



ORIGINAL RESEARCH ARTICLE

PRACTICAL APPLICATION OF NEAR-INFRARED SPECTROSCOPY FOR DETERMINING RICE AMYLOSE CONTENT AT GRAIN ELEVATOR

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ABSTRACT

The major chemical constituent contents of rice are moisture, protein and starch (amylose and amylopectin). Those constituent contents associate with eating quality of rice. Near-infrared (NIR) spectroscopy is one of the non-destructive methods for determining grain chemical contents. At grain elevator, moisture and protein contents can be measured with high accuracy using an NIR spectrometer by the effort of our research activities in Japan. However, the accuracy to determine amylose content is not sufficient. Thus, the objective of this study was to develop non-destructive method to determine rice amylose content for practical use at grain elevator. Milled rice amylose content measurement was performed using an auto-analyzer for reference (chemical) analysis. Spectra data of milled rice were obtained using an NIR spectrometer with a wavelength range of 850 to 1048 nm. Calibration model to determine amylose content was developed using non-waxy Japonica-type rice samples. Partial least squares (PLS) regression analysis was used to develop calibration model. The accuracy of the model was validated and the validation statistics were shown: coefficient of determination (r^2) was 0.72, bias was -0.04%, standard error of prediction (SEP) was 0.92%, and ratio of SEP to standard deviation of reference data (RPD) was 1.90. Production year of the validation set (2017) was different from that of the calibration set (2008 to 2016). This means the same condition as practical use of this method at grain elevator. The result obtained in this study indicated that this calibration model enables non-destructive determination of rice amylose content at grain elevator.

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1.0 Introduction

Rice is staple food for people in the large part of the world, especially in Asian countries. The major chemical constituent contents of rice are moisture, protein and starch (amylose and amylopectin). Those chemical constituents associate with eating quality of rice. The moisture content of rice is closely related to storage quality and milling characteristics. Protein and amylose contents are important constituent contents associated with texture and eating quality of cooked rice (Allahgholipour *et al.*, 2006). Texture of cooked rice greatly affects eating quality and is one of the most important quality factors of rice (Natsuga, *et al.*, 1999).

Environmental temperature during the ripening period of rice greatly affects amylose content in rice (Matsue *et al.*, 2002; Kinoshita and Sato, 2004; Igarashi *et al.*, 2009; Tanno, 2010; Yamaguchi *et al.*, 2012; Tsujii *et al.*, 2015). Lower environmental temperature during the ripening period of rice causes higher rice amylose content. Hokkaido is the northernmost island in Japan. In Hokkaido, therefore, the temperature of rice ripening period is lower than that in the other areas in Japan and rice amylose content increases than the other areas. East Asian people including Japanese, Korean and most of Chinese people prefer low amylose content rice, because it becomes soft and sticky cooked rice. Thus, Hokkaido makes effort in development of low amylose content rice cultivar.

In Hokkaido, we have bred low amylose rice cultivar called *Yumepirika* from 2008. *Yumepirika* is the original brand rice in Hokkaido. We want to make higher quality of rice. Thus, it was decided that the good taste combination of amylose and protein content about *Yumepirika*. For example, when amylose content is less than 19%, protein content is less than 7.5%, or when amylose content is 19% or more, protein content is 6.8% or less (Kawamura *et al.*, 2013). The combination is selected finely. Therefore, there is a need for the highly accurate measurement of rice protein and amylose content.

Near-infrared (NIR) spectroscopy is one of the non-destructive methods for determining grain chemical contents. There have been many studies on the usefulness of NIR spectroscopy as a non-destructive method for determining chemical constituent contents of agricultural products such as grain, fruits and vegetable. Now, it has been shown that determination of moisture and protein contents of rice by NIR spectrometer is sufficiently accurate for practical use at rice grain elevators (Fujita *et al.*, 2010; Li *et al.*, 2013). However, the accuracy for determination of rice amylose content by NIR spectrometer is lower than those of moisture and protein contents. However, rice amylose content has great impacts on the eating quality of rice and farmer's income. Thus, there is a strong need for the highly accurate measurement of rice amylose content using non-destructive method such as NIR spectroscopy. The overall objective of this study was to develop non-destructive and more accurate calibration model to determine rice amylose content for practical use at grain elevator.

