

# Authentication of Rice Using Near-Infrared Reflectance Spectroscopy

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## ABSTRACT

Cereal Chem. 80(3):346–349

The authentication of rice (Korean domestic rice vs. foreign rice) has been attempted using near-infrared spectroscopy (NIRS). Two sample sets ( $n_1 = 280$  and  $n_2 = 200$ ) were used to obtain calibration equations and the spectral regions used for this study were 500–600 nm, 700–900 nm, and 980–2,498 nm. Modified partial least square (MPLS) regression was used to develop the prediction model. The standard error of cross validation (SECV) and the  $r^2$  were 0.165 and 0.91 respectively for 1st

calibration set and 0.165 and 0.93 for 2nd calibration set respectively. The results of the independent validation ( $n_3 = 80$ ) showed that all of 80 samples were identified correctly. Even though authentication of rice was performed successfully using NIRS, the calibration statistics in this study showed that further effort is needed for implementation of NIRS for authentication of rice for industry purposes.

Rice is a staple food in Korea and the concern about rice is much greater than that for other foods. Rice markets in Korea and Japan are gradually opening to the world according to the World Trade Organization (WTO) agreements and upcoming WTO negotiations on rice will be held in 2004. The price of rice cultivated in Korea and Japan is two or three times higher than that imported from foreign countries. Because of the difference in price between imported and domestic rice, imported rice can be mislabeled or mixed into domestic rice, which is illegal in Korea. To prevent illegal marketing of rice, a method for valid authentication of rice should be established. However, information on methods for authentication of rice is not established and is scarcely found in the literature.

Authentication of foods has various aspects such as species or variety, geographical origin, age, process received and admixture with base materials. Depending on the aspects, suitable methods for authentication could be different. Frequently DNA analysis or near-infrared spectroscopy (NIRS) have been used for authentication of foods. At the standpoint of species or cultivars, DNA analysis is suitable for authentication because DNA information is identical for identical cultivars or species. However, DNA analysis is not suitable for identification of geographical origin because identical cultivars grown in different places would carry identical DNA information. Because the authentication of rice in this study was mainly for geographical origin of the samples, NIRS analysis was used for this study.

NIRS analysis has an advantage of being a nondestructive and fast method, while DNA analysis can be classified as a destructive method. NIRS is a tool with many potential advantages in authenticity testing, and it has already been applied to a number of authentication problems using a range of sample presentation and chemometric techniques (Downey 1996). For example, NIRS was used for authentication of Basmati rice (Osborne et al 1993), coffee bean cultivars (Downey and Boussion 1996), green asparagus cultivars (Perez et al 2002), fresh versus frozen then thawed beef (Downey and Beauchene 1997), fruit pulps (Wesley 1996), and measurement of adulteration of olive oils (Wesley et al 1995). For authentication of rice, Osborne et al (1993) investigated the feasibility of using near-infrared transmission spectroscopy to discriminate between individual grains of Basmati and other long grain rice using 16 Basmati and 100 other rice samples of known province. The results showed that 8% of the Basmati and 14% of

the others were misclassified on the basis of a rule based on spectra of 930 individual grains. Even though it was encouraging as a result of feasibility study, further investigation was suggested to establish whether satisfactory discrimination is possible for a wide population of Basmati samples.

The above research implies that NIRS could be a useful tool for discrimination of Korean domestic rice from other foreign rice, which will be an important issue in Korea to prevent illegal marketing of rice. Even though authentication of rice is needed not only for pure samples but also for mixed sample, as a first step, the possibility of authentication of rice (Korean domestic rice vs. foreign rice) was investigated using NIRS with only pure samples in this study.

