates extraction conditions similar to those occurring in a real fermentation scenario, viz. alcohol levels of 15% v/v and a longer extraction time (40 h). Grape samples from both extraction protocols were extracted in duplicate.

2.3. Spectrophotometric analysis of phenolic compounds

A Multiskan GO Microplate Spectrophotometer (Thermo Fisher