Prediction of Fatty acid Contents of Caviar from Caspian Sea (Iran) using NIR Spectroscopy

Hosna Mohamadi Monavar, Reza Alimardani, Mahmoud Omid, Jens Petter Wold and Hadi Razavi

Abstract—The purpose of this study was to evaluate feasibility of near infrared (NIR) spectroscopy with fibre optic probe for predicting fatty acids profile of Beluga caviar. Measurement was performed on 100 samples of Beluga. The wild caviar samples caught sturgeon comprised Huso huso. NIR calibrations were developed using partial least square regression (PLSR). Selected models for the estimation of fatty acids in this species of caviar exhibited coefficients of determination for cross validation which ranged 0.81-0.91 % with root mean square errors of (RMSE) between 2.1 and 3.0. This information suggested that in general, NIR interactance spectroscopy could provide an opportunity to measure fatty acids contents of caviars.

Keywords—Beluga Caviar, Fatty acids, Near infrared spectroscopy.

I. INTRODUCTION

The most valuable caviar are derived from wild harvested sturgeons in the area of Caspian Sea is Beluga (Huso huso), [1]. The alteration in fatty acids composition of intraperitoneal, subcutaneous and intramuscular fat from farmed sturgeon products were monitored during storage at 4 °C [2]. The effect of diets on quality of farmed white sturgeon (Acipenser transmontanus) caviars was also considered by [1]. The current reference method for analyzing fatty acid composition is gas chromatography (GC) which requires work up, such as solvent extraction and derivatization. Spectroscopic methods have gained importance in the evaluation of food quality attributes during the last decades [3,4]. The fact that NIR spectra reflect several parameters of the material suits the method for evaluating complex quality [5]. NIR spectroscopy shows promise for fast and non-destructive analysis of biological materials [6] and has been successfully used as a substitute of chemical analysis due to its recognized advantages as an accurate tool [7]. Since studies on wild caviars analysis with NIR instrument have not been found in the literature, the aim of the present study was to determine fatty acids of three kinds of caviars from Caspian Sea using NIR spectroscopy by direct application of fibre optics probe.

II. MATERIALS AND METHODS

A. Caviar samples

The caviar was withdrawn from the opened abdominal cavity of sturgeons those caught using Gill nets with the standardized mesh and dimensions set by the Iran fisheries organization during spring 2011. Then caviar packed in closed commercial glass cans and stored at 0-4°C. A total of 100 samples in the glass of 20g stored at zero (±2°C) in the refrigerated storage room between acquisition and analysis.

B. Near-infrared Spectroscopy (NIRs)

The NIR instrument (Foss NIR-system Inc., USA) was connected to a hand held interactance opti-probe. In this instrument the illumination and measurement were performed on the same side of the sample, where the illumination focused on an area adjacent and parallel to the detectors field of view. Interactance eliminates the effect of specular reflection and increases the signal received from inside the sample. The single beam spectrometer designed to perform transmission measurement by using 1.5 m long fibre optic bundles. In the probe head, the bundles were split into seven parallel arrays of alternating emitting and receiving arrays. The transmitting and receiving fibre bundles were calibrated by reference and standard probe holder to match the spectra set up with regard to optical path length. The caviar samples were measured by placing the probe in contact with them. Each recording spectra was an average of 32 scans that lasted 25s. The resulting data are given in absorbance unit in the region 400-2200 nm with spectral resolution of 0.5 nm.

C. Reference Method

Fatty acid was determined by gas-liquid chromatography according to Wirth et al. [8]. The samples were homogenised in trichloromethane by means of Ultra-Turrax and the total lipid extracted as described in Folch et al. [9]. The lipids sample was dissolved in 10% methanolic hydrogen chloride (2mL). A 0.1 ml solution of tricosanoic acid 910mgmL-1) was added as internal standard. The samples were sealed and heated at 50°C, and then 2mL of a 1M potassium carbonate solution were added to each sample. The FAMEs were
extracted with 2mL × 2mL of hexane and 1µL was injected to the gas-chromatogragh, in split mode. Fatty acids analysis was carried out on an Agilent gas-chromatograh (Model 6890 Series GC) fitted an automatic sampler (Model 7683 Series Injector) and FID detector. The relative proportion of each fatty acid in the fatty acids patterns was expressed as percentage of the sum of fatty acids resolved. The proton density of fat from Beluga is found 16.36%.

