Preliminary study on near infrared spectra of retrograde starch

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Introduction

Gelatinisation and retrogradation are important factors that cause quality deterioration of starch-based foods such as rice. Up to now, research into the mechanism of gelatinisation or retrogradation has been performed by using, say, X-ray diffraction and ^{1}NMR methods.[2,3] However, a clear explanation of the mechanism has not been given.

Near infrared (NIR) spectroscopy is now widely used for food analysis and also used for basic research on, say, hydrogen bonding related to water in food.[4]

Therefore, in this study, the effect of gelatinisation and retrogradation on NIR spectra was studied and the possibility of their NIR research was examined.

Materials and method

Samples

Wheat starch, commercially supplied by the Wako company, was used to make retrograde starch. First, 10% wheat starch solution was heated under mixing up to 95°C with an amylograph to make gelatinised starch. After that, the gelatinised starch solution was stored at a temperature of –30°C–60°C for several days to make retrograde starch. The retrograde starch solutions were washed three times with ethanol and then dried with acetone.

NIR spectra acquisition

The NIR reflectance spectra (1100–2500 nm) of the samples were measured with an NIRSystems 6500 (Foss NIRSystems, Silver Springs, Maryland, USA) using a spinning sample module and a micro-sample cup for powder samples at room temperature of 25°C. The built-in ceramic tile was used for reference readings.

Chemical analysis

The degree of retrogradation of each sample was indicated as a degree of gelatinisation analysed by the β-amylase-pullulanase (BAP) method.[5]

Data analysis

Data analysis was performed using the NSAS program (Foss NIRSystems, Silver Spring, MD, USA and the Unscrambler program, Version 7.01 (Camo, Trondheim, Norway).

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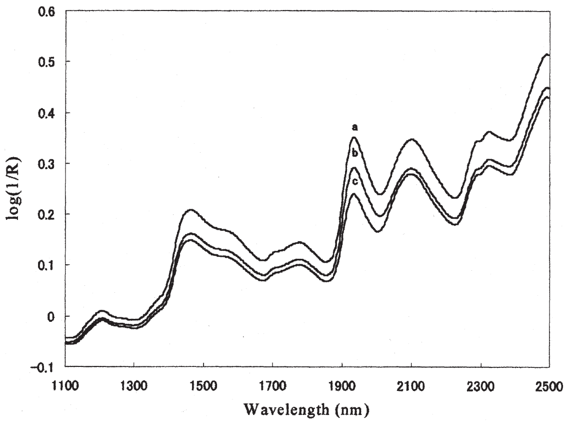

Figure 1. Original spectra of retrograded starch samples with (a) low, (b) medium and (c) high degree of gelatinisation.

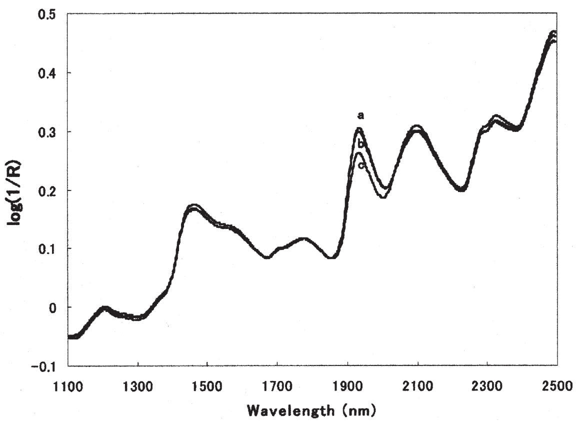

Figure 2. MSC treated spectra of retrograded starch samples with (a) low, (b) medium and (c) high degree of gelatinisation.

Results and discussion

NIR spectra of the retrograded starch

The typical spectra of samples having high (87%), medium (76%) and low (40%) gelatinisation were shown in Figure 1. The spectra were shifted upward depending on the degree of gelatinisation. Pre-processing of the spectra with multiple scatter correction (MSC) treatment removed the base line shift of the spectra (Figure 2). Characteristic changes in spectra due to retro-

Table 1. Chemical data of the degree of gelatinisation of samples used.

N	20
Maximum	93.1
Minimum	30.8
Average	72.6

N: The number of samples

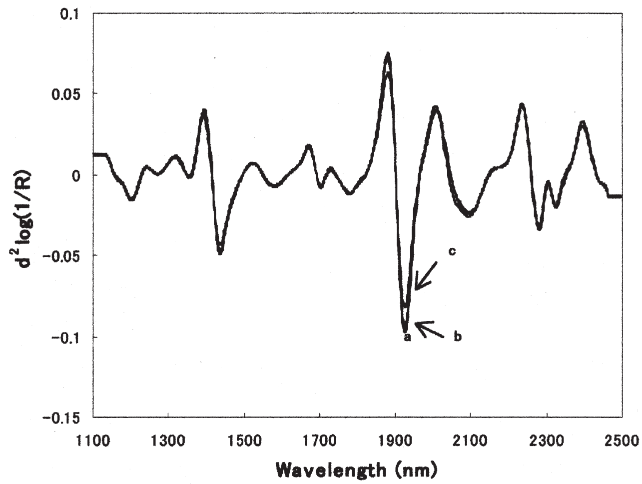

Figure 3. MSC and 2nd derivative treated spectra of retrograded starch samples with (a) low, (b) medium and (c) high degree of gelatinisation.

gradation could be observed at 2100 nm in the MSC and 2nd derivative treated spectra, as shown in Figure 3.

