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Title: Non-destructive measurement of salt using NIR spectroscopy in the herring marinating process

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Declaration of interest: none

Abstract

The salt content is one of the most important quality and safety parameters in the manufacturing process of marinated herring, which needs to be controlled during processing. Standard methods are often destructive and time consuming, and therefore a nondestructive and fast method needed. Near-infrared (NIR) spectroscopy was measured on marinade samples from herring marinating process in order to investigate the potential of NIR as a fast method to determine the salt content in marinade and in fish. The spectral region 1100-1300 nm had the highest positive correlation with the measured salt values. A principal component analysis performed on the NIR spectra showed that the first principal component described the evolution of the spectra according to the determined salt values. A partial least-squares regression model between the selected region of the NIR spectra and the salt content of the fish gave a correlation coefficient of 0.81 and a prediction error (RMSECV) of 0.41 g/100 g with the prerequisite that salt concentration in fish and marinade was in equilibrium. The results indicate that NIR spectroscopy can be used as a fast and non-destructive method for assessing the salt concentration in fish during the herring marinating process in order to ensure product safety.

Keywords: Marinated herring; Food Safety, Salt; Multivariate calibration; NIR spectroscopy

1. Introduction

Marinated herring products are traditionally consumed in Northern European countries and manufactured by a process using a solution of sodium chloride and acetic acid in order to increase the ionic strength and decrease pH and hereby preserving the fish making it available for consumption most of the year (Rodger, Hastings, Cryne, & Bailey, 1984). This process is based on passed down experience and years of traditions and often consists of an intermediate salt brining

followed by the marinating process using a solution of salt and acetic acid. Marinated herring products are semi manufactured products with no prior freezing step and no sequential heat treatment. Salt is one of the key preservatives for these herring products, but is also an important factor for the sensory characteristics (quality) of the product. One of the main safety issues is the presence and viability of the *Anisakis* larvae. A study showed that the mortality of the *Anisakis* larvae was mostly influenced by the salt concentration in the muscle liquid phase compared to the concentration of acetic acid and an adequate salt content in the fish liquid phase is important in order to achieve a safe product (Karl, Roepstorff, Huss, & Bloemsma, 1995). Salt is an important quality and safety parameter, which needs to be determined and controlled during processing.

Quality control is typically conducted at the end of the herring marinating process, where samples of fish are collected for analysis and visual evaluation. A common method for salt analysis involves an aqueous extraction of salt from the sample and titration with standardized silver nitrate (AOAC 976.18). This method is accurate, but also destructive and time consuming and difficult to run in a production setting. In some productions the final quality control is conducted using near-infrared (NIR) spectroscopy, where samples of fish are collected for analysis, however, preparing the samples for analysis is destructive and can be time consuming as well. Besides, it is known that variability between herring fillets occurs, especially in the fat content (Aidos, van der Padt, Luten, & Boom, 2002; Lane, Westgate, & Koopman, 2011; Nielsen, Hyldig, Nielsen, & Nielsen, 2005), and sampling of some fillets may not be appropriate to characterize the whole batch. Sampling of the surrounding brine is very attractive and may be more representative and indeed more accessible than sampling the whole fish during processing. In this way the concentration of the marinade, when in equilibrium with the herring muscle, can be used as a quality parameter throughout the entire herring marinating process.

Non-destructive and rapid methods for salt detection are promising and studies show that NIR spectroscopy was used to determine the salt content in aqueous solutions (Hirschfeld, 1985; Lin & Brown, 1993), in meat (Begley, Lanza, Norris, & Hruschka, 1984), in cod (Galvis-Sanchez, Tóth, Portela, Delgadillo, & Rangel, 2011), in cured salmon roe (Huang, 2001) and in hot smoked salmon (Lin, Cavinato, Huang, & Rasco, 2003).

NIR spectroscopy is a useful analytical technique for biological samples and works by measuring the amount of light, which is absorbed by the sample as a function of the wavelength (Galvis-Sanchez et al., 2011). The method is based on vibrational modes of molecules mainly C-H, O-H, and N-H functional groups, which can be observed as overtones and combinations in the NIR spectrum (Huang, 2001; Svensson, Nielsen, & Bro, 2004). While, sodium chloride (NaCl) has no specific absorption band(s) in the NIR region, it is known that salt in solution causes changes in the height, width and position of the absorbance bands of water (Hirschfeld, 1985; Lin & Brown, 1993). The bands become narrower and shift to a shorter wavelength with increasing NaCl concentration compared with the bands of pure water (Lin & Brown, 1992). For that reason, it is expected to find information about the changes in salt concentration in the marinade over time in the herring marinating process. NIR is a good choice for quality control, not only can it be used to determine the salt content during the manufacturing of marinated herring, but also simultaneously determine other parameters such as protein, sugar and fat content (Begley et al., 1984). Despite being a promising technique there are also some drawbacks to consider, e.g. water is the major constituent of herring marinade, which strongly characterize the spectral information in NIR with peaks around 1450 nm and 1886 nm.

The marinade is a heterogeneous medium consisting of fat, protein and water, which all absorbs in the NIR region resulting in overlapping signals (Grassi, Amigo, Lyndgaard, Foschino, & Casiraghi,

98 2014). For that reason, the use of chemometrics is needed in order to extract the relevant
99 information from the NIR data. The objective of the present study was to investigate if NIR
100 spectroscopy could be used to determine the salt content in fish water phase in marinated herring
101 fillets by obtained spectra of marinade. Multivariate data analysis and prediction modelling between
102 NIR spectroscopy and salt concentration in marinade and in fish were used in order to study the
103 relation between the NIR measurements and the actual salt concentration.

104 ## 2. Materials and methods

105 *2.1 Experimental data*

106 The effect of the increasing salt concentration in the spectra was studied by obtaining NIR spectra
107 of 0, 13, 16 and 26 g/100 g NaCl. The main experiment intends to mimic the industrial marinating
108 process of herring fillets, and consists on brining followed by marinating. The brining was
109 performed using different concentrations and times (Figure 1), while the marinating was carried out
110 in a solution of 6.7 g/100 g of acetic acid and 5 g/100 g salt during 35 days at 2°C. A different
111 container was used for each of the stages and each of the batches.
112 An overview of the experiments is shown in Figure 1.
113
114 At each sampling time herring fillets were drained for 1-2 min using a sieve and two individual
115 brine samples (app. 15-25 ml brine/marinade) and three fillets were taken from each bucket. Upon
116 analysis, the brine was centrifuged at 3800 g for 20 min at 5°C to remove tissue part and insoluble
117 matter and brine and fish samples were kept at -40°C until analyses were carried out. Herring fillets
118 were rinsed under running water in order to avoid excess salt crystals on the flesh surface before
119 chemical analyses were carried out. The sampling times were 0.5,1, 2, 3, 4, 5, 6, 24, 48, 72, 216,
120 432, 648 and 840 h giving 28 brine samples and 42 fillets representing each batch.

121

122 *2.2 salt and moisture content*

123 The salt content of brine, marinade and fish (flesh and skin was minced) was determined by titration
124 with $AgNO_3$ (Titrator, 785 DMP Titrino with a magnetic stirrer, Metrohm) in accordance to AOAC
125 methods (AOAC 976.18 in combination with 937.07) (AOAC, 2000a, 2000b). The dry matter
126 content of fish samples was determined after heating the sample at 105°C for 48 h where a stable
127 sample weight was achieved. The salt and dry matter content were measured on different samples
128 from the same fillet.

129

130 *2.3 Near-infrared spectroscopy*

131 NIR spectra of brine/marinade were measured with a Fourier transform spectrometer (QFA-flex, Q-
132 interline) using a cuvette with a light path length of 8 mm in transmission mode. Each sample was
133 measured with the average of 128 scans (total duration approximately 40 sec.) over the spectral
134 range of 1000 to 2500 nm (10.000 to 4.000 cm^{-1}) with a spectral resolution of 16 cm^{-1}. All samples
135 were brought to room temperature by placing the brine samples in a water bath at 21°C for 30 min
136 and in room temperature for 30 min before measuring and then the samples were measured over the
137 course of two days. Air was used as the background for all spectra obtained and measured before
138 the samples were measured each sampling day.

