Determination of degree of retrogradation of cooked rice by near infrared reflectance spectroscopy

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Near infrared (NIR) reflectance spectroscopy was used to determine the degree of retrogradation of cooked rice. Cooked rice samples were stored at 4°C for 120 hours, and the degree of retrogradation was measured every six hours during the storage time. Enzymatic method, using glucoamylase, was used as reference method for the determination of the degree of retrogradation. Spectral differences, due to retrogradation of cooked rice, were observed at 1434, 1700, 1928, 2100, 2284 and 2320 nm. 32 samples were used for calibration set and 16 samples were used for validation set. High correlations were achieved between degree of retrogradation determined by enzymatic method and by NIR with multiple correlation coefficient of 0.9753 and a standard error of calibration of 3.64%. Comparable results were obtained with 3.91% of standard error of prediction, when the calibration equation was applied to an independent group of samples. The moisture content of samples tested significantly affected the determination of degree of retrogradation by NIR. The critical moisture content for the determination of degree of retrogradation by NIR was found to be ca. 5% (W.B.). The results suggested that NIR spectroscopy might be used as a potential method for determining both the degree of retrogradation and gelatinization of cooked rice.

Keywords: NIR, near infrared, degree of retrogradation, cooked rice, starch.

Introduction

It has been well-known that the retrogradation, the changes of gelatinized starch from amorphous state to the crystalline form, are closely related with physico-chemical properties of starch molecules. Throughout the past decades, a number of procedures to measure retrogradation have been devised, based on absorption of dyes,[1] viscosity, X-ray diffraction patterns, nuclear magnetic resonance spectroscopy, differential scanning calorimetry[2] and enzymatic susceptibility.[3–5] Among these methods, enzymatic determination has been found to be one of the most sensitive and the most widely used methods for determination of degree of retrogradation of cooked rice.

However, enzymatic methods for determining the degree of retrogradation are laborious, highly time-consuming, and need a skilled expert to obtain reproducible results.

Near-infrared (NIR) reflectance spectroscopy analysis has been widely used for rapid nondestructive measurement of moisture, protein and lipid in many agricultural commodities and food. In particular, in starch based food, total starch content[6,7] and damaged starch[8] may be evaluated by NIR analysis. The degree of gelatinization of starch can also be measured by NIR. However, little work has been reported on the NIR analysis of retrogradation of cooked rice.

The objectives of this study were to determine if NIR techniques could be used to estimate the degree of retrogradation of cooked rice.

Materials and method

Preparation of samples

300 g of Japonica type rice were washed, soaked and cooked for 15 min in a rice cooker. In order to prepare the retrograded samples, cooked rice was stored at 4°C for 120 hrs. Samples were taken every six hours during the storage time, freeze-dried, milled and passed through 100 mesh standard sieve. Freeze-dried rice powders were used in both enzymatic and NIR analysis.

Moisture content and degree of retrogradation

Degree of retrogradation was determined by modified enzymatic digestibility method using glucoamylase as described by Chiang and Johnson[4] and Tsuge and Hishida.[3]

$$\text{Degree of retrogradation (DR,\%)} = \frac{\text{DG of unretrograded cooked rice} - \text{DG of sample}}{\text{DG of unretrograded cooked rice}} \times 100$$

Near-infrared spectroscopy

An NIRSystems model 4500 scanning spectrometer (NIRSystems Divisions of Perstorp Analytical, Silver Spring, MD, U.S.A) was used for NIR measurement.

NIR spectra were obtained from 48 cooked rice samples of moisture content of 5% and below. The 32 samples were selected to make calibration equation for determination of the degree of retrogradation. Samples were selected for inclusion in the calibration set by a subroutine of the NSAS software. The remaining 16 samples were used as prediction set to validate the calibrations.

Multiple linear regression analyses were performed to establish the relationship between the degree of retrogradation from enzymatic method and NIR absorbance values (log 1/*R*, d log 1/*R* and d^2log 1/*R*).

