

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

Laub-Ekgreen, Maria Helbo; Martinez Lopez, Brais; Jessen, Flemming; Skov, Thomas

Published in: Lebensmittel - Wissenschaft und Technologie

Link to article, DOI: 10.1016/j.lwt.2018.07.024

*Publication date:* 2018

Document Version Peer reviewed version

Link back to DTU Orbit

Citation (APA):

Laub-Ekgreen, M. H., Martinez Lopez, B., Jessen, F., & Skov, T. (2018). Non-destructive measurement of salt using NIR spectroscopy in the herring marinating process. *Lebensmittel - Wissenschaft und Technologie*, *97*, 610-616. https://doi.org/10.1016/j.lwt.2018.07.024

#### **General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.

- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

## Accepted Manuscript

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

Maria Helbo Laub-Ekgreen, Brais Martinez-Lopez, Flemming Jessen, Thomas Skov

PII: S0023-6438(18)30607-8

DOI: 10.1016/j.lwt.2018.07.024

Reference: YFSTL 7267

To appear in: LWT - Food Science and Technology

Received Date: 9 March 2018

Revised Date: 5 May 2018

Accepted Date: 14 July 2018

Please cite this article as: Laub-Ekgreen, M.H., Martinez-Lopez, B., Jessen, F., Skov, T., Nondestructive measurement of salt using NIR spectroscopy in the herring marinating process, *LWT - Food Science and Technology* (2018), doi: 10.1016/j.lwt.2018.07.024.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



- 1 Title: Non-destructive measurement of salt using NIR spectroscopy in the herring marinating
- 2 process
- 3
- 4 Maria Helbo Laub-Ekgreen<sup>a</sup>, Brais Martinez-Lopez<sup>a</sup>, Flemming Jessen<sup>a</sup> & Thomas Skov<sup>b</sup>
- 5 <sup>a</sup>National Food Institute, Technical University of Copenhagen
- 6 Søltofts Plads, Building 227,
- 7 2800-Kgs. Lyngby
- 8 Denmark
- 9
- 10 <sup>b</sup>Department of Food Science, Copenhagen University
- 11 Rolighedsvej 26,
- 12 1958 Frederiksberg
- 13 Denmark
- 14
- 15
- 16
- 17
- 1/
- 18 Corresponding author:
- 19 \*Maria Helbo Laub-Ekgreen (Ph.D. student)
- 20 Mail: <u>mheek@food.dtu.dk</u>
- 21 Phone: +45 45252531
- 22 Division of Industrial Food Research, National Food Institute, Technical University of Denmark
- 23 Søltofts Plads B227, 2800-Kgs. Lyngby
- 24 Denmark
- 25 Declaration of interest: none
- 26

27

#### 28 Abstract

The salt content is one of the most important quality and safety parameters in the manufacturing 29 30 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. 31 32 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 33 marinade and in fish. The spectral region 1100-1300 nm had the highest positive correlation with 34 the measured salt values. A principal component analysis performed on the NIR spectra showed 35 that the first principal component described the evolution of the spectra according to the determined 36 salt values. A partial least-squares regression model between the selected region of the NIR spectra 37 38 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 39 equilibrium. The results indicate that NIR spectroscopy can be used as a fast and non-destructive 40 method for assessing the salt concentration in fish during the herring marinating process in order to 41 ensure product safety. 42

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

#### 44 **1. Introduction**

45 Marinated herring products are traditionally consumed in Northern European countries and 46 manufactured by a process using a solution of sodium chloride and acetic acid in order to increase 47 the ionic strength and decrease pH and hereby preserving the fish making it available for 48 consumption most of the year (Rodger, Hastings, Cryne, & Bailey, 1984). This process is based on 49 passed down experience and years of traditions and often consists of an intermediate salt brining

50 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 51 52 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 53 presence and viability of the Anisakis larvae. A study showed that the mortality of the Anisakis 54 55 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 56 57 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. 58

59

Quality control is typically conducted at the end of the herring marinating process, where samples 60 of fish are collected for analysis and visual evaluation. A common method for salt analysis involves 61 an aqueous extraction of salt from the sample and titration with standardized silver nitrate (AOAC 62 976.18). This method is accurate, but also destructive and time consuming and difficult to run in a 63 production setting. In some productions the final quality control is conducted using near-infrared 64 65 (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 66 variability between herring fillets occurs, especially in the fat content (Aidos, van der Padt, Luten, 67 68 & 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 69 the surrounding brine is very attractive and may be more representative and indeed more accessible 70 71 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 72 73 entire herring marinating process.

