

VISIBLE AND NEAR-INFRARED REFLECTANCE SPECTROSCOPY FOR DETERMINING PHYSICOCHEMICAL PROPERTIES OF RICE

M. Natsuga, S. Kawamura

ABSTRACT. To assess rice grain quality, various types of analyses of the physicochemical properties of rice must be conducted. Although several methods exist, different properties require specific instruments and chemicals, and most of them are time-consuming. The authors have therefore developed calibration models for determining multiple physicochemical properties of rice using a single instrument, a visible and near-infrared (VIS/NIR) reflectance spectrometer. These models were used to measure the physicochemical properties of 61 samples of Japanese short-grain, non-waxy rice. The results of partial least squares (PLS) regression modeling with full cross-validation methods indicated that reasonably accurate models (correlation coefficient [r] of the validation greater than 0.8) could be obtained for moisture content, sound whole kernel, and appearance (whiteness, translucency, and color) of brown rice, and for moisture content, appearance, and amylogram characteristics (maximum viscosity and breakdown) of milled rice. The level of accuracy was sufficient for classifying rice samples into qualitative groups. Thus, the results demonstrate that VIS/NIR spectroscopy can be used to determine the physicochemical properties of rice and assess its quality.

Keywords. Brown rice, Milled rice, Physicochemical properties, Visible and near-infrared spectroscopy, Whole grain.

Near-infrared (NIR) spectroscopy has been used for highly accurate measurement of the chemical composition of rice grain, including such constituents as moisture, protein, and amylose (Iwamoto et al., 1986; Natsuga et al., 1992; Villareal et al., 1994; Delwiche et al., 1995; Delwiche et al., 1996; Kawamura et al., 1997a; Sohn et al., 2004). However, to assess rice grain quality, in addition to chemical composition, various physicochemical properties of the rice must be analyzed. Several studies were previously carried out to estimate quality-related parameters such as fat acidity and the gelatinization characteristics of rice (Onda et al., 1994; Li and Shaw, 1997; Bao et al., 2001; Meadows and Barton, 2002). The physicochemical properties of rice are known to be correlated with its eating quality (Chikubu et al., 1985; Kawamura et al., 1997b; Windham et al., 1997; Barton et al., 2000; Mikami et al., 2000; Champagne et al., 2001; Meullenet et al., 2001).

All common existing methods for measuring the physicochemical properties require some specific instruments and chemicals, and are labor-intensive or time-consuming. There is therefore intense interest in the rice breed improvement, culture, and production communities, as well as in the rice industry, for a quick and easy method to measure the physicochemical properties of rice. Although NIR spectroscopy

is used for measuring rice constituent contents, a method for measuring the physicochemical properties using this technology has not yet been established.

The objectives of this study were to: (1) develop VIS/NIR calibration models from brown rice and milled rice spectra to determine physicochemical properties of rice, and (2) validate the accuracy of the calibration models and determine whether VIS/NIR spectroscopy could replace various dedicated analytical methods.

MATERIALS AND METHODS

RICE SAMPLES

For this study, a total of 61 short-grain brown rice samples (at least 5 kg per sample) were collected from commercial varietal releases all over Japan. The samples consisted of 27 varieties of Japanese non-waxy rice. The brand names of the rice samples were Aichinokaori, Akitakomachi, Akitsuho, Asahi, Aya, Fukuhikari, Hananomai, Harebare, Hatsuboshi, Hitomebore, Honoka 224, Hourei, Kinuhikari, Kirara 397, Koganebare, Koshihikari, Koshijiwase, Koshinohana, Mineasahi, Mutsukaori, Nakateshinsenbon, Nipponbare, Sasanishiki, Tsugaruotome, Yamabiko, Yamahikari, and Yukihikari. The brown rice samples (at least 3 kg per sample) were processed into milled rice with a commercial friction mill (model MCM-250, Satake Engineering, Tokyo, Japan), and the yield of each milled rice sample was $90.5\% \pm 0.1\%$ of the brown rice weight.

REFERENCE ANALYSIS

The physicochemical properties of brown rice and milled rice samples were determined with the following methods. Moisture content was determined using the standard method of the Japanese Society of Agricultural Machinery; about 10 g of whole-grain rice was placed in a forced-air oven at

Submitted for review in October 2005 as manuscript number FPE 6143; approved for publication by the Food & Process Engineering Institute Division of ASABE in June 2006. Presented at the 1998 ASAE Annual Meeting as Paper No. 983036.

The authors are **Motoyasu Natsuga, ASABE Member Engineer**, Associate Professor, Faculty of Agriculture, Yamagata University, Tsuruoka, Japan; and **Shuso Kawamura, ASABE Member Engineer**, Associate Professor, Agricultural Process Engineering Laboratory, Hokkaido University, Sapporo, Japan. **Corresponding author:** Motoyasu Natsuga, Faculty of Agriculture, Yamagata University, 1-23 Wakabamachi Tsuruoka, 997-8555 Japan; phone: +81-235-28-2906; e-mail: toko@tds1.tr.yamagata-u.ac.jp.

135 °C for 24 h, and the moisture content was calculated on a wet basis. Protein content was measured with an NIR spectrometer (model Instalab-600, Dickey-John Corp., Auburn, Ill.) and calculated on a dry basis. The accuracy of the spectrometer for measurement of protein content was previously confirmed by the Kjeldahl method ($N \times 5.95$). Amylose content (apparent amylose content) of milled rice was measured using an autoanalyzer, following the protocol of Williams et al. (1958) with modifications by Inatsu (1988). The free fat acidity value was determined by the rapid method of the American Association of Cereal Chemists (AACC method 02-02), extracting free fat acid in benzene solution and titrating the extracted solution with potassium hydroxide solution.

Sound whole kernel of brown rice was judged by trained human eyes and was expressed as a percentage of weight. Bulk density was determined using a grain volume-weight tester (Brauer type, Fujiwara Engineering, Tokyo, Japan) and was expressed as grams per liter. Whiteness and translucency were measured by a whiteness meter (model C-100, Kett Electric Laboratory, Tokyo, Japan) and a rice meter (model QS-101D, Riken Instrument, Tokyo, Japan), respectively. The color of brown rice and milled rice, as defined by the Commission Internationale de l'Éclairage 1976 standard colorimetric system ($L^*a^*b^*$ colorimetric system), was measured by a color difference meter (model CR-200b, Minolta Camera, Osaka, Japan).

