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Determination of Maximum Viscosity of Milled Rice Flours Using Near-Infrared Transmittance Spectroscopy

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The objective of this study was to develop a partial least squares regression (PLS) calibration method of maximum viscosity determination of Japanese milled rice flours using near-infrared transmittance (NIT) spectroscopy. The diversity of spectra and maximum viscosity of wide ranging of rice subfamilies were much more than those of *japonica* type rices. The variations of spectra and maximum viscosity were found to influence PLS loading weights. C-H and O-H in ROH and H_2O absorbances presented by the loading weights were significant in the 8th loading of the PLS model for *japonica* type rices. The performance of this PLS calibration model (11 components) for maximum viscosity of a rapid visco analyser (RVA) was the standard error of prediction (SEP) of 17.7, square of regression coefficient (R^2) of 0.75 and the ratio of the SEP to the standard deviation of the original data (RPD) of 1.9. This method can be applied to the determination of maximum viscosity of *japonica* type rices.

Keywords: *japonica*, amylose, pasting properties, maximum viscosity, breakdown, near-infrared transmittance, partial least squares regression(PLS), rapid visco analyser, monochromator type NIT

The rice industry has begun to use near-infrared spectroscopy for evaluation of rice quality. Several calibrations were proposed to evaluate amylose content (Kobayashi *et al*., 1994) and eating quality (Champagne *et al*., 1996, Kawamura *et al*., 1997) using near-infrared transmittance (NIT) spectroscopy. The NIT method yields a desirable accuracy of reference values based on the evaluation method of apparent amylose content (AAC) of Japanese milled rice (Shimizu *et al*., 1999).

The partial least squares regression (PLS) model for a broad AAC range of rices (0–35.3%) was found to be inadequate for accurate prediction of the narrow AAC range (13.2–20.7%) of Japanese milled rice samples. The wavelengths necessary for determination of AAC using wide ranging rice subfamilies and those necessary for the narrow AAC range differ (Shimizu *et al*., 1999). The NIT method requires used of population definition and selection of suitable samples (Shenk & Westerhaus, 1991).

Among pasting properties, maximum viscosity and breakdown of rapid visco analyzer (RVA) as well as AAC are often used as indices to evaluate eating quality. Palatable rices in the Japanese rice market have been reported to show high maximum viscosity by amylography (Tani *et al*., 1969, Chikubu *et al*., 1983, 1985) or the RVA method (Fuwa *et al*., 1994, Toyoshima *et al*., 1997). The error in measurements was small in RVA tests using the same type of RVA instruments (Toyoshima *et al*., 1997), and recently the RVA method was adopted as the AACC approved method for evaluation of rice quality (AACC, 1995). A method using NIT spectroscopy with PLS to predict pasting properties has been developed (Delwiche *et al*., 1996). These methods have employed calibration samples for pasting properties based on wide ranging rice subfamilies of *indica*, *japonica*, and *javanica* rices. There is no practically applicable NIT calibration model for maximum viscosity determination of *japonica* type rices.

The objective of the present study was to develop a new calibration method for maximum viscosity of Japanese milled rice flours, a rice with narrow AAC range, using a monochromator type NIT with whole-grain milled rice as samples.

Materials and Methods

Sample and preparation Short-grain *japonica* non-glutinous type rices (341 samples; 44 varieties) harvested in 1996 and 1997 and short-grain *japonica* glutinous type rices (22 samples; 19 varieties) harvested in 1997 were collected in 37 prefectures throughout Japan. The long-grain *indica* type rices (5 samples; 5 varieties) in 1997 were harvested in Thailand, India and Hong Kong.

Milling of the 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 type TRG cylinder separator (Satake CO., Higashihiroshima).

