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Prediction of starch pasting properties in barley flour using ATR-MIR spectroscopy

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ABSTRACT

The objective of this study was to evaluate the feasibility of using attenuated total reflectance (ATR) mid infrared (MIR) spectroscopy to predict starch pasting properties in barley flour samples. A total of 180 barley flour samples sourced from the University of Adelaide germplasm collection, harvested over three seasons (2009, 2010 and 2011) were analysed using both ATR-MIR and the rapid visco analyser (RVA) techniques. Calibrations ($n = 100$) were developed using partial least squares (PLS1) regression and full cross validation. The coefficient of determination (R^2) and the standard error in cross validation (SECV) were 0.74 (SECV = 875 RVU) for peak viscosity (PV), 0.63 (SECV = 561 RVU) for trough (THR), 0.80 (SECV = 173 RVU) for breakdown (BRK), 0.74 (SECV = 126 RVU) for setback (STB), 0.77 (SECV = 679 RVU) for final viscosity (FV), and 0.73 (SECV = 0.57 s) for time to peak (TTP). The RPD values (SD/SEP) from the validation indicated that only BRK can be accurately predicted (RPD = 4). We have demonstrated that ATR-MIR spectroscopy has the potential to significantly reduce analytical time and cost during the analysis of barley flour for starch pasting properties.

1. Introduction

Starch pasting properties are influenced primarily by amylose and amylopectin contents (Batey, 2007; Booth & Bason, 2007). Analytical methods currently used to determine pasting properties in cereals and starchy foods include instrumental methods such as differential scanning calorimetry (DSC) (Mestres, Matencio, Pons, Yajid, & Fliedel, 1996) and the rapid visco analyzer (RVA) (Batey, 2007; Booth & Bason, 2007; Haase, Mintus, & Weipert, 1995; Kim, Wiesenborn, Orr, & Grant, 1995; Stevens & Elton, 1971). Instruments such as the RVA are used also in the routine analysis of cereals (wheat, barley) to determine the effects of rain damage on grain quality at the delivery point (Bason, Ronalds, Wrigley, & Hubbard, 1993; Batey, 2007; Booth & Bason, 2007; Shewayrga, Sopade, & Jordan, 2012; Zhou & Mendham, 2005).

Several authors have also reported the use of RVA as a method for determining barley and malt quality in routine analysis or as selection tool in breeding programmes (Bason et al., 1993; Batey, 2007; Booth & Bason, 2007; Zhou & Mendham, 2005). Recent studies have also reported that relationships between starch pasting properties, measured using the RVA, and malting quality parameters such as hot water extract (HWE) in barley (Bason et al., 1993; Batey, 2007; Booth & Bason, 2007; Zhou & Mendham, 2005). However, in order to use the RVA method in routine laboratory analysis and in breeding programmes, this method requires some pre-processing of the sample prior analysis (e.g. grinding). Therefore this method can be time consuming and laborious when a large number of samples needs to be analysed.

In recent years, the combination of novel instrumentation and chemometric techniques has resulted in the development of rapid analytical methods relating multivariate data analysis combined with either near infrared (NIR) or mid infrared (MIR) spectroscopy (Cozzolino, 2009; Karoui, Downey, & Blecker, 2010; Stuart, 1996; Subramanian & Rodrigez-Saona, 2009). Despite the apparent advantages of attenuated total reflectance (ATR) methods over transmission based applications this technique is still not widely employed (Barron & Rouau, 2008; Subramanian & Rodrigez-Saona, 2009; Wilson & Tapp, 1999). Thus, the driving force behind exploring ATR-MIR spectroscopy for the analysis of grains and flours is the availability of simple and small amount of sample required for analysis that makes this technique as an ideal tool for screening or phenotyping of samples in breeding or routine analysis.

