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Rapid Determination of Moisture and Protein contents in Silver Carp Surimi by Fourier Transform Near-Infrared (FT-NIR) Spectrometry

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Abstract

Moisture and protein contents in silver carp surimi were determined by Fourier transform near-infrared (FT-NIR) spectrometry in this study. Prediction error of calibration set (SEC) and validation set (SEP), correlation coefficient of calibration set (Rc) and validation set (Rv) were used to evaluate the quality of the models. The result showed that for moisture, the best calibration was developed using partial least square (PLS) with pretreatment-Normalization to Unit Length (NLE). The best calibration model of protein in surimi was also developed using PLS. The NIR, but with pretreatment- Normalization by Closure (NCL). The study demonstrated that NIR spectroscopy technology could be successfully applied as a rapid method to determine moisture and protein contents in surimi processing industry.

Introduction

As an intermediate fish product, surimi can be used to make many kinds of product. That is why surimi can be widely used as a food raw material in the world. China has rich resources of freshwater fisheries. It is very important for freshwater surimi to develop freshwater resources and offer high quality, convenient animal protein(Yinhong and Shunsheng Chen,2004).

Recent studies showed that moisture in surimi played a vital role in gel formation. The higher the moisture content, the smaller the pulling stress and gel strength, and the other way round, the pulling stress becomes larger. Another key factor is optimum protein concentration for gel strength. So in order to get good surimi gelation, the protein and moisture concentration should be adjusted to an optimum level (Guanghong and Tinghua Shi, 1999).

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Using conventional methods such as oven drying or micro-kjeldahl procedure, determination of moisture and protein contents is laborious and time consuming. NIRS is one of the fast growing and widely used green analytical technologies in the world, which is nondestructive, fast and easy to implement where no reagents are required and no waste is produced. It is well suited for determining the major components of foods, quantity and quality analysis in food industry.

Previous studies have been done by using NIRS to access the chemical component in aquatic products were concluded with satisfactory result. NIRS has been successfully applied in determination of chemical components in different kinds of fishes such as salmon, rainbow trout, freshwater fishes and so on. With the development of the technology, the object of the measure has been changed. NIRS fish analysis was initially performed on freeze-dried fillets and then on fresh minced samples. Later studies were conducted on whole fillets and intact fish. There are few reports on the estimation of the quality of the fish products by NIRS. As for surimi, Musleh Uddin used a surface interactance fibre optic accessory to collect the transmittance spectra and then established the models for water and protein (Cozzolino et al. 2002 and Musleh Uddin et al. 2006).

The advantages of FT-NIRS are listed as follows: 1) continuous spectrum; 2) fast, computer can work out the light splitting; 3) highly luminous flux, it is not essential to get the resolution by decreasing the number of narrows and reducing the energy, which lead to big noise; 4) built-in laser, wavelengths are always reliable; 5) random error of the detector is apportion into all the wavelengths, rather than produced by each wavelength.

So in this case, this research was aimed at establishing a rapid and accurate NIR calibration for evaluating the moisture and protein contents in the silver carp surimi, comparing the results shown in predecessor's and doing data accumulation on the identification of different kinds of surimi.

Materials and Methods

Sample collection

About 50 surimi samples were collected from 2004 to 2007. In this study, we did not have enough representative samples. As the reliability of a calibration will be restricted to the range of constituent values, we made some representative samples by adding the water in the surimi. Then we obtained several representative samples. Table1. shows the mean reference values, range and standard deviations for two components in the calibration and validation sets, which indicates that the sample population was well represented in both the calibration and validation sets.

Table 1. Mean reference value, range and standard deviation (S.D.) of moisture and protein in calibration set and validation set

Components	Calibration set				Validation set			
	Min.	Max.	Mean	S.D.	Min.	Max.	Mean	S.D.
Moisture/%	73.15	82.06	77.58	2.37	73.55	81.43	77.32	2.47
Protein/%	10.27	17.27	13.92	1.83	10.40	16.85	13.51	2.08

The parameter of the NIR instrument

Sample spectra were scanned by the Buchi FT-NIR NIRFlex N-500 solids (See Fig.1) with 8cm^{-1} resolution and 32 scans per sample. The instrument was conditioned over 15min before measurement. The spectrum reference was Spectralon.