Results and discussions

NIR spectra of sample

Near infrared reflectance spectra of cooked rice with different moisture content and degree of retrogradation are shown in Figure 1. Due to little differences among the spectra of each sample in Figure 1,

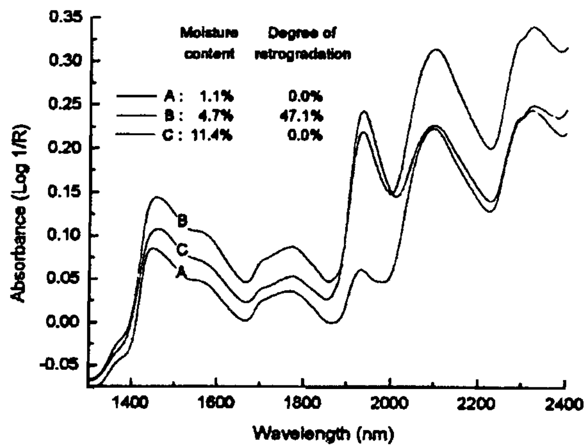

Figure 1. Near infrared reflectance spectra of cooked rice with different moisture content and degree of retrogradation.

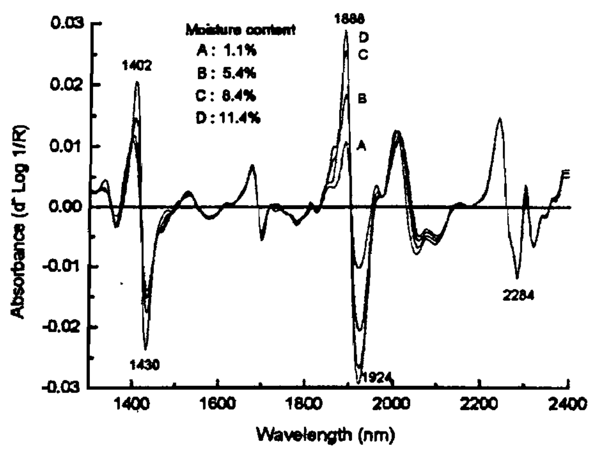

Figure 2. Second derivative of NIR spectra of cooked rice with the same degree of retrogradation and the different moisture content.

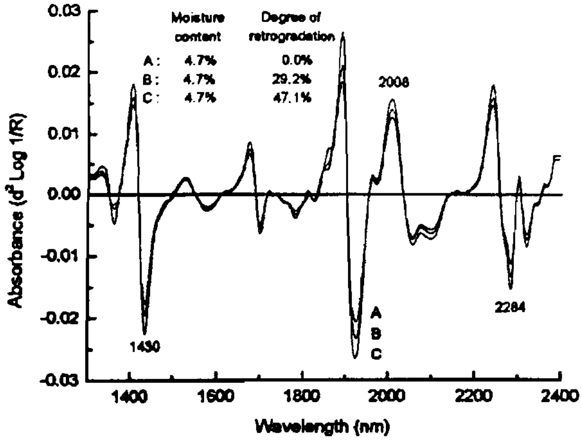

Figure 3. Second derivative of NIR spectra of cooked rice with the same moisture content and the different degree of retrogradation.

the second derivative mathematical treatment with segment 15 nm and gap 0 nm was applied to analyse spectra of samples. In Figure 2, large NIR spectral differences were noted at wavelength of 1924 and 1430 nm, which is assumed to be caused by the different moisture content of samples.

Samples of the same moisture contents also showed spectral differences at wavelength of 1360, 1700, 2240, 2284 and 2320 nm as the degree of retrogradation of samples increased (Figure 2). Additional differences in absorption bands were also found at the wavelengths of 1924 and 1430 nm due to retrogradation (Figure 3). Considering the moisture contents of samples are constant, the differences in absorption bands arose, not only from moisture variation, but also from retrogradation.[9] The absorption bands at 2282 nm wavelength region in Figure 4

Table 1. Constituent statistics of degree of retrogradation analyzed by enzymatic method.

	Number of samples	Mean (%)	S.D (%)[a]	Range (%)
Calibration set	30	28.0	15.70	0.00–47.10
Validation set	13	24.9	15.11	0.00–47.10

[a]Standard deviation

Table 2. Wavelength selected, statistical summary and calibration equations for degree of retrogradation.

