Discrimination of noodle flours using a portable near infrared spectrometer

Masanori Kumagai[a,b], Naganori Ohisa[b], Toshio Amano[c] and Nobuaki Ogawa[a]

[a]*Faculty of Engineering and Resource Science, Akita University, Tegata Gakuencho, Akita 010-8502, Japan*

[b]*Akita Research Institute of Food and Brewing, Arayamachi, Akita 010-1623, Japan*

[c]*OPT Research, Inc., Akasaka, Minato-ku, Tokyo 107-0052, Japan*

Introduction

Near infrared spectroscopy (NIRS) has been developed and used as a rapid, non-destructive and convenient technique for the qualitative and quantitative compositional analysis of many kinds of materials[1-2]. We are also conducting a thorough investigation for NIRS feasibility, and have attained some positive results [3-5]. In this work, using a portable near infrared spectrometer, we attempt to discriminate flours for making Japanese noodle (soba) not only relying on a statistical and mathematical approach, but also on chemical interpretation of NIR spectra. This study suggests a novel idea of utilizing wavelength contribution ratio spectra for interpretation of factors extracted from principal component analysis for NIR spectra. And we also described the relationship between NIR spectra and chemical analysis data.

Methods

Samples

Five kinds of buckwheat flours and ten kinds of wheat flours for making Soba noodles were obtained from a milling factory and investigated in this work.

Chemical analyses

The moisture, protein, fat, and ash content of each sample were determined according to AOAC methods [6]. The mean particle size of each sample was determined by a particle size analyser (MICROTRAC HRA, Leeds & Northrup, USA).

NIR spectroscopy

The NIR diffuse reflection spectra in the 1200 - 2400 nm wavelength region (800 data points) were measured three times for each sample with a portable near-infrared spectrometer (Figure 1), PlaScan SH (OPT Research, Inc., Japan), equipped with an acousto-optical tunable filter (AOTF) [3-6]. It is widely known that the AOTF method theoretically caused a wavelength shift. In the case of PlaScan SH, because polystyrene film is used to correct the wavelength at 1680 nm, the shift from an accurate wavelength increases as it departs from the corrected wavelength. In this work, the wavelength was re-corrected using a grating monochromator device (NIRS 6500, FOSS-NIRSystems) for the apparent observed wavelength. A white ceramic disk was used as a reference

in the diffuse reflection mode. Each flour sample was packed into a sample holder in which it was compressed against a quartz window.
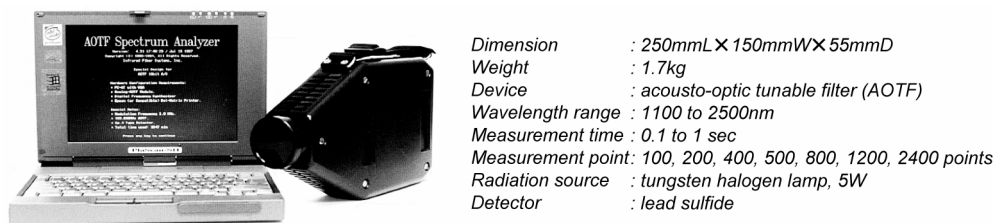
Figure 1.   Portable NIR Spectrometer PlaScan SH (OPT Research, Inc., Japan).

Data analyses

A software program (JUSE-Stat Works / V3.0, The Institute of Japanese Union of Scientists & Engineers) was employed for a spectral data analysis. Because this program allows a maximum of 256 entries for data analysis, the 800 data points in the 1200 - 2400 nm wavelength region were reduced to 200 data points by averaging four successive data points. All NIR data were subjected to a treatment by a Kubelka-Munk transformation and a standardized normalization procedure.[2] The former treatment was applied to the original NIR spectra to correct for any non-linearity of diffuse reflectance data. Utilizing the Kubelka-Munk theory, the reflectance (R) can be related to the absorption coefficient (K) and scattering coefficient (S); it is also related to the absorption (A) by the following equation:

$$K \diagup S = (1-R)^2 \diagup 2R = \cosh A - 1 \tag{1}$$

In general, the latter treatment, the standardized normalization procedure, is applied to remove any systematic variation; it reduces the effect of a baseline drift in the original NIR spectra. This treatment centres each spectrum around zero by subtracting the mean and dividing each value by the standard deviation of the entire spectrum. Spectra that have undergone a treatment by both procedures are referred to as the standardized spectra in this work. For a discrimination analysis, a principal component analysis (PCA) was applied to standardized spectral data.