D. Data Analysis

Spectra were exported from Vision software (ver. 3.2) for chemometric analysis to the Unscrambler software (ver. 9.5, CAMO, AS, Norway). Spectral pre-treatment in the form of 1st derivative using Savitzy-Golay [10] with a second order polynomial and a 50 nm wide smoothing window were performed on whole collection of spectra (calibration and test set). Partial least square regression (PLSR) was used for making calibration models between NIR spectra and fatty acid components described by Martens and Naes [11]. The reference value, $y_i$, and the predicted value, $\hat{y}_i$, of each sample were compared to calculate the prediction error of the cross-validated calibration model, expressed as the root mean square error of cross-validation (RMSECV). The RMSECV value is defined using (1).

$$RMSECV = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (y_i - \hat{y}_i)^2}.$$  

Where i is the samples from 1 to N. Both RMSECV and the multivariate correlation coefficient ($R^2$) between reference and predicted values were reported to evaluate the performance of the regression models (Naes et al., 1996):

$$R^2 = 1 - \frac{SEL}{SD}^2.$$  

Where SEL and SD are the standard error of reference method and standard deviation of the known concentrations in the validation set, respectively.

III. RESULTS AND DISCUSSIONS

A. NIR spectral features

Fig.1 shows the NIR raw mean spectrum of Beluga with fibre optic probe. The peak centered at 1200, 1700 and 2300 nm in the interactance spectra is due to absorption by fat [5]. The NIR average spectrum of water exhibits in 1400-1440 nm absorbance value. Fig.2 shows derivative of NIR average spectrum. The derivative of mean spectrum allows identification of smaller absorption bands. Around 960nm, absorption bands are related with CH2 bond, which is characteristic of fat and also there is OH second overtone near this region. Other bands corresponding to the fat contents are located around 1200 nm, which is related with the CH stretch second overtone: 1730 and 1760 nm, associated with the CH stretch first overtone [12]-[13]. The C=O and CH absorption bands of terminal double bonds and cis unsaturation around 1900 nm and 2100 nm are characteristic of fatty acid. The absorption bands at 1832 nm related with CH first overtone of carbonyl compounds.

B. Fatty acids composition

The fatty acid profiles of caviar samples used for the calibrations are shown in Table 1. The first inspection of composition results reveals an important variability, which could be favourable for calibration development. The reference results could be used to predict the lipid and moisture content of caviars as shown in Table 1.

TABLE I

<table>
<thead>
<tr>
<th>Caviar sample</th>
<th>Mean Fatty acids (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>16:0</td>
</tr>
<tr>
<td>Beluga</td>
<td>24.27</td>
</tr>
</tbody>
</table>

C. Multivariate analysis

PLS regression models were developed for each analytical parameter versus reference values (Fig. 3). It shows the correlation of the values obtained by reference method with respect to those predicted by NIR with a fibre optic probe. However it is tempting to look at the profiles corresponding to regression coefficient for established PLSR models and try to match them with the characteristic spectral features of caviars. Fatty acids of Beluga belonging to the test set were successfully predicted on the basis of constructed models. An accuracy of RMSE= 2.2% was comparable with what has been obtained on beef [14] and salmon fillet [15]. Calibration statistics reported in Table 2.
IV. CONCLUSION

This study contributed to the chemical characterization of Beluga caviar for fatty acid compositions. VIS/NIR spectroscopy with fibre optic probe is proved an adequate technique for the analysis of fatty acids in caviars with derivative pre-treatment method. The PLS regression models for fatty acids show that as long as there is a good match between spectroscopic sampling and sampling by reference methods, sufficient correlation is obtained (0.81-0.91).

ACKNOWLEDGMENT

This study was supported by Iranian Ministry for research, Science and Technology (MRST) and Tehran University. The authors gratefully appreciate technical support of the research council of Nofima Mat, Ås, Norway.

REFERENCES


[4] Nadai, B.T.; Mihalji-kengyl, V. Investigations of different equations predicting moisture, fat and protein content of raw meat by NIR-