Type of Equation	λ_1[a] (nm)	λ_2 (nm)	λ_3 (nm)	λ_4 (nm	K_0[b]	K_1[c]	K_2	r[d]	*SEC*	*SEP*
2nd derivative of log (1/*R*)										
Eq. 1	1688	1902			– 55.26	47471.60	– 3343.85	0.9685	4.11	3.22
Eq. 2	1688	2342	2284	2344	147.10	– 5.93	– 911.775	0.9791	3.36	4.66
Eq. 3	1688	2340	2292	2206	– 174.16	– 277.67	– 53.970	0.9753	3.64	3.91

[a]Selected wavelength, [b]intercept of calibration equation, [c]coefficient of calibration equation, [d]correlation coefficient.

Eq. (1) : $Yi = K_0 + K_1\, d^2\log(1/R_{\lambda 1}) + K_2\, d^2\log(1/R_{\lambda 2})$

Eq. (2) : $Yi = K_0 + K_1\, d^2\log(1/R_{\lambda 2})/d^2\log(1/R_{\lambda 1}) + K_2\, d^2\log(1/R_{\lambda 4})/d^2\log 1/R_{\lambda 3})$

Eq. (3) : $Ti = K_0 + K_1\, d^2\log(1/R_{\lambda 1})/d^2\log(1/R_{\lambda 2}) + K_2\, d^2\log(1/R_{\lambda 3})/d^2\log(1/R_{\lambda 4})$

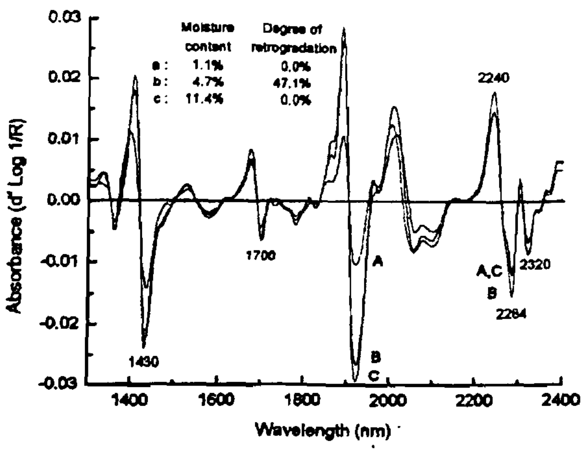

Figure 4. Second derivative of NIR spectra of cooked rice with different moisture content and degree of retrogradation.

were represented by C–H stretch and CH_3 deformation of starch molecules.[10] The degree of retrogradation of both sample A and C showed the same absorbance at 2282 nm wavelength region, whereas sample B (degree of retrogradation = 47.1%) presented different spectral absorbances. This result suggested that it was possible to produce a calibration equation for the evaluation of degree of retrogradation of cooked rice.

Preparation of calibration equations

Table 1 summarised the degree of retrogradation of samples in calibration set and validation set determined by enzymatic digestibility method. Samples selected for prediction had a degree of retrogradation range similar to those used for calibration.

The second derivatives of absorbances ($d^2\log 1/R$) were used to establish calibration equation for the determination of degree of retrogradation. The results are shown in Table 2. High correlations were achieved between degree of retrogradation determined by enzymatic method and by NIR with multiple correlation coefficient of 0.9753, and a standard error of calibration (*SEC*) of 3.64%. Comparable results were obtained with 3.91% of standard error of prediction (*SEP*), when the calibration equation was applied to independent group of samples. Linear correlationships between enzymatically determined and NIR spectroscopically predicted degree of retrogradation of cooked rices in both calibration and validation set are compared in Figure 5.

Calibration equation was applied to the sample sets of three different moisture contents; 4.0%, 7.0%

Table 3. Influence of sample moisture content on accuracy of analysis of degree of retrogradation.

Type of equation	Number of terms	4.0 ± 0.4%[a]			7.0 ± 0.6%			11.4 ± 0.6%		
		SEP	Bias	r^b	*SEP*	Bias	*r*	*SEP*	Bias	*r*
Eq. (1)	1	4.77	– 2.27	0.956	4.54	2.64	0.960	5.40	0.928	0.943
	2	3.22	8.54	0.980	4.51	20.1	0.961	7.29	18.9	0.893
Eq. (2)	1	4.71	7.36	0.980	5.34	14.9	0.944	3.33	18.0	0.979
	2	4.66	10.3	0.958	4.84	25.7	0.959	3.08	34.1	0.982
Eq. (3)	1	3.90	8.92	0.971	4.13	19.2	0.967	4.28	23.1	0.964
	2	3.90	5.66	0.971	4.19	16.5	0.966	4.61	19.9	0.959

