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Application of near-infrared spectroscopy as at line method for the evaluation of histamine in tuna fish (*Thunnus albacares*)

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ABSTRACT

The assessment of histamine levels in fishery products has emerged as a paramount issue in the context of global food safety, given its profound implications for human health and the consequential impact on food quality and trade. Histamine intoxication, stemming from the ingestion of foods containing heightened histamine levels, results from the bacterial decarboxylation of histidine under conditions of improper handling, processing, or storage. This study endeavors to provide a thorough examination of histamine contamination in frozen-thawed tuna (*Thunnus albacares*) samples, employing an integrated approach that combines near-infrared spectroscopy (NIRS) with advanced machine learning techniques. One hundred and one samples were considered, and a systematic fortification process was applied to obtain samples with 4 histamine concentrations (0; 50; 150; 250 mg/kg); the fortification levels were confirmed by the LC-MS/MS analysis. Subsequently, NIRS spectra were collected and chemometric analyses, including modified partial least squares regression (MPLS) and support vector machine (SVM), were employed for quantitative and qualitative evaluation, respectively. Histamine quantification through MPLS utilizing the full spectrum exhibited good predictive performance in cross-validation and in hold-out validation ($R^2_{CV} = 0.88$; $R^2_P = 0.74$, respectively), confirming the potential of NIRS for estimating histamine levels in tuna. SVM classification models, both binary (presence/absence) and multi-class (four levels), demonstrated high accuracy (100% and 93%, respectively). The study highlights the effectiveness of NIRS combined with machine learning for rapid and accurate histamine detection in frozen-thawed tuna, offering a non-destructive, environmentally friendly alternative to traditional methods. This approach holds significant promise for food business operators and regulatory authorities, enhancing product safety, quality control, and decision-making processes related to histamine contamination in the seafood industry.

1. Introduction

Histamine determination in fishery products is a relevant issue with global food safety and security purposes given its effects on human health and its impacts on food quality and trade. In Europe, no substantial variations in reporting histamine intoxication outbreaks were observed in 2021 compared with recent years, despite the increase observed over last ten years. Indeed, in 2021, among the overall 47 outbreaks of histamine intoxication (1.2% of the total foodborne outbreaks), 14 strong-evidence outbreaks were reported for the food category fish and fish products by the causative agent histamine (EFSA & ECDC, 2022). Additionally, from the Rapid Alert System for Food and Feed (RASFF) network 4 out of the overall 33 notifications on foodborne incidents were related to histamine poisoning (European Commission & Directorate-General for Health and Food Safety, 2022). In more detail, histamine was reported in 5.6% of RASFF notifications in 2004–2017 and 2019, mainly in tuna. These notifications (generally information notifications, but also alerts and border rejections) were transmitted mostly by Italy and concerned products from Spain, Morocco, and also from Asia. The basis for the notifications was usually an official control

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on the market, but also food intoxication and a control at the border, after which the consignment was detained (Pigłowski, 2023). Similarly, among the overall seafood recalls that occurred over the 20-year period by the United States Food and Drug Administration, tuna is the second most cited seafood group involved in recalls, and histamine was the fifth most common reason for these seafood recalls (3%) (Blickem et al., 2023).

This intoxication is caused by the consumption of foods with high level of histamine, which in turn, is formed by bacterial decarboxylation of the amino acid histidine present in the food resulting from inappropriate handling, processing or storage conditions (EFSA, 2017; FAO & WHO, 2013; Sheng & Wang, 2021; Visciano et al., 2020). The content of histamine in fish and fish products is variable within individual lots of products, and even within individual fish, and depends on a multifaceted scenario involving: i) the type of fish, in relation to the amount of histidine in the primary/raw product and the activity of the microbial enzyme histidine decarboxylase, which is directly related to the amount of these microorganisms; ii) the way the fish is handled and the relative potential for growth of microorganisms containing this enzyme; (iii) the duration, conditions and temperature of storage of the fish, also in terms of time-temperature abuse of fish (FAO & WHO, 2013). Besides, histamine is heat-stable, meaning that common industrial or domestic process such as canning, cooking and freezing do not reduce its presence. Moreover, it is not correlated with any sensory changes of fish products (Ruiz-Capillas & Herrero, 2019). Therefore, consumers' education may not be an effective means of preventing the consumption of histamine-contaminated fish. Considering all these aspects, the food testing along with good hygienic practices and temperature control throughout the chain (from fish catch to manipulation, storage and commercialization) are the main preventive measures adopted by Food Business Operators (FBOs) to effectively control this hazard. Nevertheless, it is important to acknowledge that the objective of testing is the implementation of all required control measures. FBO must identify failures in the system and take action to prevent the placing of unsafe food on the market or remove implicated products from the market, as well as to enforce the action levels performed by official surveillance programs and inspections for histamine detection (FAO and WHO, 2013). Therefore, various sampling approaches, along with their respective plans and analytical methods, are widely utilized.

In relation to food testing, there are no difficulties in analysing histamine and a number of suitable methods are available (FAO& WHO, 2013). Regulation (EC) 2073/2005 (European Commission, 2005) indicates the EN ISO 19343:2017 (ISO, 2017), that uses high performance liquid chromatography (HPLC) coupled to UV detection, as the official referenced method in Europe for the safety criteria for histamine in fishery products and fish sauces from species associated with a high amount of histidine. Moreover, the AOAC 977.13 fluorometric method established by the Codex Alimentarius is the most used. Other methods include thin-layer chromatography, gas chromatography, enzymatic-linked immunosorbent assay and biosensors (Ghidini et al., 2021). However, histamine testing by these analytical methods is rarely efficient for monitoring Critical Control Points (CCPs) and cannot be used as a tool of process control. This is primarily due to the cost and time-consuming nature of analytical procedures, the need of operators with specialized skills, and the inability to deliver real-time results. The only exception is the use of enzymatic immunosorbent assay (ELISA) and colorimetric enzymatic methods, which can be applied routinely for self-checking monitoring by FBO. However, these methods are not applicable by Competent Authorities and lack legal advice.

