Preliminary Study on the Determination of ppm-Level Concentration of Histamine in Tuna Fish Using a Dry Extract System for Infrared Coupled with Near-Infrared Spectroscopy

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ABSTRACT: Rapid and simple methods to determine histamine in tuna fish have been examined. A dry extract system for infrared (DESIR) was coupled with near-infrared spectroscopy in order to obtain the absorption of histamine in tuna fish at the ppm level. The result showed that the optimal extraction solvent for preparing DESIR samples was 75% methanol and boiling water (100 °C). Calibration equations were developed and tested by independent validation set samples. The calibration equation developed from boiling water as solvent extraction was slightly better than the equation developed from 75% methanol solvent with a coefficient of determination (R²) of 0.79, a standard error of calibration of 2.45 ppm, a standard error of prediction of 2.94 ppm, and a bias of 0.10 ppm. Furthermore, the predicted values from both equations were not significantly different from the reference values obtained from the standard method at the 95% confidence interval. Compared to the current AOAC fluorometric official method, the proposed technique simplified and reduced the preparation time.

INTRODUCTION

Nowadays, the fish processing industries are expanding due to population growth, leading to an increase in raw fish and fish product consumption. Microbial contamination during processing and storage is essential because this is the key factor that leads to histamine poisoning. The presence of histamine is due to the bacterial decarboxylation of histidine, which is an amino acid present in high levels in muscle tissues of the Scomberiscida and Scombridae families that include tuna. Among foods containing histamine, tuna is one of the most extensively consumed. Scombroid poisoning or histamine poisoning is a type of food poisoning with symptoms and treatment similar to those associated with seafood allergies. The risk of histamine poisoning is increased when fish are kept at temperatures above 4 °C. Histamine levels are therefore used as an indicator of a good manufacturing practice and preservation step.

There are numerous methods for histamine analysis. The AOAC fluorometric procedure is an official method most commonly used for histamine analysis in foods. Many other analytical techniques, including thin-layer chromatography (TLC), high-performance liquid chromatography (HPLC), capillary electrophoresis (CE), and enzymatic tests, have been developed for histamine determination in food. TLC is simple and does not require special equipment, but most of the published reports suffered from the excessive time needed for analysis and/or inaccuracy of the obtained results. CE is not so often applied for determining histamine because its detection limits is 2 ppm that is too high to detect histamine in tuna, while the detection limit of the fluorometric method is 0.5 and that of the HPLC method is 1 ppm. Enzyme-based methods offer a rapid means of detection, but enzymes are unstable and expensive test kits are needed, and these methods tend to overestimate the histamine content. The most widely used and officially accepted method to detect histamine in fish is a batch fluorescence method (AOAC 977.13). The fluorometric procedure is sensitive and reproducible but complex and time consuming.

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. NIR spectroscopy has been used to determine the matrix component and composition in fish such as moisture, fat, and protein contents in tuna fish and fat, protein, and dry matter in Atlantic halibut fillet. Histamine in fish and fish product can be found at the parts per million (ppm) level, whereas NIR spectroscopy requires concentrations above about 0.1%. However, several techniques coupled with NIR spectroscopy have overcome this limitation. Some research studies detected low-concentration analytes by developing spectra pretreatment and wavelength selection with chemometric methods. For example, orthogonal signal correction and net analyte signal were used to pretreat the NIR spectra before partial least

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squares (PLS) modeling. Some others applied NIR coupled with the preconcentration technique. For example, carbaryl and HZ818 macroporous adsorption resin were employed to detect low-concentration analytes in aqueous solution by near-infrared diffuse reflectance spectroscopy.

Another method to concentrate the amount of the analyte is the dry extract system for infrared (DESIR). In this procedure, a liquid containing the extracted constituent of interest is dried onto a solid substrate with low IR absorbitivity. The drying step allows the analyte to be more concentrated, and the solvent is removed. Then, the absorbance is acquired by NIR or IR spectroscopy. A successful DESIR technique is introduced to detect fungicide contamination on tomato surface. In that work, glass microfiber filter (GMF) paper was used as the substrate to extract analytes before NIR measurement. The best model was obtained when adding 2 mL of fungicide solution to the filter paper in a polystyrene Petri dish, with standard errors of prediction (SEPs) of 6.58 and 7.89 ppm for standard solutions and real tomato samples, respectively.

