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Application of Visible/Near-Infrared Transmittance Spectroscopy for the Improvement of Amylose Determination Accuracy

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The performance of partial least squares (PLS) calibration models developed using NIR and visible transmittance were examined in order to improve the accuracy of the calibration model for amylose content. The regression coefficients in the PLS calibration model developed by a full-cross validation using the wavelength region from 570 to 1000 nm (Model B) were smoother and the fluctuations of the coefficients were smaller than the model developed by a full-cross validation using the wavelength region from 850 to 1048 nm (Model A). Significant peaks in the regression coefficients of Model A were characterized by two absorption bands at 928 and 990 nm, and those of Model B were characterized by four absorption bands at 607, 760, 928 and 990 nm. The samples were separated into calibration sets and validation sets, and PLS calibration and validation were also performed. The statistics performance (standard error of performance (SEP), a coefficient of determination (R^2)) of the model developed using the wavelength region from 570 to 1000 nm (Model D), was better than those of the model developed using the wavelength region from 850 to 1048 nm (Model C). The SEP of 0.64% on model D examined here was smaller than that of 0.99% on Model C. Therefore, the absorption bands at 607 and 760 nm play an important function in improving the performance of the PLS calibration model.

Keywords: visible/near-infrared transmittance, near-infrared transmittance (NIT), partial least squares (PLS), regression coefficients, *japonica*, amylose

Rice is consumed mainly as cooked whole grain kernels, and the physical properties of cooked rice are important from the viewpoint of its edible quality. These physical properties of cooked rice are characterized by the apparent amylose content (amylose content) of milled rice. Therefore, amylose content is used as index of rice quality, especially for its edible quality.

In our previous study, near-infrared transmittance (NIT) apparatus (wavelength range: 833–1050 nm, type of spectroscopy: filter) for whole-grain milled rice was used to develop a partial least squares (PLS) calibration model for amylose content. The statistics performance of the model had a standard error of performance (SEP) of 1.25%, a coefficient of determination (R^2) of 0.49 and bias of -1.19% (Shimizu *et al.*, 1999). There was insufficient performance of the PLS calibration model to measure amylose content, and for *japonica* type rice in particular, which has a narrow range of amylose content, a more accurate NIT determination method is required.

Therefore, in this study, the performance of a PLS calibration model developed using NIR and visible transmittance was examined in order to improve the accuracy of the calibration model for amylose determination.

Materials and Methods

Sample and preparation Short-grain *japonica non-glutinous* type rices (125 samples; 37 varieties), harvested in 1996 were collected in 37 prefectures throughout Japan.

Milling of brown rice samples was carried out up to a milling yield of 90%, w/w, using a VP-31T friction type rice milling machine (Yamamoto CO., Tendou). Broken kernels were removed using a TGR cylinder type separator (Satake CO., Higashihiroshima). The characteristics of a sample set used to make the calibration mode are shown in Table 1.

Determination of amylose content The milled rice samples were ground with a 3010-018 model cyclone grinder (Udy, Ft. Collins, CO) equipped with a 50-mesh screen. Before amylose determination, the moisture contents of the ground samples were determined in duplicate by an oven drying method using 3 g of rice powder at 135°C for 1 h. The amylose (%) was determined in duplicate on 50-mesh milled rice flour by the iodine colorimetric method of Juliano (1971) as reported (Shimizu *et al.*, 1999).

Near-infrared spectra acquisition The whole-grain samples of milled rice were scanned using a scanning monochromator which is the prototype of the Infratec 1241 spectrometer (Foss-Tecator AB, Höganäs, Sweden). The Infratec 1241 contains a tungsten halogen lamp and a diffraction grating which

Table 1. Characteristics of sample sets of milled rice used.

	Sample sets for a full-cross validation (%)	Sample sets for calibration and validation (%)	
		Calibration	Validation
Sample No.	125	63	62
Max	20.7	20.7	20.3
Min	13.1	13.1	13.2
Mean	17.3	17.5	17.1
SD	1.53	1.53	1.57

irradiates monochromatic light. The detector was a silicon detector. Spectra were first recorded for each sample from 850 to 1048 nm, using 100 wavelength points with 2 nm steps; then were next recorded for each sample from 570 to 1000 nm, using 215 wavelength points with 2 nm steps. Milled rice grains (300 g) were supplied to the sample cell from the feeder. Each batch was scanned ten times. Ten spectra were averaged to form one spectrum ($\log(1/T)$) for each sample. The coefficient of variation in absorbance among measurements for each sample was less than 0.01.