Embryo activity, defined as the amount of succinic dehydrogenase in the embryo of rice, was measured according to the standard method of the Japan Food Agency (JFA); briefly, 100 sound brown rice kernels were soaked in a triphenyltetrazolium chloride solution (0.25% [w/w] concentration) and placed in an incubator at 25 °C for 24 h, and embryo activity was judged by trained human eyes on the basis of stained embryo color. Germination vigor and germination ratio were measured according to the JFA standard method; 100 sound brown rice kernels were soaked in hydrogen peroxide solution (1% [w/w] concentration) and placed in an incubator at 20 °C. The germination vigor and germination ratio were determined as the number of kernels that germinated within three days and seven days, respectively.

Measurement of cooking characteristics, such as water uptake ratio, extracted solids, and starch-iodine blue value, was performed by the method of Batcher et al. (1957) with modification by Chikubu et al. (1960).

Texturograms A1, A2, and A3 were defined as the first peak area, the second peak area, and the first negative peak area of the texture profile measured by a texturometer (Zenken, Tokyo, Japan). The rapid visco analyzer peak was defined as the magnitude of the curve recorded on a rapid visco analyzer (Newport Scientific, Warriewood, NSW, Australia). Amylogram maximum viscosity and breakdown were defined as the magnitude of the curve recorded on an amylograph (Brabender, Duisburg, Germany).

SPECTROSCOPIC ANALYSES

Spectra of rice samples of approximately 5 g were recorded with a visible and near-infrared spectrometer (model NIRS-6500, Foss-NIR Systems, Silver Spring, Md.). A spinning cup was used for all sample types, i.e., whole-grain brown rice and whole-grain milled rice. Reflectance (R) readings at 2 nm increments were collected over a visible

and near-infrared wavelength range of 400 to 2498 nm, averaging the values of 120 readings and transforming the values to $\log_{10}(1/R)$, giving a total of 1050 data points per spectrum. Five replicates for each rice samples, with sample repacking, were carried out and averaged for the chemometrics analysis.

CHEMOMETRICS ANALYSES

The full wavelength range of 400-2498 nm was divided into three sub-ranges: VIS (400-798 nm), NIR1 (800-1098 nm), and NIR2 (1100-2498 nm). A commercial spectral data analysis program (The Unscrambler 9.2, CAMO Software, Oslo, Norway), and the statistical method of partial least squares (PLS) regression was used to process the data and develop calibration models. The rice distribution system in Japan, from rice growers and rice processing facilities to wholesalers and retailers, is usually in the form of brown rice that is milled just before retailing. Accordingly, the calibration models to estimate the physicochemical properties of brown rice and milled rice were developed from the original spectra of brown rice at first. The calibration models to estimate physicochemical properties of milled rice were then developed from the original spectra of milled rice.

The calibration models were developed for each wavelength range (VIS, NIR1, and NIR2) and their combinations, using PLS regression with full cross-validation since the number of samples was insufficient to divide into two separate groups of calibration development and validation. The number of factors used in the PLS calibration models were those suggested by The Unscrambler software. Values of RPD (Williams and Norris, 2001) were calculated to verify the applicability of the calibrations. RPD is the ratio of the standard error of prediction (SEP) to the standard deviation (SD) of the reference data; in this study, we replaced SEP with SECV (standard error of cross-validation). For specific applications, RPD was defined using the following ranges: 0.0 to 2.3 as not recommended, 2.4 to 3.0 as very rough screening quality, 3.1 to 4.9 as screening quality, 5.0 to 6.4 as quality control, 6.5 to 8.0 as process control, and >8.1 suitable for any application.

RESULTS AND DISCUSSION

PHYSICOCHEMICAL PROPERTIES OF BROWN RICE AND MILLED RICE

The mean, minimum, maximum, and SD values of the physicochemical properties of brown rice and milled rice samples are shown in table 1. Because the rice sample set in this study only included short-grain non-waxy varieties grown in Japan, the range of each physicochemical property was smaller than it would have been if the sample set had included medium-grain and long-grain varieties grown elsewhere around the world. For example, the protein and amylose contents of the milled rice samples ranged from 6.1% to 8.8% and from 14.8% to 22.7%, respectively. This is relatively limited compared to another study (Delwiche et al., 1996) where the same properties varied from 5.20% to 10.21% and from 0.0% to 26.4%, respectively. These variations in content are due to differences in the rice variety including non-waxy and waxy type, soil in the paddy field, and the climate of the rice-growing district. These factors would produce much larger variations in protein and amylose

Table 1. Physicochemical properties of 61 rice samples.

Property	Unit ^[a]	Mean	Min.	Max.	SD
Brown Rice					
Moisture content	%	15.8	14.2	17.2	0.76
Protein content	%	7.7	6.6	9.7	0.62
Free fat acidity	mg	28.3	9.7	84.5	12.05
Sound whole kernel	%	90.0	75.3	97.6	4.58
Bulk density	g/L	830.0	796.2	854.0	12.54
Whiteness	(-)	17.2	15.7	19.0	0.81
Translucency	(-)	71.0	40.2	93.8	10.53
Color L* ^[b]	(-)	55.3	53.2	57.6	0.90
Color a*	(-)	2.7	1.9	3.3	0.35
Color b*	(-)	15.3	14.5	16.0	0.35
Color C*	(-)	15.6	14.8	16.3	0.36
Embryo activity	%	80.9	49.0	95.5	12.95
Germination vigor	%	82.4	50.8	99.0	11.93
Germination ratio	%	88.3	55.0	99.0	9.78
Milled Rice					
Moisture content	%	15.7	14.0	17.2	0.71
Protein content	%	7.2	6.1	8.8	0.56
Amylose content	%	19.0	14.8	22.7	1.60
Free fat acidity	mg	9.2	2.7	24.1	3.68
Bulk density	g/L	838.9	821.7	855.4	6.54
Whiteness	(-)	34.5	30.8	37.5	1.41
Translucency	(-)	88.6	60.0	106.0	9.13
Color L* ^[b]	(-)	61.4	57.8	63.8	1.13
Color a*	(-)	-0.5	-0.8	-0.2	0.15
Color b*	(-)	8.6	7.7	9.6	0.47
Color C*	(-)	8.6	7.7	9.6	0.46
Water uptake ratio ^[c]	%	72.8	40.7	109.0	16.82
Extracted solids ^[c]	mg	308.0	190.2	525.0	86.73
Starch-iodine blue value ^[c]	(-)	0.2	0.1	0.5	0.06
Texturogram A1	TU	14.6	11.4	17.6	1.24
Texturogram A2	TU	7.3	6.1	9.1	0.71
Texturogram A3	TU	1.0	0.6	1.4	0.14
Rapid visco analyzer peak	RVU	503.4	426.5	615.0	41.51
Amylogram max. viscosity	BU	627.1	399.0	852.0	106.34
Amylogram breakdown	BU	342.8	145.0	556.0	106.55