Few studies have reported the use of infrared (IR) spectroscopy to predict starch pasting properties in starchy foods and cereals, mainly of those were achieved using NIR spectroscopy (Bao, Cai, & Corke, 2001; Delwiche, McKenzie, & Webb, 1996; Juhasz, Gergely, Gelencser, & Salgo, 2005; Lu & Sheng, 1990; Meadows & Barton, 2002; Shashikumar, Hazelton, Ryu, & Walker, 1993; Windham et al., 1997). Although the use of ATR-MIR spectroscopy has been

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reported before as method to determine starch, protein, fatty acids and lipids content in ground cereals products (Gangidi, Proctor, & Meullenet, 2002; Iizuka & Aishima, 1999; Karoui et al., 2010; Kim, Himmelsbach, & Kays, 2007; Millar, Robert, Devaux, Guy, & Maris, 1996; Shao, Cen, He, & Liu, 2011; Subramanian & Rodrigez-Saona, 2009; van Velzen, van Duynhoven, Pudney, Weegels, & van der Maas, 2003; Wilson & Belton, 1988; Wilson, Kalichevsky, Ring, & Belton, 1987), no references were found on the use of this technique to predict starch pasting properties.

The objective of this study was to evaluate the feasibility of using attenuated total reflectance (ATR)-mid infrared (MIR) spectroscopy to predict starch pasting properties, measured using the rapid visco analyser (RVA) method, in barley flour samples, as a potential screening tool for novel genotypes in breeding programmes.

2. Materials and methods

2.1. Samples

In total, one hundred and eighty ($n=180$) barley samples (*Hordeum vulgare* L.) were sourced from commercial varieties and breeding lines from the University of Adelaide germplasm collection (Barley Breeding Programme). Commercial samples were sourced from Flagship ($n=5$), Commander ($n=5$), Schooner ($n=3$), Gairdner ($n=5$), Navigator ($n=10$), Buloke ($n=2$), Vlamingh ($n=2$), and VT Admiral ($n=10$) varieties. Details about the varieties used can be found on the Barley Australia website (http://www.barleyaustralia.com.au). Samples were collected from two localities in South Australia (Roseworthy and Charlick), two localities in Western Australia, and harvested in three consecutive years 2009, 2010 and 2011.

2.2. ATR-MIR measurements

Barley flour samples were scanned using a platinum diamond ATR single reflection sampling module cell mounted in a Bruker Alpha instrument (Bruker Optics GmbH, Ettlingen, Germany). The MIR spectra were recorded on OPUS software version 7.0 provided by Bruker Optics. The spectrum of each sample was obtained by taking the average of 64 scans at a resolution of 8 cm^{-1} and acquired between 4000 and 375 cm^{-1}, with a scanner velocity of 7.5 kHz and a background of 64 scans. The samples were hold against the ATR crystal using the pressure applicator or sample clamp mechanism supplied by the instrument manufacturer in order to assure that the same and constant pressure was applied for all samples. Duplicates of each sample were scanned twice (repacking) and the average ATR-MIR spectrum of each sample was used for further analysis. Air was used as reference background spectra. The ATR diamond surface was cleaned with ethanol (95% v/v) before each sample was scanned.

2.3. RVA analysis

Samples were milled using an Udy Cyclone Mill (Sweden) through a 0.8 mm screen, before RVA and ATR-MIR analysis. Ground barley flour samples (4.0 g of flour corrected using the moisture content of the sample, ±0.01 g) were slurried with distilled water (25.0 g as function of the amount of adjusted sample, ±0.1 g) in an aluminium can. The pasting properties of the slurries were determined with a RVA instrument (Tecmaster, Perten Instruments, NSW, Australia). The RVA test profile used was reported elsewhere (Cozzolino, Allder, Roumeliotis, & Eglinton, 2012; Cozzolino, Roumeliotis, & Eglinton, 2013). The properties calculated by the software TCW3 (Thermocline, Perten Instruments, NSW, Australia) were pasting viscosity (PV), trough (THR), breakdown (BRK), final viscosity (FV), setback (STB), time to peak (TTP), pasting temperature (PT) and peak area (PA) (Batey, 2007; Booth & Bason, 2007).

