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Application of NIR spectroscopy for monitoring quality of surimi

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Summary

Non-invasive spectroscopy in the near red range from 899 - 1699 nm (NIR) was applied with the aim to analyze commercial samples of surimi and analogs of see shrimp. In this paper the aim was to investigate the possibility of recording reflectance samples for potential monitoring in the production process and sorting of samples according the quality, in order to prevent adulteration, and classification. The surimi as shrimp analogs spectra samples were monitored at 4 °C room temperature of 21 °C over time intervals (0, 30, 60, 120 and 240 min) on both sides of the samples. The samples were treated by cooking in water and in a microwave oven in time intervals: 0; 0.5; 1 and 2 min. Analysis of the spectrums reveal changes in specific wave lengths of 919, 1177, 1201, 1343, 1458 and 1495 which correspond to O-H, C-H and N-H bonds that indicates possibility of determination of fat, protein and water in surimi and shrimp analogues enabling use of NIR for on-line monitoring of quality and selection.

Keywords: NIR spectroscopy, surimi, food quality

Introduction

One of the main challenges of food industry is to obtain reliable information of the products offered on the market (Růžičková and Šustova, 2006). Use of spectroscopy in the NIR region (near infrared region) allows a wide range of applications in the food chain production, controlling the quality indicators of row materials, intermediary products and final products (Růžičková and Šustova, 2006) in order to provide a guarantee for consumers (Damez and Clejron, 2008). NIR spectroscopy is a method used especially for the determination of the main constituents (dry matter, proteins, fat and saccharides), for example in the case of surimi.

Surimi, as an intermediate fish product defined as a refined fish protein product prepared by washing mechanically deboned fish and minced and washed fish is stabilized by cryoprotectants (Udin et al., 2006).

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Previous studies have used NIRs to assess the protein and water content of whole fish and surimi with satisfactory results (Uddin et al., 2005; Uddin et al., 2006; Folkestad et al., 2008; Uddin et al., 2006a; Shimamoto et al., 2003).
The objective of the presented study is to evaluate the use of NIR spectroscopy for the quantitative analysis of different surimi samples for the high-speed determination of fat, protein and water content tested on different surimi samples. Explored was the possibility if NIRs could find its practical application in the production process as well as in the market control.
The technique of NIR spectroscopy is based on the electromagnetic absorption at the near-infrared region but the spectral analysis has to be assisted with various chemometric techniques, such as multiple linear regression analysis, MLRA, principal component analysis, PCA and canonical variate analysis, CVA (Ding and Xu, 1999; Alishahi et al., 2010).

Materials and methods

Surimi samples

Two commercial surimi samples, from two different manufacturers were used in this study. Land of origin for the first surimi, samples P, was China and the second sample, L, was from Lithuania. P surimi samples had 42 % of white fish meat and L samples had 29 % of white fish meat. For both manufacturers, Croatia was importer country and they were purchased from a supermarket.

Sample preparation

After purchasing all the samples were kept for two days under controlled conditions in freezer at temperature of - 13 ± 1 °C prior to experiments. Measurements using NIR instrument were carried immediately after extraction of each sample from the freezer without any mechanical or chemical treatment prior to NIR spectroscopy. Each sample was unwrapped from foil and put on clean surface. The probe of NIR instrument was then leaned upon the sample slightly touching it. Both sides (white and red) of surimi were tested.

NIR measurements

Surimi NIR spectra were collected over the range of 904-1699 nm using a Control Development, Inc., NIR-128-1.7-USB/6.25/50µm shown in Fig. 1 with installed Control Development software Spec32.

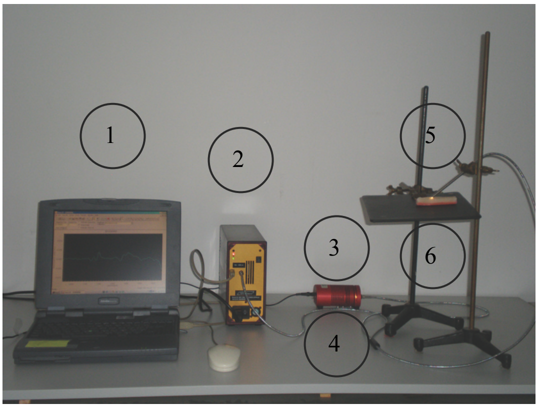

Fig. 1. NIR instrument connected to PC (Laptop with Spec32 software (1), NIR instrument (2), source of light (3), optical cable (4), measurement probe (5), surimi sample (6))