## MATERIALS AND METHODS

### Materials

Short or medium grain rice was used and long grain was excluded as samples for this study because long grain is not available in Korean market. A total of 280 rice samples were used for this study (139 domestic and 141 foreign rice samples). Among 141 foreign rice samples, 81 were from the United States, 23 from Australia, and 37 from China. Domestic and foreign rice used for this study were harvested in 1996–98. Domestic rice samples used for this study were pure Korean samples, which were those with identified cultivar and cultivated site. They were considered to be representative samples of cultivars and cultivation sites in Korea. Domestic paddy rice was obtained through the Grain Marketing Department in National Agricultural Cooperative Federation (Seoul, Korea). Paddy rice was dehulled using a rice machine (Type THU, Satake Engineering Co., Tokyo). After dehulling, the brown rice was milled using a testing rice mill (VP-31T, Fujihara Factory, Tenzusi, Japan) to 9.6% degree of milling based on brown rice.

Most of the Australian rice was harvested in Riverina district and supplied by the Rice Grower's Co-operative Limited in Australia. Most of rice samples from the United States and China were purchased individually in each country and the rest of the foreign rice samples were obtained from National Agricultural Products Quality Management System (NAPQMS) in Korea.

### Spectroscopic Measurements

Rice samples were stored in a refrigerator (5°C) until spectroscopic measurements and the rice was placed at room temperature one day before measurement. Milled rice was placed in a rectangular coarse cell (width × length × depth, 5.7 × 29.4 × 2.0 cm) using a sample transport module without any alteration of grain. The reflectance spectra of milled rice were recorded as log (1/R) on all samples between 400 to 2,500 nm in 2-nm intervals using a NIR system 6500 scanning monochromator (Foss NIRSystems, Silver Spring, MD). NIR spectral data were handled by the WinISI II software v. 1.01 (Infrasoft International, Port Matilda, PA).

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NIRS data for authentication of rice were collected for three years to establish a valid database, considering the variations of rice depending on the harvesting year and the limit in number of foreign rice samples that could be collected for any one year. NIR spectrum was recorded and stored each year after collection of rice samples.

### NIRS Calibration for Authentication of Rice

As a chemometric technique of NIRS quality analysis, a modified partial least square (MPLS) regression was used. As a first step for calibration, the reference value of "1" was assigned for 139 Korean domestic rice and the reference value of "2" was assigned for 141 foreign rice. As a second step, a prediction equation was developed relating the spectroscopic information with the assigned values (1 or 2). The regression methods chosen was MPLS and for the correction of the scatter effect, standard normal variate (SNV), and detrending (DT) mathematical procedures were applied. During the calibration process, removal of the ranges of wavelength with large standard deviation within rice groups has been attempted to find the spectral regions that are effective for authentication of rice, resulting in high  $r^2$  and low SECV for the equation. The spectral regions used for this study were 500–600 nm, 700–900 nm, and 980–2,498 nm. The spectral regions <500 nm, 600–700 nm, and 900–980 nm were not used for this study because of large variation of the spectrum within group (domestic

**TABLE I**  
Mean, Range, and Standard Deviation for Two Calibration Sets and One Validation Set

	Set	Mean	Range	SD
Calibration	N1 ( $n_1 = 280$ )	1.500	1.00–2.00	0.500
	N2 ( $n_2 = 200$ )	1.500	1.00–2.00	0.500
Validation	N3 ( $n_3 = 80$ )	1.512	1.00–2.00	0.501

**TABLE II**  
Cross-Calibration Statistics for Authentication of Rice (Korean Domestic Rice vs. Foreign Rice) with Two Different Calibration Sets<sup>a</sup>

Cross Calibration Statistics <sup>b</sup>	Calibration Set	
	N1 ( $n_1 = 280$ )	N2 ( $n_2 = 200$ )
Math treatment	2, 8, 8, 1	2, 8, 8, 1
Number of outliers	26	17
N (calibration set)	254	183
PLS factors	9	11
SECV (%)	0.165	0.165
$r^2$	0.914	0.932
RPD	3.04	3.04
RER	6.06	6.06

<sup>a</sup> Standard normal variate (SNV), and detrending (DT) mathematical procedures applied.

<sup>b</sup> PLS, partial least square; SECV, standard error of cross-validation; RPD, standard deviation (SD)/SECV; RER, (range of data: maximum data – minimum data)/SECV.