2.4. Data analysis

Spectra were exported from the OPUS software into The Unscrambler software (version X, CAMO ASA, Oslo, Norway) for chemometric analysis. Principal component analysis (PCA) was performed before partial least squares regression (PLS1) models were developed to determine any relevant and interpretable structure in the data, and to detect outliers (Brereton, 2000; Naes, Isaksson, Fearn, & Davies, 2002). Calibration models ($n=100$) between chemical compositional values and the ATR-MIR spectra were developed using the PLS1 regression method with full cross validation. The optimum number of terms in the PLS1 calibration models was indicated by the lowest number of factors that gave the minimum value of the prediction residual error sum of squares (PRESS) in cross validation in order to avoid overfitting in the models (Naes et al., 2002). Calibration statistics calculated included the coefficient of determination in cross validation (R^2) and the standard error of cross validation (SECV). The prediction accuracy of the calibration models was tested first by full cross validation using the SECV and the residual predictive deviation (RPD = SD/SECV) (Fearn, 2002; Williams, 2001). The calibration models developed were validated using the remaining samples ($n=80$). Statistics calculated included the coefficient of correlation (R), the standard error of prediction (SEP), slope and bias. The ATR-MIR spectral data was processed using the second derivative Savitsky-Golay (2nd derivative, 40 smoothing points, 2nd polynomial order) (Duckworth, 2004).

3. Results and discussion

Table 1 shows the descriptive statistics (mean, standard deviation, and range) for the RVA parameters and crude protein (CP) content in the set of barley samples analysed. The values obtained represent a wide range in composition due to the different commercial varieties and experimental lines analysed as indicated by the CP content. It is well known that collinearity in the spectral data is handled by the PLS algorithm but an important consideration with chemometric calibrations is collinearity in the analytical data (reference method), as this may result in surrogate calibrations that are actually based on the most dominant collinear analyte. Table 2 shows the Pearson correlation coefficients. High

Table 1
Mean, standard deviation, minimum, maximum and coefficient of variation of rapid visco analyser (RVA) parameters and crude protein content measured in barley flour samples.

	Mean	SD	Min	Max
CAL ($n=100$)				
PV (RVU)	1971.391	1597.977	204	5352
BRK (RVU)	1305.6	1209.68	65	3960
THR (RVU)	666.09	445.95	139	1793
FV (RVU)	1798.42	1478	102	5273
STB (RVU)	495.8	310.3	37	1387
TTP (min)	5.87	1.14	3.67	8.6
PT (°C)	76.9	3.4	69.6	84.75
CP (% dw)	11.8	2.3	8.5	18.3
VAL ($n=80$)				
PV (RVU)	1839.9	1554.3	132	5673
BRK (RVU)	1205.5	1170.0	39	4162
THR (RVU)	630.4	416.3	93	1793
FV (RVU)	1657.1	1429.5	69	5666
STB (RVU)	477.6	302.4	26	1625
TTP (min)	5.81	1.17	3.2	8.3
PT (°C)	76.65	3.76	67.35	84.7
CP (% dw)	11.7	2.2	8.5	16.9

Table 2
Correlation coefficients (Pearson $p < 0.05$) between rapid visco analyser (RVA) parameters and crude protein measured in barley flour.

	PV	BRK	THR	FV	STB	TTP	PT	CP
PV	1	0.98	0.91	0.97	0.80	0.83	0.40	−0.0001
BRK		1	0.84	0.98	0.81	0.88	0.44	−0.16
THR			1	0.83	0.73	0.67	0.27	0.05
FV				1	0.86	0.89	0.47	0.063
STB					1	0.83	0.49	−0.014
TTP						1	0.62	−0.11
PT							1	−0.16
CP								1