In this context, the faster, easier and cheaper near infrared (NIR) spectroscopy has been recently used by Ghidini and Colleagues (2021) to directly quantify istamine content in raw and processed tuna. Also attenuated total reflectance-Fourier transform infrared spectroscopy was suggested as a non-destructive, fast and accurate method for determining the histamine in tuna fish samples (Asghari et al., 2022). Further, the ultraviolet–visible (UV–VIS)-NIR spectroscopy has recently been listed, by Commission Implementing Regulation (EU) 2022/2503 (European Commission, 2022), among the official methods that can be used when the organoleptic examination gives rise to any doubt that previously frozen fish is commercially presented as fresh (Annex VI, Chapter 1, General provision B "Freshness indicators", Commission Implementing Regulation (EU) 2019/627).

The main objective of this study was to rapidly detect samples with potentially hazardous levels of contamination. In detail, the performances of NIR spectroscopy were investigated by simulating the worst-case real scenarios to directly quantify histamine in the muscle tissue in which frozen-thawed tuna samples could be tested. Unsupervised and supervised chemometric techniques were tested in the quantification and classification models, to provide valuable insights into wavelengths associated with this amine and the feasibility of identifying specific safety thresholds suitable for the self-monitoring of raw materials.

2. Materials and methods

2.1. Fish samples and histamine spiking procedure

A frozen fish sample of *Thunnus albacares,* belonging to the *Scombridae* family (one of the six families associated with a high amount of histidine included in Regulation (EC) 2073/2005), was purchased from the market and transported to the Food Safety Laboratory of the Department of Veterinary Medical Sciences, University of Bologna. The sample was defrosted keeping it in a chilling room at 4 °C for 24 h. Firstly, a fillet sample was analyzed by LC-MS/MS method to confirm the absence of histamine. The muscle tissue weighed 5.5 kg and was cut in several portions that were minced using a domestic blender for 1 min. Then, the homogenate was divided into four portions: one portion was used to prepare 12 blank samples of 50 g, while the others 3 portions were divided into 89 samples of 50 g each, fortified at different levels of histamine (namely 30 samples at 50 mg/kg, 30 samples at 150 mg/kg and 29 samples at 250 mg/kg with 0.5 mL of histamine solutions in water at 5000 ppm, 15,000 ppm and 25,000 ppm respectively). In order to both have a homogenous contamination and not modify the physiochemical composition of fish samples, 0.5 mL of histamine solutions were added into each homogenate sample and then they were manually mixed for 2 min, stored in a chilling room at 4 °C for 10 min, and mixed again for a total of three times. A total of 101 samples were prepared and analyzed. Each sample was divided in two aliquots: 10 g for the LC-MS/MS analysis to confirm the fortification level and 40 g for the NIRS analysis. All the samples were stored at −20 °C before the subsequent analysis, aiming to employ NIR spectroscopy in the most challenging conditions associated with frozen-thawed treatment. Additionally, chemical analyses of tuna samples were conducted both before and after the second frozen-thawed treatment to confirm consistent histamine levels (data not showed).

2.2. Reagents and chemicals

Histamine (purity >99.0%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile, methanol, perchloric acid, and formic acid were acquired by Merck (Darmstadt, Germany), ammonium formate was purchased from Sigma-Aldrich (St. Louis, MO, USA), all LC-MS grade. Ultrapure water was freshly produced from a Milli-Q® water purification system (Merck, Darmstadt, Germany). Paper filters and PTFE syringe filters (13 mm 0.2 μm) were purchased from Waters Corp. (Milford, MA, USA). Stock solution (50 mg of standard in 50 mL of an 80:20 methanol: water v/v solution) was prepared and stored at −20 °C.

2.3. LC-MS/MS analysis

The extraction procedure was conducted following the protocols outlined by Chen et al. (2010) and Altieri et al. (2016). Appropriate adjustments were made to adapt the method to LC-MS/MS analysis.

Thus, 1 g of grounded tuna muscle was weighted in a 15 mL polypropylene tube. 3 mL of a perchloric acid 0,1 M solution were added and the sample was homogenised with ultraturrax for 2 min. Thus, the mixture was centrifugated at 8000 rpm for 15 min at 4 °C. The supernatant was filtered with a paper filter and subsequently was further filtered with 0.2 μm filter. Finally, the sample was subjected to a double dilution: a first 1:10 and a second 1:50, with 80:20 acetonitrile: water v/v solution prior the LC-MS/MS analysis.