Figure 1. NIRFlex N-500 with sample

NIRS analysis

NIRS spectrometric analyses of surimi were conducted according to the NIR standard procedures that included selection of calibration and validation samples, reference data obtained by routine laboratory analysis, NIR spectral data obtained by scanning samples, selection of optimum equations by calibration and finally confirmation of optimum equations by validation. The established prediction model was used to measure new independent samples.

Sample preparation and reflection spectra collection

The frozen silver carp surimi was thawed overnight at 4ºC. About 50-60g of surimi was ground in a mortar, then was placed in the Petri dish. Big air bubbles were avoided at the bottom of the Petri dish by compacting the surimi. The spectra data were collected by measuring the diffuse reflectance from the surimi samples in the NIR region from 10000 to 4000 cm^{-1}. Each sample was scanned three times rotating the Petri dish to a different position, filling the surimi in Petri dish again. The original reflectance spectra are shown in Fig.2.The instrument operation and collection of NIR spectra were performed using NIRware 5.0 (software, BUCHI). All the operations were accomplished at 20-25ºC.

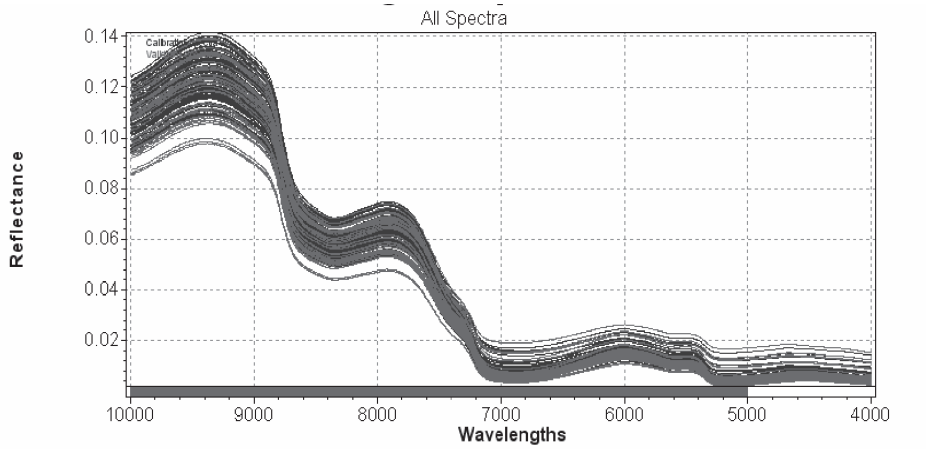

Figure 2. Typical original reflectance spectra for surimi samples

Data analysis

All calculations were performed in NIRCal5.0 (software, BUCHI). Calibrations were developed and evaluated by PCR or PLS. In each case, the spectral data were performed on raw or several pretreatment methods (Smoothing, Normalization, Derivatives and Offset) provided in NIRCal5.0.

The parameters used to evaluate the quality of the calibrations were correlation coefficient of calibration set (Rc) and validation set (Rv), the standard error of calibration set (SEC) and validation set (SEP), consistence between SEC and SEP, and the averaged difference (Bias) between predicted and reference values for all samples in the prediction set, which form a new parameter-Q-value. Q-Value is between 0 and 1. Q-value 1 means perfect and 0 means nothing.

Chemical analysis

Moisture and protein content were analyzed using AOAC methods (GB/T 5009.3-2003 and GB/T 5009.5-2003).