[a] (-) = nondimensional, TU = texturograph unit, RVU = rapid visco unit, and BU = Brabender unit.

[b] * = Commission Internationale de l'Eclairage 1976 standard colorimetric system.

[c] Cooking characteristics.

contents if the sample set included different rice varieties from various countries. Thus, the physicochemical properties of the samples in this study show typical values of commercial short-grain rice grown and sold in Japan.

PLS REGRESSION RESULTS

The results of PLS regression models developed from brown rice spectra are shown in tables 2 and 3. Performance was evaluated using the correlation coefficient (r) between reference values and NIR estimated values and the standard error of cross-validation (SECV) and RPD. A value of r greater than 0.41 indicates significance at the 0.1% level. Good calibration results in a larger r value and smaller SECV. Shaded values highlight the best models among the various wavelength ranges.

Figures 1 to 6 show scatter plots of the reference and estimated values of the physicochemical properties of brown rice. Among them, higher RPDs (>=2.4) were obtained for moisture content (5.1, NIR1), whiteness (3.2, VIS), color L* (27.7, VIS), color a* (13.2, VIS+NIR1), color b* (28.5, VIS+NIR1), color C* (26.3, VIS), and amylogram breakdown (2.4, NIR1). As Williams and Norris (2001) previously discussed, a low RPD resulting from the small SD of samples may be still valid when the sample population size is reasonable (60 or more), and we should therefore look at the other parameters, r and SECV. The results in table 2 and 3 indicate that reasonably accurate models (r >= 0.8) were obtained for sound whole kernel in all different spectroscopic ranges: (1) for color L*, color a*, color b*, and color C* in the VIS range; (2) for moisture content, translucency, color L*, color b*, color C*, amylogram maximum viscosity, and amylogram breakdown in the NIR1 range; (3) for moisture content, sound whole kernel, whiteness, translucency, color L*, color a*, color b*, color C*, water uptake ratio, amylogram maximum viscosity, and amylogram breakdown in the VIS+NIR1 range; (4) for moisture content in the NIR2 range; and (5) for moisture content, sound whole kernel, whiteness, translucency, color L*, color a*, color b*, color C*, water uptake ratio, amylogram maximum viscosity, and amylogram breakdown in the VIS+NIR2 range.

PLS regression models of slightly lower accuracy (0.5 < r < 0.8) were obtained for free fat acidity, bulk density and germination ratio in the NIR2 region; for embryo activity,

Table 2. PLS regression results developed from brown rice spectra (1).

Property	VIS (400-798 nm)				NIR1 (800-1098 nm)				VIS+NIR1 (400-1098 nm)			
	nF ^[a]	r ^[b]	SECV ^[c]	RPD ^[d]	nF	r	SECV	RPD	nF	r	SECV	RPD
Brown Rice												
Moisture content	4	0.40	0.71	1.1	2	0.98	0.15	5.1	2	0.95	0.24	3.2
Protein content	4	0.45	0.56	1.1	2	0.96	0.16	3.8	2	0.47	0.55	1.1
Free fat acidity	1	0.22	11.82	1.0	1	0.30	11.56	1.0	1	0.26	11.69	1.0
Sound whole kernel	6	0.85	2.43	1.9	5	0.68	3.42	1.3	5	0.88	2.21	2.1
Bulk density	1	-0.04	12.81	1.0	1	-0.17	12.92	1.0	1	-0.07	12.86	1.0
Whiteness	5	0.95	0.25	3.2	4	0.78	0.52	1.5	4	0.95	0.26	3.1
Translucency	7	0.75	7.01	1.5	3	0.82	6.02	1.7	7	0.83	5.95	1.8
Color L*	3	>0.99	0.03	27.7	3	0.92	0.35	2.5	3	>0.99	0.05	17.3
Color a*	5	0.99	0.04	8.1	7	0.60	0.30	1.2	7	>0.99	0.03	13.2
Color b*	5	>0.99	0.02	18.3	6	0.85	0.20	1.8	6	>0.99	0.01	28.5
Color C*	5	>0.99	0.01	26.3	3	0.82	0.22	1.7	3	0.98	0.06	5.6
Embryo activity	2	0.35	12.23	1.1	8	0.69	9.56	1.4	8	0.58	10.97	1.2
Germination vigor	1	-0.13	12.26	1.0	1	0.54	10.95	1.1	1	-0.14	12.28	1.0
Germination ratio	1	-0.07	9.98	1.0	1	0.50	8.72	1.1	1	-0.04	9.99	1.0

(cont)

Table 2. (cont) PLS regression results developed from brown rice spectra (1).