Determination of AAC The milled rice samples were ground with a model 3010-018 cyclone grinder (Udy, Ft. Collins, CO) equipped with a 50-mesh screen. Before AAC determination, the moisture contents of the ground samples were determined in duplicate by an oven dry method using 3 g of rice

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powder at 135°C for 1 h. The AAC (%) was de-termined in duplicate on 50-mesh milled rice flour by the iodine colorimetric method of Juliano (1981). The repeatability error in the AAC reference method was less than 0.5%. Amylose (Amylose type III, Lot 17H3893, Sigma Chemical CO., St. Louis, MO) and amylopectin (glutinous type rice amylopectin, Shimada CO., Niigata) were mixed (amylose to amylopectin weight fraction of 0/100, 10/90, 15/85, 20/80, 30/70 and 40/60) for calibration of AAC. Absorbance after 20 min incubation with iodine solution (I_2: 2.0 g and KI: 20.0 g diluted to 1.0 *l* with distilled water) at 26.5°C (Ohtsubo, 1995) was measured at 620 nm using a model U-2010 spectrophotometer (Hitachi CO., Katsuta).

Determination of pasting properties The pasting properties of rice flours were measured by a type 3D RVA (Newport Scientific, Warriewood, NSW, Australia). The ground sample size (3.0 g dry matter), distilled water volume (25.0 ml), and heating regime (50°C for 1.0 min, 10.75°C/min to 93°C, hold for 7.5 min, 10.75°C/min to 50°C, hold for 3.0 min to finish) were in accordance with the method of Toyoshima *et al.* (1997). The coefficient of variation of each sample was less than 0.02. One stir unit (S.U.) is equivalent to 12.6 mPa·s in the SI unit system (Kimura *et al*., 1995).

NIT spectroscopy The whole-grain samples of milled rice were scanned using an Infratec 1229 NIT monochromator type spectrometer (Foss-Tecator AB, Höganäs, Sweden). The monochromator contains a 50 W tungsten lamp and a diffraction grating which irradiates monochromatic light. The detector was a silicon photodiode array. Spectra were recorded for each sample from 850 to 1048 nm, using 100 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 of each sample was less than 0.01.

Algorithms for selecting samples The sample selection was performed by a commercial spectra analysis program with SELECT algorithms (WINISI II, Version 1.02, Infrasoft International Inc., Foss NIRSystems/ Foss Tecator, Silver Springs, MD).

The algorithm, SELECT, eliminated samples with similar spectra from a file of spectra (Shenk & Westerhaus, 1991). First, the spectra were transformed by a derivative math treatment and then by principal component analysis (using the scores in 7-dimensional space), as in the first treatment. Next, a distance matrix was formed using Mahalanobis distances (*H*) between all pairs of spectra. Any stored samples whose neighborhood *H* values were less than 0.6 *H* (Shenk & Westerhaus, 1991) from any sample in the original calibration data set were eliminated. That spectrum was retained and its neighbors discarded. This method then evaluated all remaining samples to identify the spectrum that had the nearest neighbor. Once again, that sample was retained and its neighbors discarded. This process was continued until no samples remained with neighbors closer than the minimum distance.

Modeling procedure The Unscrambler 6.11b (Camo ASA, Trondheim, Norway) was used to develop a PLS calibration model for maximum viscosity determination using 100 wavelengths.

The optimum number of PLS components used for maximum viscosity prediction was decided when the value of the least standard error of cross-validation (SECv) reached a minimum in a plot of SECv versus a number of PLS components in cross-validation (Lindbering *et al*., 1983).

The models were validated using an independent set of milled rice samples. The performance of PLS models was evaluated using the standard error of prediction (SEP) and the ratio of the SEP to the standard deviation of the original data (RPD) (Williams & Sobering, 1993).

Results and Discussion

Sample selection for maximum viscosity modeling The number of wide ranging rice subfamilies remaining in the sample set was reduced from 368 to 238 using the SELECT program. As the minimum standardized distances (*H*) between pairs of samples, 0.20 was chosen to make calibration (n=133) sets. The number of *japonica* type rices remaining in the sample set was reduced from 341 to 327 using the SELECT program. As the *H* distance between pairs of samples, 0.18 was chosen to make a calibration (n=222) and a validation (n=105) set.