Modelling

NIR spectra were recorded in EXCEL format and imported to STATISTICA v. 8. software for evaluation. Imported are the original spectra and pre-processed spectra by Savitsky-Golay "smooth" algorithm for data filtering which is available by Control Development software Spec32. Firstly, the data are collected in a matrix **X** with samples placed in rows and NIR intensities are variables placed in columns. Each vector of the variables is auto-scaled with respect to each variable (wave length) sample average and standard deviation:

$$\mathbf{X}_{i,j} \leftarrow \frac{X_{i,j} - \overline{X}_j}{\sigma_j\left(X_j\right)} \tag{1}$$

Assuming normal distribution, for each variable sample statistics is calculated by:

$$\overline{\mathbf{X}}_j = \frac{1}{n} \cdot \sum_{i=1}^{n} X_{i,j} \qquad \sigma_j^2 = \frac{1}{n-1} \cdot \sum_{i=1}^{n} \left(X_{i,j} - \overline{\mathbf{X}}_j\right)^2 \tag{2}$$

The scaled data matrix **X** is approximated by the projections into the subspace of principal components **P**:

$$\mathbf{T} = \mathbf{X} \cdot \mathbf{P} \tag{3}$$

The principal components form the loading matrix **P** and all the scores are collected in the target matrix **T**. The principal component model reconstructs the original data by the relation:

$$\mathbf{X} = \mathbf{T} \cdot \mathbf{P}^T + \mathbf{E} \tag{4}$$

In Eq. 4. **E** is the error matrix of the residuals between the experimental data and the principal component projections. Components of the error matrix are assumed to be a result of all random factors included in the experiment, such as instrument error, sample treatment and laboratory conditions. Due to high colinearity between spectra data, very significant reduction in dimension is obtained. The principal component vectors are determined by sequential maximization of the variance of the projected data with assumption of the sample based covariance. The principal components are eigenvectors of the sample covariance, while the corresponding eigenvalues are the variances:

$$\mathbf{X}^T \cdot \mathbf{X} \cdot \mathbf{P}_i = \lambda_i \cdot \mathbf{P}_i \tag{5}$$

Variance of the data matrix is given by the sum:

$$\sigma^2(\mathbf{X}) = \sum_{i=1}^{m} \lambda_i^2 \tag{6}$$

The method enables extraction of the essential deterministic information from large sets of spectra correlated data by reduction of the dimension by only the first *r* significant principal components ($\mathbf{P}_1$, $\mathbf{P}_2$ $\mathbf{P}_r$).

In this work the main purpose for principal component analysis (PCA) is to apply cluster analysis in the plane of the first two principal components for discrimination of sample origin and detection of possible product adulteration.

Results and discussion

In Fig.1 is shown the experimental setup with NIR instrument, optical cables and a sample holder. Each spectrum was digitally recorded and saved in EXCEL format for further analysis. Numerical evaluation of principal component analysis was performed by statistical software STATISTICA v. 8. Four samples of each surimi manufacturer, labelled as L and P, were subject to NIR analysis on upper and lower side of each sample. The data matrix **X** (8x796) is composed of 8 rows, 4 samples of L and P, and 796 NIR reflectance in columns. In Fig. 2 are presented two typical samples NIR reflectance spectra for L and P samples. In order to perform PCA analysis applied is numerical derivation as presented in Fig. 3. For a first estimate of the spectra similarities evaluated are Pearson's correlation coefficients. The obtained matrix of cross-correlation coefficients is given in Table 1. The spectra are highly correlated as proved by very high coefficients with average value R = 0.952. Correlation between spectra of the same sample P is very high, R =0.99, while for L samples is R=0.957. However, there is noticeable decrease in the cross correlation, R =0.91, between the two types of surimi products, L and P, which leads to possible recognition of samples based on correlation of full NIR spectra.

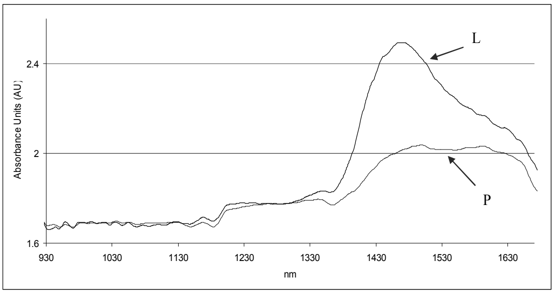

Fig. 2. NIR spectra for surimi samples P and L

Sample of NIR spectra for both surimi manufacturers are shown in Fig. 2. and their corresponding derivatives in Fig. 3.