Property	VIS (400-798 nm)				NIR1 (800-1098 nm)				VIS+NIR1 (400-1098 nm)			
	nF ^[a]	r ^[b]	SECV ^[c]	RPD ^[d]	nF	r	SECV	RPD	nF	r	SECV	RPD
Milled Rice												
Amylose content	6	0.57	1.33	1.2	6	0.54	1.37	1.2	6	0.65	1.23	1.3
Water uptake ratio	12	0.84	9.22	1.8	14	0.79	10.44	1.6	14	0.84	9.30	1.8
Extracted solids	6	0.80	52.24	1.7	4	0.72	40.01	2.2	4	0.44	50.19	1.7
Starch-iodine blue value	5	0.43	0.05	1.1	4	0.72	0.04	1.4	4	0.44	0.05	1.1
Texturogram A1	3	0.54	1.05	1.2	8	0.52	1.10	1.1	3	0.52	1.07	1.2
Texturogram A2	3	0.52	0.61	1.2	3	0.38	0.66	1.1	3	0.50	0.62	1.1
Texturogram A3	1	-0.44	0.15	0.9	1	0.42	0.13	1.1	1	-0.37	0.15	0.9
Rapid visco analyzer peak	10	0.71	30.18	1.4	13	0.76	27.51	1.5	13	0.74	28.93	1.4
Amylogram max. viscosity	12	0.81	64.01	1.7	14	0.87	51.75	2.1	14	0.81	63.50	1.7
Amylogram breakdown	12	0.89	48.78	2.2	14	0.91	43.59	2.4	14	0.89	49.17	2.2

[a] Number of factors.

[b] Correlation coefficient between reference values and NIR estimated values. A value of r greater than 0.41 indicates significance at the 0.1% level.

[c] Standard error of cross-validation.

[d] Ratio of the standard error of cross-validation (SECV) to the standard deviation of the reference data.

Table 3. PLS regression results developed from brown rice spectra (2).

Property	NIR2 (1100-2498 nm)				VIS+NIR2 (400-798 nm + 1100-2498 nm)			
	nF	r	SECV	RPD	nF	r	SECV	RPD
Brown Rice								
Moisture content	7	0.97	0.19	3.9	10	0.97	0.18	4.2
Protein content	14	0.92	0.24	2.6	20	0.88	0.30	2.1
Free fat acidity	10	0.67	9.02	1.3	5	0.58	9.95	1.2
Sound whole kernel	2	0.33	4.35	1.1	5	0.87	2.28	2.0
Bulk density	8	0.67	9.45	1.3	8	0.59	10.24	1.2
Whiteness	8	0.66	0.62	1.3	4	0.94	0.29	2.8
Translucency	6	0.78	6.63	1.6	8	0.87	5.14	2.1
Color L*	10	0.77	0.58	1.5	4	>0.99	0.05	18.8
Color a*	1	-0.13	0.36	1.0	8	0.99	0.04	7.9
Color b*	10	0.78	0.22	1.6	5	0.98	0.06	5.5
Color C*	10	0.77	0.24	1.5	5	0.99	0.06	6.0
Embryo activity	8	0.67	9.87	1.3	4	0.58	10.68	1.2
Germination vigor	6	0.32	11.70	1.0	1	0.01	12.16	1.0
Germination ratio	12	0.65	7.74	1.3	8	0.54	8.40	1.2
Milled Rice								
Amylose content	18	0.67	1.31	1.2	8	0.63	1.26	1.3
Water uptake ratio	11	0.77	11.10	1.5	16	0.81	10.33	1.6
Extracted solids	13	0.77	56.80	1.5	2	0.39	51.05	1.7
Starch-iodine blue value	16	0.64	0.05	1.2	2	0.39	0.05	1.1
Texturogram A1	8	0.52	1.07	1.2	4	0.51	1.08	1.1
Texturogram A2	3	0.39	0.66	1.1	4	0.49	0.63	1.1
Texturogram A3	1	-0.29	0.13	1.0	1	-0.27	0.14	1.0
Rapid visco analyzer peak	7	0.57	34.47	1.2	12	0.73	29.54	1.4
Amylogram max. viscosity	7	0.68	79.50	1.3	16	0.83	62.27	1.7
Amylogram breakdown	11	0.79	67.69	1.6	16	0.88	51.89	2.1

germination vigor, and starch-iodine blue value in the NIR1 region; and for texturogram A1 and texturogram A2 in the VIS region.

The results of PLS regression models developed from milled rice spectra are shown in tables 4 and 5. Figures 7 to 13 show scatter plots of the reference and estimated values of the physicochemical properties of milled rice. Among them, higher RPD values (≥ 2.4) were obtained for moisture content (6.9, NIR1), whiteness (3.8, VIS+NIR2), color b* (2.5, VIS), and color C* (2.7, VIS). Similarly to brown rice spectra, the results in tables 4 and 5 indicate that reasonably accurate models ($r > 0.8$) were obtained in the various spectroscopic ranges: (1) for whiteness, color L*, color b*, color C*, amylogram maximum viscosity, and amylogram

breakdown in the VIS range; (2) for moisture content, whiteness, translucency, color L*, water uptake ratio, extracted solids, amylogram maximum viscosity, and amylogram breakdown in the NIR1 range; (3) for moisture content, whiteness, translucency, color L*, color b*, color C*, amylogram maximum viscosity, and amylogram breakdown in the VIS+NIR1 range; (4) for moisture content, amylogram maximum viscosity, and amylogram breakdown in the NIR2 range; and (5) for moisture content, whiteness, translucency, color L*, color b*, color C*, amylogram maximum viscosity, and amylogram breakdown in the VIS+NIR2 range.

PLS regression models of slightly lower accuracy ($0.5 < r < 0.8$) were obtained for amylose content and bulk density

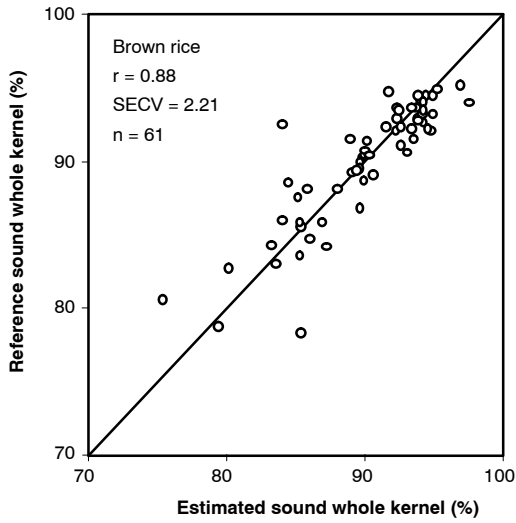


Figure 1. Correlation between reference and estimated sound whole kernel of brown rice in the VIS+NIR1 region.

