Developing wort calibrations on a FOSS XDS rapid liquid analyser

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Introduction

Quality improvement in malting barley varieties involves the analysis of many physical and chemical parameters. NIRS has long been used to evaluate the quality of barley from breeding programs[1,2] and for derived products such as malt, wort and beer,[3–6] because of its ability to predict multiple traits rapidly and simultaneously. Malt wort calibrations for soluble nitrogen, malt extract, free amino nitrogen and fermentability have been developed over several seasons (2003–2007) using a Foss-NIRSystems 6500 spectrometer in transmittance mode. These predicted parameters have assisted in selecting lines in early generations of the breeding program by providing additional information that would otherwise not have been tested with the amount of available sample. More recently a new Foss-NIRSystems XDS instrument has been purchased with dedicated liquid analysis capability. This study investigates techniques to utilise the existing NIRS6500 spectral database and calibrations for soluble nitrogen and malt extract with a Foss-NIRSystems XDS Rapid Liquid Analyser (XDS-RLA).

Materials and methods

Eighty one barley samples, consisting of current Australian varieties and advanced crossbreds, were obtained from the 2008 season crop variety testing trials grown at four diverse locations in Western Australia. Five hundred-gram cleaned samples retained over a 2.2 mm screen were micromalted in a Joe White Maltings Systems Micromalter (Joe White Malting Systems, Adelaide, Australia) using a standard program.[7] Wort samples were produced by the congress mash program (European Brewing Convention)[8] and included the analysis of hot water extract (method 4.5.1) and malt soluble nitrogen (method 4.9.3). Freshly prepared worts were scanned (32 scans) in transmittance mode (400–2498 nm) in a 2 mm pathlength cuvette on a Foss-NIRSystems 6500 spectrometer (Foss-NIRSystems, Laurel, MD, USA) at room temperature, approximately 22°C and on a Foss-NIRSystems XDS Rapid Liquid Analyser, with equilibrated cuvette temperature at 30°C. Data from seventeen samples were used to update the existing calibration library (NIRS6500), and for instrument standardisation (spectral matching between instruments). Standardisation was evaluated using two techniques, single sample standardisation (SSS) and multiple sample (MSS) standardisation. In SSS, an averaged spectrum produced from each set of seventeen spectra scanned on both instruments, was used to generate a difference spectrum correction (standardisation file),

Table 1. Composition of calibration and validation sets.

Trait	Calibration set				Validation set			
	n	Range	Mean	*SD*	*n*	Range	Mean	*SD*
Soluble Nitrogen	702	0.375–0.868	0.575	0.09	64	0.445–0.832	0.613	0.09
Malt Extract	1554	71.3–84.4	79.1	2.34	64	78.5–83.1	81.0	0.95

that was then applied to other XDS-RLA (host instrument) spectra to match NIRS6500 (master instrument) spectra. In MSS, the seventeen individual spectra scanned on both instruments were used to correct for differences in wavelength shift and photometric response, using a quadratic formula and linear slope adjustment at each wavelength for deriving the standardisation file. The remaining sixty four wort spectra were used as an independent validation set for evaluating the two standardisation techniques and prediction performance on both instruments. Spectral acquisition, analysis, standardisation and calibration development were carried out using ISIscan v2.85 and WinISI ver4 software (Infrasoft International LLC, State College, PA, USA). Table 1 shows the composition of the calibration and validation sets.

The validation set range and standard deviation for soluble nitrogen was similar to the calibration set, while for malt extract the range was narrower and with a higher average.

Results and discussion

Standardisation

Transmittance spectra showed regions where the detector response was saturated (Figure 1) including large differences in the peak heights in the water and combination band regions.