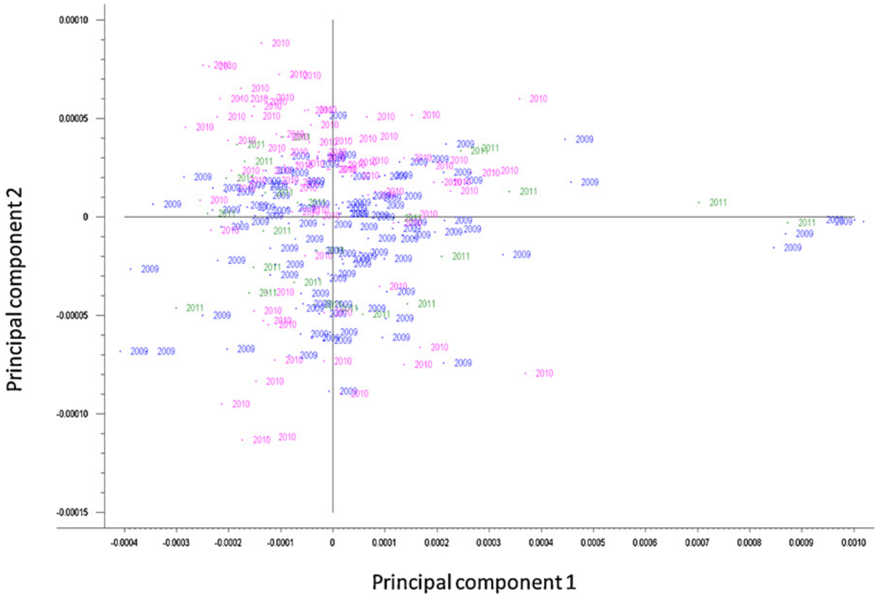

Fig. 1. Score plot of the first two principal components of barley flour samples analysed using attenuated total reflectance and mid infrared spectroscopy.

collinearity between the RVA parameters as indicated by positive and high Pearson correlations ($r > 0.75$; $p < 0.05$) between most of the RVA parameters was observed. Low and positive Pearson correlations were found between PT and most of the RVA parameters measured ($r < 0.50$). Low (positive and negative) Pearson correlations were found between the RVA parameters and CP content ($r < 0.20$).

Fig. 1 shows the score plot of the first two principal components explaining 91% of the spectral variation (PC1 86% and PC2 5% variation) of the barley samples analysed using the ATR-MIR method. The score plot derived from the PCA analysis did not show any clear separation between samples related to harvest or locality.

Statistics for the PLS calibrations developed for the RVA parameters using ATR-MIR spectra of the barley flour samples are shown in Table 3. The coefficient of determination (R^2) and the standard error in cross validation (SECV) were 0.74 (SECV = 875 RVU) for peak viscosity (PV), 0.63 (SECV = 561 RVU) for trough (THR), 0.80 (SECV = 173 RVU) for breakdown (BRK), 0.74 (SECV = 126 RVU) for setback (STB), 0.77 (SECV = 679 RVU) for final viscosity (FV), and 0.73 (SECV = 0.57 s) for time to peak (TTP). No useful calibrations were obtained for PT. More than 70% of the explained variance (as indicated by $R^2 = 0.70$) in the data set related with PV, BRK, STB, FV and TTP was explained by the PLS models based on the ATR-MIR spectra.

Table 3
Partial least squares (PLS1) calibration statistics for the prediction of rapid visco analyser (RVA) parameters measured in barley flour samples using attenuated total reflectance and mid infrared spectroscopy ($n = 100$).

	R^2	SECV	PLS terms	RPD	CV	
PV (RVU)	0.74	875	15	1.8	44.3	VRScr
THR (RVU)	0.63	561	7	0.7	84.2	NU
BRK (RVU)	0.80	173	10	6.9	13.2	Scr
STB (RVU)	0.74	126	6	2.5	25.4	VRScr
FV (RVU)	0.77	679	7	2.2	37.7	VRScr
TTP (min)	0.73	0.57	6	2.1	9.7	VRScr

The RPD value is a useful statistics to evaluate the ability of the PLS models developed to predict new samples. If the error in estimation for a constituent (SECV) is large compared with the spread in composition of that sample in the population (as SD), a relatively small RPD is obtained, therefore the ATR-MIR calibration models are considered not robust. The higher the RPD value the greater the power of the model to predict new samples. The RPD values obtained were 1.8 for PV, 0.7 for THR, 6.9 for BRK, 2.5 for STB, 2.2 for FV, and 2.1 for TTP. An RPD value greater than three is considered fair and recommended for screening purposes, while a RPD value greater than five is considered good for quality control (Fearn, 2002; Williams, 2001). However, the interpretation of the RPD values depends very much on the context and on the purpose of the measurement (Fearn, 2002; Williams, 2001). For breeding purposes, the RPD values obtained indicated that the PLS calibration models developed using ATR-MIR spectra can be used only for screening of BRK and rough screening of STB, PV and TTP starch pasting properties of novel lines or genotypes of barley.

