Prediction of moisture content of potash fertilizer using NIR spectroscopy

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Faraji, H., Crowe, T., Besant, R., Sokhansanj, S. and Wood, H. 2004. **Prediction of moisture content of potash fertilizer using NIR spectroscopy.** Canadian Biosystems Engineering/Le génie des biosystèmes au Canada **46**: 3.45 - 3.48. Near infrared spectroscopy (NIRS)was employed to explore the structure of reflectance spectra of red standard potash granules. Reflectance spectra were collected after samples had been conditioned to moisture contents in the range of 0-1%. Reflectance at selected wavelengths was incorporated with multiple linear regression (MLR) to predict sample moisture contents. Models were evaluated based on their ability to predict moisture content in the validation data set, using the adjusted coefficient of determination (r^2_{adj}) and standard error of prediction (SEP). A three-regressor model, using reflectance at 1198, 1427, and 2016 nm was selected as a model with the best ability to estimate moisture content of red standard potash. For this model r^2_{adj} and SEP were 0.92 and 0.005, respectively. **Key words:** multiple linear regression, MLR, potash, moisture measurement.

La spectroscopie à l'infrarouge rapproché (NIRS) a été employée pour analyser le spectre réfléchi de granules standards de potasse rouge. Les spectres réfléchis ont été recueillis après que des échantillons aient été conditionnés à des teneurs en eau variant de 0 à 1%. La réflexion à des longueurs d'onde pré-déterminées a été incorporée avec une régression linéaire multiple (RLM) pour prédire la teneur en eau des échantillons analysés. Différents modèles ont été évalués en termes de leur capacité à prédire la teneur en eau dans un ensemble de données de validation, utilisant un coefficient de détermination ajusté (r^2_{adj}) et une erreur standard de prédiction (SEP). Un modèle à trois paramètres de régression utilisant la réflexion à 1198, 1427 et 2016 nm a donné les meilleurs résultats pour l'estimation de la teneur en eau de la potasse rouge standard. Pour ce modèle, les valeurs de r^2_{adj} et SEP étaient respectivement 0,92 et 0,005. **Mots clés**: régression linéaire multiple, RLM, potasse, mesure de teneur en eau

INTRODUCTION

Potash fertilizer supplies the essential element, potassium, for the stimulation of plant growth. It plays a critical role in the growth process and is essential to boost yields of many major crops. Potash products are available in different types with different physical and chemical characteristics. These include red granular, red standard, white granular, white soluble, and pink standard. These products range in size from a fine powder (size ~ 0.2 mm), standard (size ~ 0.8 mm), granular (size ~ 2.5 mm), and coarse with size of almost 4 mm (Garret 1996).

Potash fertilizer is hygroscopic. It adsorbs water when it is exposed to an atmosphere with high relative humidity. If the moisture content of the potash exceeds 0.2%, caking and dust formation can occur after subsequent drying (Zhou 2000). Caking and dust formation are problematic because they impede the flow of potash during distribution and agricultural application (Peng et al. 1999).

Knowledge of moisture content in stored potash is crucial because it can be used as a product quality indicator and management tool for potash during its storage, shipment, and handling. Typically, moisture content of potash is determined by drying and weighing techniques. Reflectance measurements may represent a suitable alternative. No studies using NIR spectroscopy for determining moisture content of inorganic fertilizers have been undertaken, previously.

Use of NIRS techniques to sense moisture content has been the subject of many other investigations. It has been used to measure moisture content of food products, agricultural products, and manure. Ren and Chen (1997) used NIRS to determine the moisture content of ginseng roots. Calibration equations were developed using wavelengths in the 1100 – 2500 nm region and first order derivatives and scatter correction were used. High correlation and low SEP were attained during validation.

Near infrared reflectance spectroscopy has also been used to successfully measure moisture content of food products. Pioneering work in this field was conducted by Ben-Gera and Norris (1968a) who used NIRS to measure the near-infrared absorbance properties of meat emulsions. The difference in optical density between 1800 and 1725 nm gave a high correlation to moisture content. Ben-Gera and Norris (1968b) also used NIRS to determine moisture content of ground soybeans. In this research a calibration between moisture content and intensity of the 1940 nm water absorption band was constructed. Adamopoulos and Goula (2004) used NIRS to measure the moisture content of taramoslata, a traditional Greek food. Calibration models based upon six wavelengths were developed using multiple linear regression. Lee et al. (1997) used NIRS to measure moisture content of Cheddar cheese curds. A high degree of correlation was obtained during validation. Wold and Isaksson (1997) used NIRS to determine the moisture content of whole Atlantic salmon, wherein results showed that NIRS was suitable for non-destructive determination of moisture content.