**TABLE III**  
Validation Statistics Values for Authentication of Rice ( $n = 80$ ) with Calibration Equation Developed with 200 Samples

Validation Statistics	Values	Limit
SEP	0.164	
Mean	1.513, <sup>a</sup> 1.545 <sup>b</sup>	20% difference
Bias	-0.033	
Bias limit	0.099	
SEP (c)	0.162	
SEP (c) limit	0.214	
Standard deviation	0.503, <sup>a</sup> 0.505 <sup>b</sup>	20% difference
Slope	0.945	0.900
$r^2$	0.899	0.600
Validation set number	80	

<sup>a</sup> SEP, standard error of performance.

<sup>b</sup> Laboratory data.

<sup>c</sup> NIRS data.

vs. foreign) of rice. The derivation treatments were 2, 8, 8 and 1. The first digit is the number of the derivative, the second is the gap over which the derivative is calculated, the third is the number of the data points in a running average or smoothing, and the fourth is the second smoothing (Shenk and Westerhaus 1995). When developing MPLS equations, cross-validation was used to select the optimum number of factor bases on low SECV. The calibration equation was selected based on  $r^2$  and SECV.

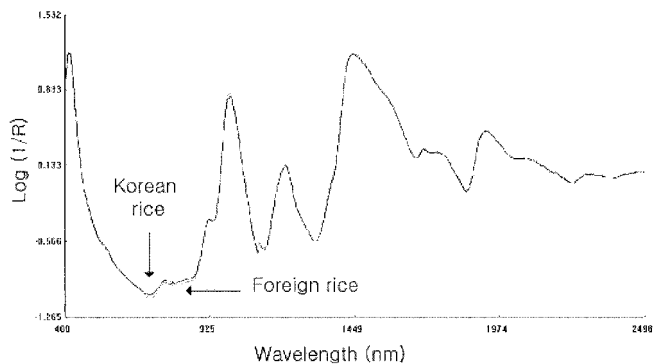
In addition to  $r^2$  and SECV, RPD, and RER were calculated as in Perez et al (2001) to investigate the possibility of the industrial use for the equation developed and the RPD and RER were calculated as:

$$RPD = \text{standard deviation (SD)/SECV}$$

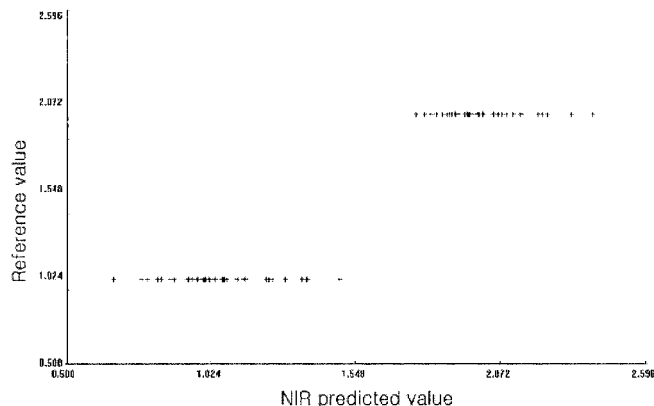
$$RER = (\text{range of data: maximum data} - \text{minimum data})/\text{SECV}$$

The outliers whose predicted values differed significantly from those of the reference, were detected based on  $t = 2.5$ . Even though SECV statistic is recognized as an adequate estimator of the prediction error, in this study an independent validation set of samples was used to evaluate the accuracy of the model. The objective of the validation procedure was to obtain an independent measure of equation accuracy expressed as standard error of performance (SEP).

In this study, independent validation was performed and calibration results were compared. For validation procedure, total 280 rice samples were divided into two subsets: 1) 200 samples (5/7 of the total) and 2) 80 samples (2/7 of the total). In 200 calibration samples, 100 rice samples for each Korean domestic rice and foreign rice were included. The validation set was made up of 39 Korean rice and 41 foreign rice. Cross-calibration statistics with 200 rice samples were compared with those of 280 total samples and it was confirmed whether or not SECV is a valid estimator for SEP with the reduced number of samples.