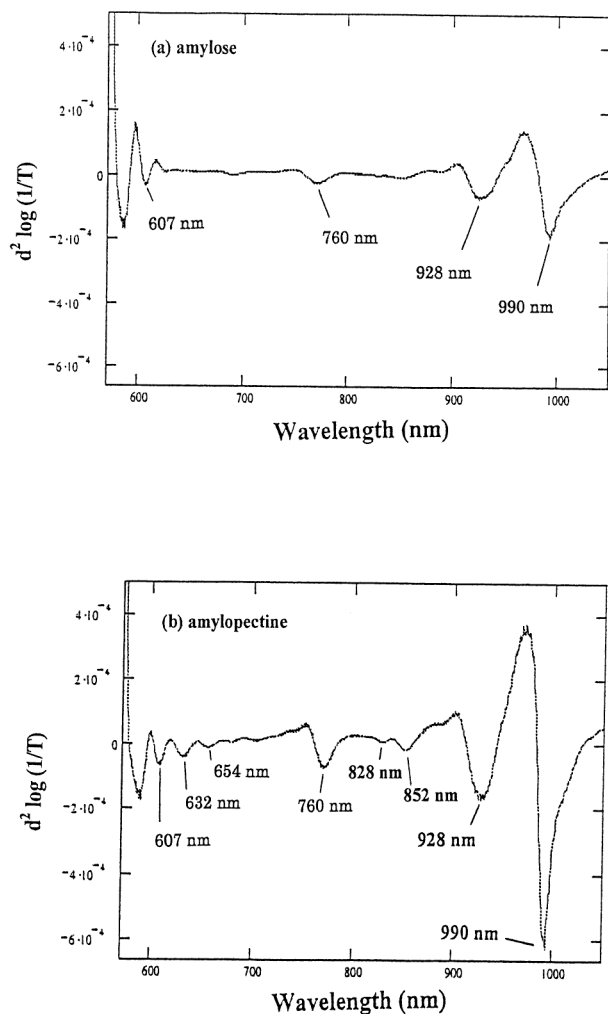
The standard amylose (Amylose type III, Lot 17H3893, Sigma Chemical CO., St. Louis, MO) and amylopectin (*glutinous*

type rice amylopectin, Shimadagakaku CO., Niigata) were also scanned using the Infratec 1241 spectrometer.

Modeling procedure The Unscrambler 6.11b (Camo ASA, Trondheim, Norway) was used to develop a PLS calibration model for amylose content determination. The full cross-validation and selection of the optimum number of PLS components were carried out as reported (Shimizu *et al.*, 1999). The PLS calibration model was also developed and evaluated using calibration ($n=63$) and validation ($n=62$) sample sets which had been selected at random.

Results and Discussion

Spectra of standard amylose and amylopectin The second derivative spectra of standard amylose and amylopectin are plotted in Fig. 1. Those second derivative spectra showed O-H absorption at 760 and 990 nm, C-H absorption at 928 nm (Osborne *et al.*, 1993) and significant absorption at 607 nm. The second derivative spectra of amylopectin also showed significant

**Fig. 1.** Second derivative spectra of standard (a) amylose and (b) amylopectine.**Table 2.** Calibration results for determining amylose content in milled rice using a full-cross validation.

