Application of near infrared spectroscopy for quality assessment of grapes, wine and spirits

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Introduction

Near infrared spectroscopy (NIR) is utilised in a number of food industry applications and over the past decade has gained an increasing level of acceptance as an analytical tool in the wine industry. The most common use of NIR in winery laboratories has been for the determination of the alcohol content of wine. Almost 10% of more than 120 company members of the Interwinery Analysis Group in Australia routinely use NIR for measuring the alcohol concentration of wines. Whilst NIR has been successfully used for the determination of sugars in various matrices, wine has not been one of them. The determination of fermentable sugar in unfermented grape must and juice (range 160–260 g L^{-1}) has found only limited application because of the ease of established methods such as hydrometry and refractometry.

To further enhance the quality of its products, the wine industry requires practical methods for objectively evaluating the composition of grapes, wine and spirits, so as to reduce the reliance in this relatively traditional industry on subjective quality assessment by expert tasters. NIR techniques offer the potential for wineries to obtain analytical data which is, at present, only attainable through expensive and slow laboratory procedures which, as a result, have had only limited uptake.

The aim of this work was to assess the suitability of NIR for the practical measurement of grape and wine compositional parameters. The NIR instrument used for this investigation was a NIRSystems 6500 (NIRSystems Inc., Silver Spring, MD, USA) scanning spectrophotometer. Spectral data were collected over the range 400–2500 nm and calibration models developed using the NSAS software package (NIRSystems).

Grape berry compositional measurements

It is common wine industry practice to assess grape quality by measuring total soluble solids (predominantly sugars, measured as degrees Brix), acidity, by visual grading and also by tasting fruit and wines following fermentation. Acidity and soluble solids measures are not sufficient as quality indicators and it is not possible to adequately assess quality by tasting alone. The Australian wine industry is seeking rapid methods for measuring grape composition in order to determine optimum harvest dates, to identify areas in the vineyard with similar composition and for the assessment of grape quality for appropriate payment.

Existing laboratory analytical methods for the measurement of grape composition are not appropriate for the demands of wine production, where rapid results and low cost of analysis are of para-

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mount importance. Red grape anthocyanin pigment measurement,[1,2] and the recently developed glycosyl–glucose (G–G) assay,[1,3] which determines the total concentration of glycosylated secondary metabolites in a sample, are useful indicators of potential wine quality[4–7] but are currently not considered as serious options by the wider wine industry because of their high cost and slow turnaround time. The conventional method for colour analysis of red grape berries requires several steps:[1]

- homogenisation of the berry sample, followed by
- a one hour ethanol extraction step
- centrifugation
- adjustment of the extract to low pH with acid and
- a three hour waiting period before a spectrophotometric reading at 520 nm is taken.

The G–G method uses the same extraction procedure but involves a subsequent solid phase extraction step followed by acid hydrolysis and ultimately an enzymatic determination of released glucose (the G–G).

For the evaluation of the utility of NIR for measurement of berry components, samples of Semillon (110 samples) and Shiraz grapes (97 samples) were analysed for total soluble solids (°Brix), pH and G–G concentration. For the Shiraz data set ,colour values were also determined. Berry homogenates of the same samples were scanned by the near infrared spectrophotometer and the spectral data correlated against the reference laboratory data using partial least squares regression (PLS).

A strong predictive model was derived from the set of homogenates of Shiraz grape berries, for total soluble solids (r^2 = 0.998, *SEP* = 0. 19 °Brix), pH (r^2 = 0.99 1, *SEP* = 0.05) and importantly, colour (Figure 1, r^2 = 0.982, *SEP* = 0.05 mg g^{-1}). The strong correlation for °Brix was expected, given that the measurement of °Brix in juices by NIR has been well established. The measurement by NIR of G–G in homogenates of Semillon grapes achieved a comparable level of accuracy to that determined by the reference method (r^2 = 0.805, *SEP* = 0.1 µmol g^{-1}, Figure 2).

The ability of NIR to determine these compositional parameters on berry homogenates is encouraging. The possibility of extending the application of NIR from carefully homogenised grape samples to either whole grapes or minimally processed berries, would be a further advantage for the wine industry. This might then permit non-destructive analysis, as has been developed in other agricultural commodities such as, for example, sugarcane[8] and peaches.[9] Such a development could have a signifi-

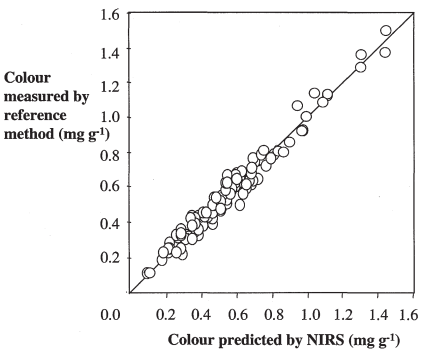

Figure 1. Relationship between colour values (determined as malvidin 3-glucoside pigment) obtained by NIR PLS calibration and by the standard laboratory method for 97 Shiraz berry homogenates (r^2 = 0.982, *SEP* = 0.051 mg g^{-1}).