74

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).

80 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-81 Sanchez et al., 2011). The method is based on vibrational modes of molecules mainly C-H, O-H, 82 83 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 84 85 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, 86 1993). The bands become narrower and shift to a shorter wavelength with increasing NaCl 87 88 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 89 90 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 91 92 determine other parameters such as protein, sugar and fat content (Begley et al., 1984). Despite 93 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 94 95 peaks around 1450 nm and 1886 nm.

96 The marinade is a heterogeneous medium consisting of fat, protein and water, which all absorbs in
97 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

The effect of the increasing salt concentration in the spectra was studied by obtaining NIR spectra of 0, 13, 16 and 26 g/100 g NaCl. The main experiment intends to mimic the industrial marinating process of herring fillets, and consists on brining followed by marinating. The brining was performed using different concentrations and times (Figure 1), while the marinating was carried out 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 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

At each sampling time herring fillets were drained for 1-2 min using a sieve and two individual brine samples (app. 15-25 ml brine/marinade) and three fillets were taken from each bucket. Upon analysis, the brine was centrifuged at 3800 g for 20 min at 5°C to remove tissue part and insoluble matter and brine and fish samples were kept at -40°C until analyses were carried out. Herring fillets were rinsed under running water in order to avoid excess salt crystals on the flesh surface before chemical analyses were carried out. The sampling times were 0.5,1, 2, 3, 4, 5, 6, 24, 48, 72, 216, 432, 648 and 840 h giving 28 brine samples and 42 fillets representing each batch.

121

#### 122 2.2 salt and moisture content

The salt content of brine, marinade and fish (flesh and skin was minced) was determined by titration with AgNO<sub>3</sub> (Titrator, 785 DMP Titrino with a magnetic stirrer, Metrohm) in accordance to AOAC methods (AOAC 976.18 in combination with 937.07) (AOAC, 2000a, 2000b). The dry matter content of fish samples was determined after heating the sample at 105°C for 48 h where a stable sample weight was achieved. The salt and dry matter content were measured on different samples from the same fillet.

129

130 2.3 Near-infrared spectroscopy

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

- 139
- 140 2.4 Data processing

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

150 Cross-validation was conducted using Venetian blinds with 10 splits including 4 samples per split 151 ensuring that replicates were kept together. The predictive performance was tested using the root 152 mean squared error of cross validation (RMSECV) and the correlation coefficient ( $R^2$ ) of the 153 predicted value and the reference value. An average value of the salt content in the fish flesh (n=3) 154 is used in order to correlate the value to the salt concentration in brine/marinade. The RMSECV is 155 given by comparing the predicted value and the reference values as shown in eq. 1.

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

163

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)

166

#### 167 **3. Results and discussion**

#### 168 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 26 169 g/100 g (w/v), which were used to study whether NIR spectroscopy could detect the salt in different 170 concentrations. The four water absorbance bands were located around 980, 1200, 1450 and 1780 171 nm (Figure 2). The main peak around 1450 nm is related to O-H first overtone of water (Grassi et 172 al., 2014), and the light is heavily absorbed by water and here considered as noise. Weaker 173 174 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 1600-175 1700 nm increasing salt concentration resulted in a decrease in absorbance intensity and the water 176 bands became narrower and shifted to the shorter wavelength (Figure 2a). Figure 2b shows a linear 177 increase in the water absorbance bands around 1200 nm with the increasing salt concentration. The 178 179 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 180 181 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.

#### 188 *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

191 simultaneous and equally abrupt increase in the salt concentration of the marinade. This behavior 192 was observed in all six batches, and can be explained by the higher salt concentration in the herring 193 water phase after brining compared to the initial salt concentration of the marinade. This way, the 194 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, 195 196 2005). As a general trend, the salt concentration in the fish water phase was a little higher compared 197 to the concentration of the marinade (Figure 3). The salt concentration ranged from 4.4-9.2 g/100 g 198 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. 199

Figure 4a shows the herring WPS concentration vs the salt concentration in the marinade for all the 200 time points for which sampling is available. In comparison, Figure 4b shows the same data, but only 201 202 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 203 marinating time (0.5-35 days) and after 24 h of storage to 35 days, confirming the positive 204 correlation between the two variables with r=0.63 and r=0.90, respectively. This higher correlation 205 coefficient for the samples taken after 24 h was expected, since that is the time point after which the 206 system can be considered in equilibrium, and gives an indication that the concentration in the 207 marinade gives a reasonable concentration of the WPS in the fish, provided that the system is in 208 equilibrium. 209