139

140 *2.4 Data processing*

141 Initial multivariate data analysis was performed by principal component analysis (PCA). The
142 spectra were pre-processed using Standard Normal Variate (SNV) in order to minimise the effect of
143 additive and multiplicative effect to the spectrum baseline (psychical effects due to the sample
144 matrix) as well as noise and highlight modifications due to the chemical composition (Rinnan et al.
145 2009).

Partial Least Squares regression (PLS) models were built, in order to relate the NIR spectra to the concentration of salt in brine/marinade based on the reference measurements from storage experiments. The spectra were pre-processed as described earlier. The pre-processed data as well as the variable to predict were mean centred before fitted with PLS models.

Cross-validation was conducted using Venetian blinds with 10 splits including 4 samples per split ensuring that replicates were kept together. The predictive performance was tested using the root mean squared error of cross validation (RMSECV) and the correlation coefficient (R^2) of the predicted value and the reference value. An average value of the salt content in the fish flesh (n=3) is used in order to correlate the value to the salt concentration in brine/marinade. The RMSECV is given by comparing the predicted value and the reference values as shown in eq. 1.

$$RMSECV = \sqrt{\frac{\sum(y - \hat{y})^2}{n}} \quad (1)$$

Where y and $\hat{y}$ represent the measured reference (salt g/100 g) and the predicted value (salt g/100 g), respectively, and n is the number of samples. The number of Latent variables (LVs) included in the models was evaluated by inspecting the root mean square error of cross-validation (RMSECV), selecting the number of LVs where the curve for RMSECV flattened out or had a minimum. Additionally, in order to find the uncertainty of the prediction error for each PLS components, an additional Monte Carlo cross validation was conducted by randomly dividing the dataset into a calibration and validation set and calculating the RMSEC, RMSECV and RMSEP 100 times.

All models were developed in the PLS Toolbox (Eigenvector Research Inc., Wenatchee, WA) working under MATLAB 2016a v. 8.1.1 (The MathWorks, Natick, MA USA)

3. Results and discussion

3.1 Influence of the increasing salt concentration on NIR spectra

Figure 2 shows the NIR spectra (SNV) of four sodium chloride solutions varying between 0 and 26 g/100 g (w/v), which were used to study whether NIR spectroscopy could detect the salt in different concentrations. The four water absorbance bands were located around 980, 1200, 1450 and 1780 nm (Figure 2). The main peak around 1450 nm is related to O-H first overtone of water (Grassi et al., 2014), and the light is heavily absorbed by water and here considered as noise. Weaker absorption was seen at 980, 1200 and 1780 nm. Dissolving different concentrations of NaCl in water resulted in changes in the wavelengths and intensity of the water bands. For the region 1600-1700 nm increasing salt concentration resulted in a decrease in absorbance intensity and the water bands became narrower and shifted to the shorter wavelength (Figure 2a). Figure 2b shows a linear increase in the water absorbance bands around 1200 nm with the increasing salt concentration. The changes in the water absorbance bands due to sodium chloride are probably related to the weakening or strengthening of the hydrogen bonding network (Lin & Brown, 1992), where chloride is thought to have the greatest effect (Begley et al., 1984).

Since water absorption is lower in the shorter wavelengths (Pedersen, 2002) and the change in salt concentration can be observed as a linear change in the water bands (around 1200 nm), it is believed that the change in salt concentration in the marinade is best observed in the shorter wavelength region. Thus, even though sodium chloride has no specific absorption bands in the NIR region it is possible to detect the change in salt concentration due to salts effect on the water absorbance bands (Huang, 2001), and these results provide a basis for the application to biological matrices.

3.2 Herring marinating study

Figure 3 shows the concentration development of the herring water phase salt (WPS) and the marinade. As it can be seen, there is an abrupt drop in salt concentration of the herring WPS and a

simultaneous and equally abrupt increase in the salt concentration of the marinade. This behavior was observed in all six batches, and can be explained by the higher salt concentration in the herring water phase after brining compared to the initial salt concentration of the marinade. This way, the transport occurs from the herring to the marinade, until the concentration in the water phase of the herring is equal to the salt concentration in the marinade (Birkeland, Sivertsvik, Neilsen, & Skåra, 2005). As a general trend, the salt concentration in the fish water phase was a little higher compared to the concentration of the marinade (Figure 3). The salt concentration ranged from 4.4-9.2 g/100 g for marinade and 6.2-10.7 g/100 g in fish water phase. One batch of fish (E) did not reach equilibrium with the marinade and was discarded from the data set.

Figure 4a shows the herring WPS concentration vs the salt concentration in the marinade for all the time points for which sampling is available. In comparison, Figure 4b shows the same data, but only for the time points between 24 h and 35 days of marinating. A Pearson correlation coefficient was computed to assess the relationship between the salt concentration in marinade and fish for the full marinating time (0.5-35 days) and after 24 h of storage to 35 days, confirming the positive correlation between the two variables with r=0.63 and r=0.90, respectively. This higher correlation coefficient for the samples taken after 24 h was expected, since that is the time point after which the system can be considered in equilibrium, and gives an indication that the concentration in the marinade gives a reasonable concentration of the WPS in the fish, provided that the system is in equilibrium.

3.3 NIR spectroscopy

Figure 5a shows the NIR spectra (SNV) collected from the marinade during the herring marinating process. The spectra were similar to the spectra collected from the salt solutions in the preliminary study with four main water absorbance bands. Light was heavily absorbed at 1450 nm (related to O-

H first over tone) and considered as noise likewise in the preliminary salt study (Figure 2). Figure 5b shows in detail the spectral region 1150-1300 nm where the increase in salt concentration is well highlighted with the increase in intensity (absorbance). A sharp decent is seen in the region 1550-1650 nm, where the intensity decreased with increasing salt concentration (Figure 5a) similarly to the preliminary salt study (Figure 2). The correlation coefficients were calculated for each wavelength of the NIR spectra (SNV) against the chemical determined salt values of the marinade in order to find the region in the spectra that had the highest correlation (Figure 5c). The region at approximately 1100-1300 nm gave the highest positive correlation with the measured salt values and the region around 1500-1800 nm gave the highest negative correlation. The average NIR spectra (SNV) were colored according to the correlation coefficients (Figure 5d) in order to visualize the wavelengths containing most information about the salt concentration changes and that could be favorable to include in the calibration model. The spectral region 1170-1290 nm was selected for further analysis because of the high correlation to the actual salt concentration values hence contributing the most to the predictive performance and the reduced impact of water in this region (Pedersen, 2002).

3.4 Principal component analysis

Prior to regression analysis, an exploratory analysis of the spectral data was performed in order to gain an overview of the data and find possible clusters among the samples collected from the six batches of marinade. PCA was conducted on the selected region 1170-1290 nm because of the high correlation between this region and the actual salt values that was described in sections 3.1 and 3.3. Figure 6a shows the score plot of the first and the second principal components, PC1 and PC2, respectively, with samples classified according to their batch number. As it can be seen, the spectra group reasonably well in function of their batch number. The differences between the six batches have two immediate explanations. The first and most evident one is the different (pre-brining)

contact time and brine concentration used for each batch. This results in the batches brined in 26 g/100 g NaCl achieved a higher salt concentration compared to those brined in 13 g/100 g NaCl. The second one is the salt diffuse to the marinade from those fillets with a higher salt concentration at the beginning of the marinating (Figure 3). Figure 6b describes the evolution of the spectra according to the salt concentration of the marinade. Marinade samples collected from batch 2 and 5 with low salt concentration have negative PC1 values and are grouped together and samples collected from batch 1, 3 and 6 with higher salt concentration have positive PC1 values are also grouped together. Samples collected from batch 6 with the highest concentration of salt, have positive PC1 values and are separated from the others.

3.5 Multivariate regression

Multivariate regression was performed in order to correlate the actual salt content of the marinade and herring to the pre-treated NIR spectra. The PLS models were evaluated in terms of root mean square error of calibration (RMSEC) and cross-validation (RMSECV). The main objective of this study was to investigate the ability of NIR spectroscopy to determine the salt concentration in herring muscle by the obtained spectra of marinade. For that reason initial PLS models were conducted for salt content in marinade in order to investigate how well the salt concentration could be predicted in the herring marinade. Comparing results from the model on the entire spectral range (without 1400-1550 nm due to full absorption of light) and the model including only the selected region, performed equally well (table 1). This confirms that the removed wavelengths do not contribute in explaining the salt content of marinade. Additionally, this reduces the number of spectral variables, hence the model complexity, which ultimately results in a better stability of the calibration model (Ye, Gao, Li, Yuan, & Yue, 2016). For the sake of comparison, the effect of using exclusively samples after 24 h of marinating resulted in an improved model using 2 LV, R^2 was 0.91 and RMSECV was 0.27 g/100 g, which is illustrated in Figure 7a. The same analysis was used

263 to determine the salt content in the herring muscle water phase leading to a 5 factor model, R^2 was
264 0.81 and RMSECV is 0.41g/100 g including samples after 24 h of marinating. As expected the
265 predictability improves including samples after 24 h of marinating compared to the full marinating
266 time (table 1) because of the effect of equilibrium described in section 3.2.

