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Development of near infrared spectroscopic methods for monitoring major nutrient elements in sugar mill byproducts

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Introduction

The Australian sugarcane industry is geographically situated in close proximity to environmentally sensitive and World Heritage listed areas of the Great Barrier Reef Marine Park and the Wet Tropics. As a result, the Australian sugar industry is subjected to a high level of scrutiny with respect to nutrient application rates and associated nutrient runoff. The Queensland State Government passed legislation at the beginning of 2010 enabling it to regulate certain farming activities. In particular, the legislation was designed to minimise the impact of fertilisers and pesticides on the quality of run-off water entering the Great Barrier Reef lagoon by controlling maximum application rates on nearby land.

Figure 1. Typical sample of mill mud (left) and boiler ash (right).

Sugar mill byproducts are a valuable source of mineral nutrients and organic matter and their application to surrounding cane farms is a mutually beneficial practice for sugarcane growers and millers. It is estimated that the value of available nutrient inputs from mill mud and ash application across the industry is approximately $36M per year. Mill mud (Figure 1) is produced as a byproduct of a juice purification process known as clarification. During clarification, predominantly high molecular weight and/or insoluble impurities present in the juice such as gums, waxes and residual fibre particles are entrapped in a flocculated calcium phosphate system. A scum or mud forms during the process and is subsequently removed. This waste product is referred to as "mill mud" and contains significant amounts of calcium (approximately 878 kg Ca per 150 wet tonnes) and phosphorous (341 kg P per 150 wet tonnes)[1] and is often combined with boiler ash (Figure 1) prior to field application. Boiler ash is the residue remaining after burning bagasse (sugarcane fibre which has had sucrose removed) in the boilers to produce steam and contains significant amounts of potassium (296 kg K per 150 wet tonnes) and silicon (3600 kg per 150 wet tonnes)[1] (internal communication). The application rate of the byproducts back to the cane field can vary between 120 and 250 wet tonnes/ha depending on the region. Transportation of the byproduct from the mill to the cane field is usually by truck; Figure 2 shows a truck waiting to be loaded via a hopper at the sugar mill. A specifically designed mechanised applicator spreader is mounted on the tailgate of the truck in order to deposit the byproduct evenly between rows in the field (Figure 3).

At present, the nutrient content of these byproducts is not included in the determination of nitrogen and phosphorus levels applied to sugarcane farms under existing legislation. The research reported in this article has been designed to produce rapid, easy to use NIR spectroscopic methods for the prediction of nutrient elements: carbon (C), nitrogen (N), silicon (Si), phosphorus (P) and potassium (K) levels in mill mud and boiler ash. This information will likely be required in the future in order to ensure that sugarcane growers comply with all aspects of the Great Barrier Reef Protection Legislation.

Figure 2. Loading a truck with mill mud at the sugar mill.

While there is considerable literature precedent for carbon and nitrogen calibrations, there are theoretical issues regarding the potential to develop NIR calibrations for inorganic materials such as silicon, phosphorus

Figure 3. Mill mud application between rows of sugarcane in the field.

and potassium. This is because there are no absorption bands for such inorganic or mineral species in the NIR spectral region. However, the mill mud and boiler ash samples do contain sub-structures which can help us from an NIR perspective. Within mill mud samples, there are organic molecular structures within the sample matrix which may also form mineral complexes and/or inclusions from which secondary correlations may be possible. Within the boiler ash samples, Si, K and P will be predominantly present in their oxide forms, and these forms can induce changes in hydrogen bonding within the sample matrix. The research described here does not attempt to determine any specific reasons why NIR calibrations were successful for inorganic nutrient constituents. Future work is likely to explore this further as we seek to enhance the quality and robustness of the preliminary calibrations developed and described here. Additionally, the sampling approach taken has attempted to provide a broad range of constituent concentrations and has also been performed at multiple sugar mills to capture variability based upon differences in the cane supply and mill process conditions.

Chemical analysis

At the sugar mill, the traditional sampling method of these byproducts for analysis involves combining "small grabs" of byproduct from the production line across a particular time period (i.e. 24 h, a week or periodically over a month). The subsequent composite sample is mixed well and an appropriate subsample is used for analysis.