The SECV and R^2 values generally indicate how well the equations will perform within the same population. However, the R^2 may not be a good indicator and some authors suggested the use of coefficient of variation (CV = SECV/mean), as the range in concentration could render R^2 values misleading. It is well known that the interpretation of the R^2 is dependent of the distribution of

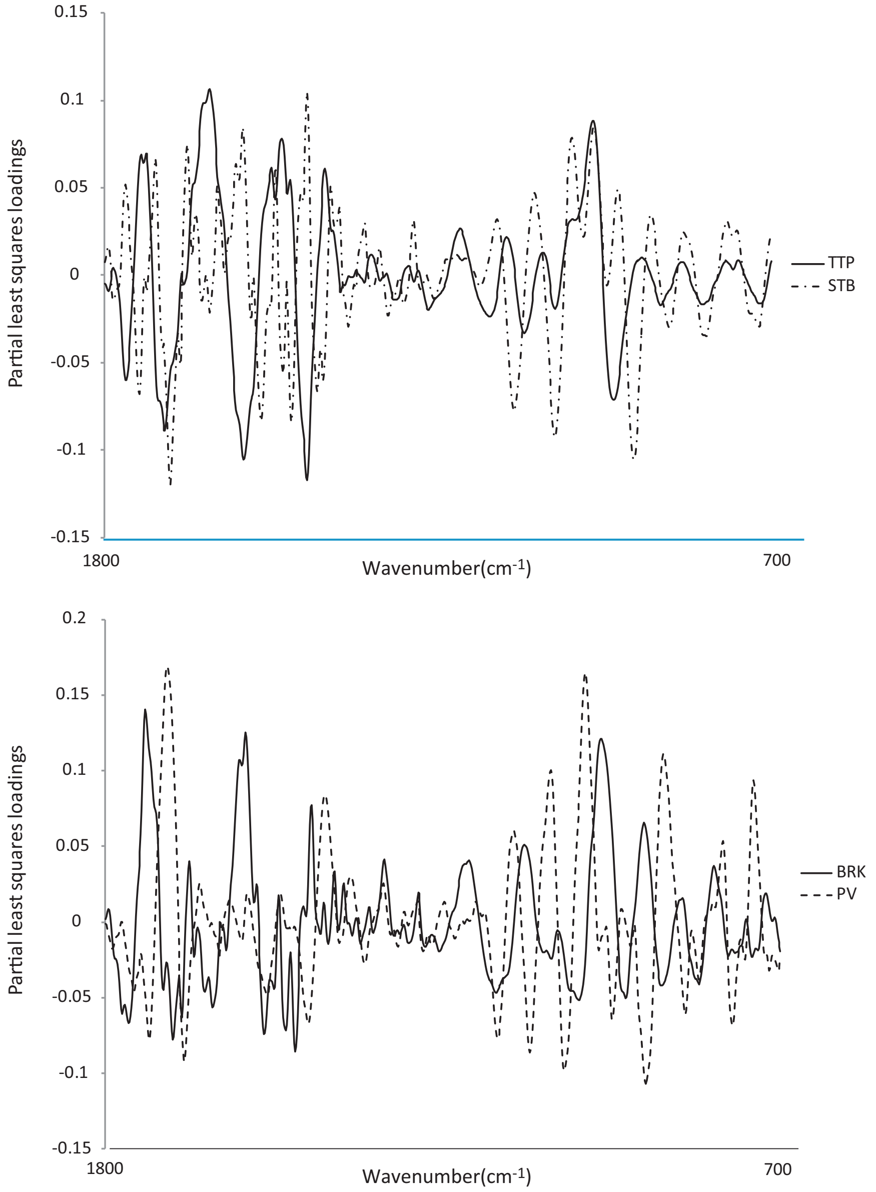

Fig. 2. Optimal partial least squares loadings used for the prediction of rapid visco analyser (RVA) parameters measured in barley flour samples analysed by attenuated total reflectance and mid infrared spectroscopy.

analytical values. Therefore, the magnitude and interpretation of the CV as a tool in evaluating calibration equations will depend partly on the source of data (distribution) and functionality. For example, CV values higher than 5% may accrue from the determination of the reproducibility of functionality parameters but in general CV values lower than 20% are considered adequate. Both BRK (CV = 13.2%) and TTP (CV = 9.7%) showed CV values lower than 20%, indicating the ability of such calibrations to predict functional parameters related to RVA starch pasting properties in barley flour.