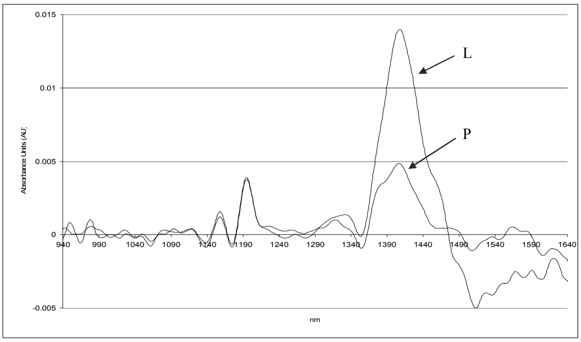

Fig. 3. Samples of the corresponding derivatives of NIR spectra for surimi samples P and L

Table 1. Matrix of correlation coefficients for the first derivative of NIR spectra for L and P surimi samples. Average correlation between L samples is $R_{L,L} = 0.957$, for P samples is 0.990, and average cross-correlation between L and P samples is $R_{L,P} = 0.911$

Variable	**L1**	**L2**	**L3**	**L4**	**P1**	**P2**	**P3**	**P4**
L1	1.00	1.00	0.99	0.93	0.93	0.93	0.90	0.95
L2	1.00	1.00	0.99	0.94	0.93	0.93	0.90	0.95
L3	0.99	0.99	1.00	0.89	0.96	0.96	0.94	0.97
L4	0.93	0.94	0.89	1.00	0.83	0.84	0.79	0.87
P1	0.93	0.93	0.96	0.83	1.00	0.99	0.99	0.99
P2	0.93	0.93	0.96	0.84	0.99	1.00	0.99	0.99
P3	0.90	0.90	0.94	0.79	0.99	0.99	1.00	0.99
P4	0.95	0.95	0.97	0.87	0.99	0.99	0.99	1.00

In order to apply NIR spectra for sample classification according to product manufacturer principal component analysis (PCA) is applied. Firstly are determined eigenvalues for the data matrix X composed of four independent measurements for each manufacturer, L and P samples. Eigenvalues are calculated by numerical matrix inversion algorithm provided by STATISTICA v.8 software. Results are presented in Table 2. and graphically as scree plots in Fig. 4. The pronounced affect of the first two eigenvalues is observed and by the cumulative effect is observed that 99.5 % of variance is accounted by the first two principal components.

Table 2. Eigenvalues of the covariance matrix of NIR spectra for L and P samples

Value number	Eigenvalue	% Total variance	Cumulative Eigenvalue	Cumulative %
1	605.357	79.9679	605.357	79.968
2	147.962	19.5459	753.320	99.513
3	2.790	0.3686	756.111	99.882
4	0.516	0.0681	756.627	99.950
5	0.285	0.0376	756.912	99.988
6	0.061	0.0080	756.973	99.996
7	0.026	0.0035	757.000	100.000

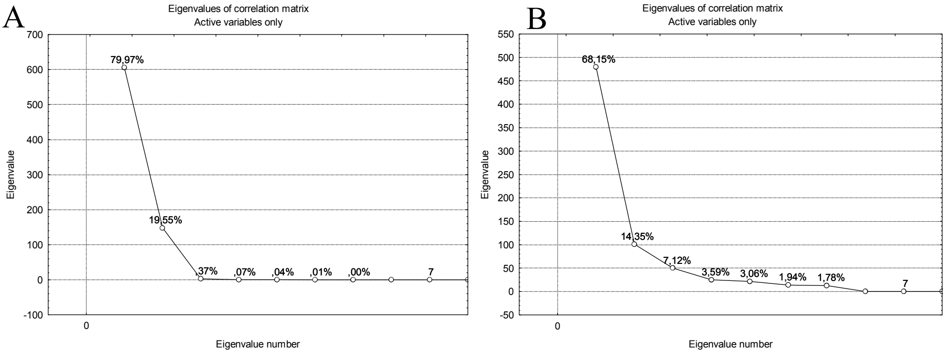

Fig. 4. Scree plots for the NIR spectra (A) and their derivatives (B)