[a]Sample moisture content
[b]Correlation coefficient

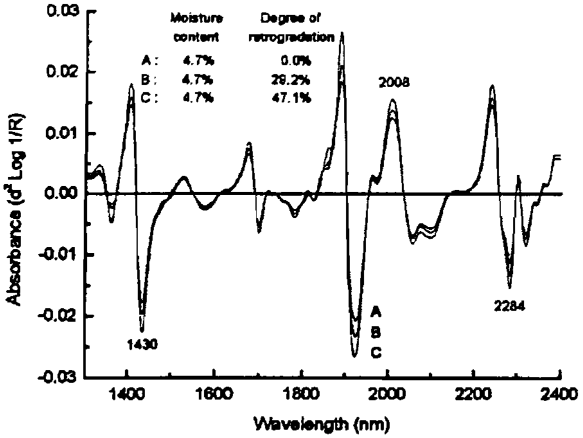

Figure 5. Plot of linear correlation between enzymatically determined and NIR spectroscopically detrmined degree of retrogradation of cooked rice.

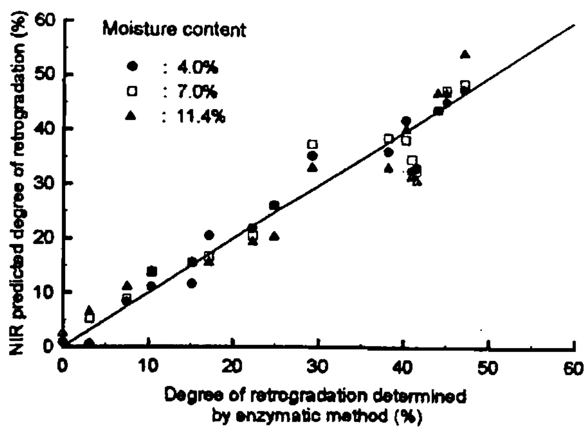

Figure 6. Effect of sample moisture content on prediction of degree of retrogradation by NIR.

and 11.4%, to know whether NIR predicted degree of retrogradation is independent from sample moisture content. The results were shown in Table 3. The moisture content of samples tested significantly affected the determination of degree of retrogradation. The higher *SEP* and biases were observed when the calibration equation was applied to the high moisture content samples. Figure 6 shows the relationship between enzymatically determined and NIR spectroscopically predicted degree of retrogradation of cooked rices with calibration equation in Table 2 after compensation of biases. Deviations from the ideal regression line were notable as the sample moisture contents were increased. The critical moisture content for the determination of degree of retrogradation by NIR was found to be 5% which is the moisture content of samples in calibration set.

The results suggested that NIR spectroscopy might be used as a potential method for determining both the degree of retrogradation and gelatinization of cooked rice.

References

1. S.K. Kim and C.F. Ciacco, *J. Food Sci.* **41**, 1249 (1976).
2. F. Nakazawa and S. Noguchi, *Agric. Biol. Chem.* **48**, 201 (1984).
3. H. Tsuge and M. Hishida, *Starch* **42**, 213 (1990).
4. B.Y. Chiang and J.A. Johnson, *Cereal Chem.* **54**, 429 (1977).
5. M. Wolton and M.A. Chaudhry, *J. Food Sci.* **45**, 1783 (1980).
6. B.A. Orman and R.A. Schumann Jr, *J. Agric. Food Chem.* **39**, 883 (1991).
7. H.O. Kim and P.C. Williams, *J. Agric. Food Chem.* **38**, 683 (1990).
8. P.L. Finney, J.E. Kinney and J.R. Donelson, *Cereal Chem.* **65**, 449 (1988).
9. P.C. Williams and K.H. Norris, "*Qualitative applications of near-infrared reflectance spectroscopy*", in *Near-Infrared Technology in The Agricultural and Food Industries.* American Association of Cereal Chemists, Inc., Minnesota, USA, p.241 (1990).
10. D.A. Burns and E.W. Ciurczak, "*Application of NIR spectroscopy to agricultural products*", in *Handbook of Near-Infrared Analysis.* Marcel Dekker Inc., New York, USA, p.395 (1992).