Results and Discussion

Sample selection

At first, all the samples were sorted by reference data for each property. The measured spectra are divided into two sets: 2/3 for calibration and the rest (1/3) for validation. The software uses only the spectra selected into the C-set referring to the calibration wavelength and data pretreatments .The spectra of the V-set will only be used to prove and judge the calibration. The sample with the highest and lowest property

values for each property should belong to C-set. Finally, according the score plot, sample selection was adjusted slightly.

Calibration development

The data acquired from NIR spectrometer contain background information and noises as well as sample information. Data pretreatments are used to eliminate non-important effects or enlarge minor effects of the measurements. Different NIR region has different information contribution for each component. In order to obtain reliable, accurate and stable calibration models, it is very necessary to pre-process spectral data and chose optimum NIR region before modeling. In this paper, by using the NIRCal5.0 wizard, 96 calibrations were developed, compared and sorted by Q value.

A good accuracy of a model was decided by a low SEC and SEP, a high Rc and Rv, a low Bias, which means high Q-value. On the basis of the criteria above, optimum spectral region, data pretreatment and the number of principal component were determined.

The result indicated that best calibration for moisture was got with Normalization to Unit Length (NLE) pretreatment and partial least square (PLS) algorithm. The best calibration model of protein in surimi was also developed by using PLS, but with Normalization by Closure (NCL) pretreatment. Both NLE and NCL can reduce the baseline variations efficiently. The optimum spectral region for moisture and protein were 10000-5000 cm^{-1}, 10000-7404 cm^{-1} and 7144-5000 cm^{-1}, respectively. The wavelength range around 7300 cm^{-1} was removed for protein calibration wavelength so that the influence from the strong first overtone of water can be decreased.

Table2. shows the NIR calibration statistics for moisture and protein in the silver carp fish surimi. For moisture model, SEC and SEP were 0.386 and 0.489 respectively. Both Rc and Rv were higher than 0.98. For protein model SEC and SEP were 0.394 and 0.511 respectively. Both Rc and Rv were higher than 0.97. The slop values were closed to 1 for both moisture and protein models. In this study, the SEP was significantly greater than the SEC. This result suggested that over fitting of the calibrations might occur.

Table 2. The NIR calibration statistics for moisture and protein in the surimi samples

Components	Calibration set			Validation set		
	Rc	SEC	Slope	Rv	SEP	Slope
Moisture/%	0.987	0.386	0.974	0.981	0.489	0.950
Protein/%	0.976	0.394	0.954	0.970	0.511	0.972

The pretreated silver carp surimi spectra are shown in Fig.3 and Fig.4. Now the original spectra (shown in Fig.2) were spaced much closer to each other, the variation due to scattering has been removed.