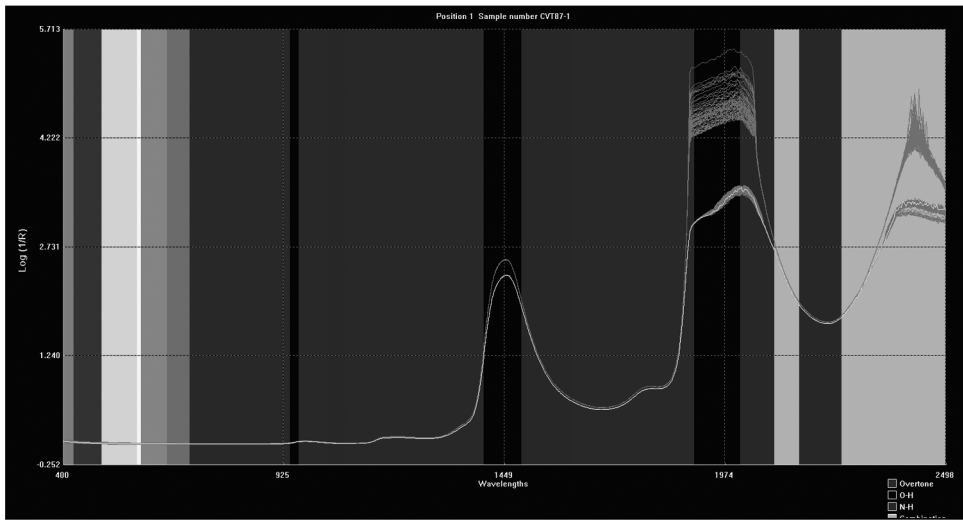

Figure 1. Wort spectra from NIRS6500 (lower) and XDS-RLA (upper).

Table 2. Standardisation comparison between NIRS6500 and XDS-RLA.

RMS(*C*)	Unstandardised	SSS	MSS
Seg. 1 (400–1098 nm)	383	97	91
Seg. 2 (1100–1850 nm)	10,613	499	498

RMS(*C*): bias corrected root mean square.

These are due to the strong absorption of water at higher wavelengths. This effect could be reduced by using a narrower path length cell, however this investigation was limited to using a 2 mm cuvette. Adjacent regions showed some variability within and between instruments, likely due to the low scattering effect of the medium. Peak displacements through temperature differences were not apparent. Both instrument specifications have an upper detector limit of about three absorbance units (AU), however some non-linearity can occur above 1.5 AU. Instrument standardisation was carried out using complete spectra, and evaluated with the "Contrast Spectra" program, excluding the 1850–2498 nm region where detector saturation was most apparent. Results showed that both SSS and MSS techniques produced similar and acceptable results [criteria <700 RMS(C)] on the validation set (Table 2).

The result for MSS is interesting, given that the correlation and slope values between individual instrument wavelengths were low, suggesting that only a bias adjustment was necessary.

Calibration Optimisation and Validation Performance

A number of strategies were tested to optimise calibrations, including selecting reduced wavelength ranges, excluding regions based on absorbance limits (<1.5, <2.0, <2.5, <3.0 AU), and different mathematical pre-treatments (data not shown). The best calibrations were achieved using modified PLS regression, SNV and detrend scatter correction and 1,10,10,1 derivative math treatment, incorporating a repeatability (REP) file and limiting wavelength regions to levels <2 AU and >850 nm (Table 3).

The REP file greatly improved calibration robustness by reducing the leverage of calibration coefficients in regions where there was high residual spectral variance. Similar validation performance was achieved with standardised host XDS-RLA spectra compared with master

Table 3. Prediction statistics for the validation set.

Statistics	Soluble nitrogen			Malt extract		
	NIRS6500	XDS-RLA (SSS)#	XDS-RLA (MSS)#	NIRS6500	XDS-RLA (SSS)#	XDS-RLA (MSS)#
SEP(*C*)	0.03	**0.02**	0.04	0.32	0.70	**0.40**
Bias	–0.01	**0.02**	0.02	0.35	0.10	**0.07**
Slope	1.13	**1.01**	1.43	0.91	0.67	**0.98**
RSQ	0.92	**0.96**	0.81	0.89	0.62	**0.82**
RPD	3.0	**4.5**	2.25	3.0	1.4	**2.4**

standardised to NIRS6500 instrument. Best performance on XDS-RLA validation set indicated in bold.

NIRS6500, but the best standardisation technique varied between the two traits, suggesting that both techniques should be evaluated to determine the optimum.

Conclusion

An existing wort spectral database was successfully utilised on a different model NIRS instrument with careful attention to standardisation and calibration optimisation. Different standardisation techniques should be evaluated to determine the best performance. A wider range of the NIR transmittance spectrum could be utilised with a narrower path-length cuvette, with the potential to improve calibration accuracy. Future dedicated calibrations wholly developed on the XDS-RLA should be more accurate, because this instrument has precise temperature control.

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