The distribution of standardized *H* from NIT spectra for different sample sets is given in Figs. 1 and 2. The *H* of 20.7 in the wide ranging rice subfamilies was 14.1 times higher than the *H* value of 1.47 in the *japonica* type rices. Thus, the diversity of spectra and maximum viscosity of wide ranging rice subfamilies were found to be much more than those of *japonica* type rices. This indicates that the two sample sets of wide ranging rice subfamilies and *japonica* type rices influence the PLS loading weights in calibration models for maximum viscosity of milled rice flours.

Table 1 is a summary of reference values of fresh milled rice flour. The range of AAC in the wide ranging rice subfamilies was from 0 to 24.4%, with the standard deviation (SD) of 3.8. The range of AAC in *japonica* type rices was from 12.3 to 21%, with an SD of 1.7; this range of *japonica* type rices understood fell in

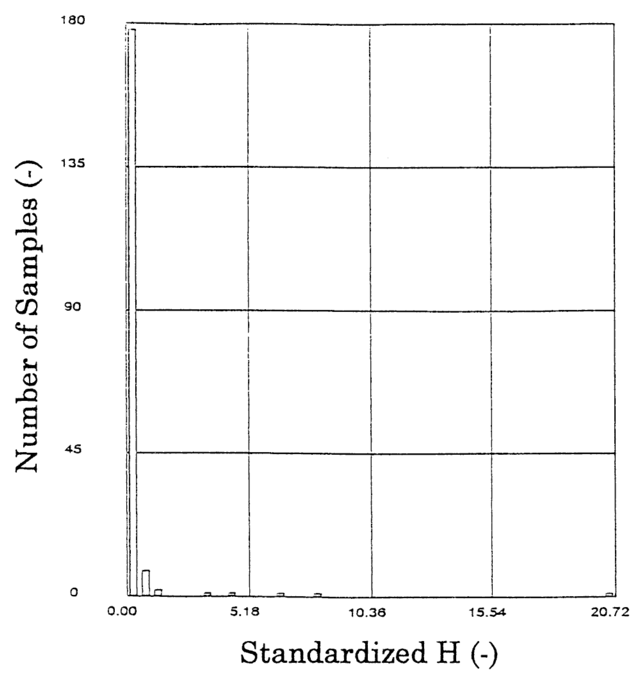

Fig. 1. Distribution of standardized Mahalanobis distance (*H*) from the mean of wide ranging rice subfamilies.

the low AAC category defined by Juliano and Villareal (1993).

The SD value of 45.2 of maximum viscosity, in which there were wide ranging rice subfamilies, was similar to those values which Fuwa *et al.* (1994) and Delwiche *et al.* (1996) reported. This SD value was 1.4 times higher than the value of the SD of 33.4 in the sample set of *japonica* type rices.

Comparison of PLS loadings for maximum viscosity of milled rice flour for two data sets: wide ranging rice subfamilies and japonica type rices Figures 3 and 4 show the relationship between the SECv and the number of PLS components for the cross-validation of maximum viscosity for the two different sample sets (wide ranging rice subfamilies, *japonica* type rices). The SECv in the PLS calibration for the former were minimum with 10 PLS components. The SECv in the PLS calibration for *japonica* type rices was minimum with 11 PLS components. The SECv of 40 in PLS calibration of wide ranging subfamilies was 2.2 times higher than the SECv value of *japonica* type.