Detection and quantification of histamine in tuna was performed using ultrahigh-performance liquid chromatography coupled with triple–quadrupole mass spectrometry (UHPLC-MS/MS) technology. The equipment employed consisted of a Waters Acquity UHPLC® binary pump coupled with a Waters Xevo® TQ-S micro triple–quadrupole mass spectrometer (Waters Corporation, Milford, MA, USA) equipped with an electrospray ionization source (ESI). Analyses were performed in positive electrospray ionization (ESI+) mode and MRM (multiple reaction monitoring) mode, following two specific transitions for the target analyte (112.0 > 95.00, 112.0 > 67.95). Capillary voltage was set at 0.50 kV, source temperature at 150 °C, and desolvation temperature at 350 °C finally, desolvation gas flow was 1000 L/h. Argon was used as collision gas. The development of the chromatographic method commenced with conditions similar to those used by Self et al. (2011) employing an analytical HILIC column. Given the polar characteristics of biogenic amines, Hydrophilic Interaction Liquid Chromatography (HILIC) with a silica stationary phase and a high organic/low aqueous mobile phase offered significant advantages (Gianotti et al., 2008). The chromatographic separation was carried out on a Waters Acquity UHPLC® BEH HILIC (50 mm × 2.1 mm, 1.7 μm) column (Waters Corporation, Milford, MA, USA) maintained at 30 °C and the chromatographic conditions were settled as follow: mobile phases were 20 mM ammonium formate in water acidified with 0.1% of formic acid (A) and acetonitrile (B). The gradient started from 0 min with 20% phase A; this percentage increased to 85% in 2 min, it was held for 1 min, then decreased linearly at 20% in 1 min. This condition was held for 1 min for column re-equilibration. Total run time was 5 min, the flow rate was 0.500 mL/min, and the volume injected was 10 μL. Thermostated autosampler was kept at 20 °C. Data were acquired and processed using Waters MassLynx™ 4.1 software (Waters Corporation, Milford, MA, USA).

The quantification of histamine in tuna was carried out through the use of six points matrix-matched calibration curve (50–300 mg/kg). The calibration curve was introduced at the beginning and end of each samples batch. The method was validated according to Regulation EU 2021/808 (European Commission, 2021).

2.4. Near infrared Spectra collection

The spectra of 101 homogenate tuna samples were collected at room temperature after the thawing process in a chilling room at 4 °C for 24 h. Spectra were acquired in reflectance mode across the 400–2500 nm (every 0.5 nm) wavelength range using a NIRS™ DS2500 (FOSS Electric A/S in Hillerød, Denmark) benchtop device and placing samples in the standard circular ring cups, (FOSS sample cups, with diameter of 6 cm). Each spectrum was an average of 32 sub-spectra recorded at eight different points by rotating the sample FOSS cup automatically. Spectra were collected in triplicate through ISIscan Nova and Mosaic software (FOSS Electric A/S, Hillerød, Denmark) and automatically converted in absorbance as log(1/Reflectance). The final representative spectrum considered for chemometric analysis was obtained by averaging the three spectral replicates for each sample.

2.5. Chemometric analysis

Two distinct methods were assessed to determine the optimal approach for the evaluation of histamine contamination in tuna fish using supervised methods. Initially, the prediction of contamination was conducted using the modified partial least squares regression (MPLS) model to estimate the histamine amount (mg/kg). Subsequently, a spatial data exploration and classification model were performed to identify contamination categories (zero, low, mid, and high) through the use of the PCA and support vector machine (SVM), respectively, using R software version 4.2.3 (R Core Team, 2023).

2.5.1. Full-spectrum prediction models and wavelength interval selection

Table 1 reported the number of samples and histamine concentration variability used to develop prediction models through the WinISI III version 1.6 (Foss and Infrasoft International LLC, State College, PA) software, using MPLS regression method. A calibration set comprising 70% of the samples (n = 73) and a validation set comprising 30% of the samples (n = 28) were proposed, ensuring a balanced representation among the histamine groups: Zero (0 mg/kg, n = 4), Low (<100 mg/kg, n = 9), Mid (≥100–200< mg/kg, n = 10), and High (≥200 mg/kg, n = 8). Several combinations for scattering corrections (i.e., no scatter correction, detrend, standard normal variate, standard normal variate and detrend, and multiplicative scatter correction) and derivative mathematical treatments (e.g., 0,0,1,1; 1,4,4,1; 1,8,8,1; 2,5,5,1; and 2,10,10,1; Cendron et al., 2023) were tested through a cross-validation in the calibration set and then validated in the validation set. If a sample exhibited a significant disparity between its predicted value and the reference value, surpassing 2.5 standard deviations (T-statistics), it was classified as an outlier and subsequently excluded from the dataset (Forte et al., 2023, pp. 1–17).

Moreover, to select the most informative wavelengths for the histamine prediction, the interval-partial least squares (iPLS) using R software, version 4.2.3 (R Core Team, 2023) was conducted. This approach tests all possible combinations of spectral regions using one or several moving windows of fixed size selecting the specific wavelengths or areas most informative according to the histamine investigated in tuna fish as reported in the study of (Asghari et al., 2022).

The selection of the best prediction model in the calibration set was based on various fitting statistics, including the number of latent factors (LF), the standard error of cross-validation (SE_{CV}), the coefficient of determination of cross-validation (R^2_{CV}), and the residual predictive deviation of cross-validation (RPD_{CV}). The calculation of these statistics followed the method proposed by Williams and Sobering (1993), where RPD values were determined as the ratio of the standard deviation of the trait to the SE_{CV}. The interpretation of R^2_{CV} values was based on the thresholds suggested by Karoui et al. (2006). Specifically, R^2_{CV} values between 0.50 and 0.65 indicated the differentiation of samples with low and high histamine concentrations; values between 0.66 and 0.81 suggested an approximate histamine prediction, while values between 0.82 and 0.90 indicated a good histamine prediction; whereas, R^2_{CV} values greater than 0.91 identified excellent histamine prediction.

2.5.2. Wavelengths selection, principal component analysis and classification models

Foremost, a binary evaluation was assessed to evaluate differences

Table 1
Description of dataset of Tuna samples (number), Histamine classes and contamination variability.