267 The external validation procedure determines the predictive ability based on a sample set, which
268 was not included in the model. In this study, the external validation was conducted using the
269 validation set of 10 samples randomly selected (100 times) from each batch. In Figure 8 the
270 prediction error (RMSEC, RMSECV and RMSEP) is given as a function of the number of PLS
271 components for the model (WPS in fish) based on the selected spectral region (1170-1290 nm). The
272 optimum model rank is 5 for RMSEC, RMSECV and RMSEP, which is also in agreement with the
273 results obtained of the PLS model of WPS illustrated in Figure 7b. The prediction error at 5 LV is
274 given 0.36 g/100 g ± 0.02 g/100 g, 0.40 g/100 g ±0.02 g/100 g and 0.39 g/100 g ±0.06 g/100 g for
275 RMSEC, RMSECV and RMSEP, respectively, and these results indicate that the predictive ability
276 of the model was good as the difference between RMSECV and RMSEP was small.

277 **4. Conclusion**

278 The prediction of the equilibrium concentration of NaCl in the marinade and the herring WPS is
279 presented here to show the potential of NIR spectroscopy for fast and non-destructive determination
280 of salt during the herring marinating process. Sampling of marinade is easily performed compared
281 to sampling of the herring fillets. The preliminary salt study suggested that NIR spectroscopy in the
282 range of 1170-1290 nm carry information related to the changes in salt concentration of sodium
283 chloride solutions. A PCA and inspections of the NIR spectra also confirmed that the spectral
284 region (1180-1290 nm) carried information associated with the change in salt of herring marinade.
285 Calibration models were established for salt in the marinade and the fish muscle water phase

independent on the different brining procedures applied to the six batches. NIR measurements area good alternative to the time-consuming sampling and chemical analysis of herring fillets in order to determine the salt content and have potential to be implemented in the herring marinating industry. Moreover, it opens up for new opportunities for faster measurements of the change in salt during processing and with the benefit of measuring several parameters simultaneously. These results contribute to the optimization of the process control in the herring marinating industry; however, further studies are needed. “Lab models are a good first approach to study the feasibility of NIR for process control, however, building calibration models to be used in large scale industrial food processes should be conducted in the industrial setting. The samples chosen for the calibration should span the variability in both the process (such as storage time, temperature, humidity and raw material variability) and the target constituents (such as variation in salt and acetic acid concentration). Emphasis should be put on correct sampling to ensure that both the NIR measurements and the reference sampling (that is required for making calibration models) are conducted with a good representation of the entire batch”.

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References:

Aidos, I., van der Padt, A. V., Luten, J. B., & Boom, R. M. (2002). Seasonal changes in crude and

lipid composition of herring fillets, byproducts, and respective produced oils. *Journal of Agricultural and Food Chemistry*, *50*(16), 4589–4599. http://doi.org/10.1021/jf0115995

AOAC. (2000a). AOAC Method no. 937.07 “Fish and marine products. Treatment and preparation of sample procedure.” Arlington, VA.: Official Method of Analysis, AOAC.

AOAC. (2000b). AOAC Method no. 976.18 "Salt (Chlorine as Sodium Chloride) in Seafood. Potentiometric Method. Arlington, VA.: Official Method of Analysis, AOAC.

Begley, T. H., Lanza, E., Norris, K. H., & Hruschka, W. R. (1984). Determination of sodium chloride in meat by near-infrared diffuse reflectance spectroscopy. *Journal of Agricultural and Food Chemistry*, *32*(5), 984–987. http://doi.org/10.1021/jf00125a007

Birkeland, S., Sivertsvik, M., Neilsen, H. H., & Skåra, T. (2005). Effects of Brining Conditions on Weight Gain in Herring (Clupea harengus) Fillets. *Journal of Food Science*, *70*(7), 418–424. http://doi.org/10.1111/j.1365-2621.2005.tb11470.x

Galvis-Sanchez, A. C., Tóth, I. V., Portela, A., Delgadillo, I., & Rangel, A. O. S. S. (2011). Monitoring sodium chloride during cod fish desalting process by flow injection spectrometry and infrared spectroscopy. *Food Control*, *22*(2), 277–282. http://doi.org/10.1016/j.foodcont.2010.07.022

Grassi, S., Amigo, J. M., Lyndgaard, C. B., Foschino, R., & Casiraghi, E. (2014). Beer fermentation: Monitoring of process parameters by FT-NIR and multivariate data analysis. *Food Chemistry*, *155*, 279–286. http://doi.org/10.1016/j.foodchem.2014.01.060

Hirschfeld, T. (1985). Salinity Determination Using NIRA. *Applied Spectroscopy*, *39*(4), 740–741. http://doi.org/10.1366/0003702854250293

Huang, Y. (2001). Detection of sodium chloride in cured salmon roe by SW-NIR spectroscopy. *Journal of Agricultural and Food Chemistry*, *49*(9). http://doi.org/10.1021/jf001177f

Karl, H., Roepstorff, A., Huss, H. H., & Bloemsma, B. (1995). Survival of Anisakis larvae in marinated herring fillets. *International Journal of Food Science & Technology*, *29*(6), 661–670. http://doi.org/10.1111/j.1365-2621.1994.tb02107.x

Kojić, D., Tsenkova, R., Tomobe, K., Yasuoka, K., & Yasui, M. (2014). Water Confined in the Local Field of Ions. *ChemPhysChem*, *15*(18), 4077–4086. http://doi.org/10.1002/cphc.201402381

Lane, H. A., Westgate, A. J., & Koopman, H. N. (2011). Ontogenetic and temporal variability in the fat content and fatty acid composition of Atlantic herring (Clupea harengus) from the Bay of Fundy, Canada. *FISHERY BULLETIN*, *109*(1), 113–122.

Lin, J., & Brown, C. W. (1992). Near-IR Spectroscopic Determination of NaCl in Aqueous Solution. *Applied Spectroscopy*, *46*(12), 1809–1815. http://doi.org/10.1366/0003702924123539

Lin, J., & Brown, C. W. (1993). Near-IR spectroscopic measurement of seawater salinity. *Environmental Science & Technology*, *27*(8), 1611–1615. http://doi.org/10.1021/es00045a017

Lin, M., Cavinato, A. G., Huang, Y., & Rasco, B. a. (2003). Predicting sodium chloride content in commercial king (Oncorhynchus tshawytscha) and chum (O. keta) hot smoked salmon fillet portions by short-wavelength near-infrared (SW-NIR) spectroscopy. *Food Research International*, *36*(8), 761–766. http://doi.org/10.1016/S0963-9969(03)00070-X

Nielsen, D., Hyldig, G., Nielsen, J., & Nielsen, H. H. (2005). Lipid content in herring (Clupea harengus L.)—influence of biological factors and comparison of different methods of analyses:

solvent extraction, Fatmeter, NIR and NMR. *LWT - Food Science and Technology*, *38*(5), 537–548. http://doi.org/10.1016/j.lwt.2004.07.010

Pedersen, D. K. (2002, June 14). *Spectroscopic and chemometric exploration of food quality: Early prediction of meat quality*.