Results and discussion

The original spectra (Fig.2) may contain some variance arising from scattering and spread, which gradually increase with the wavelength number. The observation results could be explained by the differences of the samples' powder surface in particle size, orientation, etc., which would induce variations in the diffuse reflection spectra. Consequently, in order to remove these extraneous systematic variations, the standardized normalization treatment including a Kubelka-Munk transformation was applied for the original NIR spectra. Relatively narrow data-spreads, compared to the original spectra, are essentially represented by the component differences of the investigated flour samples (Figure.3).
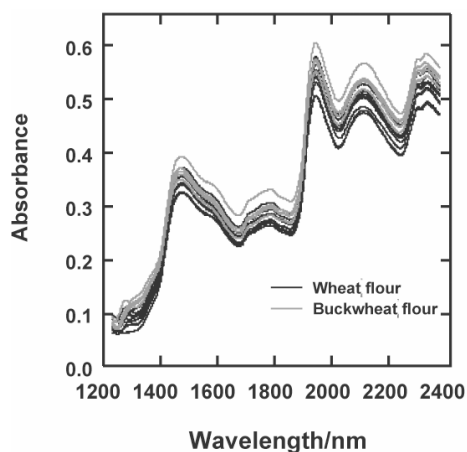
Figure 2. Original NIR spectra of flour samples. (with permission from [3])
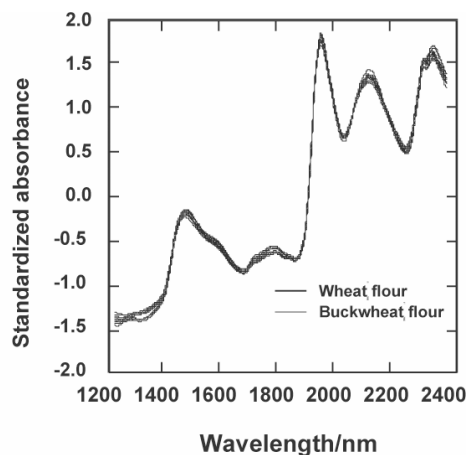
Figure 3. NIR spectra of flour samples after the standardized treatment. (with permission from [3])

A principal-component analysis (PCA) was applied to both the original and standardized NIR spectral data to reveal the sample characteristics more clearly. Using the original spectra, the separation between buckwheat flours and wheat flours was achieved with a few outliers, which is not significant. Fig. 4, however, which is score plots based on standardized NIR spectra, shows a clear distinction between them. For the case of the standardized spectra, the first three principal components accounted for 54.5, 20.1 and 10.7% of the total variance, respectively. The principal component 2 (PC2) could associate strongly with the discrimination.

To interpret PCA results, a correlation coefficient of the principal component with the chemical-analysis data was calculated, including the particle size of the samples (Table1). For the original spectra, the PC1 is generally correlated with the particle sizes. PC2 and 3 are considerably correlated with the carbohydrate and protein contents, respectively. On the other hand, after the standardized treatment, the effect of the particle size on PC1 vanished; consequently, PC1 are highly correlated with the carbohydrate. PC2 are remarkably correlated with the ash and the protein; PC3 are well correlated with the moisture.
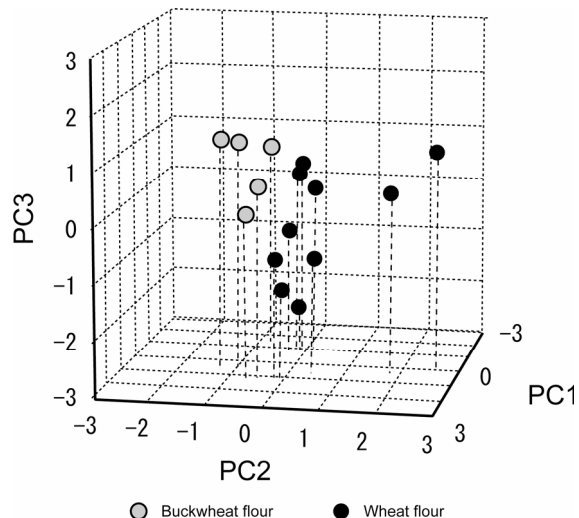
Figure 4. Three dimensional score plots of PC1, PC2 and PC3 for flour samples based on standardized spectra.