The correlation coefficients of the relationship between the estimated sample scores from each PLS component and the reference values of maximum viscosity for the two sample sets are given in Table 2. Figure 5 shows the loading weight of each of the 1st, 3rd and 8th PLS components on maximum viscosity. Estimated sample scores from the 1st PLS component had the highest correlation with maximum viscosity (r=0.46) (Fig. 5). Estimated sample scores from the 3rd PLS component had the second highest correlation understood (r=0.36) and heavy loading weights related to O-H absorption at 970 nm (Fig. 5) (Osborne *et al.*, 1993). Estimated sample scores from the 8th PLS component had the third highest correlation with maximum

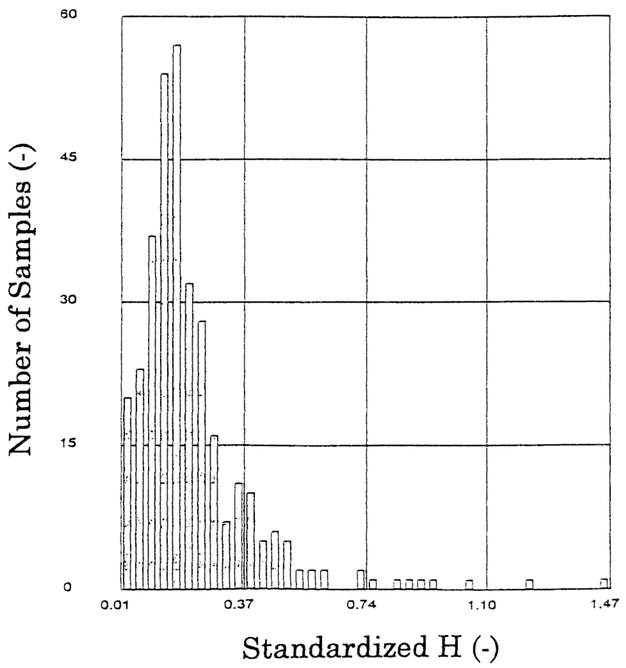

Fig. 2. Distribution of standardized Mahalanobis distance (H) from the mean of *japonica* type rices.

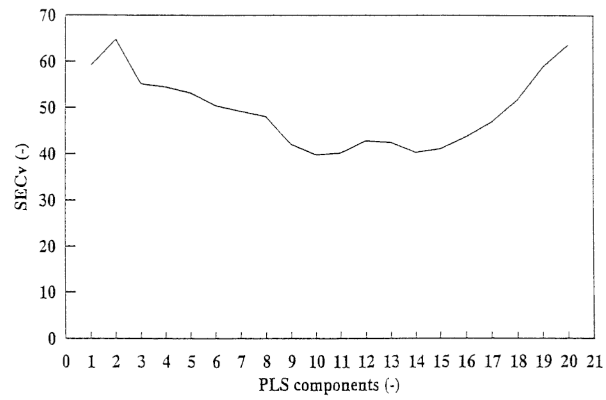

Fig. 3. Plot of SECv versus PLS components of wide ranging rice subfamilies.

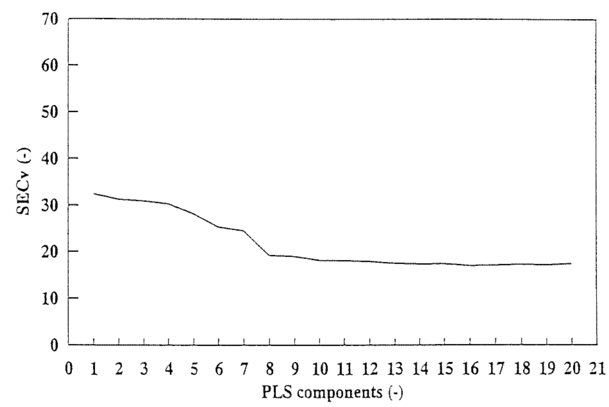

Fig. 4. Plot of SECv versus PLS components of *japonica* type rices.

Table 1. Reference maximun viscosity and AAC of wide ranging rice subfamilies and *japonica* type rices.

	Minimum	Maximum	Mean	SD
AAC				
Wide range[a] (n=238)	0	24.4	15.7	3.8
japonica type rices (n=327)	12.3	21	16.4	1.7
Max viscosity, S.U.				
Calibration for wide range[a] (n=133)	95.2	543.3	307.9	45.2
Calibration for *japonica* (n=222)	241.6	405.6	309.6	33.4
Validation (n=105)	257.6	390.3	308.1	32.8

1 S.U.=12.6 mPa·s
[a]wide ranging rice subfamilies such as *indica*, *japonica* and *non-glutious* type rices.

Table 2. The correlation coefficients of relationships between the estimated sample scores from each PLS component and maximum viscosity.

