Determination of histamine levels in fresh fish using Near Infrared (NIR) technology

Vladimir Kitanovski[1,*], and *Sani* Demiri[1]

[1] Department of Food Technology, Faculty of Technological Sciences, University Mother Teresa, 1000 Skopje, North Macedonia

Abstract. Fresh fish and fish products are highly perishable food. Development of fast, secure and non-destructive technique for estimation the presence and quantity of components which are related with safety of food products is of great interest for science but also and for the industry sector. Above-mentioned idea is the aim of this research work, precisely, determination of histamine levels in fresh fish with the use of different near infrared handheld devices. Histamine is one of biogenic amines among putrescine, cadaverine, tyramine which are non-volatile amines produced post mortem and are formed from decarboxylation of specific free amino acids in fish or shellfish tissue. Reason why we choose to developing technique for evaluation of histamine levels is EU Regulation 2073/2005 requires the determination of histamine at three different levels: 100, 200 and 400 mg/kg. For reaching the goal we decided to use paper-based technology for collecting samples for evaluation using Whatman grade 2 qualitative filter papers. In the first phase for validation of NIR devices specifications, and for creation of calibration curve we used histamine solution with 0.5, 1, 2.5 and 5 %. Results showed regression of R2 = 0.69 which indicates that NIR devices can be promising tools for spotting histamine beside small molecular weight.

1 Introduction

Accumulation of histamine in fish products can be considered as a good indicator for spoilage [1], because biogenic amines (BAs) are nitrogenus compounds nitrogenous compounds resulting from the free amino acid decarboxylation or the amination of carbonyl-containing organic compounds through the metabolism of different microorganisms.

Classification of BAs can be based on chemical structure or it can be based on the number of amine groups into monoamines (tyramine and phenylethylamine), diamines (histamine, putrescine, and cadaverine), or polyamines (spermidine and spermine) [2].

Histamine is present in especially large amounts in fish tissues of the *Scombridae, Clupeidae, Coryphaenidae, Engraulidae, Pomatomidae*, and *Scomberesocidae* families [3]. Histamine formation in fish is related to the presence of exogenous histidine decarboxylase released from microflora associated with the specimens or surrounding seawater, the free histidine content of the fish muscle, and certain environmental conditions [4]. Increased histamine contents accompany the loss of freshness and putrefaction in mackerel (2.7 - 245.8 mg/kg), herring (9.1 - 271.4 mg/kg), sardine (19.5 - 203 mg/kg), anchovy (14-2007 mg/kg), and saury (9.1 - 262.8 mg/kg) [5].

At fish species that contains very low histamine levels, production can emerge by the postharvest exposure of fish to high temperatures, which enhance the multiplication of histidine decarboxylase-producing bacteria during fish decomposition at processing plants or even immediately after catching [6]. Histamine poisoning is a type of food poisoning with symptoms and treatment similar to those associated with seafood allergies [7]. The risk of histamine poisoning is increased when fish are kept at temperatures above 4°C [8]. Near-infrared (NIR) spectroscopy has attracted a great deal of attention owing to its rapidity and simple analysis. NIR spectroscopy can be used to identify and quantify most organic molecules from vibrational absorption at specific frequencies [9]. NIR spectroscopy has been used to determine the matrix component and composition in fish such as moisture, fat, and protein contents in tuna fish [10]. Determination of presence and quantity of specific molecules using NIR can be a, very challenging and can be affected by various factors, like for example molecular mass of the components in the matrix. This factor has a big impact on the analyses of histamine because of the very low molecular weight of 111.15 g/mol. Various techniques for determination of histamine levels in fish are developed because of the extraction method of the components from the matrix and defining the molecular path. Aim of this work was to set up base for determination of histamine levels in fish using NIR device as a tool and paper-based method for separation of the matrix.

* Corresponding author: vladimir.kitanovski@unt.edu.mk

2 Materials and methods

Analyses for evaluation of possibilities for determination of histamine levels in fish using NIR spectroscopy were conducted in the laboratories of Biotechnological faculty at Cattolica University in Porto, Portugal. Project design was developed on the basis of paper technology. We used different types of filter paper, Whatman grade 2 and grade 3 qualitative filter paper. Five paper carriers for each replica of each concentration of histamine solution, in total 25 papers of Whatman grade 2 and 25 papers from grade 3. Whatman 2 circles: 42.5 mm to 500 mm; Particle retention 1: 8µm; Nominal thickness: 190 µm; Nominal basis weight: 97 g/m^2; Nominal ash content 2: 0.06%. Whatman grade 3 circles: 23 mm to 320 mm; Particle retention1: 6 µm; Nominal thickness: 390 µm; Nominal basis weight: 185 g/m^2; Nominal ash content 2: 0.06%. Filter papers were infused in the center area with one drop of 2 mL pure histamine standard (Sigma-Aldrich) with five different concentrations starting at 0.5, 1, 2.5, 5 and 10%. Scanning was made with handheld NIR device, which was prototype device and was given from the industry sector on testing period so we can't share performances of the device. Obtained data was analyzed with MATLAB 9.4 version, and pre-treatment of the spectra was made with Standard Normal Variate (SNV).

3 Results and discussion

Very weak peak near 1500 nm related to amino acids is attributed to the N−H stretching and NH_3^+ deformed vibration.