Samples for analysis are usually received frozen and are allowed to defrost before being sub-sampled for final analysis. Traditional analysis utilises standard chemical methods for C, N, Si, P and K. The defrosted subsamples are dried at 45°C for 48 h and subsequently ground to a particle size of less than 0.5 mm using a Culatti MFC micro-hammer mill (Kinematica AG, Lucerne, Switzerland). All analyses for the mill mud and boiler ash samples are performed in duplicate as a standard laboratory procedure.

Carbon and nitrogen concentrations are determined by the Dumas combustion method using an Elementar Vario Max CN analyser (Elementar Analysensysteme GmbH, Hanau, Germany) with a thermal conductivity detector. Phosphorus and potassium concentrations are determined by a nitric-perchloric acid digestion[2] followed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). A Varian Vista simultaneous ICP-AES (Varian Analytical Instruments, Walnut Creek, USA) is used with a Sturman–Masters double pass spray chamber and V groove nebuliser. Silicon concentration is determined using the dry ashing and alkali fusion method[3] which has been modified for ICP-AES detection.[4]

Traditional laboratory techniques provide high levels of accuracy and reproducibility for the individual sub-samples analysed. However, the sub-sampling method can easily fail to provide meaningful data for the "bulk sample" when very large volumes of product are produced with such diverse and complex matrices. Additionally, the traditional laboratory methods of analysis are time-consuming, taking approximately one week to provide results after sample receipt. Rapid analytical methods based on NIR technology are capable of overcoming many of these shortcomings as well as providing additional benefits such as increased throughput, decreased cost per unit analysis and permitting the generation of data in environments where traditional wet chemistry methods could not possibly be applied. In addition to the more common use of NIR instruments in the chemical laboratory, NIR systems can be developed to provide data in factory situations in real-time by developing appropriate sample preparation techniques and robust instruments.

Methods and materials

Seventy-eight mill mud and mill mud/boiler ash mixed samples were obtained from three different sugar mills in the Mackay region across the 2009 and 2010 crushing seasons. Samples for analysis were received frozen and were allowed to defrost before being sub-sampled twice. The laboratory results obtained for these samples using standard chemical methods of analysis are presented in Table 1. Standard errors of laboratory analysis (*SEL*) were determined in a previous study.[5]

NIR spectra were collected using a Foss XDS NIR spectrometer (Foss NIRSystems, Hillerød, Denmark) fitted with a Rapid Content Analyser. Each sample was scanned and absorbance readings were recorded over a wavelength range of 400–2500 nm, with 128 co-added scans being averaged to provide the final spectrum in each case. Spectral data pretreatments studied included truncating the raw spectra to 1130–2300 nm, converting raw spectra to the first derivative using a gap of zero and segment length of 4 nm, and applying the standard normal variate function (SNV) as shown in Figure 4.

Table 1. Laboratory data for the mill mud and mixed mill mud/boiler ash samples.

	Mill mud					Mixed mill mud/boiler ash				
	Min	Max	Mean	*SD*[a]	*SEL*[b]	Min	Max	Mean	*SD*[a]	*SEL*[b]
C	16.2	38.1	30.0	5.14	0.59	8.71	35.9	22.8	7.08	1.14
N	0.40	1.77	1.29	0.31	0.04	0.20	1.60	0.81	0.37	0.05
Si	3.59	29.3	13.5	4.38	1.01	5.45	27.2	18.1	6.78	2.02
P	0.42	2.01	1.30	0.34	0.06	0.24	1.51	0.85	0.38	0.15
K	0.16	0.46	0.27	0.06	0.02	0.26	0.85	0.59	0.14	0.05

[a]*SD*: Standard deviation of all mill mud and mill mud/boiler ash samples; [b]*SEL*: Standard error of laboratory analysis; All units expressed as percentage dry matter