PLS component	Wide range[a]	*japonica* rices
1st	0.46	0.18
2nd	0.21	0.27
3rd	0.36	0.14
4th	0.19	0.21
5th	0.21	0.38
6th	0.22	0.40
7th	0.22	0.18
8th	0.31	0.48

[a]wide ranging rice subfamilies such as *indica*, *japonica* and *non-glutinous* type rices.

viscosity (r=0.31) and heavy loading weights, with large intensity related to C-H absorption at 913 and 938 nm (Fig. 5) (Osborne *et al.*, 1993).

Figure 6 shows the loading weight of each of the 5th, 6th and 8th PLS components of maximum viscosity for *japonica* type rices. Estimated sample scores from the 8th PLS component had the highest correlation with maximum viscosity (r=0.48), loading weights related to C-H absorption at 882 and 930 nm, and O-H absorption in ROH and H_2O bands at 974 and 1004 nm (Fig. 6) (Osborne *et al.*, 1993). Estimated sample scores from the 6th PLS component had the second highest correlation with maximum viscosity (r=0.40) and loading weight related to C-H absorption at 934 nm (Fig. 6). Estimated sample scores from the 5th PLS component had the third highest correlation with maximum viscosity (r=0.38) and loading weights related to C-H absorption at 900 and 922 nm (Fig. 6) (Osborne *et al.*, 1993).

Two PLS models for maximum viscosity determination of milled rice flour Figure 7 shows the NIT-predicted maximum viscosity over wide ranging rice subfamilies. The performance of this PLS calibration model (10 components) was SEP of 22.0, R^2 of 0.53 and RPD of 1.5. The SEP of 22.0 by the present calibration model was similar to the SEP of 23.7 by a previous model (Delwiche *et al.*,1996). The accuracy of calibration based on wide ranging rice subfamilies was not adequate when applied to NIT prediction of *japonica* type rice samples.

Figure 8 shows the NIT-predicted maximum viscosity on the *japonica* type rices and the B-coefficients calculated are shown in Fig. 9. The performance of this PLS calibration model (11 components) was SEP of 17.7, R^2 of 0.74 and RPD of 1.9. The SEP of 17.7 determined here was better than the SEP of 23.7 by a previous model (Delwiche *et al.*,1996).

The developed PLS model for *japonica* type rices might be applicable to practical nondestructive evaluation of maximum viscosity in Japanese milled rices.

Equation validation for japonica type rices Figure 10 shows the relationship between residuals (=reference maximum viscosity−NIT-predicted maximum viscosity) versus the reference maximum viscosity (N=105). The range of maximum vis-