Tuna Samples (n.)	Histamine Class	Mean (mg/kg)	Standard. Dev (mg/kg)	Min (mg/kg)	Max (mg/kg)
12	Zero (0 mg/kg)	0	0	0	0
30	Low (<100 mg/kg)	48.41	7.52	35.34	65.3
33	Mid (≥100–200< mg/kg)	154.88	27.08	108.04	199.63
26	High (≥200 mg/kg)	232.81	28.09	201.42	271.15

between the presence and absence of histamine (presence/absence set) in the examined tuna samples. Following this, a multiclass evaluation considered four different histamine contaminations (multiclass set; zero, 0 mg/kg; low, <100 mg/kg; mid, ≥100–200< mg/kg; high, ≥200 mg/kg) as reported in Table 1.

Similarly to the prediction process, spectral data were processed for derivative mathematical treatments using 'prospectr' package for R software, version 3.2.5 (R Core Team, 2022). Prior to identifying the most significant wavelengths, the binary (presence/absence set) and multiclass spectral datasets were divided into the training sets (70% of samples; n = 73) and the testing sets (30% of samples; n = 28) using the 'createDataPartition' function in the 'caret' package for R (Kuhn, 2008). The Random Forest (RF) feature selection procedure was performed on the training sets utilizing the Boruta algorithm (Boruta package) (Kursa & Rudnicki, 2010) with a wrapper approach. Feature selection method was employed to select bands that contained the most informative data while eliminating irrelevant and noisy data points (Ayyıldız & Arslan Tuncer, 2020; Currò et al., 2022). After the data treatment with RF, the PCA, as an unsupervised method, was performed as a descriptive tool for data visualization on both sets.

Support Vector Machine (SVM), a supervised model, was used to investigate the NIR classification capability before and after the RF feature selection procedure. The SVM was modelled by the use of the 'caret' package, through both the SVM Linear and SVM Radial kernels applied to the training dataset with repeated cross-validation. The C-value (Cost) in the Linear classifier and the Radial Basis Function sigma were customized, adopting a grid search. The performance of histamine classification models developed on the training sets (binary and multiclass) were then evaluated through the hold-out validations. In detail, the best model was developed on the training sets models through repeated cross-validation (setting number = 10 and repeats = 5), and then tested on the testing set (30%). A confusion matrix was allowed to evaluate the accuracy, sensitivity and specificity of the classification models (Bisutti et al., 2019).

3. Results and discussion

3.1. Prediction models and wavelength selection

The LC-MS/MS analyses of the 4 sets of tuna samples prepared for the validation of the NIR technique confirmed the expected fortification levels (Table 1): blank samples (0.0 ± 0.0 mg/kg); samples 50 (48.4 ± 7.6 mg/kg); samples 150 (152.9 ± 28.9 mg/kg); samples 250 (235.0 ± 30.0 mg/kg).

Among the several mathematic treatments, the most relevant outcome was reported in Table 2, which showed detailed statistical results of the calibration and prediction in cross-validation and in hold-out validation. In detail, the best prediction performance was observed for data without scattering corrections but optimized with the first derivatization and considering the whole spectrum (400–2500 nm). Basically, the optimal calibration model (No scatter correction 1441), developed using the calibration set (70% of samples), demonstrated an R^2 of 0.98 and a SE_C of 11.79 in calibration. Cross-validation within the calibration set revealed an R^2_{CV} of 0.88, with an SE_{CV} of 31.03 and an RPD_{CV} of 2.87, surpassing the threshold of 2.5, thereby confirming the model's suitability for the specified analytical objective (Karoui et al., 2006; Sinnaeve et al., 1994). The hold-out validation of the model on the validation set resulted in an R^2_P of 0.74, a SEP of 45.38, and an RPD of 1.86. In the hold-out validation, approximate performance predictions were observed, influenced by biases introduced by samples characterized by the lowest histamine concentrations (<50 mg/kg).

On the other hand, slightly lower performance of prediction after the iPLS wavelength selection was observed (Table 3); indeed, this approach for variable selection to extract the most informative features may lead to information loss. However, according to the iPLS analysis, it was evident that only a limited number of wavelengths held significance in predicting histamine content, with the most crucial interval spanning from 1182.5 to 1242 nm, indicative of the presence of -OH and -CH_3 groups (Workman Jr. & Weyer, 2012). The prediction of histamine levels in tuna has previously been explored by other researchers (Asghari et al., 2022; Ghidini et al., 2021) showing excellent prediction performance. However, these studies significantly differed from the current investigation in terms of experimental design, results, and applicability. In detail, the study of Ghidini et al. (2021) focused on exploring histamine contamination by utilizing solutions (0.1 mL) with seven different concentrations (0, 10, 50, 100, 200, 400, and 1000 mg/L) of histamine. Each solution was introduced into 1 g of minced raw tuna sample and then analyzed utilizing a NIR reflectance apparatus using shorter wavelength range (1000–2500 nm) compared to the present study. Through this methodology, Ghidini et al. (2021) achieved histamine predicition capability of 0.92 R^2_P in external validation. However, the present study showed less prediction performance in cross-validation (with an R^2_{CV} of 0.88) and in hold-out validation (with an R^2_P of 0.74) that can be largely attributed to the sample status (frozen-thawed), that could affect physicochemical properties. In detail, the differences on the physical status, on the water retention or dispersion, scattering effects of the fish matrix can interfere with the NIRS spectrum measurements (Pasquini, 2018), making the histamine prediction process more complex. The absorption is primarily associated with the chemical constituents found in the food matrix, while the scattering may be attributed to the food matrix physical structure (Pasquini, 2018). The smaller amount of matrix (1 g) used for the measurements and predictions of histamine in the study of Ghidini et al. (2021) could have reduced the scattering effect compared to the present study which used an aliquot of 40 g of muscles, therefore resulting in a sample more representative for the analysis. Even though lower performance was observed in this study, the results suggest that this could still be

Table 3
Fitting statistics of prediction models for histamine concentration (mg/kg) in thawed tuna developed using cross-validation results through interval Partial Least Square regression (iPLS).

