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Phenolic profiling of grapes, fermenting samples and wines using UV-Visible spectroscopy with chemometrics

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ABSTRACT

Phenolic compounds play and important role on colour, flavour and mouthfeel attributes of wines. The acquisition of information related to phenolic compounds during the winemaking process is therefore becoming a necessity. Ultraviolet-Visible (UV-Vis) spectroscopy appears as an affordable option to monitor phenolic composition and levels during winemaking. To investigate this, a large number of samples collected from industrial fermentations over two vintages as well as commercial wine samples, spanning a wide range of vintages, were analysed for phenolic compounds using high performance liquid chromatography (HPLC). Methyl cellulose precipitable (MCP) tannins, anthocyanins, total phenols and colour density were also analysed. Partial least-squares (PLS) calibration models, based on UV-VIS spectra and reference measurements, were constructed and their performance evaluated in terms of the residual predictive deviation values. The accuracy and robustness of the calibrations were further evaluated by a combined test on slope and intercept, interclass correlation coefficients and standard error of measurement. Limit of detection and limit of quantification of the PLS models were also reported and evaluated. Furthermore, PLS models for an additional data set including 130 grape samples was also investigated for MCP tannins, anthocyanins, total phenols and colour density measurements. Phenolic compounds were extracted following two different protocols, namely wine-like and homogenate methods.

1. Introduction

Phenolic compounds are bioactive substances that are widely distributed in plants and fruits and therefore also occur in some food products including wine (Teixeira, Eiras-Dias, Castellarin, & Gerós, 2013). Wine and grape derived phenolic compounds can be classified into non-flavonoids (hydroxycinnamates, hydroxybenzoates and stilbenes) and flavonoids (flavan-3-ols, flavonols and anthocyanins) (Garrido & Borges, 2013). Flavonoids and hydroxycinnamates are found in grapes and wines in high concentrations while the other non-flavonoid phenolics are found at lower levels (Teixeira et al., 2013). The importance of phenolic compounds resides in their role in colour, flavour and mouthfeel attributes of wines (Cheynier et al., 2006; Fulcrand, Dueñas, Salas, & Cheynier, 2006). Additionally, the health benefits of highly containing phenolic foods, such as wine, have been extensively documented (Aleixandre, Aleixandre-Tudó, Bolaños-Pizarro, & Aleixandre-Benavent, 2013). In combination with its antioxidant properties, protective effects against cardiovascular diseases (Chiva-blanch, Arranz, Lamuela-raventos, & Estruch, 2013), some cancers (Arranz et al., 2012, pp. 759–781) and neurodegenerative (Sun, Wang, Simonyi, & Sun, 2010, pp. 375–383) or inflammatory (Casas et al., 2012) diseases have been reported.

Grapegrowing and winemaking techniques can influence the levels of these compounds in the final product (Sacchi, Bisson, & Adams, 2005; Smith, Mcrae, & Bindon, 2015). The time-efficient quantification of phenolic compounds during the winemaking

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process is thus a necessity. Traditionally, ultraviolet-visible (UV-Vis) spectrophotometric based methods have been used for the analysis of the phenolic composition. UV-Visible methods are suitable for phenolic analysis because of the ability of these compounds to absorb UV (provide a protective effect in plants against UV radiation) and visible light (they are mostly coloured compounds) (Lorrain, Ky, Pechamat, & Teissedre, 2013). The intensity of the UV-Visible spectrum is attributed to the electronic transition of the π type orbitals, which depends on the number and the location of the OH, OCH_3 and glycoside groups of the different classes of polyphenols (Sanna et al., 2014). Intermolecular interactions and the conditions of the medium (pH, metals, SO_2) define the UV-Visible absorption of the phenolic pool (Hassane, Gierschner, Duroux, & Trouillas, 2012).

Spectrophotometric analyses of phenolic compounds are achieved through a number of protocols (Aleixandre-Tudo, Buica, Nieuwoudt, Aleixandre, & du Toit, 2017). These methods generally provide an estimation of the overall content of a specific subclass of phenolic compounds. A lack of specificity and reproducibility have been ascribed to these methodologies (Sun, Leandro, Ricardo da Silva, & Spranger, 1998). However, they have also been defined as reliable, simple, cost effective and fast procedures, which make them suitable for routine analytical practices (Aleixandre-Tudo et al., 2017; Harbertson & Spayd, 2006). On the other hand, high performance liquid chromatography (HPLC) analysis provide more accurate and precise quantification of phenolic compounds. In this case individual phenolics can be quantified thanks to the separation of the compounds after passing through the HPLC column (Boido, Alcalde-Eon, & Carrau, 2006). After elution, the phenolic compounds can be quantified at different wavelengths using a UV-Visible detector (Hassane et al., 2012). The main drawbacks of HPLC techniques are found in the necessity of skilled personnel, the costs involved in instrumentation and reagents and the lengthy analysis time.