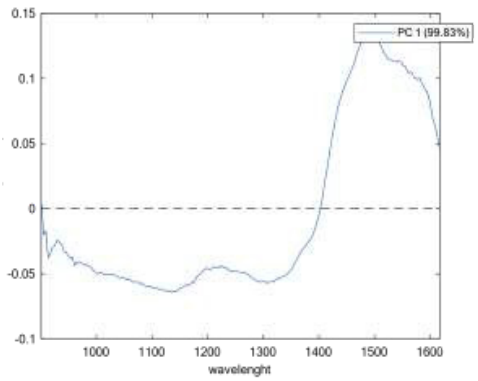

Fig. 1. Original peak of histamine in the range of 1400 - 1600 nm

Regarding quantification of histamine with the use of NIR technology we used linear regression plot, so we can be sure that tested NIR device is capable for detecting histamine levels.

From results we spot only 0.57 multiple linear regression of the responses in vector of histamine concentration for Whatman 2 and 0.641 for Whatman filter papers grade 3. Unfortunately, we can't say that obtained results are in accordance with the results of researchers that were investigating similar technology for non-destructive determination of histamine levels [11, 12, 13].

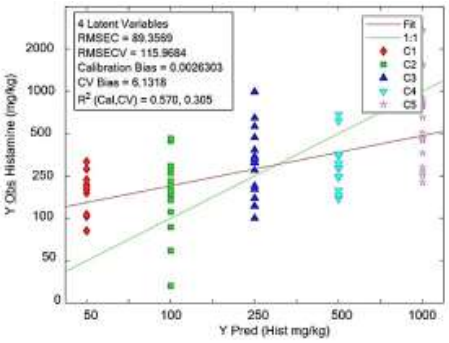

Fig. 2. NIR predicted vs observed histamine levels in the regression model of Whatman 2 samples. Concentrations are: C1 - 0.5 mg/kg; C2 - 1 mg/kg; C3 - 2.5 mg/kg; C4 - 5 mg/kg; C5 - 10 mg/kg

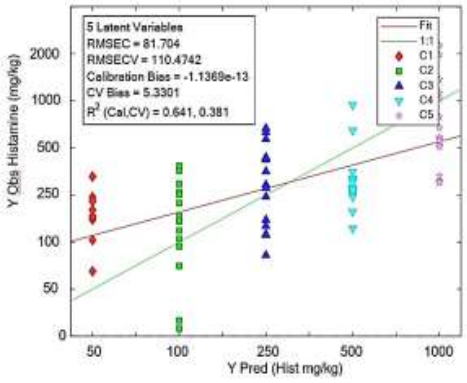

Fig. 3. NIR predicted vs observed histamine levels in the regression model of Whatman 2 samples. Concentrations are: Concentrations are: C1 - 0.5 mg/kg; C2 - 1 mg/kg; C3 - 2.5 mg/kg; C4 - 5 mg/kg; C5 - 10 mg/kg

Our believes are that in our case, this can be due to need for improvements in the design of the carrier system of the histamine.

Complexity of the experimental design and innovative technology for development of non-destructive fast and secure techniques for quality and safety assessment of food products, is limited in the discussion of the obtained results, because of today's situation that every scientist that is working on this field is trying to develop unique model for NIR spectroscopy.

4 Conclusions

Obtained results encouraged us and actually directed us and set the path for future actions. We are now focused on paper carrier design, so the NIR technology can be fully implemented for reaching this article objectives, which are determination of safety and quality characteristics of fish, with the use of non-destructive, fast and secure techniques.

References

1. X. Zhong, D. Huo, H. Fa, X. Luo, Y. Wang, Y., Zhao, C. S. Hou, Actuators B Chem. **274**, 464 (2018)
2. K. B. Biji, C. N. Ravishankar, R. Venkateswarlu, C. O. Mohan, T. K. Srinivasa Gopal, J. Food Sci. Technol. **53**, 2210 (2016)
3. L. Prester, Food Addit. Cont.: Part A. **28**, 1547 (2011)
4. H.-T. Chang, I.-L. Tsai, C.-H. Lin S. Chen, Y.- K. Chuang, LWT - Food Sci. Technol. **145,** 111524 (2021)
5. P. Visciano, M. Schirone, R. Tofalo, G. Suzzi, Front. Microbiol. **3**, 188 (2012)
6. V. Economou, M. M. Brett, C. Papadopoulou, S. Frillingos, T. Nichols, Food Addit. Cont. **24**, 820 (2007)
7. J. M. Hungerford, Scombroid poisoning: A review. Toxicon. **56**, 231 (2010)
8. W. P. Evangelista, T. M. Silva, L. R. Guidi, P. A. S. Tette, R. M. D. Byrro, P.Santisgo-silva, C. Fernandes, M. B. A. Gloria, Food Chem. **211**, 100 (2016)
9. P. Suttahatai, R. Ronnarit, ACS Omega. **4**, 19164 (2019)
10. K. Khodabux, M. S. S. L'Omeletted, S. Jhaumeer-Laulloo, P. Ramasami, P. Rondeau, Food Chem. **102**, 669 (2007)
11. U. Acharya, P. Subedi, K. Walsh. AJAC. **3/8**, 524 (2012)
12. P. Ong, C. Hsin-Tze, T. I-Lin, L. Che-Hsuan, C. Suming, C. Yung-Kun, LWT. **145**, 111524 (2021)
13. S. Pochanagone, R. Rittiron, ACS Omega. **4**, 19164 (2019)