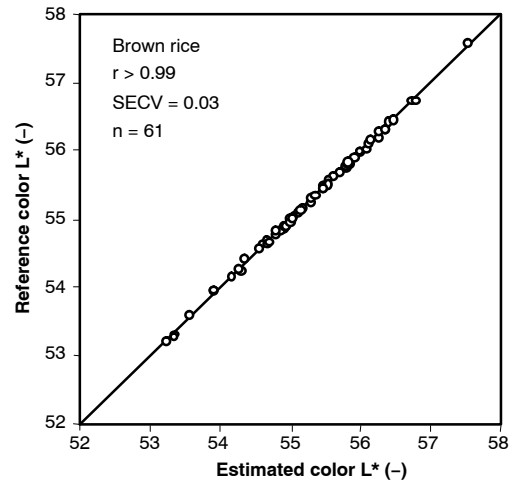


Figure 4. Correlation between reference and estimated color L^* of brown rice in the VIS range.

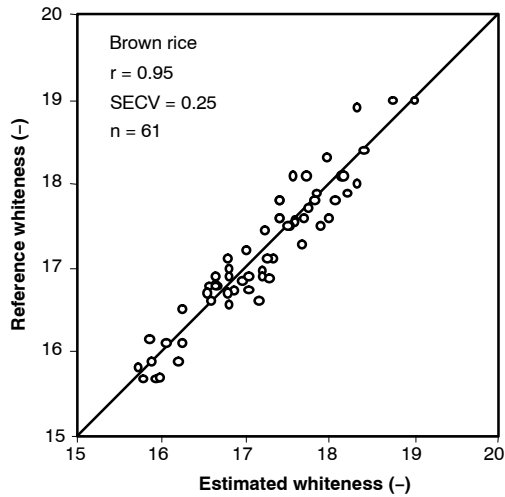


Figure 2. Correlation between reference and estimated whiteness of brown rice in the VIS range.

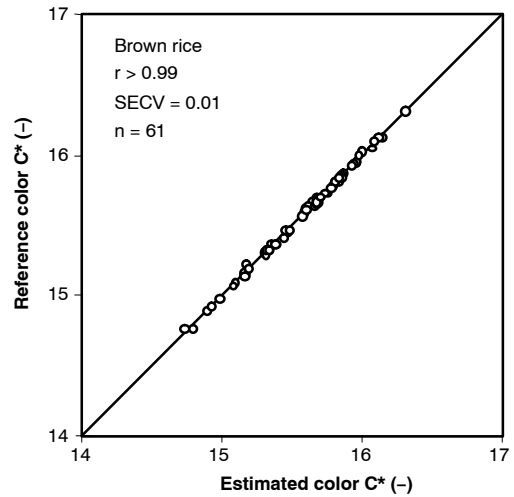


Figure 5. Correlation between reference and estimated color C^* of brown rice in the VIS range.

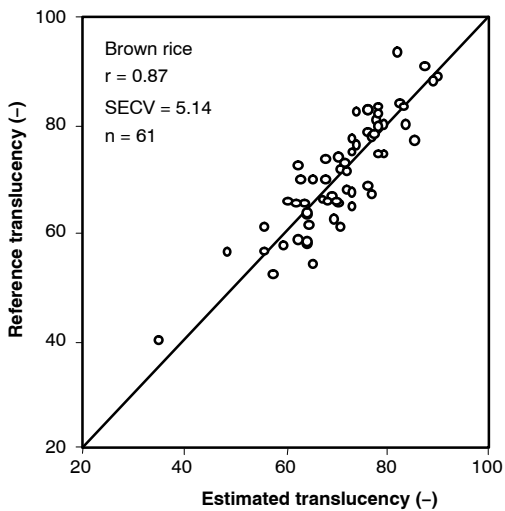


Figure 3. Correlation between reference and estimated translucency of brown rice in the VIS+NIR2 range.

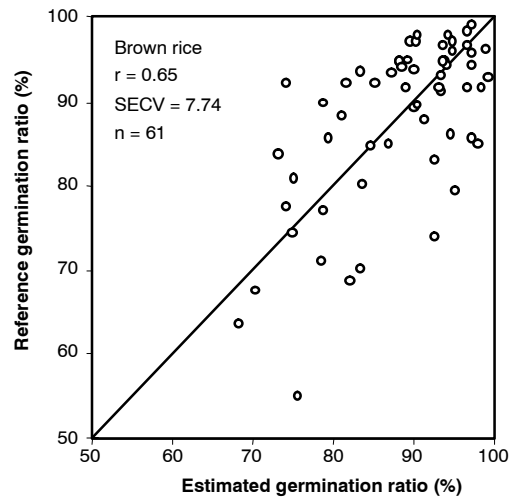


Figure 6. Correlation between reference and estimated germination ratio of brown rice in the NIR2 range.

Table 4. PLS regression results developed from milled rice spectra (1).