Range wavelengths (nm)		LF	RMSE	R^2_{CV}
462.5	522	7	44.14	0.75
1122.5	1182	10	37.77	0.82
522.5	582	13	36.19	0.83
1182.5	1242	12	35.56	0.84

LF, number of latent factors selected; RMSE, Root Mean Square Error; R^2_{CV}, coefficient of determination of cross-validation.

Table 2
Fitting statistics of calibration and prediction model in cross-validation (calibration set, N = 73) and of hold-out validation (validation set, N = 28) for histamine concentration (mg/kg) in frozen-thawed tuna through the Modified Partial Least Square Regression.

Math.	Mean	SD	SE_C	LF	R^2c	SE_{CV}	R^2_{CV}	RPD_{CV}	SE_P	R^2_P	RPD
NONE 1441	130.04	89.14	11.78	8	0.98	31.03	0.88	2.87	45.38	0.74	1.86

Math, mathematical treatment; NONE, no scatter correction; SD, standard deviation; SE_C, standard error of calibration; LF, number of latent factors selected; R^2c, coefficient of determination of calibration; SEcv, standard error of cross-validation; R^2cv, coefficient of determination of cross-validation; RPDcv, ratio of performance to deviation of cross-validation; SE_P, standard error of hold-out validation; R^2_P, coefficient of determination of hold-validation; RPD, ratio of performance to deviation in hold-out validation.

Table 4
Performance of classification using support vector machine model to classify frozen-thawed tuna sample according to the histamine contamination level in hold-out validation.

Predicted	Reference of histamine class			
	Zero (0 mg/kg)	Low (<100 mg/kg)	Mid (≥100–200< mg/kg)	High (≥200 mg/kg)
Zero	3	0	0	0
Low	2	7	0	0
Mid	0	0	9	0
High	0	0	0	7
Sensitivity (%)	60	100	100	100
Specificity (%)	100	91	100	100
Balanced Accuracy (%)	80	95	100	100
Overall Accuracy (%)	93			

considered a positive aspect for the adoption of this technology in routine histamine control by Food Business Operators (FBOs), especially those who typically analyze larger sample quantities (see Table 4).

In contrast to the investigation undertaken by Asghari et al. (2022), wherein the prediction model yielded an R^2_{CV} of 0.965 subsequent to the wavelength selection process employing iPLS, this divergence is likely ascribed to disparate technological modalities and/or distinct data filtration methodologies (notably, the automatic Whittaker filter). Alternatively, it may be explicable by the comparatively limited variability (5–100 ppm) within contamination levels and the more restrained sample size (n = 38; 4 samples per concentration) considered, relative to the parameters encompassed in the present study.

3.2. Clusterization and classification model on wavelength selected

In this study, PCA was conducted following feature selection of the treated spectra to eliminate irrelevant attributes. This analysis reduces the dimensionality of the spectra, allowing for a visual depiction of the samples spatial distribution to underline the clusterization according to sample characteristics. In particular, Figs. 1 and 2 display the score plots of the first three principal components of the binary and multiclass sets, respectively. In detail, the binary score plot showed the highest variance explanation 97.5% (PC1 = 70.7%; PC2 = 20.1%; PC3 = 6.7%), whereas in the multiclass score plot the PC1, PC2 and PC3 explained 46.6%, 29% and 13.6% of the total variance, respectively. The graphical distribution of binary and multiclass set data depicted in noterworthy clusterization among groups suggesting a promising segregation using a linear classification model.

The data classification may offer advantages when confronted with complicated results, aiming for a simple threshold classification that can aid in decision-making regarding the risk of histamine contamination. A classification approach was implemented through the application of two distinct models, specifically binary and multiclass. In the binary approach, the spectral patterns of tuna categorized by the presence (>0 mg/kg) or absence (0 mg/kg) of histamine, demonstrating remarkable resemblances, including absorbance characteristics (Fig. 3). Nonetheless, subtle distinctions in absorbance were discernible within the spectral range of 490–680 nm and 1388 nm, where tuna samples devoid of histamine exhibited heightened absorbance. Out of the 4202 wavelengths examined, the RF selection identified 210 wavelengths. Specifically, the selected wavelnghts are located mainly within the visible part (ranging from 480 to 500.5 nm, and 648–687.5 nm) and within the first part of the NIR region (ranging from 752 to 762.5 (OH phenolic and CH), 781–814.5 nm (C-OH, and and CH) which encompasses the third and second overtones in which the analysis of the sample molecular structure is more refined (Workman Jr. & Weyer, 2012).

Nevertheless, the multiclass analysis of spectral patterns across the four histamine levels (0; <100; ≥100–200<; and ≥200 mg/kg) revealed distinct absorption peaks associated with varying histamine contamination levels. In detail, tuna spectra with zero or low histamine levels generally exhibited higher absorbance values compared to those with high histamine contents. These discrepancies could stem from the histamine quantity, exerting an influence on the absorbance peak, or they might arise due to the intricate molecular interactions between histamine and the tuna's inherent molecular matrix. Nonetheless, it is crucial to consider that the food spectrum represents the fingerprinting of a sample, reflecting the internal characteristics originating from chemical components (Fakayode et al., 2020); Additionally, it is important to take into account molecular vibrations, intermolecular interactions such as hydrogen bonding, and the general effects of the chemical environment, which contribute significantly to what is known as 'matrix effects' in analytical spectroscopy (Bázár et al., 2015; Beć et al., 2022). Notably, amines engage in interactions with carboxylic acids through hydrogen bonding and/or electrostatic attractions thereby forming aggregates (Nakamura et al., 2011). Thus, the interaction of histamine with other chemical compounds in the food matrix may affect the variation in spectrum absorbance.