The use of spectroscopy combined with chemometrics to quantify the levels of phenolic compounds in grapes and wines has been extensively reported (Cozzolino, 2015; Dambergs, Gishen, & Cozzolino, 2015; Ricci, Parpiniello, Laghi, Lambri, & Versari, 2013; Versari, Parpinello, & Laghi, 2012). The benefits claimed include reliability, rapidness, cost-effectiveness and simplicity (Dambergs et al., 2015; Gishen, Dambergs, & Cozzolino, 2005). Additionally, this multiparametric technique is highly suitable for on-line and in-line systems, which makes it appropriate for the control and monitoring of wine fermentation and aging processes (Cozzolino, 2015; Gishen et al., 2005). Although a large part of the published studies uses near and mid infrared spectroscopy, UV-Visible spectral information has been shown to also be useful for the quantification of wine phenolics (Aleixandre-Tudo, Nieuwoudt, Aleixandre, & Du Toit, 2015; Beaver & Harbertson, 2016; Dambergs, Mercurio, Kassara, Cozzolino, & Smith, 2012; García-Jares & Medina, 1995; Skogerson, Downey, Mazza, & Boulton, 2007). As mentioned, the ability of phenolics to absorb UV light and the fact that they are mostly coloured compounds make UV-Visible spectroscopy a suitable technique for this purpose.

A number of attempts to quantify phenolic content in fermenting samples and finished wines using UV or the combination of UV-Visible spectroscopy have been reported in the literature (Aleixandre-Tudo, Nieuwoudt, Aleixandre, & Toit, 2015; Beaver & Harbertson, 2016; Dambergs et al., 2012; García-Jares & Medina, 1995; Skogerson et al., 2007). The first research aiming to predict anthocyanin and tannin content using UV-Visible spectroscopy was reported by García-Jares and Medina (1995). Despite the limitations of the reference methods, due to non-specificity, and the limited sample set, the results showed the potential of UV-Visible spectroscopy to predict phenolic levels in wines. More recently, Dambergs et al. (2012) reported accurate multiple linear regression (MLR) and partial least-squares (PLS) regression calibrations for the quantification of methylcellulose precipitable tannins (MCP) using UV spectroscopy. A number of fermenting samples from small scale fermentation trials were included in the calibration set as well as in validation. In another study in finished wines, UV-Visible PLS prediction models for MCP and bovine serum albumin (BSA) tannins were also reported (Aleixandre-Tudo et al., 2015). Moreover, Skogerson et al. (2007) reported PLS models with varying level of accuracy, for commercial fermenting samples collected over one vintage for the Adam-Harbertson assay phenolic parameters (Harbertson, Picciotto, & Adams, 2003). An updated research investigating the effect of several factors on the accuracy of UV-Visible spectroscopy models to quantify the Adam-Harbertson phenolic parameters was recently reported (Beaver & Harbertson, 2016). The effect of wine dilution, pH stability and cultivar (Shiraz and Cabernet Sauvignon samples were included) on model performance was investigated (Beaver & Harbertson, 2016). The updated BSA assay protocol reported by Harbertson, Mireles, and Yu (2015) was in this case used as reference method. Again, prediction models with varying accuracy were reported.

Surprisingly, no references were found in the literature regarding attempts to provide calibration models for grape phenolic composition using UV-Visible spectroscopy. Several publications reported prediction models for grape phenolic analysis using infrared spectroscopy (Chen et al., 2015; Fernandes et al., 2011; Ferrer-Gallego, Hernández-Hierro, Rivas-Gonzalo, & Escribano-Bailón, 2011; Fragoso, Aceña, Guasch, Busto, & Mestres, 2011). Moreover, different methods for the extraction of phenolic compounds from the solid part of the berries with varying extraction conditions have been reported in the literature (Bindon et al., 2014; Iland, Ewart, Sitters, Markides, & Bruer, 2000). One of the most widely accepted methods relies on the phenolic extraction of blended or homogenized berries. Although strong correlations for colour and anthocyanins measurements in grape and wine data were reported (Bindon et al., 2014; du Toit & Visagie, 2012; Jensen, Werge, Egebo, & Meyer, 2008), moderate to weak correlations were observed between the tannin levels in grapes and those measured in the corresponding wines (du Toit & Visagie, 2012; Jensen et al., 2008). On the other hand, a method simulating the phenolic extraction that occurs during the fermentation process was recently reported by Bindon et al. (2014). Strong positive correlations for MCP tannin levels in Cabernet Sauvignon and Shiraz grapes and the wines made thereof were reported. The investigation of prediction models using UV-Vis spectroscopy in grapes extracts would thus provide scientists and winemakers with additional suitable techniques that might be used for the quantification and monitoring of phenolic composition during grape ripening as well as at harvest.

Taking into account that UV Visible spectroscopy is generally a more affordable and available technique for medium and small sized wineries (compared with infrared technology), the main aim of this research was thus to firstly investigate the suitability of UV-Visible spectroscopy for the determination of the phenolic profile of wine samples during fermentation as well as for finished wines. A total of 27 individual phenolic compounds were quantified from the HPLC analysis of a large number (569) of fermenting samples and wines. Moreover, conventional methods were used to measure MCP tannins, anthocyanins, total phenolics and wine colour density. PLS prediction models for HPLC and spectrophotometric analyses were built and validated. The second aim of the study corresponds to the investigation of PLS prediction models for the quantification of phenolic composition of grape berry extracts using two different extraction protocols.