- 210
- 211 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-

215 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 216 217 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 218 the preliminary salt study (Figure 2). The correlation coefficients were calculated for each 219 wavelength of the NIR spectra (SNV) against the chemical determined salt values of the marinade 220 221 in order to find the region in the spectra that had the highest correlation (Figure 5c). The region at 222 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 223 spectra (SNV) were colored according to the correlation coefficients (Figure 5d) in order to 224 225 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 226 selected for further analysis because of the high correlation to the actual salt concentration values 227 hence contributing the most to the predictive performance and the reduced impact of water in this 228 region (Pedersen, 2002). 229

230 *3.4 Principal component analysis* 

Prior to regression analysis, an exploratory analysis of the spectral data was performed in order to 231 gain an overview of the data and find possible clusters among the samples collected from the six 232 batches of marinade. PCA was conducted on the selected region 1170-1290 nm because of the high 233 234 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, 235 respectively, with samples classified according to their batch number. As it can be seen, the spectra 236 group reasonably well in function of their batch number. The differences between the six batches 237 have two immediate explanations. The first and most evident one is the different (pre-brining) 238

239 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. 240 241 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 242 according to the salt concentration of the marinade. Marinade samples collected from batch 2 and 5 243 with low salt concentration have negative PC1 values and are grouped together and samples 244 collected from batch 1, 3 and 6 with higher salt concentration have positive PC1 values are also 245 246 grouped together. Samples collected from batch 6 with the highest concentration of salt, have positive PC1 values and are separated from the others. 247

#### 248 3.5 Multivariate regression

249 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 250 251 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 252 herring muscle by the obtained spectra of marinade. For that reason initial PLS models were 253 254 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 255 (without 1400-1550 nm due to full absorption of light) and the model including only the selected 256 region, performed equally well (table 1). This confirms that the removed wavelengths do not 257 contribute in explaining the salt content of marinade. Additionally, this reduces the number of 258 spectral variables, hence the model complexity, which ultimately results in a better stability of the 259 260 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<sup>2</sup> was 261 0.91 and RMSECV was 0.27 g/100 g, which is illustrated in Figure 7a. The same analysis was used 262

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

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

#### **4.** Conclusion

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

286 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 287 determine the salt content and have potential to be implemented in the herring marinating industry. 288 Moreover, it opens up for new opportunities for faster measurements of the change in salt during 289 processing and with the benefit of measuring several parameters simultaneously. These results 290 291 contribute to the optimization of the process control in the herring marinating industry; however, 292 further studies are needed. "Lab models are a good first approach to study the feasibility of NIR for 293 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 294 295 should span the variability in both the process (such as storage time, temperature, humidity and raw 296 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 297 measurements and the reference sampling (that is required for making calibration models) are 298 conducted with a good representation of the entire batch". 299

300

#### 301 Acknowledgements

302 Skagerak Pelagic a/s, Denmark that provided the raw material is acknowledged for pleasant and
 303 professional cooperation. The authors are grateful for the assistance with lab work from Sara Aaslet
 304 and Yuka Omura Lund. This work was supported by *Green Development and Demonstration* 305 *Program, GUDP, Ministry of Food, Agriculture and Fisheries, Denmark*