Moreover, the RF process for wavelength selection according to the multiclass approach showed that 199 wavelengths retained significance to detect differences among the four histamine concentrations. Notably, the wavelengths selected ranged within the visible spectrum from 434 to 437 nm; 485–487 nm; 512 nm; 648–672 nm; 692–701 nm; 712–738 nm and in the NIR spectrum from 1063 to 1079 nm; 1462–1476 nm and 1741–1744 nm; 1769 nm, 2045–2047.5 nm and 2057.5 nm (Fig. 4). In contrast to the wavelengths selected within the binary class, it is salient

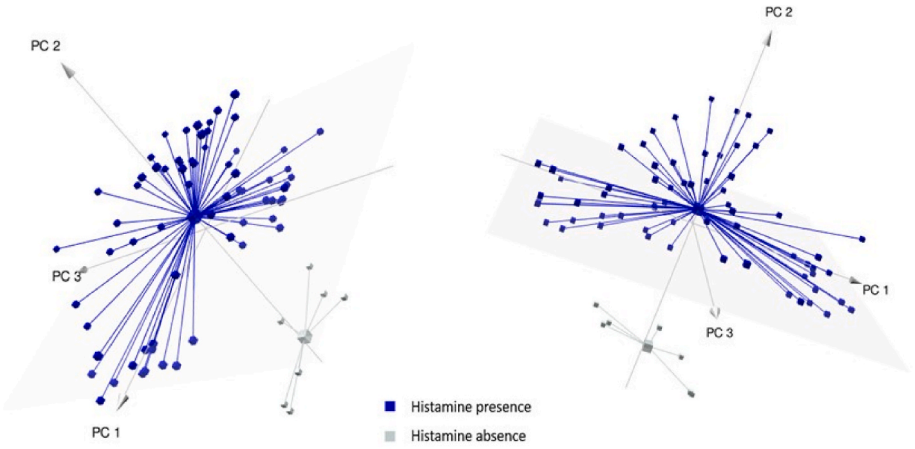

Fig. 1. Principal component score plot for PC1, PC2 and PC3 of frozen-thawed tuna with histamine presence and absence.

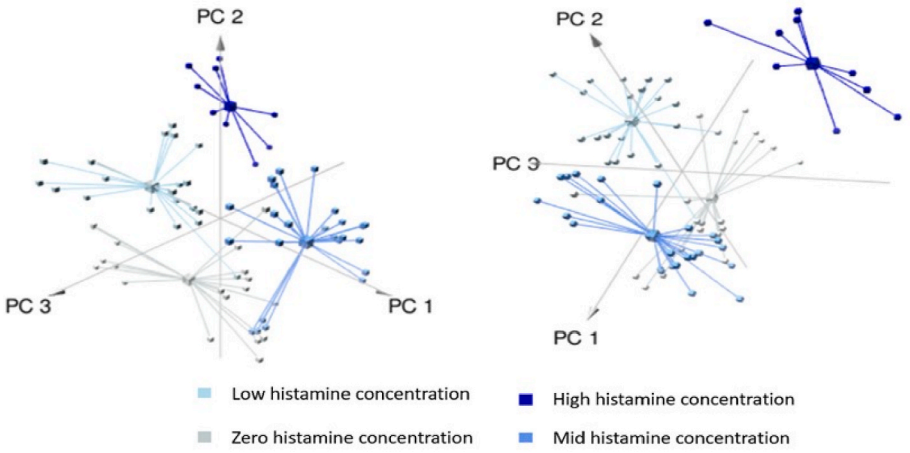

Fig. 2. Principal component score plot for PC1, PC2 and PC3 of frozen-thawed tuna with zero (0 mg/kg), low (<100 mg/kg), mid (≥100–200< mg/kg) and high (≥200 mg/kg) histamine concentration.

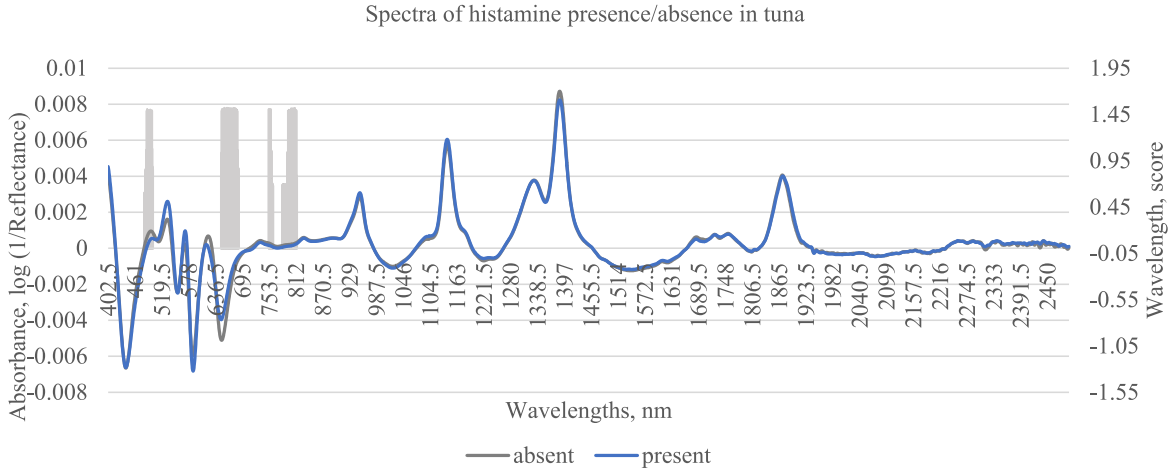

Fig. 3. NIR spectra (mean) of frozen-thawed tuna without histamine contamination (grey line) and with histamine contamination (blue line) collected using bench-top spectrometer (FOSS DS 2500). Grey areas show the most informative wavelengths selected by Random Forest on the training set (n = 73) for binary purpose.

