Measurement of moisture and protein content for single kernel rice by spectroscopy

Chang-Hyun Choi*[a] and Jae-Min Kim[b]

[a]*Sungkyunkwan University, Department of Bio-Mechatronic Engineering, Suwon 440-746, Korea.*

[b]*Korean Food Research Institute, Songnam 463-420, Korea.*

Introduction

Near infrared (NIR) spectroscopic techniques can be used to measure the intrinsic and external properties of agricultural products nondestructively. NIR spectra are due to light absorption by organic molecules. Agricultural products are composed of constituents possessing functional groups of atoms that absorb in the NIR region. The wavelength of an absorption band often reveals the nature of the chemical bonds responsible for the absorption. The frequency characteristics of C–H, N–H, O–H bands are influenced by strengths of the chemical bonds and remaining portions of the molecule. Results of several studies[2,3] show that visible/NIR spectroscopic techniques can be used to determine quality-related properties of agricultural products.

The objectives of this study were to develop models to predict moisture and protein contents of single kernel brown rices by visible and NIR spectroscopic techniques.

Materials and methods

Three rice varieties, Dongjin, Chuchung and Ilpum, were tested in this study. They are major varieties of rice cultivated in Chunbuk, Chungbuk and Kyunggi provinces in 1996. The varieties of rice were harvested in the fall of 1996, shipped to the laboratory, held in polyethylene bags and stored in the storage facility at 0ºC during experiments.

A spectrophotometer, equipped with a single-beam scanning monochromator (NIRSystems, Model 6500, Silver Springs, MD, USA) and a horizontal setup module were used to collect reflectance data from a rice kernel. The reflectance spectra were measured in wavelength ranges of 400 to 2498 nm with 2 nm intervals. Thirty-two repetitive scans were accumulated in the computer memory. The scans were averaged, transformed to $\log(1/R)$, then were stored in a microcomputer file, forming one spectrum per measurement. A sample holder was made and attached to the horizontal setup module to maintain the position of rice kernels constantly. A white Teflon block was used for referenced reflectance measurements and a reference spectrum was collected every five measurements.

The moisture content of rice kernels was measured by the oven drying method at 135ºC and then converted to the moisture content at 105ºC. After the moisture content of the rice kernels was measured, the samples were tested to measure the protein content using an Auto Nitrogen Analyzer (Model NA-1500, Italy). Based on American Association of Official Analytical Chemistry (AOAC) standards, the protein content of the rice kernels was found by multiplying the constant 5.95 to the Nitrogen content measured by the Auto Nitrogen Analyzer.

Samples were divided into a calibration set and a validation set. The calibration set was used during model development and the validation set was used to predict moisture and protein contents from unknown spectra. Multiple linear regression (MLR) and partial least square (PLS) analysis were used to develop the models of each constituent.

The first and second derivatives of raw spectra were also used to develop the models with a proper smoothing gap. The multiplicative scatter correction (MSC) and the standard normal variate and detrending (SNVD) preprocessing were applied to all spectra to minimise sample-to-sample light scatter differences. On completion of the calibration, the models were used to predict moisture and protein content from the validation set. Model performance was reported as the coefficient of determination (R^2), the standard error of prediction (*SEP*), the average difference between measured and predicted values (bias) and the model error which was calculated as the ratio of the *SEP* to the mean of the prediction values (*SEP*/mean).

Results and discussion

The MLR and PLS models for the moisture content of single kernel brown rice was developed. The models showed better results in the wavelength range of 1100 to 1400 nm for the MLR model and 1100 to 1500 nm for the PLS model, rather than whole range. The MLR model, using six wavelengths from the first derivative spectra (10 nm of gap) with *SNVD* preprocessing, showed the best results for predicting the moisture content of the brown rice. The wavelengths selected for the MLR models were 1166,1174,1262,1300,1364 and 1388 nm from the first derivative spectra with 10 nm of gap. As shown in Table 1 and Figure 1, the model had 0.987 of R^2 and 0.189% of the maximum *SEP*.