Table 4 shows the validation statistics including the standard error of prediction (SEP), slope, bias and coefficient of correlation obtained using the validation set. The SEP indicates the variability in deviations of ATR-MIR predicted values and reference data, while the bias shows the average amount by which the results differ (Williams, 2001). In general, the SEP values encountered in this study were considered adequate for the prediction of BRK. On the other hand, very rough screening of samples for starch pasting properties can be achieved for PV, FV, and TTP (sorting for low, medium or high starch pasting values).

The regression coefficients (loadings) for the optimal PLS1 calibrations for BRK, STB, PV and TTP measured using the RVA are shown in Fig. 2. The characteristic MIR bands of starch are located at wavenumbers between 1010 and 1020 cm^{-1}, 1080 and 1150 cm^{-1}, associated with the coupled C—O and C—C stretching vibrations of the polysaccharide molecules. Structural carbohydrates (e.g. cellulosic compounds) were related to peak around 1240 cm^{-1},

Table 4
Partial least squares (PLS1) validation statistics for the prediction of rapid visco analyser (RVA) parameters measured in barley flour samples using attenuated total reflectance and mid infrared spectroscopy.

	n	*R*	SEP	Bias	Slope	RPD
PV (RVU)	75	0.73	1140	178	0.79	1.3
THR (RVU)	79	0.60	1060	265	0.59	1.0
BRK (RVU)	77	0.74	297	73.7	0.66	4.0
STB (RVU)	74	0.63	295	39.6	0.74	1.0
FV (RVU)	77	0.64	1306	455	0.69	1.0
TTP (min)	77	0.50	1.03	0.05	0.43	1.0

while starch can be associated with absorbance values located between 1184 and 951 cm^{-1} wavenumbers with a peak at 996 cm^{-1} associated with C—O and C—C stretching vibrations and C—O—H deformation (Goodfellow & Wilson, 1990; Van Soest, Tournois, De Wit, & Vliegenthart, 1995; Zhang & Yu, 2012). Positive peaks were observed for BRK, TTP and PV at wavenumbers between 1050 and 1070 cm^{-1}, associated with amylose and amylopectin (Goodfellow & Wilson, 1990; Van Soest et al., 1995; Zhang & Yu, 2012). Negative peaks were observed at wavenumbers between 960 and 990 cm^{-1} also associated with amylose (Goodfellow & Wilson, 1990). The influence of this loadings suggested that calibration for BRK, TTP and PV were using similar MIR information.

4. Conclusions

The practical implications of this study showed that ATR-MIR spectroscopy confers valuable benefits for the grain industry and in particular for breeding. These results showed that ATR-MIR spectroscopy is capable of measuring starch pasting properties evaluated using the RVA method. Rapid quality assessment methods are of particular importance to breeding programmes (high throughput screening). Screening samples using ATR-MIR spectroscopy will eliminate time consuming and expensive preprocessing when large amount of samples are analysed. Infrared spectra can effectively represent a 'fingerprint' of the sample being analysed and can be used to simplify methods, reduce analytical times and used as phenotype trace during breeding. These advantages, together with the ability to provide detailed chemical information and simultaneously measure several analytes are the attractive of using such methods. Compared to traditional laboratory methods, spectroscopic techniques often give new and better insight into complex problems by measuring a great number of chemical compounds at once. These methods are attractive due to their inherent features of versatility, flexibility, effectiveness and richness of information. Further, the technology offers the exciting prospect of potentially providing for the development of new applications of IR spectroscopy.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.03.001.

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