2.0 Materials and Methods

2.1 Rice Samples

For this study, a total number of 1069 milled rice samples were collected from Hokkaido, Japan. Table 1 shows the detail of the rice samples collected. The rice samples consisted of 14 cultivars of non-waxy Japonica-type rice grown in Hokkaido, Japan from 2008 to 2017. The cultivar names of the rice samples were *Aya*, *Ayahime*, *Daichinohoshi*, *Fukkurinko*, *Hoshimaru*, *Hoshinoyume*, *Kitakurin*, *Kirara397*, *Nanatsuboshi*, *Oborozuki*, *Sorayuki*, *Yukihikari*, *Yumepirika* and *Yukisayaka*. *Ayahime*, *Aya*,

Oborozuki, *Yumepirika* and *Yukisayaka* are low amylose content rice cultivars, and the others are ordinary amylose content rice cultivars.

2.2 Reference (Chemical) Analysis of Amylose Content

Amylose content measurement was performed using an auto-analyzer (Bran-Luebbe, Solid Prep III Tokyo, Japan) for reference (chemical) analysis following the protocol of Williams *et al.* (1958) with modifications by Inatsu (1988). The absorption of the amylose-iodine complex was measured at 620 nm with a spectrophotometer, and the apparent amylose content was quantified against a calibration curve. In this study, *Hoshinoyume* cultivar of rice (moisture content: 13.09%, amylose content: 21.12%) grown in Hokkaido and *Hakuchoumochi* cultivar of glutinous rice (amylose content: 0%) grown in Hokkaido were used as standard amylose contents to calculate the apparent amylose content (AAC) of each sample. Apparent amylose content was expressed as a percentage (%).

Table 1. Rice sample used in this study

Production year	A	B	C	D	E	F	G	H	I	J	K	L	M	N	Total
2008	2	1	3	10		18		33	41	12					120
2009			16	9		14		12	11	13			45		120
2010			7	4		19		20	25	19			42		137
2011			1	10		6		18	25	8			42		110
2012				3					5				34		42
2013			9	13		7	6	18	27	5			15		100
2014			6	7		4	2	27	28	3		1	21		99
2015			10	11		9	11	8	36	12	14		32		144
2016			4	13	6	1	4	6	29	3	2		33	1	102
2017			2	20	5		1	4	25	2	2		33	1	95
Total	2	1	58	100	12	78	24	147	252	77	18	1	297	2	1069

A=Ayahime, B=Aya, C=Daichirinko, D=Fukkurinko, E=Hoshimaru, F=Hoshiyome, G=Kitakurinn, H=Kirara 397, I=Nanatuboshi, J=Oborozuki, K=Sorayuki, L=Yukihikari, M=Yumepirika, N=Yukisayaka



Figure 1. NIR spectrometer, model BR-5000

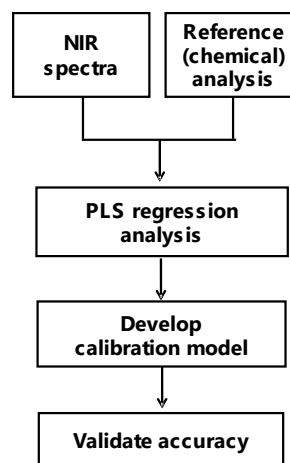


Figure 2. Flow chart of developing Calibration model and validating the accuracy

2.3 Calibration Model from NIR Spectrometer

Spectra data of milled rice were obtained using an NIR spectrometer (Shizuoka Seiki, BR-5000, Fukuroi, Japan) (Figure 1) with a wavelength range of 850 to 1048 nm with 2-nm intervals.

The Savitzky-Golay derivative was used for pretreatment. The chemometric techniques partial least squares (PLS) regression within the statistical software The Unscrambler (Version 10.3 Upgrade 10.3.0r4) were used for processing the data.

Calibration model to determine amylose content was developed using the rice samples (calibration set, n=974, including 14 cultivars) grown from 2008 to 2016. And Partial least squares (PLS) regression analysis was used to develop calibration model. The accuracy of the calibration model was validated using the other rice samples (validation set, n=95, including 10 cultivars) grown in 2017. Figure 2 shows the flow chart of developing calibration model and validating the accuracy.