306 **References:** 

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

308	lipid composition of herring fillets, byproducts, and respective produced oils. Journal of
309	Agricultural and Food Chemistry, 50(16), 4589–4599. http://doi.org/10.1021/jf0115995
310	AOAC. (2000a). AOAC Method no. 937.07 "Fish and marine products. Treatment and preparation
311	of sample procedure." Arlington, VA.: Official Method of Analysis, AOAC.
312	AOAC. (2000b). AOAC Method no. 976.18 "Salt (Chlorine as Sodium Chloride) in Seafood.
313	Potentiometric Method. Arlington, VA.: Official Method of Analysis, AOAC.
314	Begley, T. H., Lanza, E., Norris, K. H., & Hruschka, W. R. (1984). Determination of sodium
315	chloride in meat by near-infrared diffuse reflectance spectroscopy. Journal of Agricultural and
316	Food Chemistry, 32(5), 984–987. http://doi.org/10.1021/jf00125a007
317	Birkeland, S., Sivertsvik, M., Neilsen, H. H., & Skåra, T. (2005). Effects of Brining Conditions on
318	Weight Gain in Herring (Clupea harengus) Fillets. Journal of Food Science, 70(7), 418-424.
319	http://doi.org/10.1111/j.1365-2621.2005.tb11470.x
320	Galvis-Sanchez, A. C., Tóth, I. V., Portela, A., Delgadillo, I., & Rangel, A. O. S. S. (2011).
321	Monitoring sodium chloride during cod fish desalting process by flow injection spectrometry
322	and infrared spectroscopy. Food Control, 22(2), 277-282.
323	http://doi.org/10.1016/j.foodcont.2010.07.022
324	Grassi, S., Amigo, J. M., Lyndgaard, C. B., Foschino, R., & Casiraghi, E. (2014). Beer
325	fermentation: Monitoring of process parameters by FT-NIR and multivariate data analysis.
326	Food Chemistry, 155, 279–286. http://doi.org/10.1016/j.foodchem.2014.01.060
327	Hirschfeld, T. (1985). Salinity Determination Using NIRA. Applied Spectroscopy, 39(4), 740–741.
328	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
- 331 Karl, H., Roepstorff, A., Huss, H. H., & Bloemsma, B. (1995). Survival of Anisakis larvae in
- 332 marinated herring fillets. International Journal of Food Science & Technology, 29(6), 661–
- 333 670. http://doi.org/10.1111/j.1365-2621.1994.tb02107.x
- 334 Kojić, D., Tsenkova, R., Tomobe, K., Yasuoka, K., & Yasui, M. (2014). Water Confined in the
- 335 Local Field of Ions. *ChemPhysChem*, *15*(18), 4077–4086.
- 336 http://doi.org/10.1002/cphc.201402381
- 337 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
- 341 Solution. *Applied Spectroscopy*, *46*(12), 1809–1815.
- 342 http://doi.org/10.1366/0003702924123539
- Lin, J., & Brown, C. W. (1993). Near-IR spectroscopic measurement of seawater salinity.
- 344 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
- 346 commercial king (Oncorhynchus tshawytscha) and chum (O. keta) hot smoked salmon fillet
- 347 portions by short-wavelength near-infrared (SW-NIR) spectroscopy. *Food Research*
- 348 *International*, *36*(8), 761–766. http://doi.org/10.1016/S0963-9969(03)00070-X
- 349 Nielsen, D., Hyldig, G., Nielsen, J., & Nielsen, H. H. (2005). Lipid content in herring (Clupea
- 350 harengus L.)—influence of biological factors and comparison of different methods of analyses:

- 351 solvent extraction, Fatmeter, NIR and NMR. *LWT Food Science and Technology*, 38(5),
- 352 537–548. 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-
- 356 processing techniques for near-infrared spectra. *TrAC Trends in Analytical Chemistry*, 28(10),
- 357 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
- 359 Acid into Herring and Their Subsequent Effect on the Muscle Tissue. *Journal of Food Science*,

360 49(3), 714–720. http://doi.org/10.1111/j.1365-2621.1984.tb13194.x

- 361 Svensson, V. T., Nielsen, H. H., & Bro, R. (2004). Determination of the protein content in brine
- 362 from salted herring using near-infrared spectroscopy. *LWT Food Science and Technology*,
- 363 37(7), 803–809. http://doi.org/10.1016/j.lwt.2004.03.004
- 364 Ye, M., Gao, Z., Li, Z., Yuan, Y., & Yue, T. (2016). Rapid detection of volatile compounds in apple
- 365 wines using FT-NIR spectroscopy. *Food Chemistry*, 190, 701–708.
- 366 http://doi.org/10.1016/j.foodchem.2015.05.112
- 367
- 368 Figure captions:
- **Figure 1**: The experimental set-up for the herring marinating experiment.
- 370
- 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
- 375 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.
- 3/9 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.
- 391

387

- 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.

396

397

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

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

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).

CEP CEP

Raw Material	Brining	Marinating
Herring fillets	$\begin{array}{c c} NaCl \\ (g/100 g) \\ \hline 13 \\ 13 \\ 15 h \\ 5 \\ \hline 13 \\ 4 days \\ 2 \\ \hline 16 \\ 15 h \\ 1 \\ \hline 16 \\ 4 days \\ 3 \\ \hline 26 \\ 15 h \\ 6 \\ \hline \end{array}$	<ul> <li>6.7 g/100 g Acetic acid</li> <li>5 g/100 g NaCl</li> <li>[0.5, 1, 2, 4, 6, 24,</li> <li>48, 72, 216, 432,</li> <li>648, 840l h</li> </ul>
	26 4 days 4	



























#### 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

CHR MAN