2013 2nd International Conference on Nutrition and Food Sciences
IPCBEE vol.53 (2013) © (2013) IACSIT Press, Singapore
DOI: 10.7763/IPCBEE. 2013. V53. 12

Identification of Fresh Shrimp and Frozen-Thawed Shrimp by Vis/NIR Spectroscopy

Anhong Zhang and Fang Cheng+

College of Biosystems Engineering and Food Science, Zhejiang University, 310058, China

Abstract. Shrimp is an important breeding and export aquatic product in china. It is of great significance to do the identification of fresh shrimp and frozen-thawed shrimp. Vis/NIR spectral analysis technology combined with chemometrics methods have been applied in this study. Discriminant Analysis (DA), Discriminant partial least-squares (DPLS), Least Squares-Support Vector Machine (LS-SVM), three different pattern discrimination methods combined with different spectral preprocessing methods were used to establish qualitative models for differentiating these two kinds of shrimps. The result shows that spectra collected on the first and the third point after Savizky-Golay 19 point smoothing, DA model can realize correct classification of all samples. DPLS combined with Savizky-Golay 7 point smoothing can realize correct classification of all samples.

Keywords: Visible/near infrared spectroscopy, fresh shrimp, frozen-thawed shrimp, identification

1. Introduction

With high economic value and annual output, shrimp is one of the most important breeding and export aquatic products in china [1]. Shrimp is popular with people because of its high nutritional value. With fresh shrimp as the raw material, the processing product is delicious and tender, succulent soft and emits an appealing flavour of freshness [2]. But under the action of microorganisms and some endogenous enzyme, shrimp would rotten soon and lose its edible value [3]. If people eat metamorphic serious shrimp would cause food poisoning. So during the process of shrimp transportation, processing and storage, certain measures should be taken to ensure the fresh degree of raw materials [4]; on the other hand, the shrimp as the raw materials should be dynamic monitored.

Raw materials of many shrimp products are derived from frozen-thawed shrimps. The freshness and quality of shrimp will change in the process of freezing. So it is necessary to do the identification of fresh and thawed shrimp [5]. There is less report about the identification of fresh shrimp and frozen-thawed shrimp in recent years. But many researchers have done the research for qualitative analysis of aquatic products using Vis/NIR spectroscopy [6] and [7].

Vis/NIR optical fiber probe is used to establish prediction model on the kramer shear force value of the Atlantic salmon stiffness before and after rigid. Through the kramer shear force value, Atlantic salmon is divided into high, medium and low three categories [8]. (Isaksson et al. 2001)

Near infrared reflectance spectra in near infrared region (1100-2500 nm) combined with chemometrics methods were utilized to identify different batch of fish meal. Three methods of Principal Component Analysis (PCA), Discriminant partial least-squares (DPLS) and Linear Discriminant Analysis (LDA) based on principal component score were used to identify different species of fish meal. The result shows that 82%

+ Corresponding author. Tel.: +86 571 88982713; fax: +86 571 88982713.
E-mail address: fcheng@zju.edu.cn

of fish meal samples can be correctly classified by the cross validation of the DPLS model. More than 80% of fish meal samples can be correctly classified by the LDA calibration model [9]. (Cozzolino et al. 2005).

In order to classify different species of exopalaemon by Vis/NIR spectra, successive projections algorithm (SPA) combined with uninformative variable elimination (UVE) were used to select effective wavelengths from Vis/NIR bands. Twelve effective wavelengths were selected by UVE-SPA,and they were 392,431,517,55l,595,627,676,734,760,861,943 and 1018 nm. These selected effective wavelengths were set as inputs of least square-support vector machine (LS-SVM) for the classification of three typical exopalaemon species, namely, E.earincauda, E.modestus and E.orientis. The correct rate is 92.00% for classifying samples in prediction set by LS-SVM model. The overall results demonstrate that it is feasible to utilize Vis-NIR spectroscopy to classify different species of exopalaemon,and UVE-SPA can extract the most effective wavelengths to build the LS-SVM model with all optimal classification result [10]. (Wu et al. 2008)

Near infrared reflectance spectra of silver carp surimi, grass carp surimi and freshwater surimi were collected region from 1000 to 2500 nm. According to spectral characters, three different pattern discrimination methods were used to establish qualitative models for differentiating these three different kinds of surimi. Combined with different pretreatment methods and some statistical regression method, these three different kinds of surimi have been quickly classified [11]. (Huang 2008)

Vis/NIR spectroscopy combined with dynamometric analysis were used to discriminate concrete tank–cultured sea bass from sea cage-cultured sea bass. PLSR was conducted on 198 samples individually at 48 and 96 h post-mortem to determine whether textural and spectral parameters can discriminate between these two different kinds of sea bass. The results of this analysis demonstrated that spectral measurements better discriminate individual animals at 48 h post-mortem (87% in the independent test) with respect to 96 h post-mortem (66.7% in the independent test). The correlation coefficient of DPLS model is 0.905 [12]. (Cost et al. 2011)

The possibility of using NIRS for the authentication of wild European sea bass (Dicentrarchus labrax) was investigated in the study of Ottavian (2012) [13]. Three different chemometric techniques to process the NIR spectra were developed, and their ability to discriminate wild sea bass from farmed sea bass samples was evaluated.