Correlation plots

Correlation plots between MSC-treated spectra and the degree of gelatinisation (DG) (Table 1), and between 2nd derivative values of MSC treated spectra and DG were calculated (Figures 4 and 5). The major negative peaks of 1544 nm and 2258 nm and major positive peaks of 1460 nm, 1602 nm, 1766 nm and 2136 nm could be observed, indicating that NIR absorption at the positive peak wave-

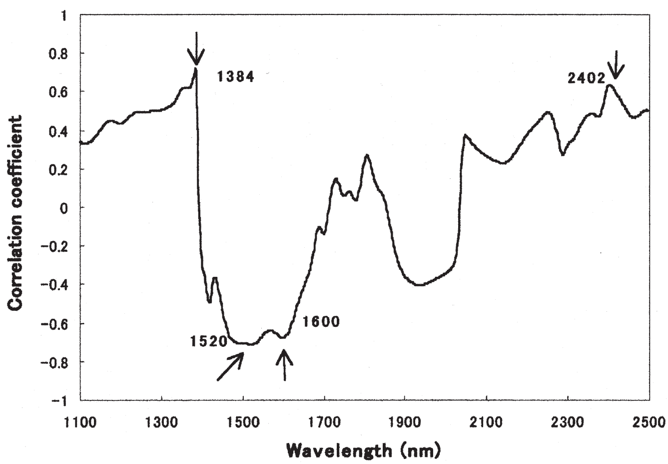

Figure 4. Correlation plots for selecting the first wavelength for the calibration equation developed using MSC treated spectra and degree of gelatinisation.

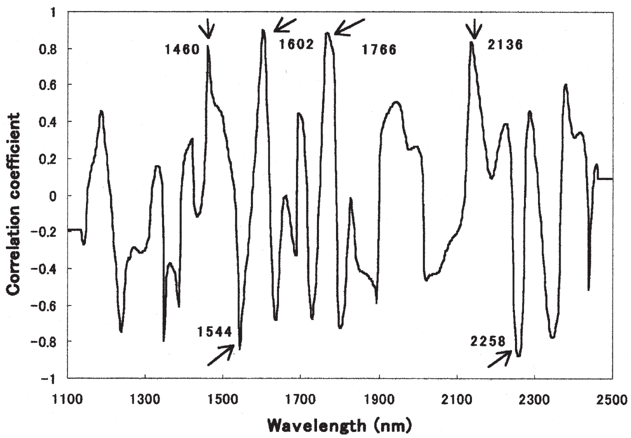

Figure 5. Correlation plots for selecting the first wavelength for the calibration equation developed using 2nd derivative values of MSC treated spectra and degree of gelatinisation.

lengths became weaker while the NIR absorption at the negative peak wavelengths became stronger as the degree of gelatinisation increased.

A simple calibration equation

In order to find wavelengths related to retrogradation, a simple regression base on the 2nd derivative values of MSC treated spectra was performed to obtain a simple calibration equation with two op-

Table 2. Results of making calibraiton equation with two optical terms for determining the degree of gelatinisation.

	Wavelength (nm)	*R*	*SEC*	*SEP*	Bias
MSc	2252, 2158	0.95	5.5	6.5	0.09
	1804, 1596	0.94	6.3	7.5	0.15
	1600, 1688	0.95	6.0	7.1	– 0.01
	1936, 2124	0.94	6.1	7.0	0.03
MSC + D2	1766, 2252	0.96	5.3	6.2	0.04
	1944, 1642	0.97	4.7	5.6	0.06
	1348, 1766	0.96	5.4	6.3	0.11
	1384, 2128	0.96	5.3	6.2	0.05
	1634, 1714	0.97	4.7	5.6	0.04
	1728, 2000	0.96	5.2	6.1	0.20
	2258, 1764	0.96	5.4	6.3	0.12

MSC: Multiplication scatter correction.
MSC + D2: MSC treated and 2nd derivative

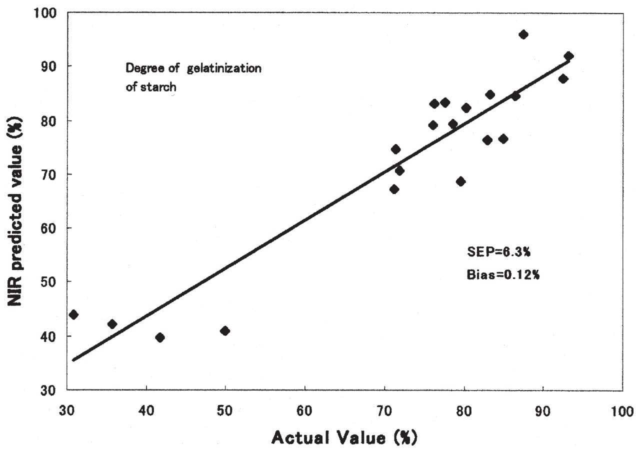

Figure 6. Relationship between actual values and NIR predicted values of the degree of gelatinisation.

tical terms (Table 2). A good calibration equation, which included 2258 nm as the first wavelength and 1764 nm as the second one, was obtained (Figure 6).

Further study is needed to find the assignment of the bands related to retrogradation.

Conclusions

Since a good calibration equation for determining the degree of gelatinisation was obtained, it is concluded that retrogradation of starch contributes to the NIR spectra of the samples.

References

1. A. Yamamoto, *J. Food Sci.* **60,** 1307 (1995).
2. C.E. Mendes Da Silva, C.F. Cialcco, G.E. Barberis, W.M.R. Solano and C. Rettopi, *Cereal Chem.* **73,** 297 (1996).
3. C.H. Teo and C.C. Seow, *Starch* **44,** 288 (1992).
4. M. Iwamoto, S. Kawano and H. Abe, *NIR news* **6(3),** 10 (1995).
5. K. Kainuma, A. Matsunaga, M. Itagawa and S. Kobayashi, *J. Jap. Soc. Starch Sci.* **28,** 235 (1981).