Rinnan, Å., Berg, F. van den, & Engelsen, S. B. (2009). Review of the most common pre-processing techniques for near-infrared spectra. *TrAC Trends in Analytical Chemistry*, *28*(10), 1201–1222. http://doi.org/10.1016/j.trac.2009.07.007

Rodger, G., Hastings, R., Cryne, C., & Bailey, J. (1984). Diffusion Properties of Salt and Acetic Acid into Herring and Their Subsequent Effect on the Muscle Tissue. *Journal of Food Science*, *49*(3), 714–720. http://doi.org/10.1111/j.1365-2621.1984.tb13194.x

Svensson, V. T., Nielsen, H. H., & Bro, R. (2004). Determination of the protein content in brine from salted herring using near-infrared spectroscopy. *LWT - Food Science and Technology*, *37*(7), 803–809. http://doi.org/10.1016/j.lwt.2004.03.004

Ye, M., Gao, Z., Li, Z., Yuan, Y., & Yue, T. (2016). Rapid detection of volatile compounds in apple wines using FT-NIR spectroscopy. *Food Chemistry*, *190*, 701–708. http://doi.org/10.1016/j.foodchem.2015.05.112

Figure captions:

Figure 1: The experimental set-up for the herring marinating experiment.

Figure 2: NIR spectra (SNV) of salt solutions of 0, 13, 16 and 26 g/100 g NaCl for the region 900-1900 nm (a) and a zoom of the region 1150 to 1300 nm (b).

Figure 3: Change in salt concentration of the brine and the fish water phase (WPS). Filled circles represents the salt concentration in the fish (water phase), and the empty circles represents the salt concentration of marinade during storage for one representative experimental batch.

Figure 4: Salt concentration in the marinade and the fish (WPS). Salt concentration of the marinade vs. the water phase salt (WPS) in the fish during the full storage time, 0.5-35 days, r=0.63, n=156 (a), and from 24 h to 35 days, r=0.90, n=84 (b), (-line) the target line for concentration equilibrium between the marinade and the fish muscle.

Figure 5: NIR spectra (SNV) collected from the marinade in the region 900-1850 nm (a), and detail of the region 1150-1300 nm (b) both colored according to salt concentration (g/100 g). Correlation coefficients of the NIR spectra (SNV) and the measured salt concentration (g/100 g) (c) and the average NIR spectra (SNV) colored according to the calculated correlation coefficients (d).

Figure 6: Principal component analysis (PCA) of the NIR spectra collected. Score plot of PC2 vs. PC1 colored according to batch number (a) and PC2 vs. PC1 colored according to the measured salt concentration in the marinade (b) for the selected region 1170-1290 nm.

Figure 7: Predicted vs. measured salt concentration in marinade (g/100g) (a) predicted vs. measured salt in fish water phase (g/100g) (b) from PLS models of the NIR spectra of 1170-1290 nm using the samples taken after 24 h of marinating, (-line) best fit through data, red line.

Figure 8: Predictions errors RMSEC (g/100 g), RMSECV (g/100 g) and RMSEP (g/100 g) vs. the model complexity from external validation of WPS model. Average error (-) and the standard deviation (- - -) from 100 repetitions, LV: latent variables.

Table 1: Statistics of calibration models of salt concentration in marinade and fish samples.

Table 1: Statistics of calibration models of salt concentration in marinade and fish samples.

Parameter	Spectral region (nm)	Calibration				
		n	*RMSEC (g/100g)*	*RMSECV (g/100g)*	R^2 *(CV)*	*LV*
Marinade	900-1400;1550-1850	156[a]	0.29	0.30	0.88	4
Marinade	1170-1290	156[a]	0.29	0.30	0.88	4
Marinade	1170-1290	84[b]	0.26	0.27	0.91	2
WPS	1170-1290	156[a]	0.60	0.62	0.64	5
WPS	1170-1290	84[b]	0.35	0.41	0.81	5

WPS: fish water phase salt (g/100g), *RMSEC*: root mean square error of calibration, *RMSECV*: root mean square error of cross validation, R^2: determination coefficient for calibration set, a: all samples included (0.5 h to 35 days), b: samples after equilibrium included (1-35 days).

Raw Material

Herring fillets

Brining

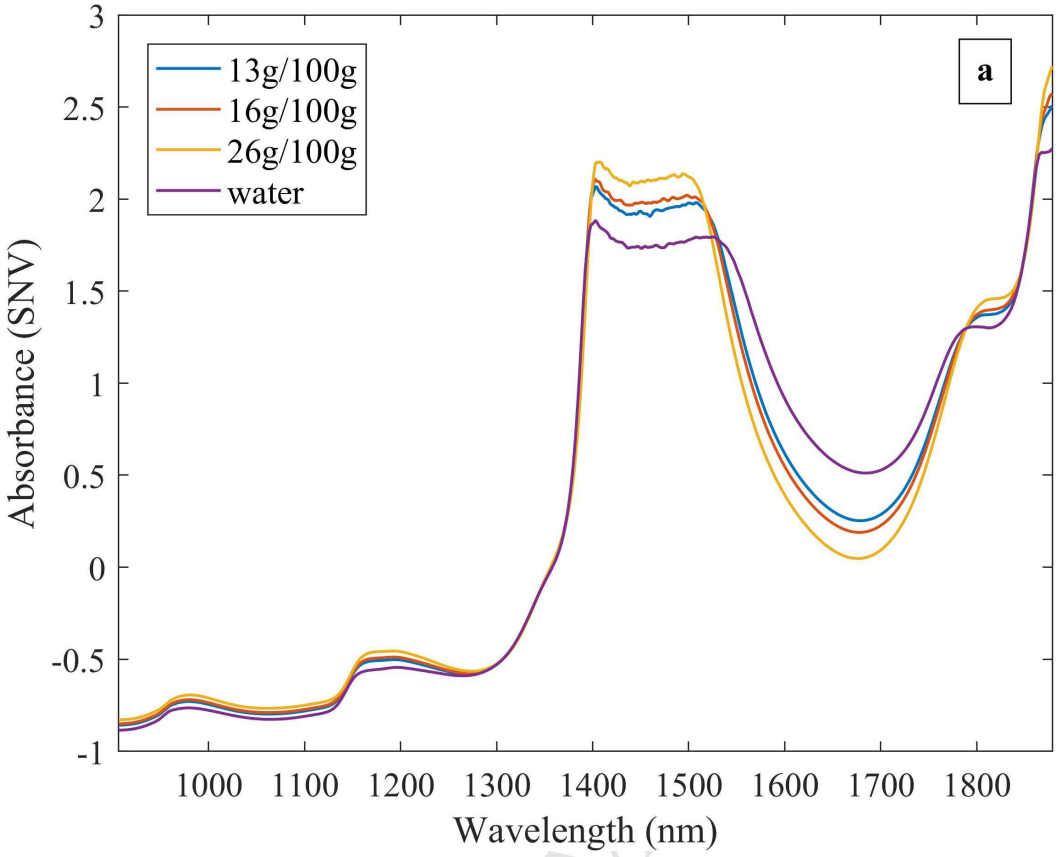
NaCl (g/100 g)	time	Batch#
13	15 h	5
13	4 days	2
16	15 h	1
16	4 days	3
26	15 h	6
26	4 days	4