Many researchers have applied DESIR for quantification and authentication applications such as beverages, milk, wine, beer, coffee, tea, and meat by drip or centrifuged meat juices. One important step for DESIR is sample extraction by a solvent. In the fluorometric method, 75% methanol in water is used as the extraction solvent for derivatization before measuring fluorescence in canned tuna. Since the result of the DESIR combined with the NIR technique depends on the solvent and extraction method, this study aimed to compare the efficiency of three solvents, namely, 75% methanol, 100% methanol, and boiling water (100 °C), for extracting histamine in tuna fish and to create a calibration model to determine histamine content using NIR spectroscopy.

## MATERIALS AND METHODS

### Reference Analysis. The histamine content was determined according to the AOAC 977.13, 1990 official fluorometric method. Frozen tuna fish samples were thawed by a microwave oven (R-240, Sharp, Thailand) before being ground by a rotating knife chopper (FP200, Kenwood, Japan). Fifty grams of tuna fish was ground and thoroughly homogenized (Eurostar digital, Ika Werke, Germany) with 75% methanol, and then, the volume was adjusted with 75% methanol until it reached 50 mL. After warming at 60 °C for 15 min in a water bath, the sample solution was filtered through Whatman filter paper no. 1. A 1 mL aliquot of clear filtrate was passed through a resin column into a beaker and rinsed with distilled water until the total volume was 40 mL. Two milliliter of sample solution was put on a glass microfiber filter (GMF) paper that was placed in a Petri dish. GMF was used as a solid support in DESIR sample preparation because it is a fast drying medium and has low adsorption ability in the NIR region, which makes it suitable for NIR spectroscopy. The solvent was removed by drying at 130 °C in an oven. The time to remove solvent was recorded. The dried GMF (or DESIR) samples were kept in a desiccator until they reached room temperature of about 25 °C. Solvents that gave the lowest error for calibration equations would be used in experiment 2.

In experiment 2, samples were prepared by the DESIR method using the selected solvent and calibration equations were created. The accuracy of equations was tested according to ISO 12099 (2017) using an independent validation set.

### Spectral Acquisition. The spectra of DESIR samples in all experiments were measured using a Fourier transform (FT-NIR) spectrometer (model MPA, Bruker, Ettlingen, Germany) in the wavelength range of 4000–12500 cm⁻¹ in diffuse reflectance mode at a resolution of 16 cm⁻¹. An integrating sphere equipped with a lead sulfide (PbS) detector was used for spectrum measurement. The average of 32 scans and reference spectrum was measured in every sample. The reference material of FT-NIR spectrometer was internal reference coated with gold. The DESIR sample or GMF paper was placed at the measuring area on top of the spectrometer and then a stainless steel reflector was put on top of the GMF paper to reflect transmitted light back to the detector.

### Data Analysis. All calibration equations were performed using OPUS software (version 6.5, Bruker Optics, Billerica, MA). Partial least squares (PLS) regression was carried out to construct calibration equations with spectral preprocessing methods containing vector normalization (SNV), multiplicative scatter correction (MSC), first derivative, second derivative, first derivative and SNV, and first derivative and MSC. The best spectral preprocessing method was selected by trial and error to obtain calibration equations with the lowest errors. Twenty-nine samples were used in experiment 1 for
selecting the optimal extraction solvent. PLS regression was validated by a “leave-one-out” cross-validation method because there are a few samples for a separate test set. The same samples were used for both developing the equation and validating it. However, 82 more samples were used for validating in experiment 2. The samples with minimum and maximum histamine contents were set into the calibration set to ensure that the range covered the content for samples in the validation set. The remaining samples were randomly split into the calibration and validation sets with a 3:2 ratio resulting in 51 and 31 samples, respectively. Calibration equations were developed from calibration set samples, and the accuracy of the equations was tested against values for the samples in the validation set.