Property	VIS (400-798 nm)				NIR1 (800-1098 nm)				VIS+NIR1 (400-1098 nm)			
	nF	r	SECV	RPD	nF	r	SECV	RPD	nF	r	SECV	RPD
Milled Rice												
Moisture content	5	0.65	0.54	1.3	7	0.99	0.10	6.9	11	0.97	0.18	3.8
Protein content	2	0.51	0.48	1.2	9	0.95	0.18	3.1	20	0.87	0.29	1.9
Amylose content	7	0.44	1.50	1.1	9	0.52	1.42	1.1	7	0.52	1.42	1.1
Free fat acidity	4	0.39	3.44	1.1	5	0.42	3.39	1.1	4	0.35	3.52	1.0
Bulk density	7	0.39	6.30	1.0	6	0.57	5.41	1.2	7	0.52	5.76	1.1
Whiteness	3	0.96	0.39	3.6	9	0.87	0.71	2.0	3	0.96	0.38	3.8
Translucency	5	0.79	5.62	1.6	4	0.89	4.10	2.2	7	0.89	4.26	2.1
Color L*	1	0.88	0.53	2.1	5	0.81	0.67	1.7	2	0.88	0.53	2.1
Color a*	5	0.74	0.10	1.5	5	0.63	0.12	1.3	6	0.75	0.10	1.5
Color b*	3	0.91	0.19	2.5	10	0.79	0.29	1.6	4	0.92	0.19	2.5
Color C*	3	0.93	0.17	2.7	10	0.79	0.29	1.6	4	0.91	0.19	2.5
Water uptake ratio	18	0.78	10.87	1.5	10	0.81	9.97	1.7	18	0.74	11.67	1.4
Extracted solids	10	0.77	57.69	1.5	12	0.87	42.85	2.0	12	0.75	59.32	1.5
Starch-iodine blue value	4	0.29	0.05	1.0	11	0.65	0.04	1.3	3	0.27	0.05	1.0
Texturogram A1	7	0.38	1.20	1.0	7	0.41	1.16	1.1	8	0.45	1.16	1.1
Texturogram A2	4	0.38	0.67	1.1	7	0.42	0.66	1.1	3	0.24	0.70	1.0
Texturogram A3	3	0.25	0.14	1.0	7	0.39	0.13	1.1	4	0.24	0.14	1.0
Rapid visco analyzer peak	9	0.73	29.38	1.4	11	0.75	27.70	1.5	11	0.72	29.99	1.4
Amylogram max. viscosity	9	0.83	59.11	1.8	11	0.83	60.25	1.8	12	0.84	59.13	1.8
Amylogram breakdown	10	0.87	52.23	2.0	11	0.88	51.00	2.1	11	0.88	50.42	2.1

Table 5. PLS regression results developed from milled rice spectra (2).

Property	NIR2 (1100-2498 nm)				VIS+NIR2 (400-798 nm + 1100-2498 nm)			
	nF	r	SECV	RPD	nF	r	SECV	RPD
Milled Rice								
Moisture content	6	0.99	0.12	5.8	9	0.99	0.10	6.8
Protein content	12	0.94	0.19	2.9	15	0.94	0.20	2.8
Amylose content	17	0.75	1.13	1.4	14	0.75	1.10	1.5
Free fat acidity	6	0.56	3.07	1.2	7	0.65	2.83	1.3
Bulk density	8	0.59	5.34	1.2	9	0.56	5.60	1.2
Whiteness	8	0.79	0.88	1.6	4	0.96	0.37	3.8
Translucency	2	0.75	6.08	1.5	7	0.87	4.51	2.0
Color L*	7	0.70	0.82	1.4	2	0.88	0.53	2.1
Color a*	1	0.26	0.15	1.0	6	0.70	0.11	1.4
Color b*	8	0.77	0.30	1.6	5	0.91	0.19	2.4
Color C*	8	0.77	0.29	1.6	5	0.91	0.19	2.4
Water uptake ratio	11	0.78	10.60	1.6	13	0.75	11.42	1.5
Extracted solids	11	0.67	64.93	1.3	13	0.79	54.99	1.6
Starch-iodine blue value	11	0.60	0.04	1.2	13	0.55	0.05	1.1
Texturogram A1	3	0.45	1.11	1.1	6	0.47	1.12	1.1
Texturogram A2	5	0.49	0.62	1.1	3	0.24	0.70	1.0
Texturogram A3	1	-0.67	0.10	1.3	4	0.24	0.14	1.0
Rapid visco analyzer peak	13	0.80	25.26	1.6	11	0.72	29.99	1.4
Amylogram max. viscosity	12	0.84	58.57	1.8	12	0.84	59.13	1.8
Amylogram breakdown	16	0.90	46.70	2.3	11	0.88	50.42	2.1

in the NIR2 region, for free fat acidity in the VIS+NIR2 region, and for starch-iodine blue value in the NIR1 region.

The constituent contents of rice (moisture and amylose) estimated by PLS regression models in the VIS+NIR2 range reported here are almost the same as those reported by Iwamoto et al. (1986), Natsuga et al. (1992), and Kawamura et al. (1997a). Villareal et al. (1994) and Delwiche et al. (1995, 1996) previously reported similar SEP (SECV) values but higher r values. However, their sample set included a wider range of rice samples such as medium-grain and long-grain rice varieties and waxy-type rice. A wider constituent range usually yields a higher r value with similar SEP (SECV), and we thus conclude that our results are in good agreement with these studies.

Because the VIS/NIR spectrometer used in this study could collect visible range spectra, its performance for estimating the appearance (whiteness, translucency, and color) of brown rice and milled rice was satisfactory in the VIS range. The observed SECV values for milled rice whiteness of 0.37% were better than the SEP values of 0.60% reported by Delwiche et al. (1996) and the SECVs of 0.70% and 1.92% of Barton et al. (2000).

Regarding the cooking characteristics and rheological characteristics (texturogram, rapid visco analyzer, and amylogram characteristics) of milled rice, although texturogram parameters could not be estimated accurately by VIS/NIR spectroscopy, both rapid visco analyzer and amylogram characteristics had relatively high r and low

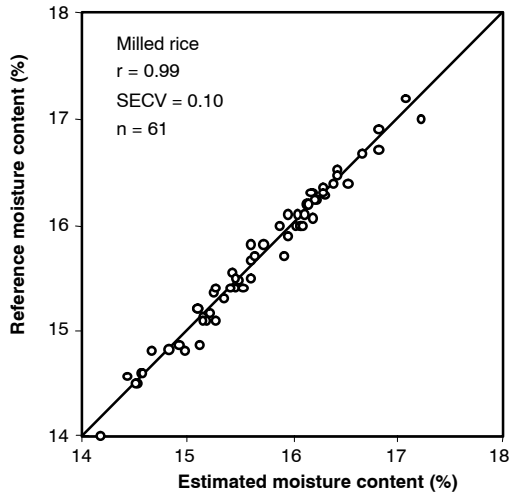


Figure 7. Correlation between reference and estimated moisture content of milled rice in the NIR1 region.