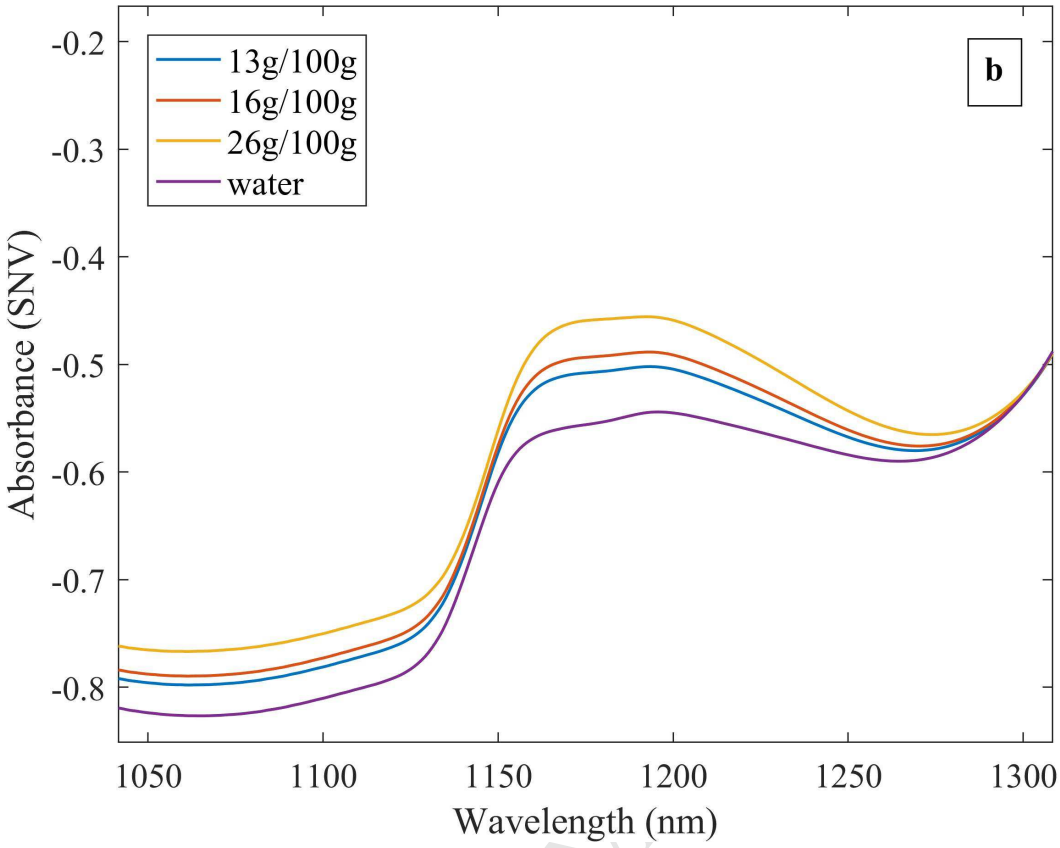
Marinating

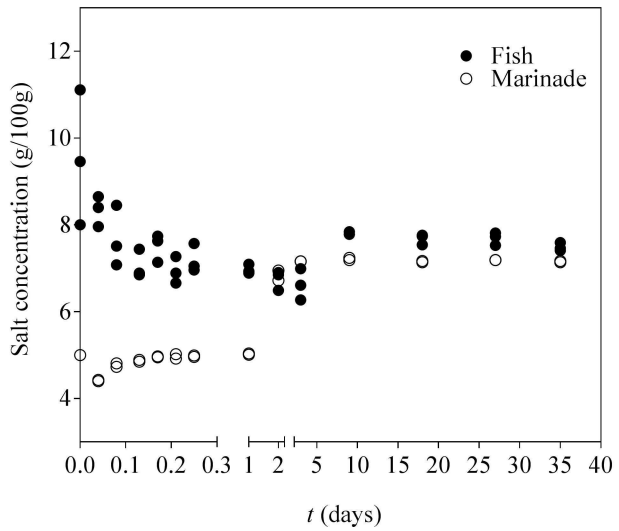
6.7 g/100 g Acetic acid

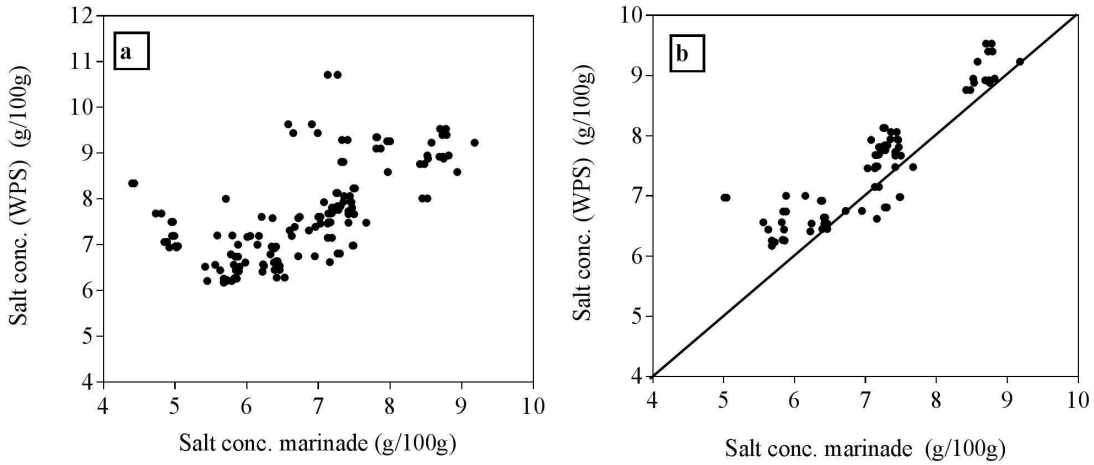
5 g/100 g NaCl

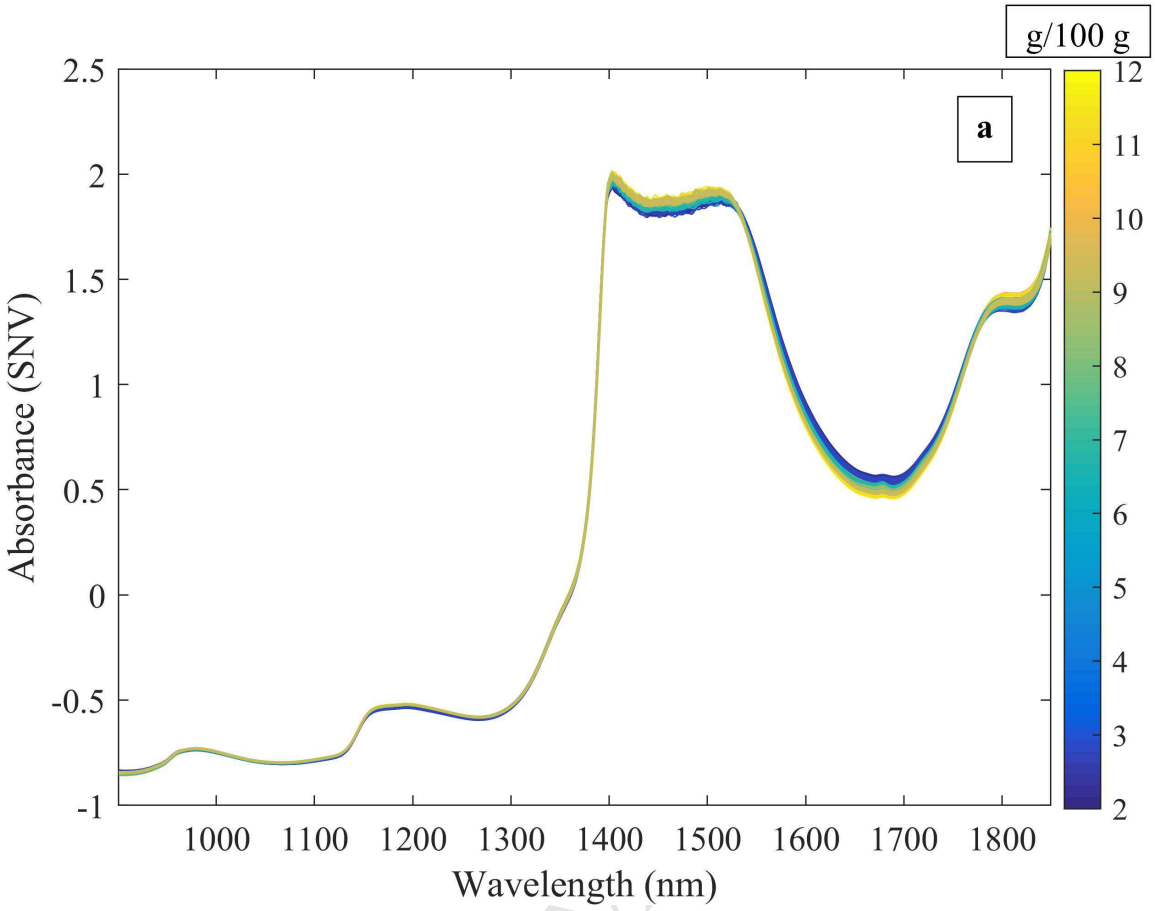
[0.5, 1, 2, 4, 6, 24, 48, 72, 216, 432, 648, 840] h