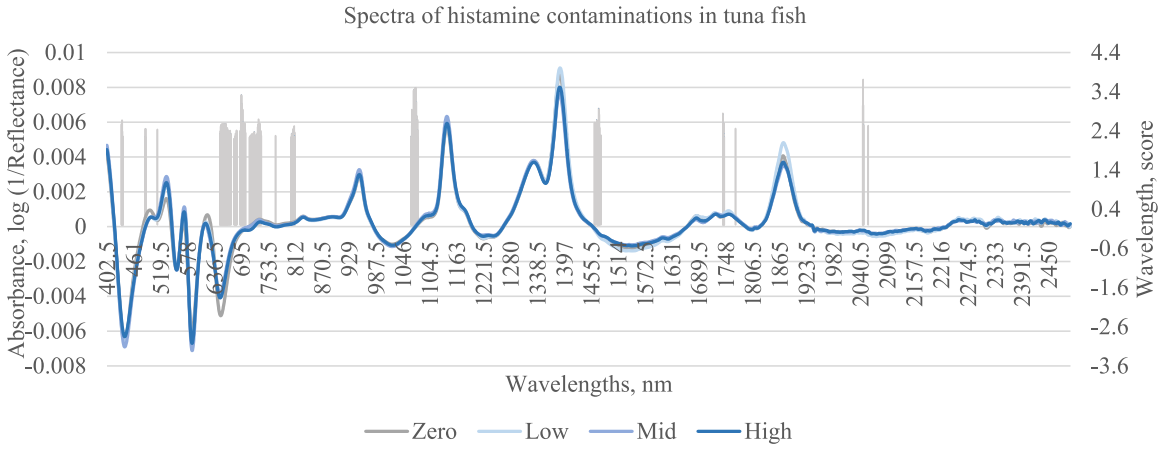

Fig. 4. NIR spectra (mean) of frozen-thawed tuna without histamine contamination (grey line), with low (<100 mg/kg; light-blue line), mid (≥100–200< mg/kg; blue line) and high (≥200 mg/kg; dark blue line) level of histamine contamination collected using bench-top spectrometer (FOSS DS 2500). Grey areas show the most informative wavelengths selected by Random Forest on the training set (n = 73) for multiclass purpose.

to observe that the chosen wavelengths not only traverse the VIS range but also exhibit a more extensive expansion into the NIR spectrum. This extension is particularly notable as it takes into consideration the combination band region, where interactions among vibrational modes manifest, enabling a more comprehensive investigation into the intricate details of molecular structures due to the distinction among the four histamine contamination levels.

In particular, this spectral range, which is of interest for the identification of the class of histamine, is associated with functional groups such O-H combination band, alcohols or water (1065 nm); N-H or N-H_2 (Amide/Protein; 1463 nm); N-H for secondary amine as (R-NH-R; 1465 nm); N-H combination band from primary amides (R-C=O – NH_2; 1470 nm); N-H Amide with N-R group (Amide/protein; 1471 nm); N-H primary aromatic amine (Aromatic amine; 1472 nm); -SH, CH_3 groups (1740, 1744 and 1770 nm, respectively); and N-H group between 2040 and 2060 nm (Workman Jr. & Weyer, 2012). The variations observed in the selection of significant wavelengths can likely be attributed to distinctions between the two approaches, which diverged in their objectives and the number of samples per class. The binary approach primarily focuses on distinguishing the presence or absence of histamine in the samples, potentially prioritizing critical wavelengths specific to this discrimination task. This constitutes a crucial element for the innovation of food safety; indeed, the optimization of the targeted spectral range permits to enhance a smooth and rapid screening process to verify and ensure the freshness of marketed tuna in the first stages of the supply chain. Moreover, in certain sampling planes where individual samples containing over 50 ppm were coupled with organoleptic analyses for sample rejection, and are considered decomposed (e.g., FDA), a simple model could be useful in the screening process (DeBeeR et al., 2021).

Conversely, the multiclass approach is more complex, necessitating the inclusion of a broader set of variables from the NIR spectrum to assess histamine levels and their interaction with the food matrix. The inclusion of extra wavelengths in this expanded set of variables leads to a more efficient approach, providing greater benefits according to the real-time analysis in product destination decisions based on the relevant contamination level at each phase of the supply chain. Another contributing factor may be the lower number of samples considered for each class in the second approach, which could require a greater number of variables to account for the differences observed among the samples.

Classification offers more straightforward data interpretation and enhances data learning efficiency compared to prediction algorithms. This distinction arises from the objective of categorizing data into specific groups rather than predicting precise numeric values. The binary classification task aimed to distinguish between the absence and presence of histamine in frozen-thawed tuna fish. Specifically, the predictive performance was assessed by comparing samples with no histamine (0 mg/kg) against samples with histamine (50–250 mg/kg), where the latter category included all tuna samples with the three different levels of histamine. For this specific binary classification task, the combined SVM Linear model demonstrated exceptional performance during hold-out validation. In particular, the model effectively differentiated samples based on the presence or absence of histamine content, achieving the highest levels of accuracy, sensitivity, and specificity (100%).

