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Quantitative analysis of minerals and electric conductivity of red grape homogenates by near infrared reflectance spectroscopy

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ABSTRACT

The use of near infrared (NIR) reflectance spectroscopy to measure the concentration of minerals and electric conductivity (EC) in red grape homogenates was investigated. Wine grape samples ($n = 209$) from two vintages, representing a wide range of varieties and regions were analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES) for the concentrations of calcium (Ca), potassium (K), magnesium (Mg), phosphorus (P), sulphur (S), iron (Fe), and manganese (Mn) and scanned in reflectance in a NIR instrument (400–2500 nm). The spectra were pre-processed using multiple scatter correction (MSC) before developing the calibration models using partial least squares (PLS) regression and cross validation. Coefficients of determination in cross validation (R^2) and the standard errors of cross validation (SECV) obtained were for Fe (0.60 and 1.49 mg kg^{-1}), Mn (0.71 and 0.41 mg kg^{-1}), Ca (0.75 and 60.89 mg kg^{-1}), Mg (0.84 and 12.93 mg kg^{-1}), K (0.78 and 285.34 mg kg^{-1}), P (0.70 and 40.19 mg kg^{-1}), S (0.88 and 14.45 mg kg^{-1}) and EC (0.87 and 7.66 mS). The results showed that Mg, S and EC in grape berries might be measured by NIR reflectance spectroscopy.

1. Introduction

There is an increasing need to update information on crop nutrition to adequately establish nutrient requirements as well as to fine-tune fertiliser rates. This is due to the need to optimise fertilisation programmes in order to maximise the yield of high quality grape fruit, to minimise the amount of chemical fertilisers applied to the vineyard and to reduce the risks of environmental impact (Etchebarne et al., 2009).

Nutrients are essential for the proper metabolic functioning of grapes and vines, and to ensure desirable commercial and sustainable wine production. Elements such as nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), copper (Cu), iron (Fe), zinc (Zn) and manganese (Mn) are macro and micronutrients associated to growth, yield and grape quality and vary considerably with growing region, soil type, age of the vineyard, and rootstock, among others factors (Clarksson and Hanson, 1980; Etchebarne et al., 2009). The use of irrigation in viticulture is a standard practice as an effective means for regulating water availability to grapevines in order to manage grape development, fruit setting and ripening, in many producing countries (Ribéreau-Gayon et al., 1975; Possner and Kliewer, 1985; Coombe, 1987, 1992, 1995; Iland and Coombe, 1988; McCarthy 1997; Morris et al., 1983; Etchebarne et al., 2009).

Grape berry growth is supported by imports of carbohydrates, water and mineral nutrients. The description of these imports provides some information about the compounds required to support berry development. Additionally, grape berry mineral composition plays an important a role in fruit development, disease resistance and wine chemical composition (Hale, 1977; Morris et al., 1983; Donèche and Chardonnet, 1992; Mpelasoka et al., 2003; Etchebarne et al., 2009; Chardonnet and Donèche, 1995). The mineral nutrient status of the grape berry is of concern not only to the viticulturist, but also to the oenologist because there is a direct impact of berry nutrition on must and wine composition. Many factors may affect the net accumulation of mineral nutrients in the berry through their effects on root cation uptake, translocation from root to shoot, re-translocation of cations from shoot back to root, the mineral nutrient reserve, and the number of berries and berry growth rates in relation to vine vigour (Etchebarne et al., 2009).

Near infrared (NIR) reflectance spectroscopy is being widely adopted for routine analysis of many agricultural products, but requires consistent sample handling and a calibration method which converts spectral (NIR absorption) information into laboratory reference method information (McClure, 2003; Cozzolino et al., 2006). The NIR spectrum of an organic material gives a global signature of composition based on the assessment of the organic chemical structures containing O—H, N—H and C—H bonds (Murray and Cowe, 2004). NIR reflectance spectroscopy has been used to determine macro and micro elements in a wide range of agricultural products and foods (McClure, 2003). However, the determination of inorganic compounds is more challenging compared to

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organic compounds owing to the lack of a direct relation between the element involved and the spectra obtained (Clark et al., 1987). NIR reflectance spectroscopy has been used for determining mineral concentration in plant tissues, due to the association between minerals and organic functional groups in the food matrix and the effect on O—H bonding. The estimation of mineral elements by NIR reflectance spectroscopy is therefore generally dependent on the presence of those elements in mixtures of organic or hydrated compounds and salts (cations and anions) (Cozzolino et al., 2008). In agricultural products, NIR reflectance spectroscopy has been used to measure mineral content in plant parts, forages, woody materials and meat samples (Menesatti et al., 2010; Moros et al., 2009; Tremblay et al., 2009; Wu et al., 2009; Fernandez-Ahumada et al., 2008; Petisco et al., 2005; Gonzalez-Martin et al.; 2002; Cozzolino and Moron, 2004; Murray and Cowe, 2004). Despite the reports of many satisfactory calibrations for mineral elements for a particular material, it is difficult to apply the results from one food to another because the form of the organic molecule/mineral compounds can vary seasonally and/or among species, type of food and processing methods (Cozzolino et al., 2008; Murray and Cowe, 2004). This may lead to unstable calibrations, inconsistent results and difficulty to expanding calibrations beyond a well characterised population (Cozzolino et al., 2008). Therefore, the development of universal calibrations for minerals is difficult.