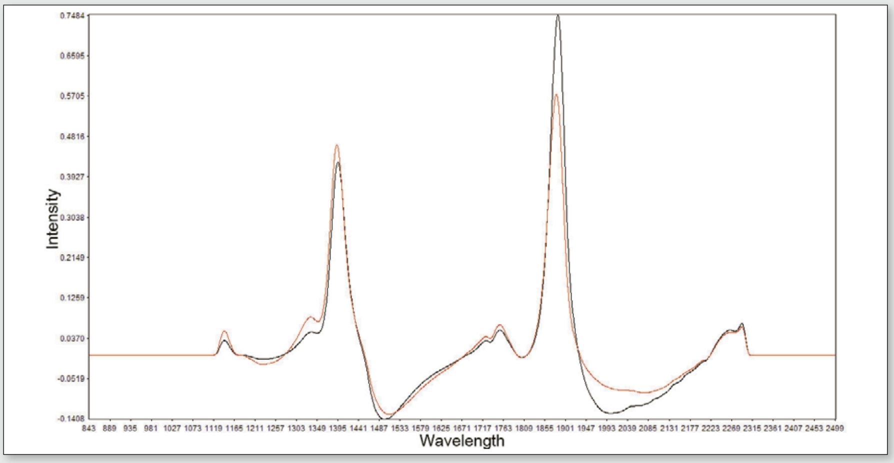

Figure 4. Overlay of typical examples of first derivative NIR spectra from mill mud (black) and mixed mill mud/boiler ash samples (red).

Calibration development

Regression models were constructed using partial least squares (PLS) and cross-validation methods within the Vision Software supplied with the instrument. Regression model properties for all nutrient calibrations are presented in Table 2 which reports the number of samples used (*n*), the number of principal components used, standard error of calibration (*SEC*), standard error of cross-validation (*SECV*), coefficient of determination for cross-validation (R^2_{cv}) and the residual predictive deviation (*RPD*) which is expressed as the ratio of *SECV* to the standard deviation. The *RPD* value was used to provide a crude evaluation of the performance of the models, with values greater than 2.5 considered adequate for analytical purposes.

The analysis of calibration performance was conducted by considering the set of five nutrient calibrations as two subsets, one containing C, N and P which are considerably higher in mill mud samples, and the other containing Si and K which are higher for the mill mud/boiler ash samples. The calibrations within the first subset (C, N and P) exhibited good levels of performance ($RPD \geq 4$) while the Si and K models performed slightly worse, having *RPD* values of 3.76 and 2.46, respectively. Considering that the data used in model development was obtained over two crushing seasons and from three different sugar mills, these results are encouraging and clearly show that the NIR models are capable of producing high quality predictive results across the range of nutrient constituents tested.

Future applications

Based on the success of this proof of concept work, there are a number of NIR applications that could be subsequently developed for application. Clearly, there is considerable value in knowing the *in situ* nutrient content of mill mud and boiler ash products prior to their use in the field. To address this, NIR methods could be developed for use in the sugar mill where these products are produced and mixed together.

Table 2. Partial least squares regression model properties for all constituents.

Nutrient	*n* (calibration)	R^2_{cv}	Factors	*SECV*	Mean[a]	*SD*[b]	*RPD*
C	151	0.96	9	1.54	27.6	6.7	4.4
N	151	0.97	8	0.09	1.1	0.4	4.5
Si	151	0.95	8	1.55	13.7	6.2	4.0
P	151	0.95	8	0.11	1.2	0.4	3.8
K	151	0.89	7	0.07	0.4	0.2	2.5

n = number of samples; [a]Mean of reference data in *SECV* step; [b]Standard deviation of reference data in *SECV* step; *RPD* = residual predictive deviation = *SD*/*SECV;* All units expressed as percentage dry matter

Further applications are also envisaged at the point of byproduct loading onto trucks prior to being transported so as to provide "truck average" determinations, or as an in-field analysis method where byproduct materials can be sampled and analysed in the field immediately after being applied. This diversity of possible applications is likely to include different types of NIR instrumentation, with the use of laboratory instruments, on-line instruments as well as portable systems that are better suited to field sampling situations.

Conclusions

With increasing environmental scrutiny of nutrient application rates in the Australian sugar industry, information on the nutrient content of mill byproducts is likely to become important in the near future. NIR based analytical techniques offer a means of monitoring the concentrations of nutrient constituents present in mill byproducts in working environments where traditional chemical analysis cannot be applied. The results reported here are encouraging and demonstrate that NIR calibrations may be feasible for all nutrient constituents examined. Additional research is underway to further develop robust NIR calibrations and to produce value-adding applications for use within sugar mill laboratory or field situations.

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