**Fig. 1.** Average reflectance spectra of Korean domestic rice ( $n = 139$ ) and foreign rice ( $n = 141$ ).



**Fig. 2.** Reference value vs. NIRS predicted value corresponding to 80 rice samples used for independent validation of the prediction model.

## RESULTS AND DISCUSSION

Average spectra of Korean domestic rice and foreign rice are in Fig. 1, showing that the difference between the average spectra of two sample groups was not noticeable. The use of chemometric methods was required because of similarity in spectra, which was suitable for extracting relevant information related to each group (Korean domestic rice vs. foreign rice).

The mean and standard deviation of the two calibration sets and the validation set were alike (Table I). Cross-validation statistics with two different calibration sets (Table II) showed similar  $r^2$ , SECV, RPD, and PER values. The coefficient of determination ( $r^2$ ) values indicated that 91 and 93% variability could be explained by the chemometric model for calibration set 1 and calibration set 2, respectively, in authentication of rice. Considering  $r^2 = 0.93$  for reduced number ( $n_2 = 200$ ) of calibration set and  $r^2 = 0.91$  for calibration set with  $n_1 = 280$ , calibration set with reduced number was better in this study and identical result was shown by Perez et al (2001). The RPD and RER values were 3.04 and 6.06, respectively, regardless of calibration sets. Williams and Sobering (1996) suggested the limit of 3 and 10 for RPD and RER, respectively, as an equation sufficiently sound to be included in quality control in industrial processes. Based on the information that acceptable values for RPD and RER are higher than 3 and 10, respectively, RPD value in the study was acceptable while RER value was not. The results of this study showed that the chemometric model developed in this study could be used effectively for authentication of rice; however, it was not sufficient for industrial use.

The validation statistic values for the authentication of rice using an independent validation set are in Table III. The limits in Table III are those recommended by Shenk et al (1989) and the validation results were within those limits. The SEP (0.164) in Table III was similar to that of SECV (0.165) in Table II, confirming that SECV is a valid estimator of SEP. Bias (0.033) and SEP (c) (0.164) was less than the maximum recommended limit (0.099 and 0.214 for bias limit and SEP [c] limit, respectively).

The reference values versus NIR predicted values of 80 rice samples used for the independent validation set are given in Fig. 2. Reference value, NIR predicted values, and residuals (reference value – NIR predicted value) for 80 independent validation samples using NIRS equations developed using 200 calibration samples are given in Table IV. In addition to low bias value (–0.03) in Table III, the results of  $t$  test to test the difference between reference value and NIR predicted value showed no difference between the two values. Except for one Korean rice (sample number 38 cultivar Illpoom) that had NIR predicted value of 1.49, all of 79 samples were identified correctly.

The correct identification of rice could be caused by environmental, genetic or processing differences between domestic rice and foreign rice. Environmental conditions for Korean samples were different from foreign rice. For example, summer in Korea is typically hot and humid, and winter is cold and dry, while summer in the United States, especially in California, is hot and dry, and winter is cool and rainy or humid. All of the U.S. rice samples for this study were cultivated in California. And all of the Chinese rice was cultivated in Manchuria, which is located in the north of the Korean Peninsula. Considering that all of the Korean samples were harvested in southern part of the Korean peninsula, the weather condition for Chinese rice is different from that for Korean rice. Also, the storage or aging time (after harvesting to testing) for Australian rice was different from rice from other countries because the harvesting season in Australia is different from that in other countries.