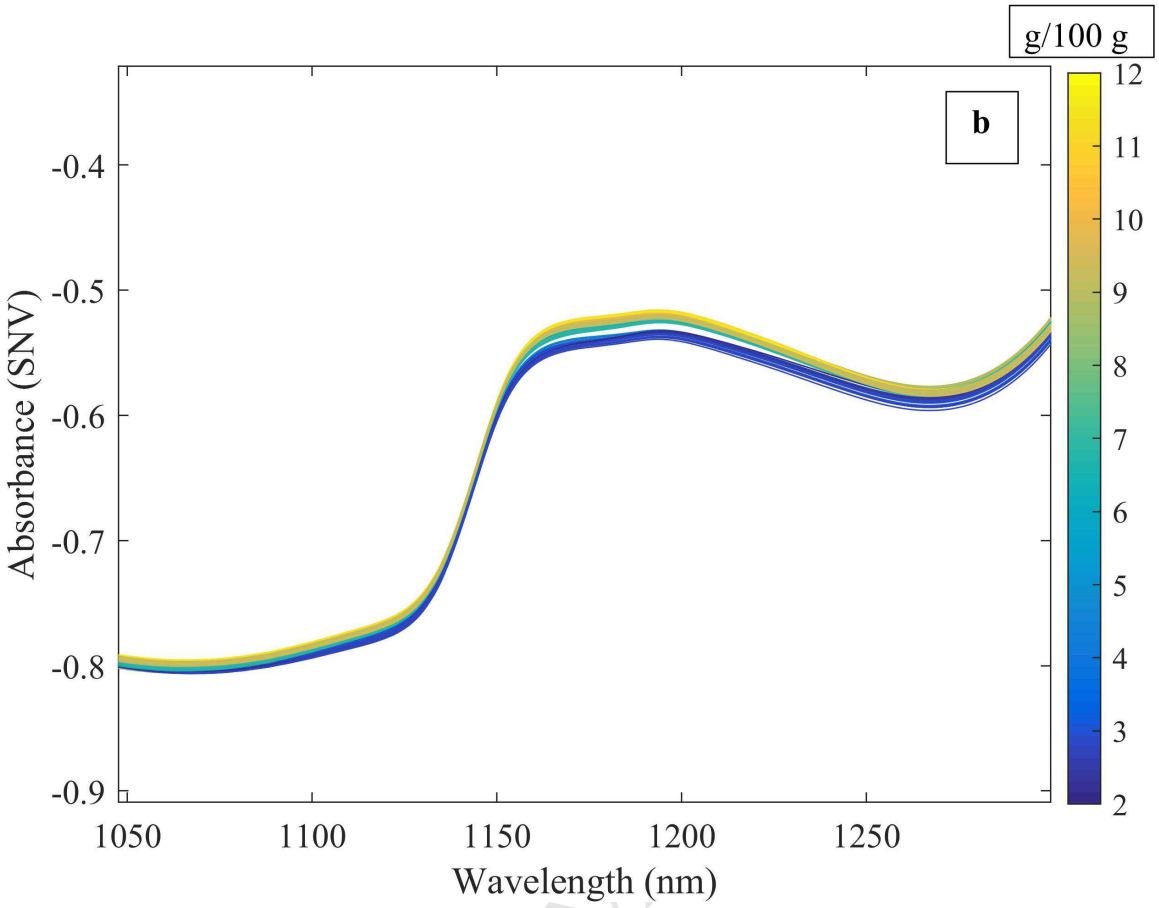


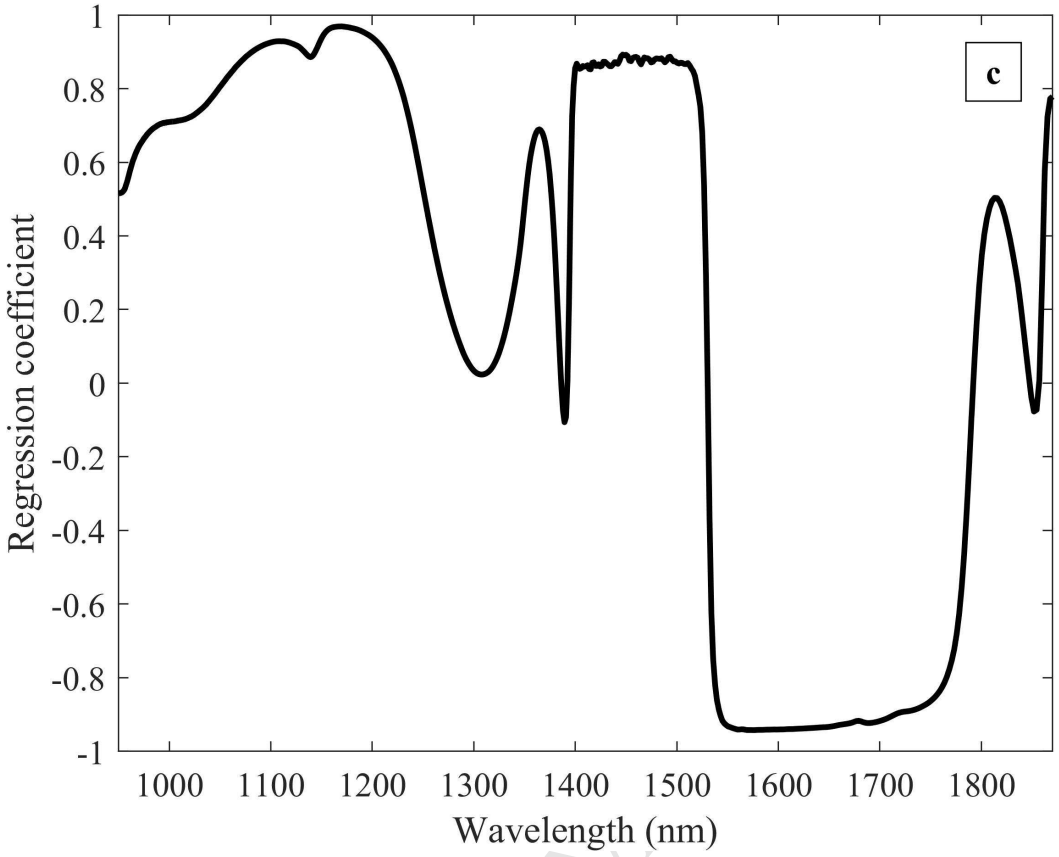


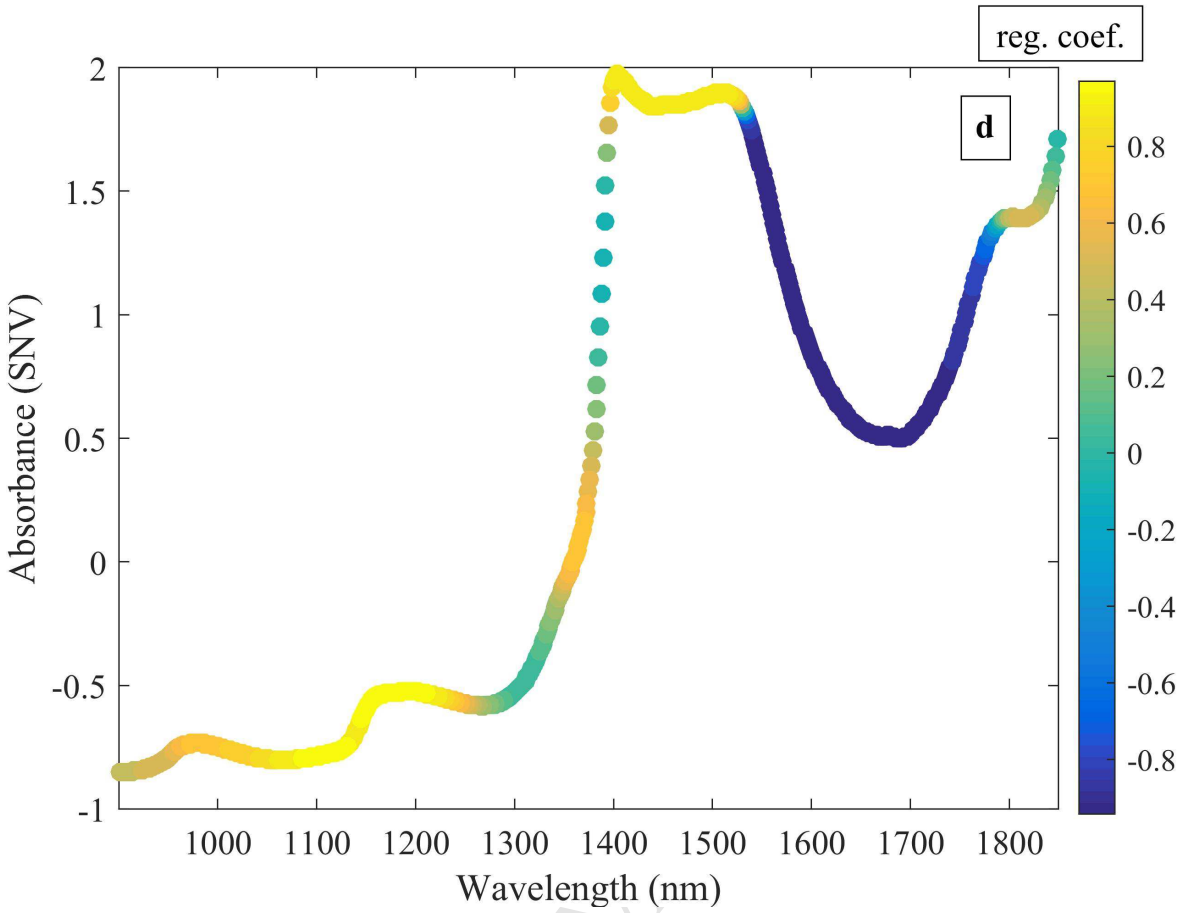


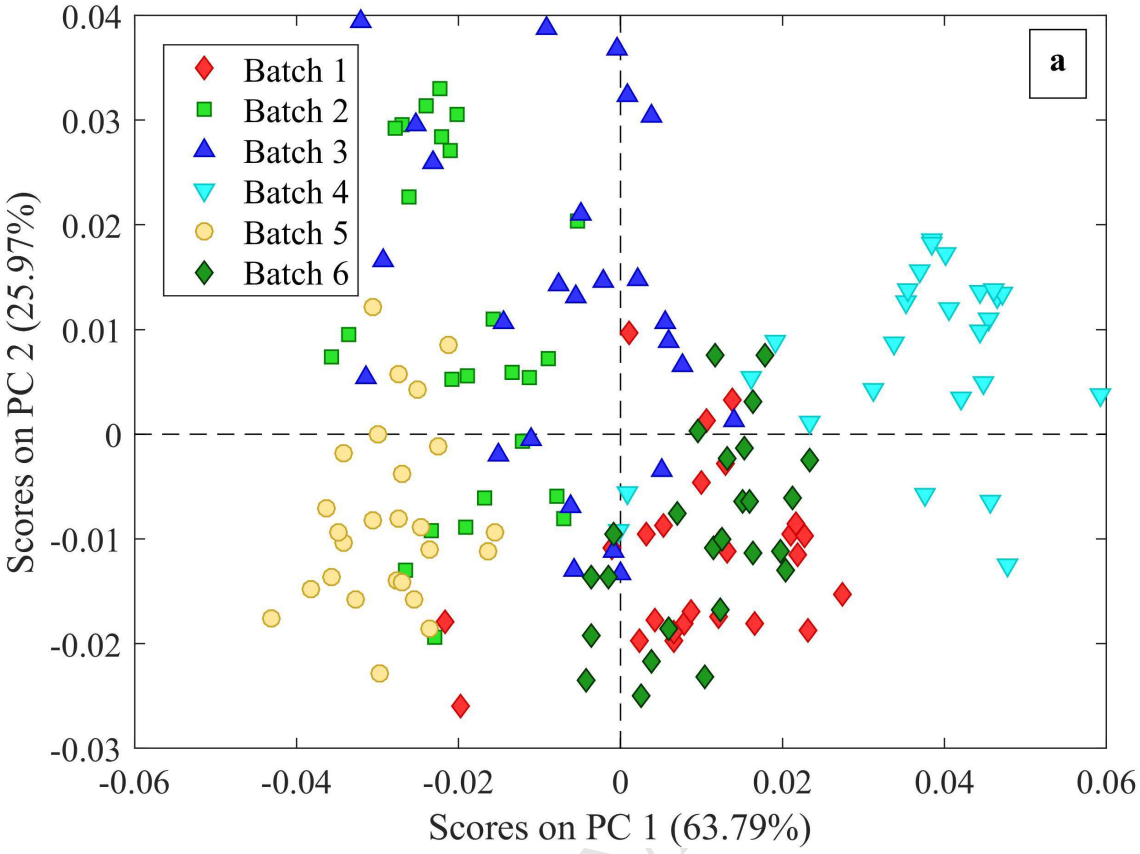


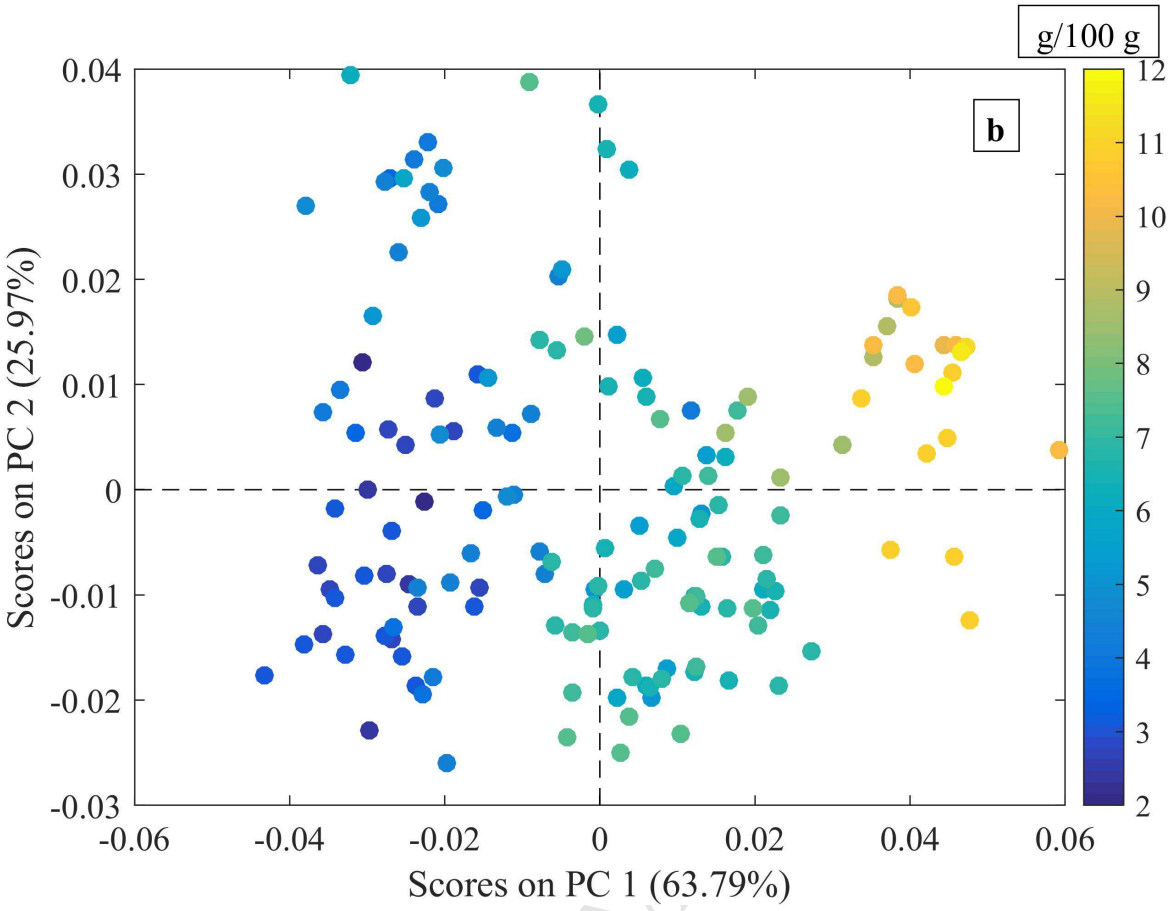


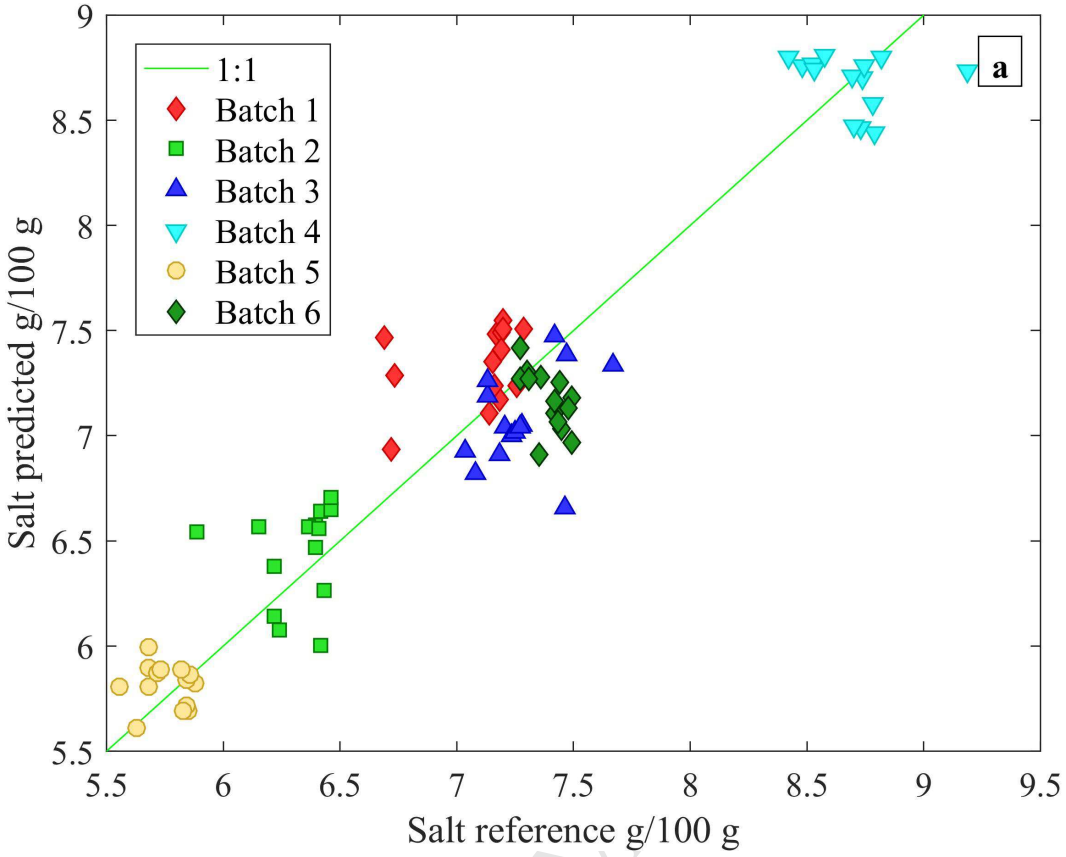