Finally, NIRS has been used by several researchers to measure the moisture content in manure from several species. Reeves (2001) used NIRS to determine the moisture content of poultry manure. In this research, partial least squares regression

Table 1. Ranges of moisture content used in experiments.

Moisture content (%)	Number of samples
0.0 - 0.1	9
0.1 - 0.2	16
0.2 - 0.3	23
0.3 - 0.4	35
0.4 - 0.5	13
0.5 - 0.6	15
0.6 - 0.7	9
0.7 - 0.8	19
0.8 - 0.9	16
0.9 - 1.0	9

(PLS) was used to develop calibration models and spectral data were treated using either multiplicative scatter correction or mean and variance scaling. Malley et al. (2002) used NIRS to determine the moisture content of hog manure in pits and lagoons, with good results. Models were developed using multiple linear regression and first and second order derivatives were used for data smoothing.

OBJECTIVES

The goal of this research was to investigate the correlation between moisture content and spectral reflectance for red standard potash with moisture content between 0 and 1%. This could lead to the development of an ability to remotely sense moisture content in potash piles. Specific objectives were:

1. To investigate reflectance properties of red standard potash in the visible and near infrared portions of the electromagnetic spectrum, and
2. To select optimum wavelengths and develop models for moisture content prediction based on these wavelengths.

EXPERIMENTAL PROCEDURE

Red standard potash samples were sieved to achieve a range of particle sizes ranging from 1.18 to 1.4 mm. After sieving, an environmental chamber was used to condition 168 samples to a range of moisture content between 0 and 1%, on a dry basis. The ranges of moisture content and the number of samples in each range are listed in Table 1.

The environmental chamber was set to relative humidity values of 66, 69, and 74% to condition the samples. The amount of time each sample was left in the chamber was determined in a separate empirical study and documented in Faraji (2001). Samples within each range of moisture content were randomly assigned to calibration or validation data sets using a random number generator. This ensured that each sub-range of moisture content was equally represented in the calibration and validation data sets.

The moisture content of the samples was determined by weighing them before and after drying. Samples were oven-dried at 75˚C until there was no change in the mass of the sample. Care was taken to minimize exposure of the samples to the atmosphere when they were transferred between the environmental chamber, the drying oven, the scale, and the spectrophotometer.

After sieving and conditioning the samples, a spectrophotometer (Cary 5G, Varian Inc., Mulgrave, Victoria, Australia) and software (WinUV version 1.0, Varian Inc., Mulgrave, Victoria, Australia) were used to measure and record their reflectance spectra over the range of 250 to 2500 nm. It should be noted that reflectance data in the range of 800 to 900 nm were not used due to noise generated by the spectrophotometer when it changed detectors. Thus, reflectance measurements were made at 2150 discrete wavelengths, resulting in 2150 possible regressors.

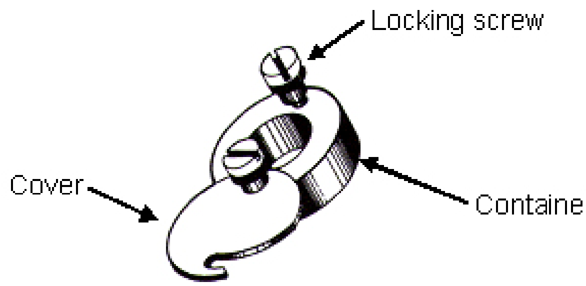

Fig. 1. Schematic of the sample container with the volume of nearly 3 mL (Varian Inc. 1995)

The Cary 5 used a deuterium arc lamp to emit radiation in the UV range of the spectrum and a halogen lamp for the visible and NIR ranges. A photomultiplier tube was used to detect radiation in the 250 to 850 nm range and a lead-sulfide detector was used for the 850 to 2500 nm range. Integration time was set to 0.2 s, the wavelength spacing of the recorded spectra was 1 nm, and the slit width was set to automatic.