Table 1 Correlation coefficient matrix of chemical analysis data, particle size and principal components. (with permission from [3])

	Original spectra			After the standardized treatment		
	PC1	**PC2**	**PC3**	**PC1**	**PC2**	**PC3**
Moisture	0.580	-0.211	0.103	0.234	-0.291	0.876
Protein	-0.178	-0.276	-0.613	0.312	0.542	-0.043
Ash	0.599	-0.417	0.330	0.433	-0.588	0.468
Fat	0.462	-0.435	0.098	0.493	-0.285	0.527
Carbohydrate	-0.367	0.546	0.348	-0.602	-0.090	-0.562
Particle size	0.723	-0.404	-0.053	0.389	-0.404	0.503

We also showed that one could evaluate real meanings of the factor axes and associate with the chemical information to the NIR spectra. Moreover, in order to examine the results of PCA, especially to interpret the factor axes, we calculated the wavelength contribution ratio at every wavelength. The contribution of the absorbance at each wavelength to the principal component was considered using the following formula:

$$\text{Contribution ratio (\%)} = \text{(factor loadings)}^2 / \text{(total number of wavelengths)} \qquad (2)$$

where factor loading indicates the correlation coefficient between the principal component and the original variable, which is for the absorbance at each wavelength.

Figure 5 shows the wavelength contribution ratio spectrum for PC2 which was generally correlated with the ash and protein, as shown in Table 1; because the contribution ratio is high at the wavelength of the band assigned to protein, the PC2 axis mainly denotes the protein content.
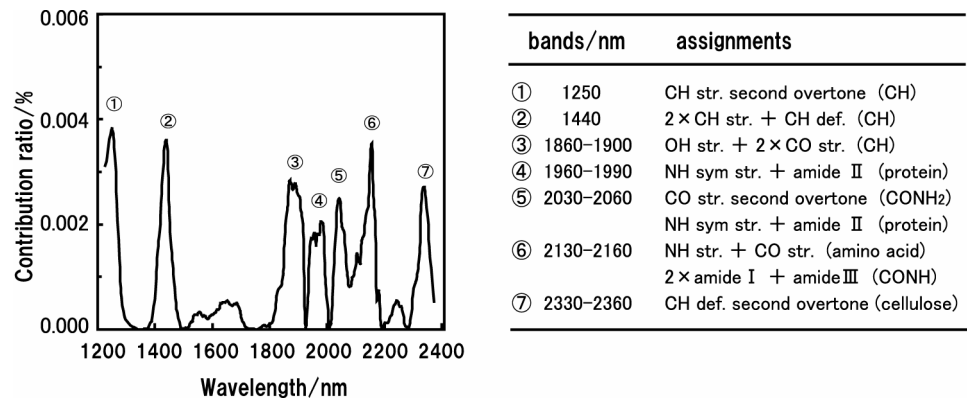
bands/nm		assignments
①	1250	CH str. second overtone（CH）
②	1440	2×CH str. ＋ CH def.（CH）
③	1860–1900	OH str. ＋ 2×CO str.（CH）
④	1960–1990	NH sym str. ＋ amide Ⅱ（protein）
⑤	2030–2060	CO str. second overtone（CONH2）
		NH sym str. ＋ amide Ⅱ（protein）
⑥	2130–2160	NH str. ＋ CO str.（amino acid）
		2×amide Ⅰ ＋ amideⅢ（CONH）
⑦	2330–2360	CH def. second overtone (cellulose)