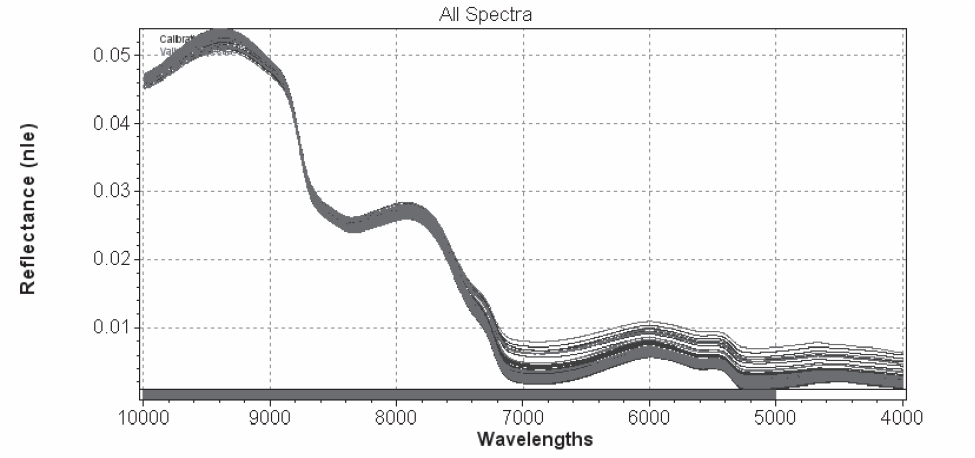

Figure 3. NLE-treated surimi spectra

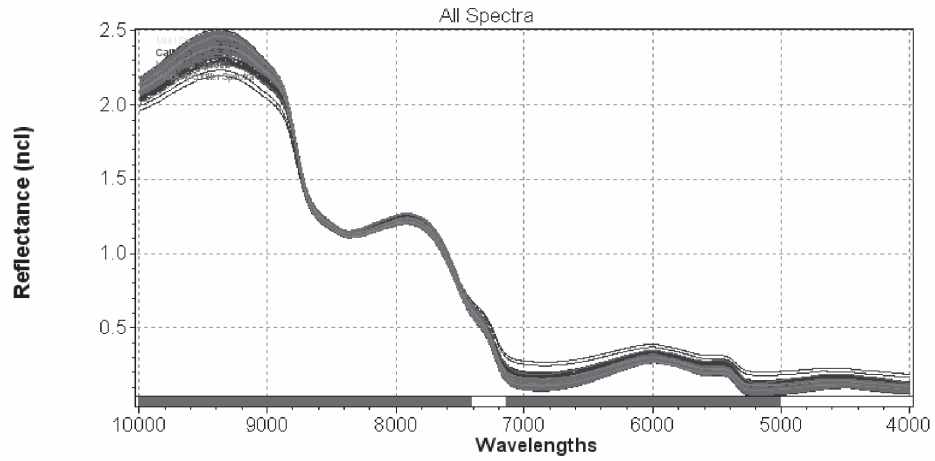

Figure 4. NCL-treated surimi spectra

The good fit of samples is demonstrated in the scatter plots for protein and moisture in Fig.5 and Fig.6. The samples are nicely positioned along the regression line. For protein model, there were three outliers which were marked red in Fig.6 were detected by calculating the property Residuum. After moving the outliers we got a better result.

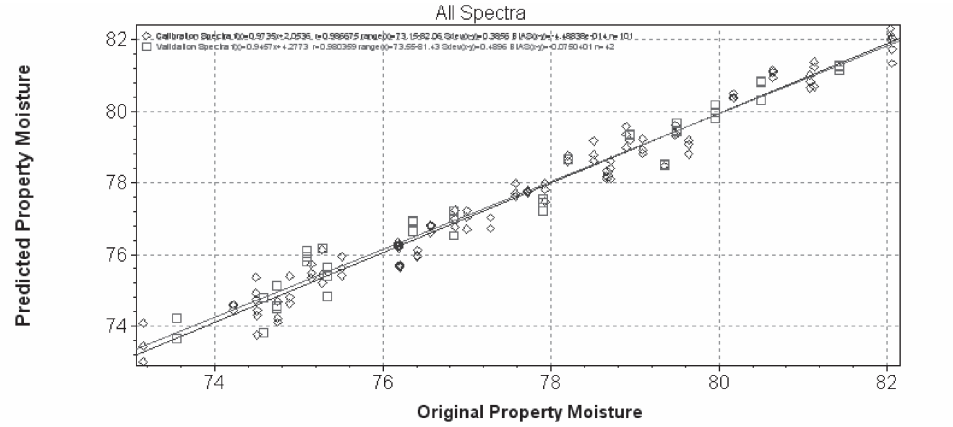

Figure 5. Scatter plot of the reference and NIR predicted values for surimi moisture model

(◊ Calibration spectra; □Validation spectra)