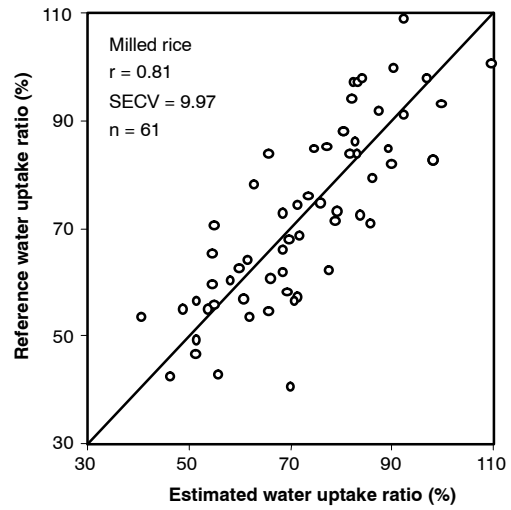


Figure 10. Correlation between reference and estimated water uptake ratio of milled rice in the NIR1 region.

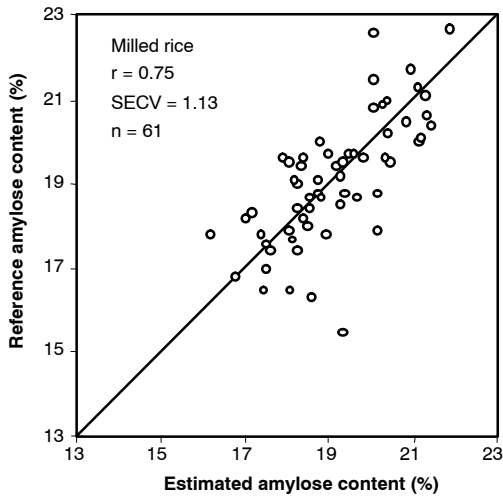


Figure 8. Correlation between reference and estimated amylose content of milled rice in the NIR2 region.

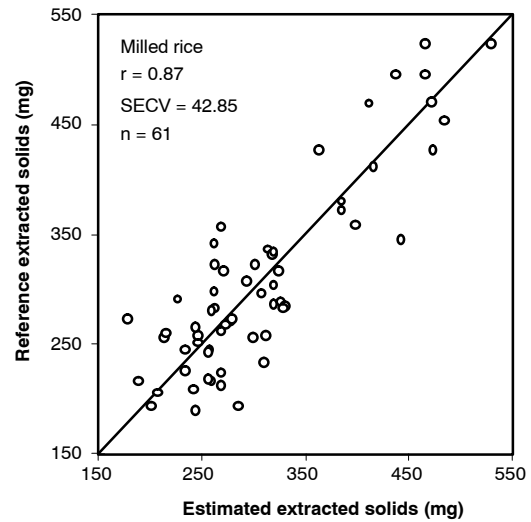


Figure 11. Correlation between reference and estimated extracted solids of milled rice in the NIR1 region.

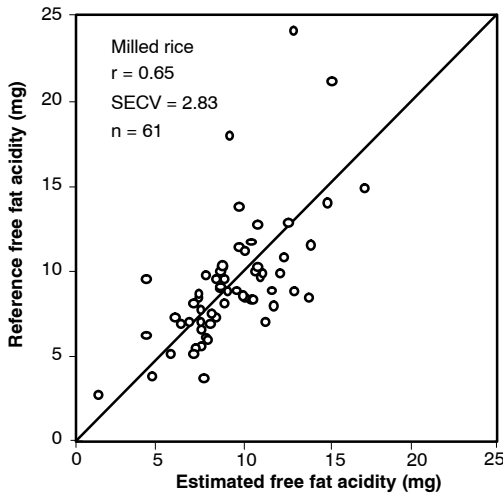


Figure 9. Correlation between reference and estimated free fat acidity of milled rice in the VIS+NIR2 region.

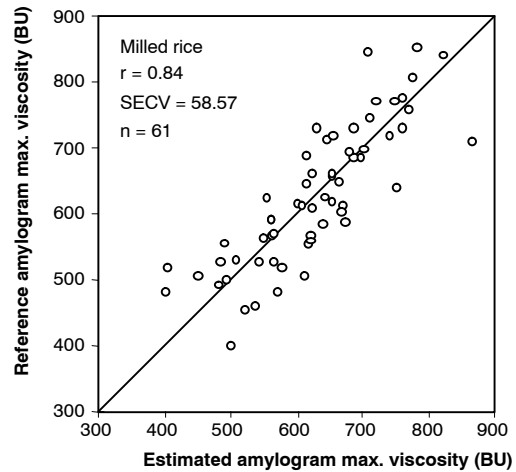


Figure 12. Correlation between reference and estimated amylogram maximum viscosity of milled rice in the NIR2 region.

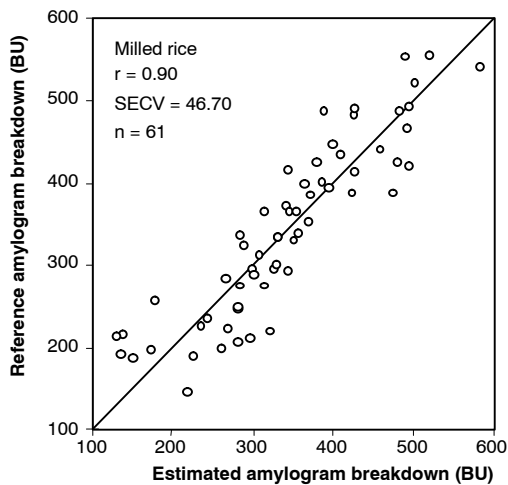


Figure 13. Correlation between reference and estimated amylogram breakdown of milled rice in the NIR2 region.

SECV: (1) a rapid visco analyzer peak of $r = 0.76$ and $SECV = 27.51$, amylogram maximum viscosity of $r = 0.87$ and $SECV = 51.75$, and amylogram breakdown of $r = 0.91$ and $SECV = 43.59$ for brown rice spectra; and (2) a rapid visco analyzer peak of $r = 0.80$ and $SECV = 25.26$, amylogram maximum viscosity of $r = 0.84$ and $SECV = 58.57$, and amylogram breakdown of $r = 0.90$ and $SECV = 46.70$ for milled rice spectra. These values were slightly less accurate than those reported by Bao et al. (2001), with an SECV of 18.5 for rapid visco analyzer peak. Since it has been shown that these characteristics are closely associated with the eating quality of rice (Chikubu et al., 1985; Kawamura et al., 1997b), VIS/NIR spectroscopy could be used for classifying rice samples according to eating quality.

