Predicting malting quality in whole grain malt compared with whole grain barley by near infrared spectroscopy

Cassandra K. Black and Joseph F. Panozzo

Agriculture Victoria - Horsham, Victorian Institute for Dryland Agriculture, Private Bag 260, Horsham, 3401 Australia

Introduction

Near infrared (NIR) reflectance technology is a non-destructive, cost effective and rapid tool for simultaneous prediction of multiple constituents in agricultural products. In southern Australia, NIR technology is currently implemented to streamline the breeding of new, improved cultivars of malting barley.[4] Constituents of particular interest to the malting and brewing industry include hot water extract, diastatic power, free α-amino nitrogen (FAAN), soluble protein, wort β-glucan and β-glucanase. After harvest, the barley requires approximately two months of post-harvest maturation to break dormancy and allow the assessment of brewing attributes. Post-harvest dormancy in barley is the main contributor to delays in providing quality data to the breeder for the selection of superior malting quality breeding lines before the next sowing season (a four-month period). NIR calibrations developed on whole grain barley, before the grain was malted, would allow breeding lines to be evaluated for malting quality immediately after harvest.

The aim of this study was to determine the applicability of NIR spectroscopy in predicting malting quality of whole grain barley as compared with whole grain malt.

Materials and methods

Barley samples

The barley-breeding programme at the Victorian Institute for Dryland Agriculture generously supplied the barley samples. Thesamples represented an array of breeding generations grown at various sites throughout Victoria in 1999. The barley samples were tested by NIR before and after they were malted and then analysed for the various quality constituents.

Laboratory reference methods

The barley samples were malted[3] and analysed for hot water extract according to a small-scale version of the European Brewing Convention (EBC) fine grind method (grist : liquor ratio of 10 g : 70 mL).[2] Malt samples were ground on an FN3100 Mill (Falling Number, Stockholm, Sweden) to pass a 0.8 mm sieve and analysed for diastatic power[1] and β-glucanase according to the Megazyme method (Megazyme, Australia). Wort from the hot water extract was analysed for FAAN using the ninhydrin method;[3] soluble protein using the Dumas combustion method on a CNS-2000 (Leco Corporation, St Joseph, MI, USA) and wort β-glucan using the Megazyme method (Megazyme Australia).

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NIR analysis

Instrumentation

Reflectance spectra, log (1/*R*), were collected on a Model 6500 monochromator (NIRSystems, Silver Springs, MD, USA) equipped with a transport module and a standard coarse NIR sample cell. Spectra were recorded across a range of 400–2498 nm with 2 nm wavelength increment. Diffuse reflectance readings off a ceramic tile were referenced before and after each sample scan. Both barley and malt samples were equilibrated to 21°C for 24 hours prior to analysis.

Math treatment

The spectra were first corrected for scatter with standard normal variate (SNV) and detrending and then a mathematical treatment of second order derivative with gap and smooth sizes of five and five data points, respectively, was applied.

Calibration development

The spectral population was structured to lie within three Global H units. The calibration set was optimised with a neighbourhood *H* value of 0.3. Calibrations were developed using a modified partial

Table 1. Statistical data of near infrared calibration and validation samples for malt quality constituents of whole grain barley and malt.

	Calibration Set					Validation Set			
Quality Parameter	N^a	Range	No. of Terms	$R^{2\,b}$	SEC^c	N^a	Range	$R^{2\,b}$	SEV^d
Whole grain barley set									
Hot water extract (%)	277	77–87	7	0.87	0.6	131	76–81	0.78	1.1
Diastatic power (WKE)	279	179–549	5	0.57	45	131	225–545	0.39	57
FAAN (mg L^{-1})	263	92–228	5	0.54	16	131	116–239	0.10	31
Soluble protein (%)	201	4–6	5	0.60	0.2	131	4–6	0.01	0.5
Wort β-glucan (mg L^{-1})	267	0–1089	9	0.77	104	131	0–760	0.25	240
β-Glucanase (units kg^{-1})	276	297–868	7	0.60	66	131	322–788	0.02	135
Whole grain malt set									
Hot water extract (%)	276	77–87	7	0.89	0.6	131	76–81	0.76	1.0
Diastatic power (WKE)	279	179–549	8	0.75	35	131	225–545	0.54	54
FAAN (mg L^{-1})	268	92–228	9	0.89	8	131	116–239	0.63	17
Soluble protein (%)	203	4–6	9	0.79	0.2	131	4–6	0.53	0.3
Wort β-glucan (mg L^{-1})	268	0–1089	9	0.83	93	131	0–760	0.51	165
β-Glucanase (units kg^{-1})	271	297–868	8	0.70	56	131	322–788	0.47	97