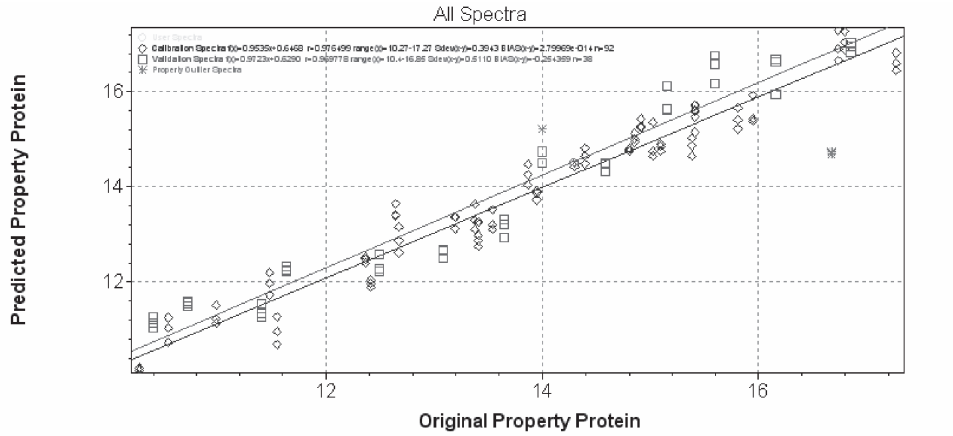

Figure 6. Scatter plot of the reference and NIR predicted values for surimi protein model

(◊ Calibration spectra; □Validation spectra; * Outlier spectra)

In this study, protein calibration model had less effect than moisture. This result was different from the Musleh Uddin's. The correlation coefficient between reference and predicted protein values in Musleh Uddin's study was somewhat higher than what is shown in this work. The reason for that was likely due to the relatively poor accuracy of the reference data.

Detecting the accuracy and adaptability of the calibration models

Table3. shows that the relative average deviation for protein and moisture are both less than 1%. The prediction results of two models were satisfactory. Using the t-test, which can assess whether the means of two groups are statistically different from each other, we found that when the confidence lever were 95%, no significant difference was found between the NIR analysis and reference analysis. This meant NIRS analysis was an alternative to the conventional chemical analysis to determine the moisture and protein contents in silver carp surimi Lu Xu (2004).

According to Table 3. we found that the samples with medium content got an excellent prediction result. It is possible that the number of the samples with medium content in the model were larger than the samples with low and high content. Obviously, in order to raise the adaptability of the model, we have to add more samples with low content and high content in the calibration in the following study.

Table 3. Comparisons of reference values and NIR values of the moisture and protein in independent surimi samples

Sample Number	Moisture			Protein		
	Chemical /%	NIR /%	Deviation /%	Chemical /%	NIR /%	Deviation /%
1	74.67	75.20	-0.53	16.33	15.90	0.43
2	75.02	75.39	-0.37	15.55	15.71	-0.16
3	75.48	76.10	-0.62	14.96	14.80	0.16
4	76.65	76.63	0.02	15.23	15.29	-0.06
5	77.56	78.03	-0.47	14.22	14.02	0.20
6	78.76	78.5	0.26	14.52	14.24	0.28
S.D./%			0.35			0.22
MRD/%			0.37			0.93

Stability test of the calibration models

One sample was selected from the sample set by random. We filled the sample in the Petri dish repeatedly, then got 11 reflectance spectra. Prediction value and RSD were used to access the stability of the models. The result showed that RSD for moisture and for protein are 0.32% and 1.5%, respectively. RSD for moisture and protein were low enough. This meant the models were stable.

Conclusions

The optimum calibration for the prediction of moisture was produced following PLS treatment of NLE spectra. The prediction results clearly indicated that NIR was well suited as a quick method to determine moisture and protein in surimi. The adaptability of the calibration models was good. At the same time, the models exhibited good stability in this study.

In this work, the variety range of the protein and moisture content were not wide enough. In order to get a better and robust calibration, we should add more samples with more representative reference values in surimi products in terms of the moisture content and the protein content.

Prospects

In this work, only two components (moisture and protein) of silver carp surimi were determined by FT-NIR spectrometry. In future, more sophisticated chemical and physical information on surimi may be analyzed by NIRS. The silver carp surimi was the single object in this study. We are beginning to establish the models for nutrition ingredients in other freshwater surimi and do the feasibility study for identifying the different kinds of the surimi.

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