Potash granules were loosely poured into the sample holder (Fig. 1) and were not packed. The sample holder was positioned at 0, 120, and 240˚. At each angular position three reflectance measurements were taken at each wavelength. A final reflectance value for each wavelength was determined by averaging the nine reflectance measurements.

Correlation analysis and wavelength selection (MLR)

A regression analysis was performed using SAS (SAS Institute Inc., Cary, NC) to reduce the number of regressors from 2150 to a smaller subset. In total, five calibration equations were developed, using the MINR option. The models assumed the form:

$$MC = a_o + \sum_k a_k R_{\lambda k} \tag{1}$$

where:

MC = predicted moisture content of the sample,
a_o, a_k = regression coefficients, and
$R_{\lambda k}$ = reflectance at a wavelength λ, corresponding to the k^{th} term in the model.

Hruschka (1987) stated that for each regressor in the model, five to fifteen observations should be available. With 79 scans in the calibration data set, the number of regressors in the model was allowed to vary between one and five.

After the model generation process was completed, the linear equations were used to predict moisture content of samples in the calibration and validation data sets. Further, residuals versus actual moisture content were plotted to visually evaluate the performance of the models. To quantify the predictive ability of the models, the adjusted coefficient of

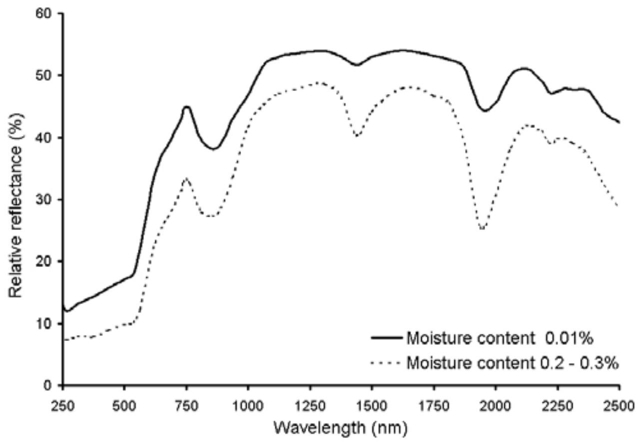

Fig. 2. Reflectance spectra of potash samples at different moisture contents.

determination (r^2_{adj}), standard error of prediction (SEP), and standard error of calibration (SEC) were determined.

RESULTS and DISCUSSION

Reflectance spectra

Figure 2 shows typical spectra of two moist potash samples. The presence of water gave rise to the characteristic absorption bands that appear as localized minima near 1450 and 1950 nm. It was also observed that samples containing higher moisture contents had lower reflectivity across their spectra.

Some of the variation in these spectra could be caused by variations in particle size between samples. Particles with identical chemical properties, but different sizes will display a vertical shift in the amount of radiation scattered (Hruschka 1987). Small variations in reflectance spectra corresponding to samples with similar moisture values were attributed to variations in particle size as well as uncertainties in the measurement of the spectra and uncertainties in the measurement of moisture content in the samples.

MLR results and best model selection

The selected wavelengths, regression coefficients, and the corresponding r^2_{adj} and SEP for the calibration data set are listed in Table 2. Models with fewer regressors are usually more desirable because they have fewer errors resulting from high correlation between regressors and they reduce the problem of over-fitting the calibration data (Hruschka 1987). It was observed that increasing the number of regressors in the calibration models improved their performance (i.e. higher r^2_{adj} and lower SEC) until they began to over-fit the calibration data. Over-fitting occurred when more than three regressors were included in the model, at which point the r^2_{adj} for validation data decreased and SEP increased. This is shown in Table 3. Based upon these results, the three-regressor model was selected as the best model. In this model, moisture content was predicted using reflectance values at 1198, 1427, and 2016 nm, resulting in:

Table 3. Calibration and validation performance of linear models.