The above differences might contribute to the discrimination of domestic rice from foreign rice using NIRS in this study. Also, most of the Korean rice was different from foreign rice genetically. However, an identical cultivar, Jinmi was included in this study both in domestic rice and in foreign rice. The difference in milling process between domestic rice and foreign rice might contribute to the correct identification of rice. While domestic rice was milled in the laboratory, all of the foreign rice was commercially available milled rice. The difference in milling process

TABLE IV  
Reference and NIR Predicted Values of 80 Rice Samples Used for Independent Validation

No.	Cultivated Region in Korea	Cultivar	Reference Values	Nir Predicted Value	Residuals	No.	Cultivated Country	Cultivar or Brand (Manufacturer Provider)	Reference or Values	Nir Predicted Value	Residuals
1	Kyunggido	HwaJung	1.00	0.98	-0.03	40	U.S.A.	Ontario <sup>a</sup>	2.00	1.82	0.18
2	KyungsangNamdo	Hwanam	1.00	1.06	-0.06	41	U.S.A.	Ontario <sup>a</sup>	2.00	1.90	0.10
3	Chullabookdo	Gaehwa	1.00	0.95	0.05	42	U.S.A.	Ontario <sup>a</sup>	2.00	1.97	0.03
4	Chungchongnamdo	Chuboo	1.00	0.83	0.17	43	U.S.A.	M-401	2.00	2.05	-0.05
5	Chungchongbookdo		1.00	1.00	0.00	44	U.S.A.	M-401	2.00	1.94	0.06
6	Chungchungnamdo		1.00	0.67	0.33	45	U.S.A.	Homai	2.00	1.96	0.04
7	Chungchungnamdo		1.00	0.80	0.21	46	U.S.A.	Homai	2.00	1.95	0.05
8	Chungchungnamdo		1.00	1.04	-0.04	47	U.S.A.	Homai	2.00	1.91	0.09
9	Chullabookdo		1.00	0.88	0.12	48	U.S.A.	Homai	2.00	1.92	0.08
10	Chullabookdo	Dongjin	1.00	1.01	-0.01	49	U.S.A.	Homai	2.00	2.01	-0.01
11	Chullanamdo	Gaehwa	1.00	0.95	0.05	50	U.S.A.	Maruyo	2.00	1.95	0.05
12	Chullanamdo	Gaehwa	1.00	0.98	0.02	51	U.S.A.	Maruyo	2.00	1.99	0.01
13	Chullanamdo	Gaehwa	1.00	1.07	-0.07	52	U.S.A.	Maruyo	2.00	1.96	0.04
14	Kaangwondo	Hwasung	1.00	1.14	-0.14	53	U.S.A.	Jinmi	2.00	1.87	0.14
15	Kyunggido	Bongkwang	1.00	0.77	0.23	54	U.S.A.	SP411	2.00	2.01	-0.01
16	Chungchongbookdo	Chuchong	1.00	1.02	-0.02	55	U.S.A.	Hanmi	2.00	2.12	-0.12
17	Chungchongbookdo	Illpoom	1.00	1.22	-0.22	56	U.S.A.	Kokuho Rose	2.00	2.10	-0.10
18	KyungsangNamdo	Saamback	1.00	0.85	0.16	57	U.S.A.	SP311 (Pirmi)	2.00	2.14	-0.14
19	KyungsangNamdo	Saamback	1.00	0.94	0.06	58	U.S.A.	WRS-1369 (Pirmi)	2.00	1.80	0.20
20	KyungsangNamdo	Saamback	1.00	0.99	0.01	59	U.S.A.	(Commodity)	2.00	1.99	0.01
21	Kyungsangbookdo	Dongjin	1.00	1.02	-0.02	60	U.S.A.	American Rice Inc.	2.00	2.07	-0.07
22	Chungchongbookdo	Youngdong	1.00	1.37	-0.37	61	U.S.A.	Nishiki	2.00	2.21	-0.21
23	Chungchongbookdo	Youngdong	1.00	1.24	-0.24	62	U.S.A.	NAPQMS <sup>b</sup>	2.00	1.99	0.01
24	Kyungsangnamdo		1.00	1.37	-0.37	63	U.S.A.	NAPQMS <sup>b</sup>	2.00	1.95	0.05
25	Kyungsangbookdo		1.00	1.23	-0.23	64	Australia	Bogan	2.00	2.15	-0.15
26	Kyunggido	HwaJoong	1.00	0.94	0.06	65	Australia	Jarrah	2.00	2.05	-0.05
27	Kyungsangnamdo	Hwaseung	1.00	0.96	0.04	66	Australia	Millin	2.00	1.77	0.23
28	Kyungsangnamdo	Dongjin	1.00	0.89	0.11	67	Australia	Amaroo	2.00	2.07	-0.07
29	Kyunggido	Chuchong	1.00	1.15	-0.15	68	Australia	Namaga	2.00	2.22	-0.22
30	Kyungsangnamdo	Youngnam	1.00	1.08	-0.08	69	Australia	Millin	2.00	1.89	0.11
31	Kyungsangnamdo	Youngnam	1.00	1.12	-0.12	70	Australia	Illabong	2.00	2.41	-0.41
32	Kyungsangbookdo	Illpoom	1.00	1.00	0.00	71	China	NAPQMS <sup>b</sup>	2.00	2.08	-0.08
33	Kaangwondo	Jinmi	1.00	1.00	0.00	72	China	GapKang 19	2.00	1.96	0.04
34	Chullanamdo	Dongjin	1.00	1.29	-0.29	73	China	NAPQMS <sup>b</sup>	2.00	1.84	0.16
35	Chullabookdo	Paalgong	1.00	1.07	-0.07	74	China	NAPQMS <sup>b</sup>	2.00	2.01	-0.01
36	Chullabookdo	Dongjin	1.00	1.29	-0.29	75	China	(Daewoo Inc.)	2.00	2.00	0.00
37	Chungchongnamdo	Ahnjoong	1.00	1.24	-0.24	76	China	NAPQMS <sup>b</sup>	2.00	1.99	0.01
38	Chungchongnamdo	Illpoom	1.00	1.49	-0.49	77	China	NAPQMS <sup>b</sup>	2.00	1.91	0.09
39	Chungchongbookdo	Odae	1.00	1.35	-0.35	78	China	NAPQMS <sup>b</sup>	2.00	1.88	0.12
						79	China	NAPQMS <sup>b</sup>	2.00	2.24	-0.24
						80	China	NAPQMS <sup>b</sup>	2.00	2.33	-0.33