Figure 5. Wavelength-contribution ratio spectrum for PC2. (with permission from [3])
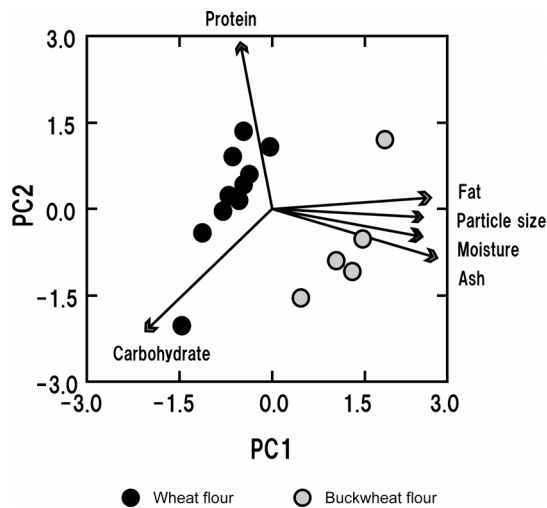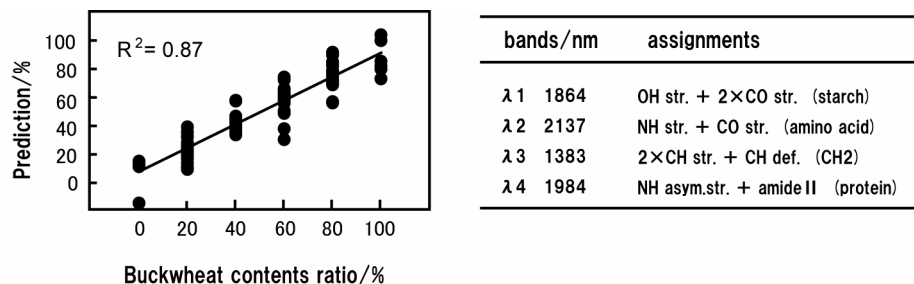

Figure 6. Score plots of PC1 vs. PC2 for flour samples based on chemical analysis data and particle size. (with permission from [3])

It is easy to signify dimensional space by overlapping the factor loadings as a vector expression on the score plots (Figure 6). Hence, buckwheat and wheat flours are isolated. From factor-loading information, the axes for discriminating these flours are classified into the three dimensions of protein, carbohydrate, and the groups of fat, particle size, moisture, and ash contents. Although the NIR spectra are overlapped by numerous broad bands of functional group frequencies, they simultaneously contain multiple compositional characteristics of samples. This fact indicates the superb functionality of NIRS; it also means that measuring of the NIR spectra makes it possible to distinguish flour types rapidly based on compositional and chemical differences.

bands/nm		assignments
λ1	1864	OH str. + 2×CO str. (starch)
λ2	2137	NH str. + CO str. (amino acid)
λ3	1383	2×CH str. + CH def. (CH2)
λ4	1984	NH asym.str. + amide II (protein)

Predicted buckwheat contents ratio/% = -631+1226 × (A$_{λ1}$)-547 × (A$_{λ2}$)-1263 × (A$_{λ3}$)-971 × (A$_{λ4}$)

Figure 7. Prediction of buckwheat contents ratio by NIR spectra.

Soba, a popular Japanese noodle, is a thin brownish noodle made from buckwheat flour, or from a mixture of buckwheat flour and wheat flour. Wheat flour can be used as a binding agent and a texture modifier for Soba noodles. Therefore, there are many mixing ratios of these flours for Soba noodles.

We can significantly demonstrate the prediction of buckwheat-flour-content ratio estimation in mixed flours performed by a calibration equation. By the Japanese Agricultural Standards (JAS), soba noodle should contain over 30% of buckwheat flour. Therefore, we need to predict the content ratio of buckwheat in soba noodles.

References

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