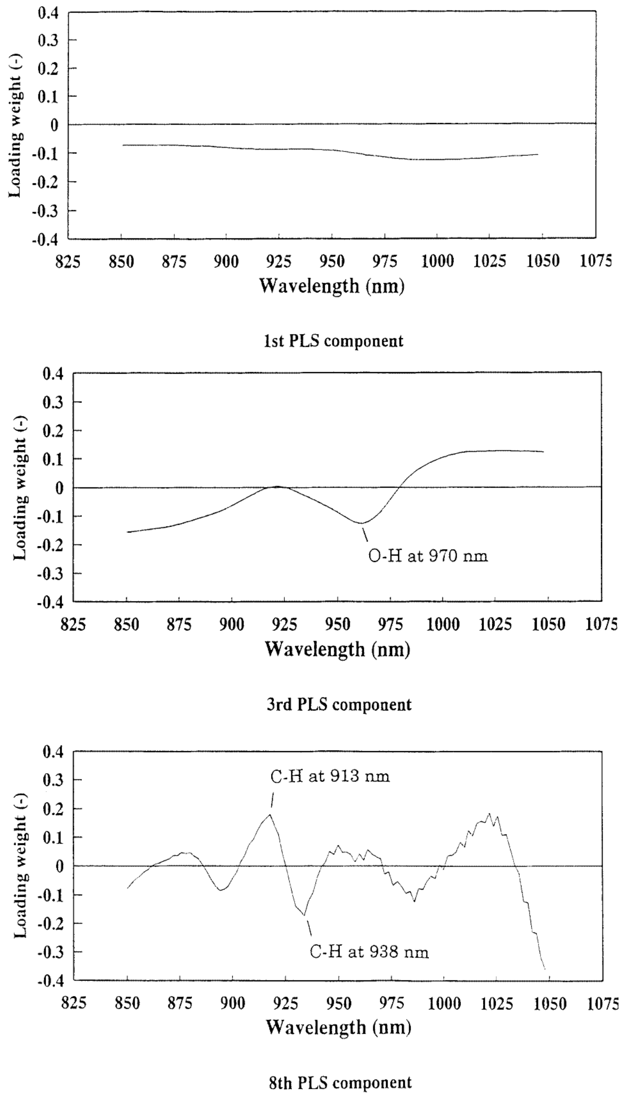

Fig. 5. Loading weights of PLS components of maximum viscosity for wide ranging rice subfamilies.

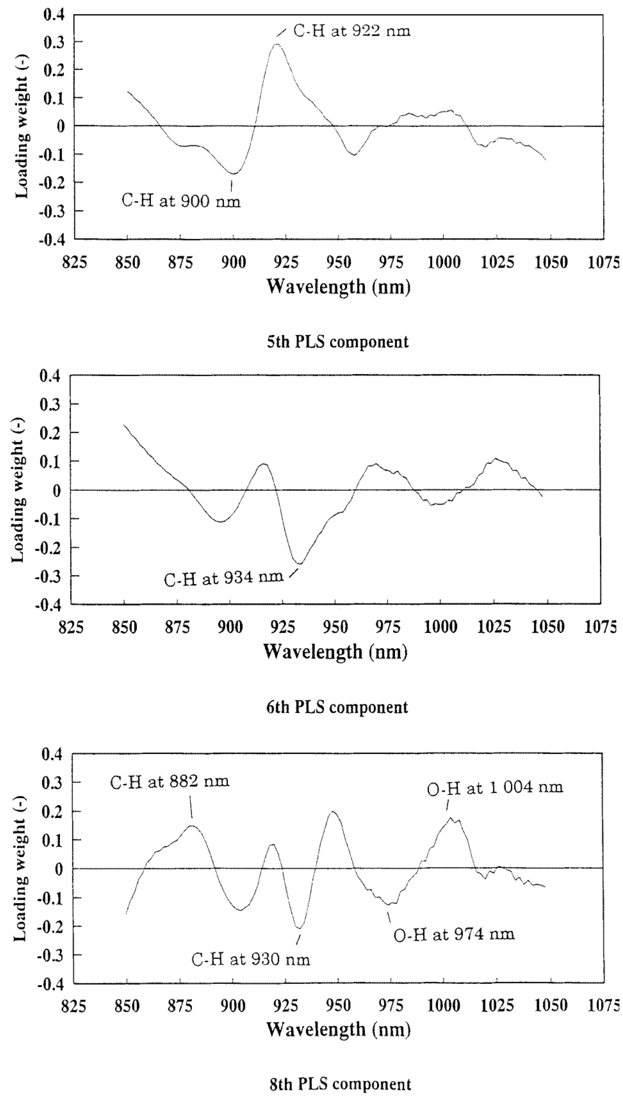

Fig. 6. Loading weights of PLS components of maximum viscosity for *japonica* type rices.