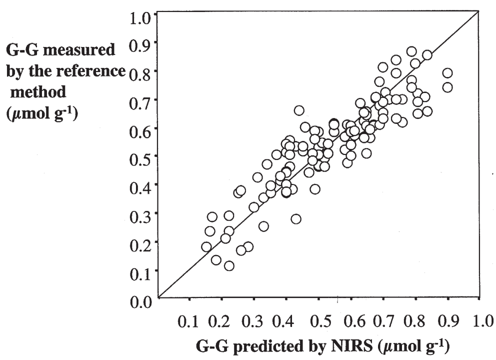

Figure 2. Relationship between (G–G) values obtained by NIR PLS calibration and by the standard laboratory method for 110 Semillon berry homogenates (r^2 = 0.805, *SEP* = 0.1 mol g^{-1}).

cant impact on the industry as it could provide rapid assessment of the compositional quality of grapes whilst still on the vine. Any further development of small scale, cheap and portable instruments, would find enormous application in vineyards to monitor the quality of fruit.

Wine grade assessment

In the Australian wine industry there is extensive use made of expert, experienced wine tasters to evaluate overall wine quality for processing decision making, particularly blending decisions, and for identifying suppliers of high quality grapes. In addition, an important aspect of the industry in Australia is the system of wine shows, where producers will enter wines for judging in a competition. In these shows it is common for three expert tasters to assess a set of submitted wines of a particular grape variety or wine style. The identity of the wines is masked and each judge assesses the wines in isolation, giving a quality score out of a maximum of 20 points.

NIR methods may have potential to assist winemakers in the task of quality assessment. In evaluating NIR for this purpose, wines were obtained from a wine show, scanned and the quality scores which were assigned to the wines were related to the spectral data. The correlations determined using multiple linear regression were promising, with coefficients of determination ranging from: 0.69, for a set of 18 red wines; 0.78, for a set of 25 white wines; and 0.99, for nine fortified sweet wines. For the fortified wines, the wavelengths used for the calibration indicated that the alcohol and sugar concentration may have been important quality determining factors. In this preliminary assessment, only relatively small numbers of samples were scanned and more sophisticated sensory assessments will be carried out on larger data sets in future experiments.

This application could provide a rapid assessment or pre-screening tool to add to the range of analyses available to winemakers. For example, it could allow preliminary blend allocation of large numbers of batches of wines prior to sensory assessment.

Winemakers may be able to develop 'profiles' for their blends as in-house NIR calibrations.

Nitrogen nutrient status and protein concentration of grapes

A common issue in commercial winemaking is the nutrient requirements of yeast. Wine yeasts require sufficient concentration of nitrogenous compounds in juice—approximately 250 mg L^{-1} yeast assimilable nitrogen (YAN)—to be able to carry out the fermentation to completion without producing off flavours. It is of interest to winemakers to be able to measure the YAN value in juice before inoculation of yeast. Current methods for determining this are either inaccurate, or else relatively slow and expensive.

A further industrial problem for white wine production is the susceptibility of some wines to the development of a protein haze. Soluble protein can aggregate and precipitate in bottled wines as a result of storage or due to exposure to elevated temperatures. The removal of these proteins in wines is relatively simple, but non-specific, expensive and detrimental to flavour. Early prediction of susceptibility to protein haze by rapid analysis of grapes or wine would be desirable.

Both of these applications have been assessed in preliminary experiments and the NIR data obtained to date appear promising. Calibrations achieved have resulted in coefficients of determination from 0.7 to 0.9 and indicate that NIR might be appropriate for winemaking production purposes. Further investigation will establish the appropriateness of NIR for these analyses.

Methanol concentration of grape spirit

Grape spirit is produced by distillation of wine or wine/grape derived process waste and is used in the production of fortified wines. The methanol concentration in the final product must be minimised to comply with food regulations and operating continuous stills can be difficult without rapid methanol analysis.

Samples of grape spirit containing methanol spanning the range 0.02 to 4.85 g L^{-1}, as previously analysed by gas chromatography (GC), were scanned and the spectra correlated with the reference data. A coefficient of determination of 0.989 was achieved, with a standard error of prediction of 0.13 g L^{-1} (Figure 3). When a number of other samples of spirit from different distillation plants were scanned, some bias was observed, which will be investigated further. These results show the potential of NIR to replace the current analysis by GC with monitoring by NIR, potentially on-line.

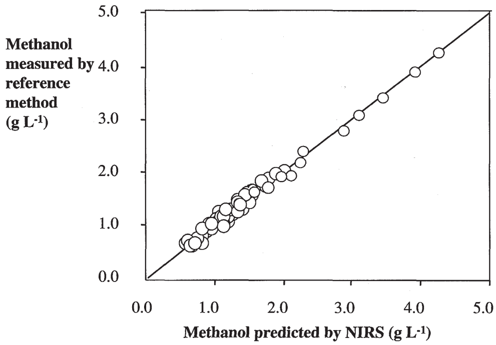

Figure 3. Relationship between methanol values obtained by NIR PLS calibration and by the standard gas chromatography method for 46 spirit samples obtained from a continuous still (r^2 = 0.989, *SEP* = 0.13 g L^{-1}).

Conclusion

This preliminary evaluation of the applicability of NIR for grape and wine analysis has shown that the technique has considerable promise and may have immediate application in the wine industry. NIR has the potential to dramatically reduce analytical times and could mean a fundamental change in the ability of winemakers and grape growers to assess the quality of their product.

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