Regarding the multiclass analysis, the 73 tuna samples of the training set were reclassified based on the four levels of histamine contamination (zero, 0 mg/kg; low, <100 mg/kg; mid, ≥100–200< mg/kg; and high, ≥200 mg/kg). Utilizing the significant RF wavelengths from the training set, the results of the SVM Radial Grid supervised model achieved a notable classification of 93%. However, complete classification was not achieved, as some misclassification occurred. In detail, two samples from the zero category were identified as belonging to the low-class with the lowest level of contamination (<100 mg/kg).

This modelling approach proved suitable as a rapid screening method in identifying the true positive tuna samples contaminated with the highest levels of histamine, representing a valid approach for the control of raw materials that enter the food chain, and allowing the implementation of precautionary measures to prevent health risks associated with the consumption of foods contaminated with histamine. However, the results suggest that the developed model may require further refinements or enhancements, as it appears to respond particularly to samples with low levels of histamine contamination. Nonetheless, the capability to distinguish between samples with minimal to no histamine and those with moderate to high levels remains highly valuable for FBOs. It aids them in avoiding the distribution of food products to consumers that contain hazardous levels of histamine. It is important to note that while EFSA identified a no observed adverse effect level (NOAEL) of 50 mg/kg for histamine (EFSA, 2011), most histamine poisonings are associated with products that exhibit abnormally high histamine levels, often exceeding 200 mg/kg (EFSA, 2011). This underscores the practical significance of this method in ensuring food safety. In detail, with NIRS being an untargeted approach, the histamine contamination could be associated with specific functional chemical groups, highlighting the capability of NIRS to classify frozen-thawed tuna according to the histamine amount. Specifically, this differentiation may be attributed to the molecular phenotype variations among histamine contaminations, reflecting their distinct expression according to the interaction with histamine and organic molecules of the tuna matrix. On the other hand, the untargeted nature of this approach is one of its primary advantages. With a single instrument, FBOs could gather a wealth of information regarding both the safety aspects (specifically related to histamine) and the physicochemical characteristics of the product (Khodabux et al., 2007; Li et al., 2020; Reis et al., 2017). It is worth noting that several models have already been validated for the latter purpose, further enhancing the versatility and value of this method.

4. Conclusion

Due to the widespread consumption of fishery products, histamine control is of utmost importance for both FBOs and food control authorities in the decision-making process to prevent intoxication issues resulting from histamine contamination. This study addresses the need for a prompt detection of histamine contamination in frozen-thawed tuna fish using an untargeted methodology. The VIS-NIR analysis results offer an accurate, non-destructive, rapid, and environmentally friendly method for assessing the presence and level of histamine contamination in frozen-thawed tuna. For the quantification prediction, the MPLS using the full spectrum exhibited good (R^2_{CV} = 0.88) and approximate (R^2_P = 0.74) predictive performance in estimating histamine amount in frozen-thawed tuna. Conversely, the support vector machine classification combined with wavelength selection approach excelled in sample identification. Specifically, the binary classification model accurately distinguished between the presence and absence of histamine, achieving a flawless 100% accuracy. In the multiclass approach, the model exhibited a commendable classification accuracy of 93%, successfully identifying classes with concentrations higher than 100 mg/kg. However, the multiclass model adopted a cautious approach, as two samples from the zero class were identified as belonging to the low class.To the best of our knowledge, this study represents the first attempt to explore wavelength selection and construct a classification model based on the presence/absence of histamine, as well as its four distinct levels, in frozen-thawed tuna. Therefore, the analyzed tuna dataset offers compelling evidence regarding the efficacy of this approach when integrated with machine learning for both qualitative and quantitative objectives. It enables a prompt evaluation, proving particularly beneficial in scenarios demanding quick decisions, such as food safety inspections and regulatory compliance checks, especially for perishable foods like fish. This approach offers several advantagesas as it allows testing all samples rather than just a representative subset, thus improving the sampling plans or identifying contamination in lots with low prevalence.

Moreover, the user-friendly technique, coupled with the ability to assess quality, verifies the physical status of fish product (Regulation EU 2022/2503) (European Commission, 2022), and ensure its safety in detecting and quantifying histamine, emphasizes its significance. This approach is valuable for both FBOs and Competent Authorities. In conclusion, this approach offers rapid and straightforward results, making a positive contribution to consumer safety and enhancing business operations in the quality control of raw material as well as supplier qualification. Further studies should be performed to evaluate different fish matrices in order to determine the feasibility of near-infrared applications, the presence of matrix interferences as well as matrix interactions with artificial compounds.

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CRediT authorship contribution statement

Sarah Currò: Writing – review & editing, Writing – original draft, Formal analysis. **Federica Savini:** Writing – review & editing, Visualization. **Luca Fasolato:** Writing – original draft, Conceptualization. **Valentina Indio:** Writing – review & editing. **Federico Tomasello:** Writing – review & editing, Investigation, Data curation. **Giulia Rampazzo:** Investigation. **Elisa Zironi:** Investigation. **Giampiero Pagliuca:** Writing – review & editing, Resources. **Teresa Gazzotti:** Writing – original draft, Investigation, Data curation. **Laura Prandini:** Writing – review & editing. **Damiano Accurso:** Writing – review & editing. **Andrea Serraino:** Writing – review & editing, Conceptualization. **Valerio Giaccone:** Writing – review & editing. **Federica Giacometti:** Writing – review & editing, Writing – original draft, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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