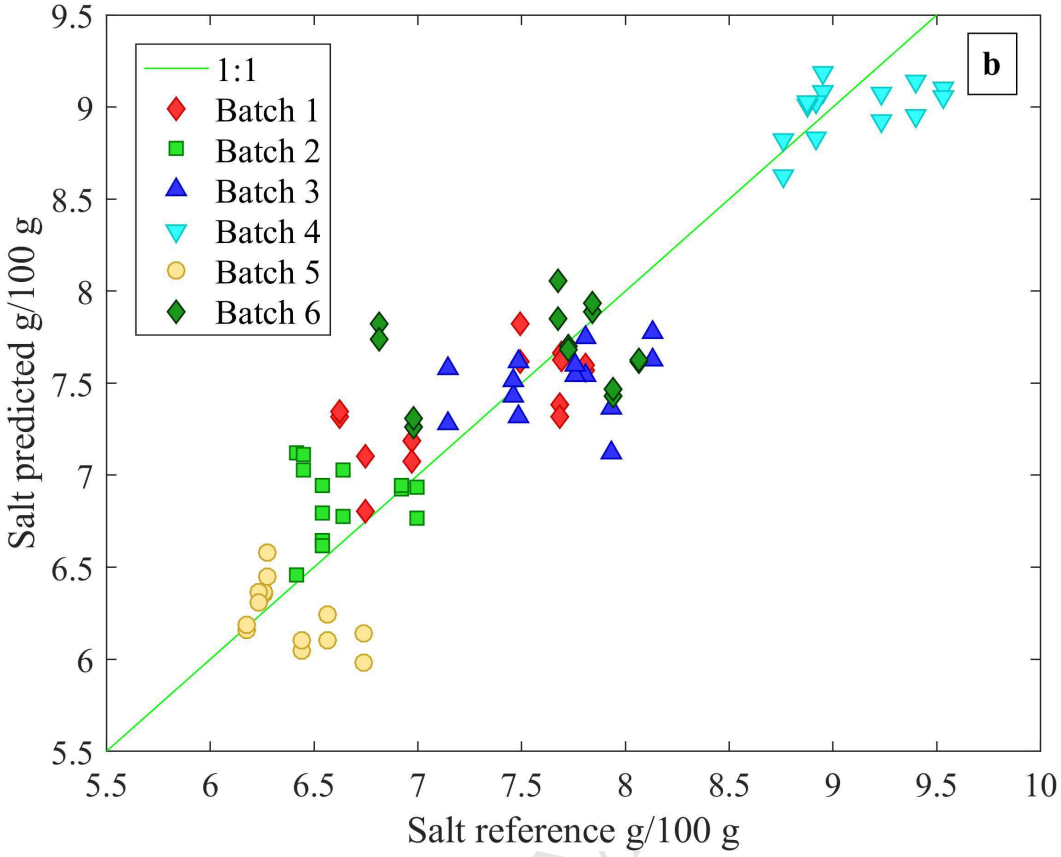


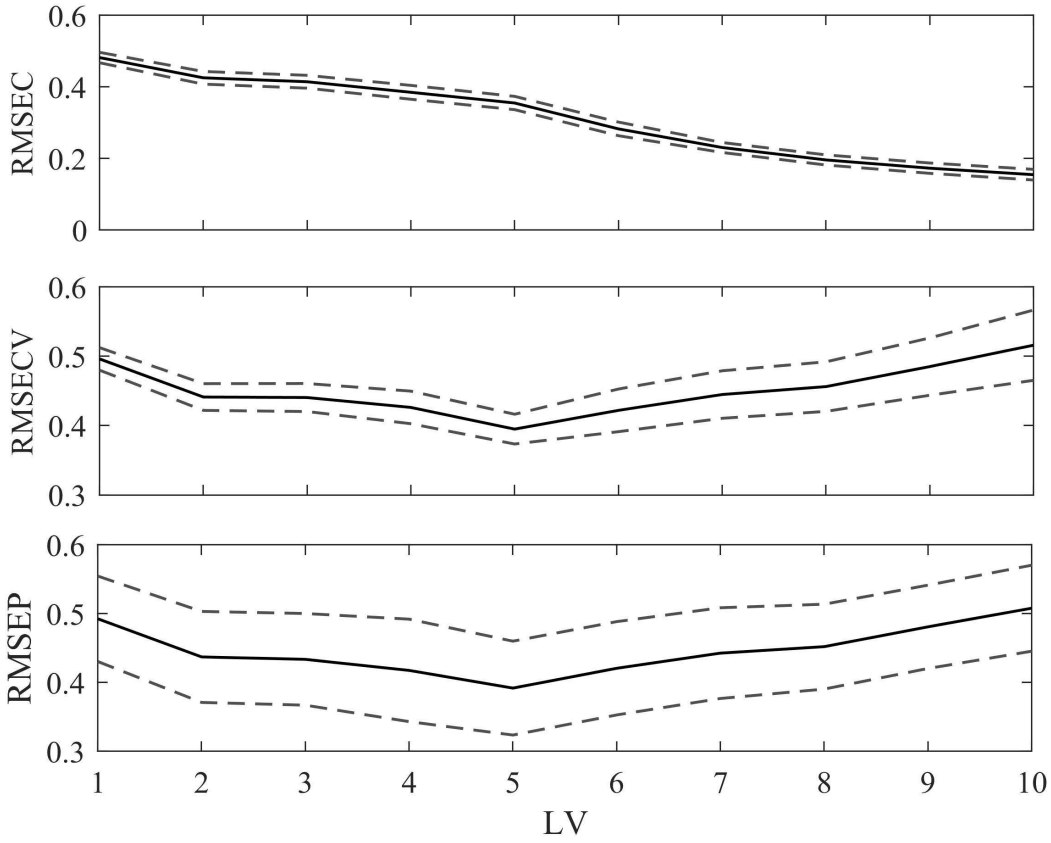












Highlights

- NIR region 1170-1290 nm carried information in relation to salt changes
- PCA described the evolution of the spectra according to the salt concentration of the marinade
- Calibration models were established for salt in marinade and fish independent on processing
- NIR can be used as a fast and non-destructive method for assessing the salt conc. in marinated herring