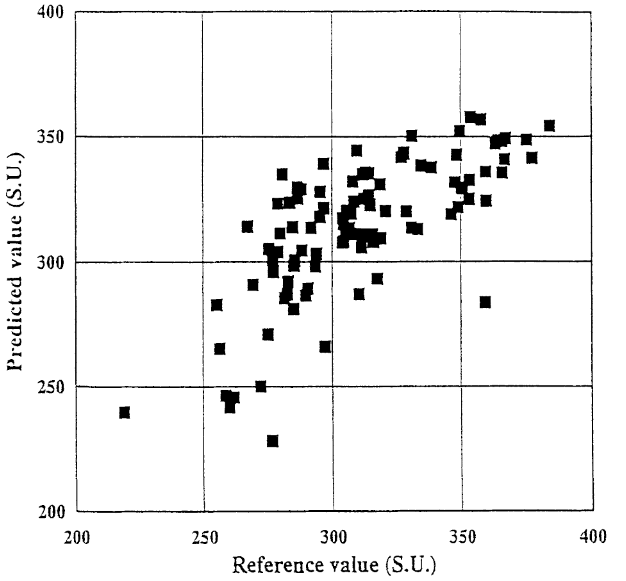

Fig. 7. Relationship between reference values of *japonica* type rices and predicted maximum viscosity for wide ranging rice subfamilies.

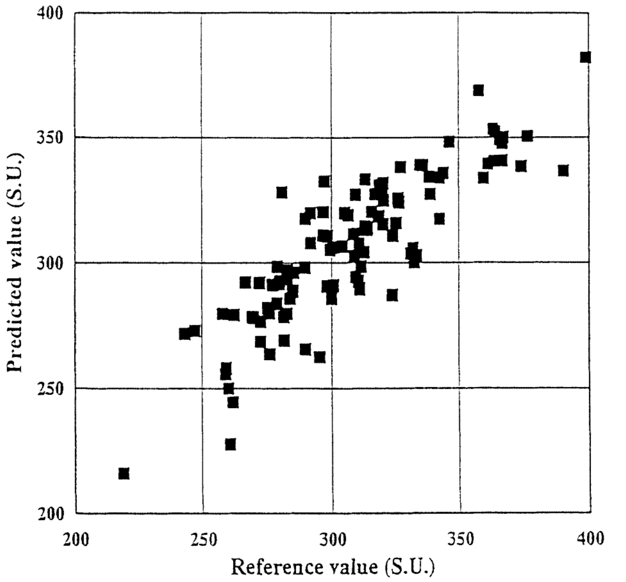

Fig. 8. Relationship between reference values of *japonica* type rices and predicted maximum viscosity for those rices.

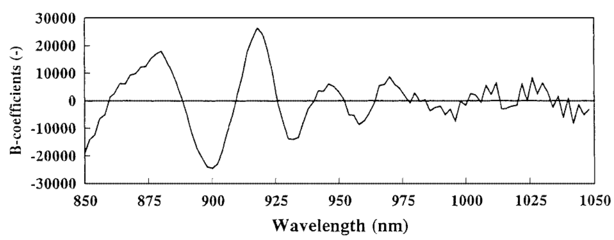

Fig. 9. B-coefficients of PLS for predicting maximum viscosity in *japonica* type rices.

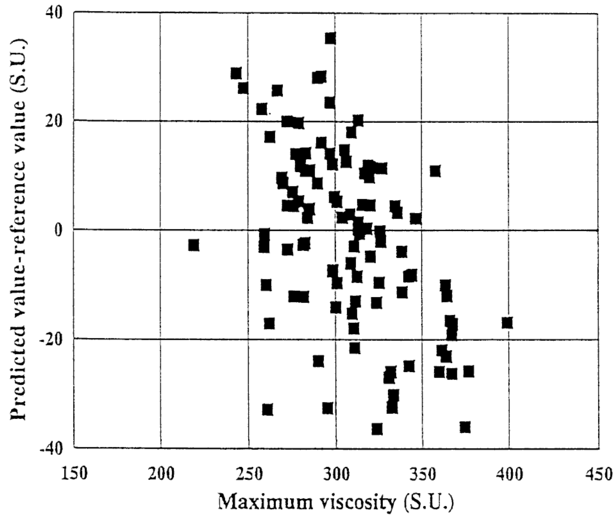

Fig. 10. Relationship between residuals in maximum viscosity versus reference maximum viscosity.