[a] Number of samples
[b] Coefficient of determination
[c] Standard error of calibration
[d] Standard error of validation

least squares (MPLS) algorithm using a cross-validation technique. ISI software V 4.01 (Infrasoft International, Silver Springs, MD, USA) was used for all data processing.

A population of 131 barley samples from separate trials of the 1999 harvest was used for validating the performance of calibrations.

Results and discussion

The NIR calibration and validation statistics for each constituent are presented in Table 1. The hot water extract value indicates the concentration of fermentable sugars in the malt. Near infrared (NIR)

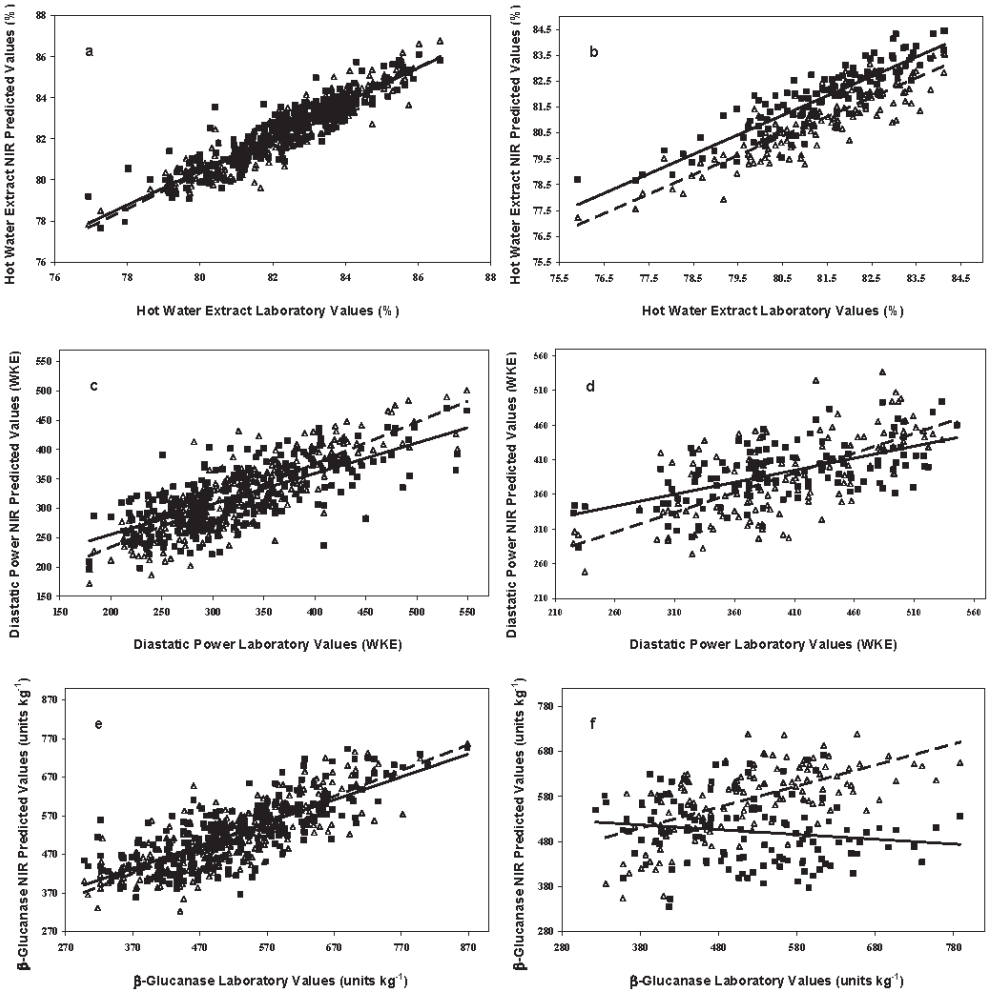

Figure 1. Scatter plots of the laboratory reference data and NIR predicted values for three constituents for whole barley and whole malt samples. (a) Hot water extract, calibration set; (b) hot water extract, validation set; (c) Diastatic Power, calibration set; (d) Diastatic Power, validation set; (e) β-Glucanase, calibration set; and (f) β-Glucanase, validation set (barley samples, △ malt samples).