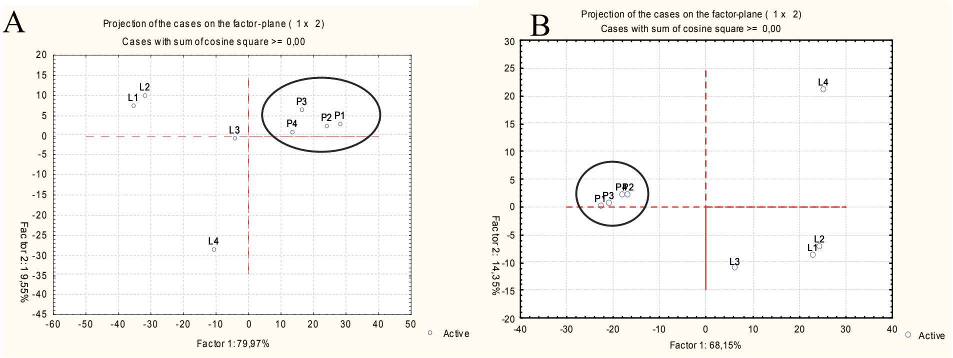

Fig. 5. Classification of L and P samples based on NIR spectra (A) and their corresponding derivatives (B) in the plane of the first two principal components

In Fig. 4 are compared scree plots for NIR spectra and its first derivative. The similar distribution of eigenvalues is obtained, showing the "knee point" after the second eigenvalue, at which occurs separation of deterministic information from random effects. However, account of random effects in the derivative of the spectra is higher, about 10 %. Projections of the samples on the first two principal component planes are presented in Fig 4. Clustering of the samples according to product manufacturer is observed in both cases, PCA 1-2 of NIR spectra Fig. 5A, and PCA 1-2 of the first derivatives Fig. 5B. The clustering effect based on NIR first derivative is more pronounced compared to the original NIR spectra, yielding very close scores for P and distinct from L samples.

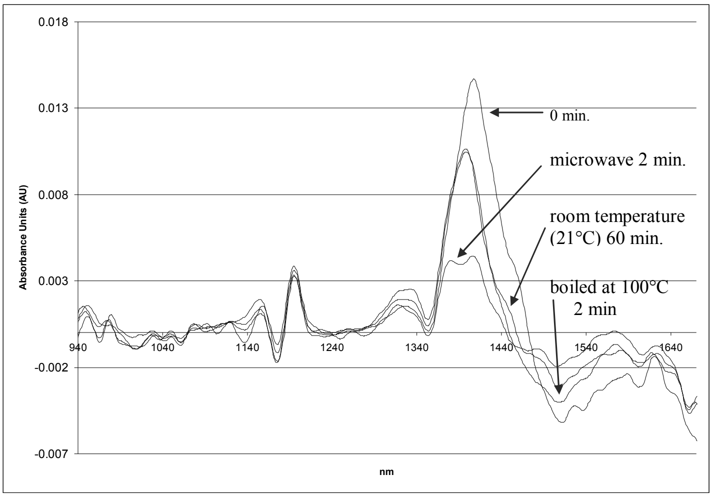

Fig. 6. Derivatives of NIR spectra of four surimi samples L after thermal treatment. First sample was recorder in immediately after it was taken from a freezer (-12±1 °C), i.e. at time 0 min. The second was micro waved for two minutes, the third was thawed by leaving for 60 minutes at room temperature (21 °C) and the fourth sample was boiled in water at 100 °C for 2 minutes.

The scores of L samples show relatively large distance and a sub-cluster for L1 and L2 samples. Nevertheless, P and L scores are clearly discriminated by the second principal component, i.e. all P samples are on the left-hand side and L samples are on the right hand side. These results support the main objective to use NIR and PCA analysis for sample recognition and possible detection of product adulteration.

Effects of various thermal treatments of surimi can be monitored by NIR spectra. In Fig. 6 are given the effects on the first derivative after sample thawing for 60 minutes at room temperature, after 2 minutes of exposition in a microwave oven, and after boiling in water for 2 minutes at temperature 100 °C. These are preliminary results, which support the main hypothesis that NIR spectrometer with optical cables is applicable for on-line process monitoring and control.

Conclusions

A NIR process analyzer with optical cables proved to be versatile and sufficiently accurate for recognition of surumi origin and for monitoring of thermal processes.
Applied is principal component analysis for sample clustering and sample origin classification. The analysis is applied on auto-scaled data and numerical derivatives of the smoothed spectra. The scree plot of eigenvalues reveals that the first two principal components account for 90 % of extracted deterministic information.
Based on scores on the plane of the first two principal components successfully are performed classifications of two surimi products of different origin (manufacturer).
By NIR spectra are monitored effects of applied thermal treatments thawing, micro-wave frying and boiling. Each of the thermal treatments has a characteristic NIR signature enabling on-line process monitoring and control.

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