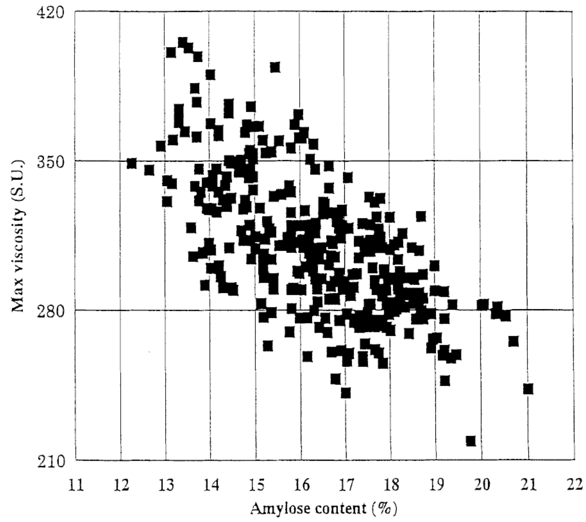

Fig. 11. Relationship between milled rice AAC and maximum viscosity.

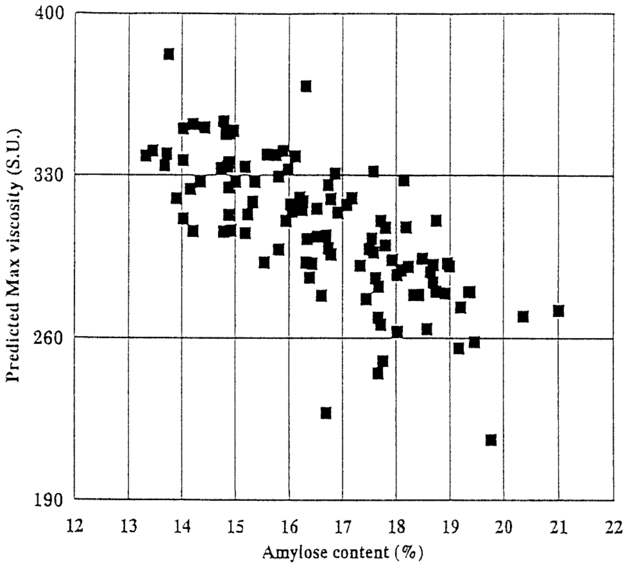

Fig. 12. Relationship between milled rice AAC and NIT-predicted maximum viscosity.

cosity residuals was from −37 S.U. to 37 S.U., and these residuals were randomly distributed.

The maximum viscosity of fresh milled rice flours was significantly affected by amylose content in milled rice (Inatsu, 1988). Figure 11 shows the relationship between the reference of maximum viscosity and AAC in milled rices. Maximum viscosity is negatively correlated with AAC ($r = -0.66$). Figure 12 shows the relationship between AAC and NIT-predicted maximum viscosity. NIT-predicted maximum viscosity shows a significant negative correlation with AAC ($r = -0.54$). The present NIT-predicted maximum viscosity could be used as one of the quality indices for evaluation of rice edible quality.

Conclusions

A simple and rapid technique for determination of maximum viscosity using NIT spectroscopy was developed based on near-infrared transmittance spectra. The accuracy of maximum viscosity calibration based on wide ranging rice subfamilies was insufficient when applied to NIT prediction of *japonica* type rices. The statistical performance of maximum viscosity PLS calibration model (11 components) for narrow AAC range of rices was SEP of 17.7, R^2 of 0.74 and RPD of 1.9. The present method by NIT can be used to determine the maximum viscosity of *japonica* type milled rice flours.

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