predicted hot water extract values of the calibration samples were highly correlated with the laboratory reference data for both whole grain barley ($R^2 = 0.87$) and whole grain malt ($R^2 = 0.89$), and were associated with low standard errors of calibration (0.6 and 0.6, respectively). The validation data for hot water extract reflected those of the calibration samples, displaying good correlations and low standard errors (Table 1). Scatter plots of the laboratory reference data and the NIR predicted values of calibration and validation barley samples are presented in Figure 1(a) and 1(b). The data in this study are in agreement with findings of other researchers and this constituent has been routinely analysed by NIR for the past three years on whole grain barley to aid in the screening of early generation lines in southern Australian barley breeding programmes.[3,4]

Diastatic power is the ability of the enzymes present in the malt to convert starch to fermentable sugars.[1] NIR predicted values for diastatic power were moderately correlated to the laboratory reference values ($R^2 = 0.57$) for calibrations developed for whole grain barley [Table 1 and Figure 1(c)]. Validation statistics for diastatic power indicate a weak relationship between the NIR predicted values and the reference data [Table 1 and Figure 1(d)]. However, the size of the standard error of validation may suggest that NIR analysis could be useful for classification of early generation barley cultivars into high or low groups. In contrast, high correlation was observed between NIR predicted values and laboratory method for whole grain malt ($R^2 = 0.75$). Calibrations developed on whole grain malt are currently used for the evaluation of diastatic power in lines pre-selected with the aid of whole barley calibrations.

Soluble protein, FAAN, wort β-glucan and β-glucanase are complex malting constituents that influence the production of beer during the brewing process. Calibrations for these constituents, developed on whole grain barley, displayed a reasonably good relationship between the NIR predicted and laboratory reference values [Table 1 and Figure 1(e)]. Unexpectedly, this relationship was not confirmed by statistics observed for the validation samples (Table 1). The scatter plot of the laboratory reference data and the NIR predicted data for the constituent β-glucanase is depicted in Figure 1(f).

Calibrations developed on whole grain malt for soluble protein, FAAN, wort β-glucan and β-glucanase had high values for the coefficient of determination ($R^2 > 0.70$) and were associated with low standard errors of calibration (Table 1). The statistics observed for the validation samples were in agreement, displaying acceptable correlations with low standard errors (Table 1). Calibrations developed for these complex constituents on whole grain malt are suitable for the evaluation of early to mid-generation barley lines from a breeding programme.

Conclusion

NIR calibrations developed on whole grain barley for hot water extract display similar precision and accuracy as calibrations developed on malted grain. The validation data for diastatic power indicated a weak relationship between NIR predicted values and reference values, therefore a two step operation was employed. The calibration developed on whole grain barley was used to categorise early generation barley samples into low–high groups. The selected samples of interest were malted and the calibration developed on malted grain applied. The gain is in the reduced number of samples going through the lengthy process of micro-malting. The validation data for soluble protein, FAAN, wort β-glucan and β-glucanase demonstrated that the calibrations developed on whole grain barley could not be applied to the analysis of these constituents. This can be explained by the complex nature of these constituents. The unmalted barley has proteins and starches in the storage form. The composition of barley is modified by the action of enzymes throughout the steeping and germination stages and by heating during the kilning stage of the malting process.

Calibrations developed for hot water extract, diastatic power, soluble protein, FAAN, wort β-glucan and β-glucanase on malted barley are suitable for the evaluation of early to mid-generation

barley lines from a breeding programme, although there is the added expense of micro-malting the samples.

The ability to apply barley and malt calibrations to different generations is an advantage to a barley breeding programme that requires thousands of samples to be assessed each year.

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