VIS/NIR spectroscopy for differentiating between fresh and frozen-thawed cod fillets had been evaluated. Results show that frozen-thawed cod fillets can be fully separated from fresh fillets using a small subset of wavelengths in the visible region [14]. (Agnar et al. 2011)

In a word, near infrared spectrum analysis technique is widely used with the classification of aquatic products (especially on fish)[15] and [16], so this study also try to use Vis/NIR spectra to identify the fresh and frozen-thawed shrimps.

2. Materials and Methods

2.1. Samples

159 fresh shrimps were bought from Hangzhou Sandun market, which were divided into two parts. The shrimp weight varied from 8 to 10 g, length varied from 80 to 100 mm. The fresh group had 82 shrimps, which were stored in a cold room (4-5 ℃) packed in plastic bags, after 12 h spectra would be measured; another group, the frozen group had 77 shrimps, which were stored in a refrigerator (-20 ℃) also packed in plastic bags. After four weeks shrimp of the frozen group were thawed over night at 4-5 ℃, then spectra would be measured.

2.2. Preparation

Nexus intelligent Fourier transform near infrared spectrometer was chose as sample spectra acquisition instrument.

- Spectral acquisition positions: three detecting points of shelled shrimp, the center of the first, third and last section muscle, respectively.

- The scanning parameters: Scanning for 64, a resolution of 2 cm^{-1}, lens moving speed of 0.9494cms^{-1}, and gain is 8.

3. Result and Discussion

Fig. 1 is the Vis/NIR spectra of fresh and frozen-thawed shrimp on average acquisited by intelligent Nexus Fourier transform near infrared spectrometer equipped with Si detector (670-1100 nm). There is an obvious absorption peak of water at 980 nm. According to spectral characters, there is also some significant difference between fresh and frozen-thawed shrimp samples.

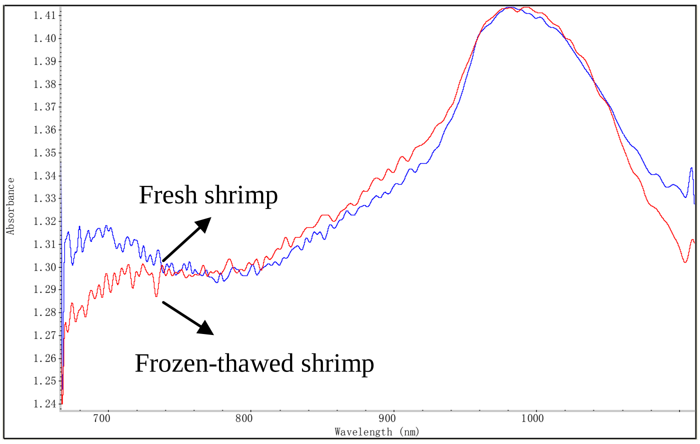

Fig. 1: The average visible and NIR transmission spectra of fresh and thawed shrimp samples

The total number of samples was 157 after eliminating two abnormal samples. There were 105 samples in calibration set (the number of fresh shrimps and frozen-thawed shrimps was 55 and 50, respectively). The number of prediction set was 52 (the number of fresh shrimps and frozen-thawed shrimps was 27 and 25, respectively). Samples were randomly distributed. According to spectral characters, three different pattern discrimination methods were used to establish qualitative models for differentiating fresh and frozen-thawed shrimps combined with different preprocessing methods.

Spectra of fresh and frozen-thawed shrimps were collected on these three detecting points, respectively. The method of discriminant analysis was used to establish classification models. Compared with models established in the range from 670 nm to 1100 nm, the correct rate of models established in the range from 900 nm to 1100 nm was much better. In the range from 900 nm to 1100 nm, on the first point, the correct rate was 91.42% and 98.08% for classifying samples in calibration set and prediction set by DA model, respectively. On the second and third point, the correct rate was 96.19% and 98.08% for classifying samples in calibration set and prediction set by DA model, respectively.

On this basis, different spectral preprocessing methods were utilized to optimize these models. Results show that spectra collected on the first and the third point after Savizky-Golay 19 point smoothing, DA model can realize correct classification of all samples, the classification schematic diagram is shown in Fig. 2; spectra collected on the second point after Savizky-Golay 11 point smoothing, the correct rate was 98.10% and 98.08% for classifying samples in calibration set and prediction set by DA model, respectively.