Although other parameters such as embryo activity and germination vigor ratio of brown rice were not predicted well having lower RPD values, results obtained by VIS/NIR spectroscopy in this study suggest that these parameters could nonetheless be used for classifying rice samples according to their biological characteristics.

CONCLUSIONS

The results of VIS/NIR calibration modeling and validation presented in this study showed that VIS/NIR technology can be used for estimating not only the chemical compositions but also the appearance and the biological, cooking, and rheological characteristics of brown rice and milled rice. The accuracy of the VIS/NIR models was sufficient to classify rice samples into qualitative groups, and VIS/NIR technology can thus be used to determine the physicochemical properties to assess rice quality.

REFERENCES

Bao, J. S., Y. Z. Cai, and H. Corke. 2001. Prediction of rice starch quality parameters by near-infrared reflectance spectroscopy. *J. Food Sci.* 66(7): 936-939.

Barton, F. E., D. S. Himmelsbach, A. M. McClung, and E. T. Champagne. 2000. Rice quality by spectroscopic analysis: Precision of three spectral regions. *Cereal Chem.* 77(5): 669-672.

Batcher, O. M., P. A. Deary, and E. H. Dawson. 1957. Cooking quality of 26 varieties of milled white rice. *Cereal Chem.* 34(4): 277-285.

Champagne, E. T., K. L. Bett-Garber, C. C. Grimm, A. M. McClung, K. A. Moldenhauer, S. Linscombe, K. S. McKenzie,

and F. E. Barton. 2001. Near-infrared reflectance analysis for prediction of cooked rice texture. *Cereal Chem.* 78(3): 358-362.

Chikubu, S., T. Iwasaki, and T. Tani. 1960. Studies on cooking and eating qualities of white rice (part 1) comparison between Japanese rice and foreign rice. *J. Japanese Society of Food and Nutrition* 13(3): 137-140.

Chikubu, S., S. Watanabe, T. Sugimoto, N. Manabe, F. Sakai, and Y. Taniguchi. 1985. Relation between palatability evaluations of cooked rice and physicochemical properties of rice. *J. Japanese Society Starch Sci.* 32(1): 51-60.

Delwiche, S. R., M. M. Bean, R. E. Miller, B. D. Webb, and P. C. Williams. 1995. Apparent amylose content of milled rice by near-infrared reflectance. *Cereal Chem.* 72(2): 182-187.

Delwiche, S. R., K. S. McKenzie, and B. D. Webb. 1996. Quality characteristics in rice by near-infrared reflectance analysis of whole-grain milled samples. *Cereal Chem.* 73(2): 257-263.

Inatsu, O. 1988. Studies on improving the eating quality of Hokkaido rice. Report No. 66: 3-7. Hokkaido, Japan: Hokkaido Prefectural Agricultural Experiment Stations.

Iwamoto, M., T. Suzuki, N. Kongseree, J. Uozumi, and O. Inatsu. 1986. Analysis of protein and amino acid contents in rice flour by near-infrared spectroscopy. *Nippon Shokuhin Kogyo Gakkaishi* 33(12): 848-853.

Kawamura, S., M. Natsuga, and K. Itoh. 1997a. Determining undried rough rice constituent content using near-infrared transmission spectroscopy. *Trans. ASAE* 42(3): 813-818.

Kawamura, S., M. Natsuga and K. Itoh. 1997b. Visual and near-infrared reflectance spectroscopy for rice taste evaluation. *Trans. ASAE* 40(6): 1755-1759.

Li, W. S., and J. T. Shaw. 1997. Determining the fat acidity of rough rice by near-infrared reflectance spectroscopy. *Cereal Chem.* 74(5): 556-560.

Meadows, F., and F. E. Barton. 2002. Determination of rapid visco analyser parameters in rice by near-infrared spectroscopy. *Cereal Chem.* 79(4): 563-566.

Meullenet, J. F., A. Mauromoustakos, T. B. Horner, and B. P. Marks. 2001. Prediction of texture of cooked white rice by near-infrared reflectance analysis of whole-grain milled samples. *Cereal Chem.* 79(1): 52-57.

Mikami, T., T. Kashiwamura, Y. Tsuchiya, and N. Nishio. 2000. Palatability evaluation for cooked rice by a visible and near-infrared spectroscopy. *J. Japanese Society for Food Sci. and Tech. - Nippon* 47(10): 787-792.

Natsuga, M., S. Kawamura, and K. Itoh. 1992. Precision and accuracy of near-infrared reflectance spectroscopy in determining constituent content of grain. *J. Japanese Society of Agric. Eng.* 54(6): 89-94.

Onda, T., H. Abe, A. Matsunaga, Y. Komiyama, and S. Kawano. 1994. Analysis of gelatinization of starch by near-infrared spectroscopy. *J. Japanese Society for Food Sci. and Tech. - Nippon* 41(12): 886-890.

Sohn, M., F. E. Barton, A. M. McClung, and E. T. Champagne. 2004. Near-infrared spectroscopy for determination of protein and amylose in rice flour through use of derivatives. *Cereal Chem.* 81(3): 341-344.

Villareal, C. P., N. M. Cruz, and B. O. Juliano. 1994. Rice amylose analysis by near-infrared transmittance spectroscopy. *Cereal Chem.* 71(3): 292-296.

Williams, P., and K. Norris, eds. 2001. *Near-Infrared Technology in the Agricultural and Food Industries*. 2nd ed. St. Paul, Minn.: American Association of Cereal Chemists.

Williams, V. R., W. T. Wu, H. Y. Tsai, and H. G. Bates. 1958. Varietal differences in amylose content of rice starch. *J. Agric. Food Chem.* 6(1): 47-48.

Windham, W. R., B. G. Lyon, E. T. Champagne, F. E. Barton, B. D. Webb, A. M. McClung, K. A. Moldenhauer, S. Linscombe, and K. S. McKenzie. 1997. Prediction of cooked rice texture quality using near-infrared reflectance analysis of whole-grain milled samples. *Cereal Chem.* 74(5): 626-632.