<sup>a</sup> U.S. rice purchased in Canada.

<sup>b</sup> NAPQMS, National Agricultural Products Quality Mangement System in Korea.

between Korean rice and foreign rice might contribute to the correct identification of rice by NIRS.

In previous studies, the correct identification using NIRS varied depending on the studies. For example, Perez et al (2001) correctly identified the green asparagus cultivar 100% using NIRS and a chemometric model and the results proved that the technique can be easily implemented in industry. Wesley (1996) also showed that NIRS in conjunction with discriminant analysis could be used to classify apple pulps by cultivar with a 100% success rate. Wesley et al (1995) attempted to measure the level of adulteration using NIRS with a set of virgin and extra virgin olive oils adulterated with corn oil, sunflower oil, and raw olive residue oil. As a result, the level of adulteration was correctly identified for 98% of the spectra, and the identification of the adulteration was correct for 75% of the samples. Osborne et al (1993) demonstrated the feasibility of using NIR transmission spectroscopy for authentication of Basmati rice by showing 8 and 14% misidentification rate for Basmati rice and the others, respectively.

The results of this study showed that NIRS is a potential tool for discriminating Korean domestic rice from foreign rice. However, the calibration statistics suggested that further research is required for implementation of the results for industrial use.

### CONCLUSIONS

The results of this study showed that authentication of rice could be done successfully using NIR reflectance spectroscopy. Those correct identification of rice could be caused by environmental differences between Korean rice and foreign rice. However, application of this technique for industrial purposes still remains to be solved. Further research on authentication of rice is needed for the implementation of this technique at industry level.

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[Received June 27, 2002. Accepted February 28, 2003.]