3.0 Results and Discussion

The accuracy for determining amylose content of milled rice was shown in the following. Table 2 shows that when the production years for calibration set increased, standard error of prediction (SEP) values decreased and ratio of SEP to standard deviation of reference data (RPD) values increased. This means that the accuracy was improved by increasing production years of calibration sample set and this method got a step closer to practical use at grain elevator.

Amylose content of rice is affected by environmental temperature during the ripening period. In other words, the environmental temperature of each production years was different, amylose content of rice changed by each production year. Natsuga (1995) reported that to obtain high accuracy of calibration model, it is necessary to use samples collected over a period of several years. By increasing production years of calibration set, the information of variation in temperature and amylose content was added to the calibration model, and then the accuracy of determination of milled rice amylose content was improved. This is the reason why the accuracy for calibration model increases when the production years for calibration set increases.

The correlation between reference (chemical) amylose content of milled rice and predicted amylose content of milled rice (calibration set: 2008 to 2016, validation set: 2017) is shown in Figure 3. The coefficient of determination (r^2) was 0.72, bias was -0.04%, SEP was 0.92% and RPD was 1.90. The production years of validation set (2017) was isolated from calibration set (2008 to 2016). This is the same condition in practical use of this non-destructive method at grain elevator. The result indicates that this method enables non-destructive determination of rice amylose content at grain elevator.

Table 2. Change of accuracy for determining amylose content of milled rice

calibration set	n (2017)	r^2	Bias(%)	SEP(%)	RPD	Regression
3 years (2008-2010)	95	0.25	0.26	1.94	0.90	$y=0.41x+12.5$
4 years (2008-2011)	94	0.46	-0.99	1.40	1.25	$y=0.67x+7.50$
5 years (2008-2012)	95	0.41	-0.89	1.55	1.12	$y=0.58x+9.19$
6 years (2008-2013)	95	0.50	-2.00	1.27	1.37	$y=0.80x+5.75$
7 years (2008-2014)	95	0.49	-1.79	1.29	1.35	$y=0.78x+6.09$
8 years (2008-2015)	95	0.65	0.41	1.03	1.69	$y=1.01x-0.72$
9 years (2008-2016)	94	0.72	-0.04	0.92	1.90	$y=0.99x+0.20$

n: the number of validation set, r^2 : coefficient of determination, Bias: difference of average values between predicted values and reference (chemical) values, SEP: standard error of prediction, RPD: ratio of SEP to standard deviation of reference data, Regression line: Regression line from predicted value (x) to reference value (y).

Figure 3 shows that the result which we validated the calibration model using 9-year production samples (2008-2016) for calibration set and 1-year production sample (2017) for validation set. Regression line is $y=0.99x+0.20$, $r^2=0.72$, Bias=-0.042%, SEP=0.92%, RPD=1.90, and n (the number of validation sample set)=94 (This result shown at the most bottom of Table 2.)

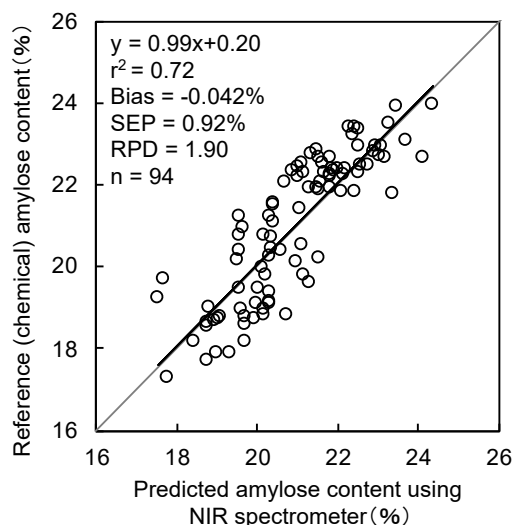


Figure 3. Correlation between reference (chemical) amylose content of milled rice and predicted amylose content of milled rice

4.0 Conclusion

The validation statistics between reference (chemical) amylose content and NIR spectrometer-predicted amylose content indicate that when the production years for calibration set increase, the accuracy for determining amylose content of milled rice improves. And in this study, the production year of validation set was isolated from that of calibration set. Thus, this is the same condition in practical use of this non-destructive method at grain elevator. The result obtained in this study indicates that the calibration model (developed using 9-year production samples (2008-2016)) enables non-destructive determination of rice amylose content at grain elevator.

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