Model No.	Calibration r^2_{adj}	SEC	Validation r^2_{adj}	SEP
1	0.900	0.007	0.899	0.007
2	0.921	0.005	0.878	0.008
3	0.937	0.004	0.921	0.005
4	0.956	0.003	0.916	0.006
5	0.961	0.003	0.902	0.007

$$MC = 1.06 + 0.06R_{1198} - 0.14R_{1427} + 0.06R_{2016} \tag{2}$$

None of the selected wavelengths were within the UV or visible wavelength bands. This was consistent with previous work by Ben-Gera and Norris (1968a, 1968b) that used spectrophotometric techniques for moisture determination. It was interesting to note that two of the regressors were reflectance values at 1427 and 2016 nm, wavelengths relatively close to the recognized water absorption bands at 1450 and 1950 nm.

Plots of predicted versus measured moisture content and residuals are shown in Figs. 3 and 4, respectively. Note that the data points were generally grouped about the 1:1 line in Fig. 3, with almost 95% of the residuals being less than 0.1% (Fig. 4).

CONCLUSIONS and FUTURE WORK

A three-regressor model was found to be optimal for estimating the moisture content of red standard potash having moisture content in the range of 0 to 1%. This model used reflectance at wavelengths of 1198, 1427, and 2016 nm. The three-parameter model performed well, with r^2_{adj} and SEP values equal to 0.921 and 0.005, respectively. Predictive performance of the models deteriorated when there were more than three regressors, suggesting over-fitting problems with models of higher dimensionality. The high correlation between reflectance at similar wavelengths suggests that principle component analysis could be a viable option for analysis (Joliffe 1986).

Table 2. Optimum wavelengths and regression coefficients for the linear models.

Model No.	Optimum wavelengths (nm)	a_0	a_1	a_2	a_3	a_4	a_5
1	1406	2.43	-0.05				
2	1943, 2497	2.02	0.12	-0.17			
3	1198, 1427, 2016	1.06	0.06	-0.14	0.06		
4	1043, 1073, 1415, 1892	1.36	-0.4	0.46	-0.15	0.06	
5	1043, 1073, 1121, 1388, 1854	1.81	-0.73	1.06	-0.23	-0.21	0.07

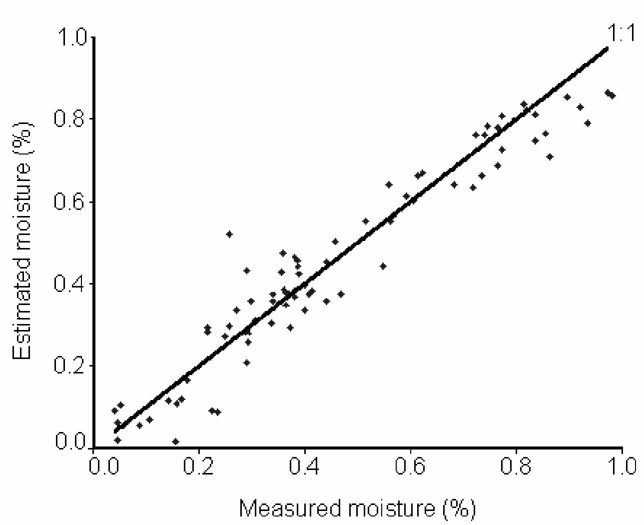

Fig. 3. Estimated versus measured moisture content for the three-regressor model. r^2_{adj} = 0.920 and SEP = 0.005 for the validation data set.

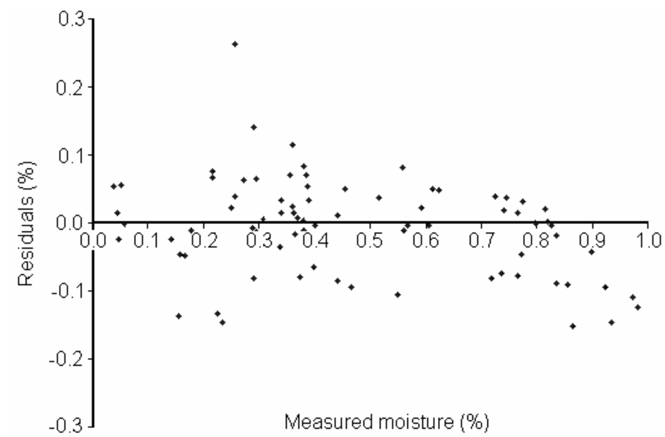

Fig. 4. Prediction residuals versus measured moisture content for the three-regressor model. r^2_{adj}= 0.92 and SEP = 0.005 for validation.

ACKNOWLEDGEMENTS

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