$$\text{Moisture Content (\%)} = 14.975 - 19.262\ W_{1388} - 163.749\ W_{1300} + 81.093 W_{1262} + 97.891\ W_{1174} + 35.703\ W_{1364} - 66.252\ W_{1166}$$

The PLS model, using raw spectra with MSC preprocessing, also gave a good performance for predicting the moisture content from unknown samples. The results of the PLS models for moisture contents are shown in Table 2. The minimum R^2 was 0.988 and the maximum *SEP* was 0.225%. Considering 0.5% of the measurement error of the moisture content in the rice processing complex, the MLR and the PLS models developed in this study could be useful to predict the other short grain rice varieties which are produced in Korea.

The MLR and PLS models showed good correlations between the predicted and measured protein content using single kernels of brown rice samples. The MLR model used the second derivative spec-

Table 1. Validation results of MLR models for the moisture content of brown rice.

Varieties	Mathematical treatment	Preprocessing	*N*	R^2	*SEP*	Bias	*SEP*/mean (%)
Dongjin	None	SNVD	52	0.985	0.264	–0.008	1.63
	1st derivative	SNVD		0.987	0.148	–0.060	0.91
	2nd derivative	None		0.986	0.275	0.013	1.69
Ilpum	None	SNVD	52	0.992	0.240	–0.007	1.45
	1st derivative	SNVD		0.992	0.137	–0.026	0.83
	2nd derivative	None		0.985	0.296	0.002	1.79
Chucheong	None	SNVD	53	0.988	0.288	–0.028	1.80
	1st derivative	SNVD		0.991	0.189	0.007	1.18
	2nd derivative	None		0.988	0.219	0.067	1.37

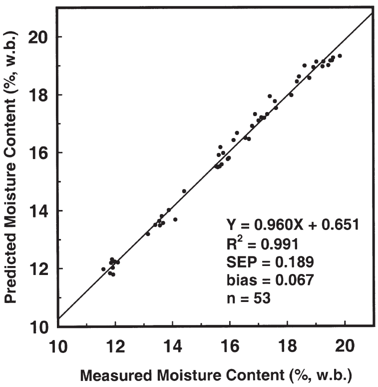

Figure 1. Comparison of measured and predicted values of moisture contents of Chucheong using MLR model (Model conditions: 1st derivative, 6 wavelengths).

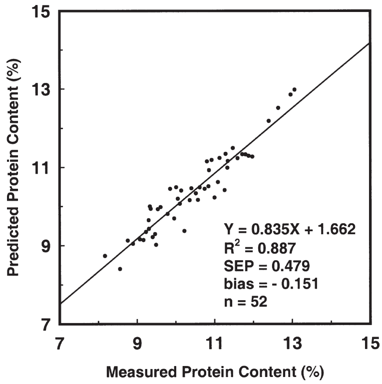

Figure 2. Comparison of measured and predicted values of protein contents of Ilpum by PLS (Model conditions: 1st derivative, 1100–1500 nm, 13 factors).

tra (10 nm of gap) with SNVD preprocessing over the wavelength 1100–2000 nm. The results of the MLR model were a maximum R^2 of 0.819 and a minimum *SEP* of 0.485% the as shown in Table 3. The PLS model was developed over the wavelength 1100–1500 nm. The first or the second derivative pretreatments did not affect the PLS model performance. The PLS model, using the second derivative spectra (4 nm of gap) with SNVD preprocessing, showed better prediction performance than the MLR model, and had 0.837 of the maximum R^2 and 0.479% of the minimum *SEP* as shown in Table 4 and Figure 2.

Conclusion

The MLR and PLS models were developed to predict the moisture content and the protein content of single kernels of brown rice by visible and NIR spectroscopic techniques. The models showed better results in the wavelength range of 1100 to 1400 nm for the MLR model and 1100 to 1500 nm for the PLS model, rather than the whole range. The MLR model, using six wavelengths with SNVD pre-

Table 2. Validation results of PLS models for the moisture content of brown rices.