Discriminant partial least-squares method was applied to establish models for differentiating fresh and frozen-thawed shrimp based on the third point spectra, combining with different spectral preprocessing methods to optimize these models. Results showed that discriminant partial least squares combined with Savizky-Golay 7 point smoothing can realize correct classification of all samples, the classification schematic diagram is shown in Fig. 3.

There were two bands, ranging from 680 to 1100 nm and 900 to 1100 nm, respectively. These two bands were set as inputs of least square-support vector machine (LS-SVM) for the classification of fresh and frozen-thawed shrimp, respectively.

The results are shown in Table I. The correct rate of LS-SVM models based on band of 900 to 1100 nm was much better. The correct rate on the first and third point was 98.73%, the third point was 96.82%.

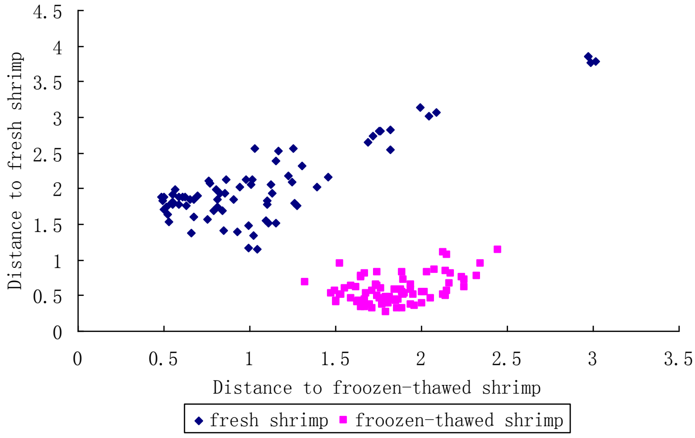

Fig. 2: Classification plot for fresh and thawed shrimp by DA with Savizky-Golay 19 smoothing

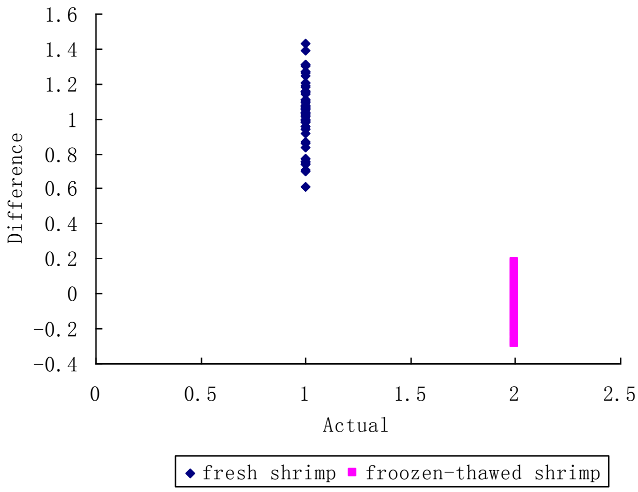

Fig. 3: Classification plot for fresh and thawed shrimp by DPLS with Savizky-Golay 7 smoothing

Table I: The discriminant analysis results of different detecting points of different bands

detecting point	Total correct rate (%)	
	680-1100 (nm)	900-1100 (nm)
first	91.72	98.73
second	94.90	96.82
third	95.54	98.73

To reduce the number of input variables and improve the speed of classification, the top ten principal component scores of the range from 900 nm to 1100 nm were set as inputs of least square-support vector machine (LS-SVM) for the classification. The results of these three points were shown in Table II.

The correct rate was 100% for classifying samples in calibration set by LS-SVM model on these three points. The correct rate was 98.08% for classifying samples in prediction set by LS-SVM model on the second point, which is much better than other two points. The total correct rate was 98.73% on the first and third point. The second point is 96.82%, which was a bit poor compared with other two points.

Conclusion can be drawn from the above analysis that results were different when different methods were utilized to establish models based on the spectra collected at three detecting points. The main reason may be caused by uneven muscle surface thickness of the shell shrimp. And directions of the lighting from the fiber optic diffuse probe were not unified, so that it would cause certain influence to the original spectrum collection, and would affect subsequent modelling results. It can be seen from the overall modelling results that the correct rate of models based on spectra collected on the third point were much better. The explanation might be the third point located at the tail section, whose muscle was thin and relatively homogeneous. So the fiber optic diffuse lighting direction would also be unified, which could reduce the effect on collected spectra and the results would be relatively good.

Table II: Fresh and thawed shrimp discrimination overall results developed by LS-SVM with the first ten principal component scores of three detecting

detecting point	the correct rate of calibration set (%)	the correct rate of prediction set (%)	the total correct rate (%)
first	100.00	86.54	95.54
second	100.00	98.08	99.36
third	100.00	96.15	98.73

All results showed that frozen-thawed shrimps could be fully separated from fresh shrimps based on visible/near infrared spectral analysis technology combined with chemometrics methods.

4. Acknowledgements

We thank the National Key Technologies R&D Program of China (2012BAD29B04) for funding of this project.

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