Calibration Model	Wavelength used (nm)	F	R ²	SEC	SECv
A	850–1050	9	0.63	0.83	0.96
B	570–1000	12	0.85	0.45	0.56

F: Number of factors used for making calibration model, SEC: Standard error of calibration, SECv: Standard error of cross-validation

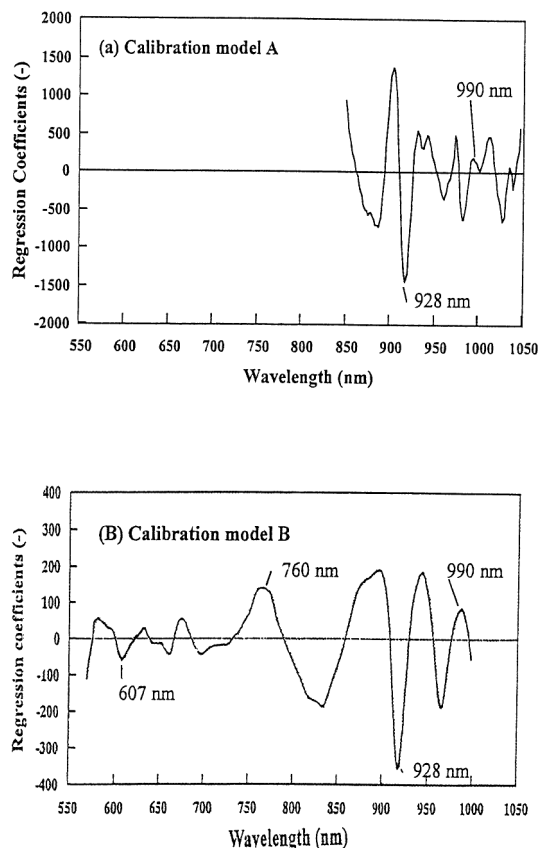
**Fig. 2.** The regression coefficients of the PLS calibration models A and B in Table 2.

Table 3. Results of calibration and validation for determining amylose content in milled rice.

Calibration Model	Wavelength used (nm)	F	R^2	SEC	SEP	Bias
C	850–1050	10	0.77	0.72	0.99	0.03
D	570–1000	11	0.86	0.55	0.64	0.13

F: Number of factors used for making calibration model, SEC: Standard error of calibration, SEP: Standard error of performance.

absorption at 632 and 654 nm, and these $d^2\log(1/T)$ were larger than those of amylose spectra.

New PLS calibration model for amylose content in milled rice Table 2 shows the result of PLS calibration by a full-cross validation. The first PLS calibration model (Model A) was developed using the wavelength region from 850 to 1048 nm, and the second understood model (Model B) was developed using the wavelength region from 570 to 1000 nm. Model B showed about a 20% improvement of R^2 compared to the PLS calibration model A (Table 2).

Figure 2 shows the regression coefficients at each wavelength in Model A and B. The variation in these coefficients ranged from -1434 to 1387 in Model A and ranged from -350 to 200 in Model B. Compared to Model A, the regression coefficients in Model B were smoother and the fluctuations were smaller.

There were several significant peaks in the regression coefficients (Fig. 2) corresponding to absorption bands at 607 nm, 760 nm (O-H), 928 nm (C-H), and 990 nm (O-H) in the second derivative spectra of amylose (Fig. 1). The significant peaks in the regression coefficients of Model A were characterized by two absorption bands at 928 and 990 nm while those of Model B were characterized by four absorption bands at 607, 760, 928 and 990 nm.

The results of calibration and validation for determining amylose content in milled rice are shown in Table 3. The SEP of 0.64% on Model D examined here was smaller than that of

0.99% on Model C. The better model showed that the SEP was smaller and the R^2 was higher. The statistics performance of Model D was better than that of Model C.

The absorption bands at 607 and 760 nm in Models B and D play an important role in improving the performance of the PLS calibration model for amylose content. Therefore, the statistics performance of this model examined here was improved by the use of a visible/near-infrared region.

Conclusions

The performance of PLS calibration models (Models A, B, C, and D) developed using NIR and the visible transmittance were examined to improve the accuracy of the calibration model for amylose content. The regression coefficients in PLS calibration Model B were smoother and the fluctuations were smaller compared to Model A. Significant peaks in the regression coefficients of Model A were characterized by two absorption bands at 928 and 990 nm while those of Model B were characterized by four absorption bands at 607, 760, 928 and 990 nm. The SEP of 0.64% on Model D was smaller than that of 0.99% on Model C. Therefore, the absorption bands at 607 and 760 nm have an important function in improving the performance of the PLS calibration model for amylose content.

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