Varieties	Mathematical Treatment	Preprocessing	*N*	R^2	*SEP*	Bias	*SEP*/mean %
Dongjin	None	MSC	52	0.989	0.225	– 0.050	1.39
	1st derivative	MSC		0.989	0.100	0.029	0.62
	2nd derivative	MSC		0.988	0.122	0.024	0.75
Ilpum	None	MSC	52	0.993	0.225	– 0.007	1.36
	1st derivative	MSC		0.994	0.154	– 0.008	0.93
	2nd derivative	MSC		0.993	0.114	0.010	0.69
Chucheong	None	MSC	53	0.994	0.189	– 0.005	1.18
	1st derivative	MSC		0.993	0.094	– 0.010	0.59
	2nd derivative	MSC		0.992	0.148	– 0.011	0.93

Table 3. Validation results of MLR models for protein content of brown rice.

Varieties	Mathematical treatment	Preprocessing	*N*	R^2	*SEP*	Bias	*SEP*/mean %
Dongjin	None	SNVD	51	0.591	0.817	0.168	7.80
	1st derivative	SNVD		0.644	0.732	– 0.029	6.99
	2nd derivative	SNVD		0.803	0.570	0.163	5.47
Ilpum	None	SNVD	52	0.774	0.681	0.157	6.47
	1st derivative	SNVD		0.819	0.613	0.179	5.82
	2nd derivative	SNVD		0.876	0.485	– 0.021	4.61
Chucheong	None	SNVD	51	0.760	0.537	– 0.278	4.23
	1st derivative	SNVD		0.766	0.485	– 0.187	6.15
	2nd derivative	SNVD		0.777	0.471	– 0.179	5.97

Table 4. Validation results of PLS models for protein content of brown rice.

Varieties	Mathematical treatment	Preprocessing	*N*	R^2	*SEP*	Bias	*SEP*/mean %
Dongjin	None	MSC	51	0.851	0.475	–0.053	4.54
	1st derivative	SNVD		0.857	0.463	0.014	4.42
	2nd derivative	MSC		0.829	0.508	0.018	4.85
Ilpum	None	MSC	52	0.924	0.400	–0.081	3.80
	1st derivative	SNVD		0.887	0.479	–0.151	4.55
	2nd derivative	MSC		0.901	0.433	0.066	4.11
Chucheong	None	MSC	51	0.830	0.427	–0.183	5.41
	1st derivative	SNVD		0.837	0.412	–0.184	5.22
	2nd derivative	MSC		0.838	0.450	–0.247	5.71

processing, showed the best results to predict the moisture content of the brown rice. The wavelengths selected for the MLR models were 1166,1174,1262,,1300,1364 and 1388 nm from the first derivative spectra with 10 nm of gap.

The PLS model, using raw spectra with MSC preprocessing, also performed in predicting the moisture content from unknown samples. The MLR model for protein content used the second derivative spectra (10 nm of gap) with SNVD preprocessing over the wavelength of 1100 to 2000 nm. The PLS model, using the second derivative spectra (4 nm of gap) with SNVD preprocessing, showed better results than the MLR model in predicting the protein content.

References

1. G.D. Batten, A.B. Blakeney, M.G. Holmes, R.J. Henry, A.C. McCaffery, P.E. Bacon and D.P. Heenan, *J. Sci. Food Agric.* **54(1),** 191 (1991).
2. S.R. Delwiche, M.M. Bean, R.E. Miller, B.D. Webb and P.C. Williams, *Cereal Chem*. **72(2),** 182 (1995).
3. W.S. Li and J.T. Shaw, in *Food Processing Automation IV.* Proceedings of the FPAC IV Conference, pp. 288–302 (1995).
4. P.C. Williams and K.H. Norris, in *Near-Infrared Technology in the Agricultural and Food Industries.* A.A.C.C. Inc., St Paul, Minnesota, USA (1987).