The aim of this study was to evaluate the potential of NIR reflectance spectroscopy as a method to quantitatively measure minerals and EC in red grape homogenates.

2. Materials and methods

2.1. Samples

Wine grape (*Vitis Vinifera* L.) samples ($n = 209$) of Cabernet Sauvignon, Shiraz, Merlot, Pinot Noir and Chardonnay cultivars were collected during two consecutive vintages (2009 and 2010) at harvest (20–24 °Brix), as whole berries and stored frozen (−18 °C) for up to six months before analysis. Samples (approximately 100 g) were homogenised using a commercially available homogeniser (8,000 rpm for 20 s on a Retsch Grindomix GM200, Retsch GmbH & Co., Germany). Frozen samples were always thawed overnight at 4 °C prior to homogenisation. Samples were homogenised cold (<10 °C) and analysed on the day of homogenisation at room temperature (approx. 24–25 °C) (Cynkar et al., 2004; Cozzolino et al., 2005).

2.2. Reference analysis

The samples were analysed for calcium (Ca), potassium (K), magnesium (Mg), manganese (Mn), phosphorus (P), iron (Fe) and sulphur (S) after acid digestion using Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES), performed by the Waite Analytical Services, School of Agriculture and Wine, University of Adelaide. Samples were digested with nitric acid and hydrochloric acid (http://www.adelaide.edu.au/was/). All analysis were done in duplicate and expressed as mg per Kg. Electric conductivity (EC) was measured using an Orion Portable pH-Meter (Model 250A, Thermo-Orion, USA). Measurements were taken in duplicate by directly immersing the pH electrode in the homogenate at room temperature (ca. 22 °C).

2.3. Spectral and chemometric analysis

Grape homogenate samples were scanned in reflectance mode (400–2500 nm) using a scanning monochromator FOSS NIRSystems6500 (FOSS NIRSystems, Silver Springs, MD, USA). Spectral data collection was made using Vision software (version 1.0, FOSS NIRSystems, Silver Spring, USA). Samples were scanned in a rectangular cuvette with a 10 mm path-length. The spectrum of each sample was the average of 32 successive scans (1050 data points per scan) (Cozzolino et al., 2005).

Calibration models ($n = 120$) for the measurement of the elements and EC were performed using partial least squares regression (PLS) (The Unscrambler software, version 9.7, CAMO, ASA, Norway) using samples collected during the 2009 vintage (1100–2500 nm wavelength range). Calibration models were developed using full cross validation and the number of terms in the PLS calibration models were determined by the PRESS (prediction residual error sum of squares) function in order to avoid overfitting of the models (Naes et al., 2002). The PRESS value is a statistical parameter that helps to know how well a calibration model can predict the level of analytes omitted during cross-validation. It was calculated from the prediction errors in cross-validation and plotted as a function of the number of factors used in the PLS calibration. The PLS method is a soft-modelling method (Wold et al., 2001; Naes et al., 2002) for constructing predictive models when the factors are many and highly collinear and allows a model to be calculated that was tested on external samples observing its prediction ability.

The predictive ability of the NIR calibration models developed was demonstrated using an independent validation set. Validation of the PLS calibration models was carried out using samples from 2010 vintage ($n = 89$). Before PLS models were developed Multiplicative Scatter Correction (MSC) was used as transformation method in order to compensate for additive and/or multiplicative effects in spectral data (The Unscrambler software, version 9.7, CAMO, ASA, Norway) (Naes et al., 2002; Duckworth, 2004). The predictive ability of calibrations was assessed from the r^2, the standard error of prediction (SEP) and the ratio of standard error of prediction to standard deviation, RPD value (SD/SEP).

3. Results and discussion

The mean, range, standard deviation (SD) and coefficient of variation (CV) for the elements and EC in both the calibration and validation sets measured in red grape homogenates are shown in Table 1. The samples analysed varied considerably in elemental composition as shown by the range and CV. High CV was observed for Fe (46%) and Mn (81%) possibly due to the different varieties, regions (e.g. soil chemical and physical properties, agronomic and vineyard management) used. The variability in elemental composition and EC in both calibration and validation sets was considered suitable for developing NIR calibrations for this elements.

Statistics for the PLS calibration models developed for elements and EC using the NIR wavelength region (1100–2500 nm) and after MSC correction are shown in Table 2. Coefficients of determination in cross validation (R^2) and the standard errors of cross validation (SECV) obtained were for Fe (0.60 and 1.49 mg kg^{-1}), Mn (0.71 and 0.41 mg kg^{-1}), Ca (0.75 and 60.89 mg kg^{-1}), Mg (0.84 and 12.93 mg kg^{-1}), K (0.78 and 285.34 mg kg^{-1}), P (0.70 and 40.19 mg kg^{-1}), S (0.88 and 14.45 mg kg^{-1}) and EC (0.87 and 7.66 mS).

Table 3 shows the validation statistics (SEP, r^2, slope and bias) for the elements and EC measured in grape berries. Good predictions were obtained for EC (SEP: 13.4 mS), Ca (SEP: 79.27 mg kg^{-1}) and S (SEP: 34.5 mg kg^{-1}) while intermediate predictions were obtained for the other elements. The results showed that Mg and S might be measured by NIR reflectance spectroscopy in red grape homogenates.

The RPD values obtained for the calibration models were lower than three indicating that the PLS calibrations could be used only