The performance of various calibration methods developed from DESIR samples prepared by different extraction solvents was compared by calculating the standard deviation of prediction errors on a validation set for each method. The prediction error is expressed as the standard error of prediction (SEP) and bias to indicate the predictive performance of PLS regression. SEP is calculated from variables in the validation set. SEP is compared by calculating the standard deviation of prediction errors on a validation set for each method. The SEP expresses the accuracy of NIR results relative to the reference method values. The unexplained error confidence limit (T_UE) is calculated from an F-test as follows

\[
T_{UE} = \text{SEC} \sqrt{F(a,v,M)}
\]

where T_{UE} is the unexplained error confidence limits; v = n − 1 is the numerator degree of freedom associated with the SEP of the test set; in which n is the number of samples in the validation process; and M = n_k − p − 1 is the denominator degree of freedom associated with the SEC, in which n_k is the number of calibration samples and p is the number of factors (PLS equation).

If SEP is less than T_{UE} then the SEP can be accepted.

The slope, b, of the simple regression equation \( y = a + b \hat{y} \) is often reported in NIR publications. The slope can be calculated to check the hypothesis that \( b = 1 \)

\[
t_{obs} = |b - 1| \sqrt{\frac{s^2_y (n - 1)}{s^2_{res}}}
\]

where \( n \) is the number of independent samples, \( s^2_y \) is the variance of the \( n \) predicted values, and \( s_{res} \) is the residual standard deviation as defined in the following equation

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s_{res} = \sqrt{\frac{\sum_{i=1}^{n} (\hat{y}_i - a - b \bar{y})^2}{n - 2}}
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In which \( a \) is the intercept of equation; \( a = \bar{y} - b \bar{y} \), where \( \bar{y} \) is the mean of predicted values, \( \bar{y} \) is the mean of reference values, and \( b \) is the slope; \( \gamma_i \) is the \( ith \) reference value; and \( \bar{y}_i \) is the \( ith \) predicted value obtained when applying the multivariate model.

The slope, b, is considered as different from 1 when \( t_{obs} \geq t_{(1-\alpha/2, v)} \) where \( t_{obs} \) is the observed \( t \) value, calculated according to above equation, and \( t_{(1-\alpha/2)} \) is the \( t \) value obtained from the \( t \) distribution table for probability of \( \alpha = 0.05 \).

### RESULTS AND DISCUSSION

**Optimal Conditions for Solvent Removal.** Extraction solvent and other elements that can absorb in the NIR region might interfere and overlap with the absorption of the target compound such as histamine. Elimination of the solvent hence reveals important data about the trace analyte. Investigation of optimal conditions to remove the solvent was an important step for the DESIR sample preparation. In this research, an oven drying method and an operating temperature of 130 °C were selected. However, this temperature is higher than the boiling point of 75% methanol (about 69 °C), 100% methanol (64.7 °C), and water (100 °C), which were the extraction solvents in this study. Moreover, histamine is not destroyed or

\[
T_b = \pm \frac{t_{(1-\alpha/2, v)} \text{SEP}}{\sqrt{n}}
\]

where \( T_b \) is the bias confidence limit, \( \alpha \) is the probability of making a type I error, t is the appropriate Student’s \( t \) value for a two-tailed test with degrees of freedom associated with SEP and the selected probability of a type I error, and \( n \) is the number of independent samples.

If the bias value is less than \( T_b \), the bias is not significantly different from zero.

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deteriorated at this temperature. The evaporation time in the oven was investigated by comparing weights of the GMF before and after drying using a four-digit analytical laboratory balance. When weights of the GMF before and after drying were not completely different, it indicated that GMF was completely dried. In this step, water was selected as the solvent for testing the conditions of evaporation because the boiling point of water is the highest among the solvents used. Two milliliters of distilled water was put on a GMF that was laid in a Petri dish. Then, the drying time of GMF at 130 °C was compared. Figure 1 demonstrates the result of time for removing water solvent in an oven dryer at 130 °C.

From Figure 1, weights of GMF before and after drying were not significantly different from 11 min onward. This implied that there was no more solvent left on GMF after 11 min of drying. Therefore, the suitable condition for removing solvent in DESIR samples preparation was drying at 130 °C for 11 min.

**Experiment 1: Effect of Different Solvents on Extraction of Histamine for DESIR.** Sample preparation for the DESIR method was modified from the official AOAC 977.13 fluorometric method with the intention to reduce the assay time and increase the number of samples analyzed for routine analysis. The heating step and chemical solutions added for making a fluorescent compound, which are not required and necessary in NIR analysis, were eliminated. Furthermore, added chemical can obscure histamine absorption. Therefore, the DESIR technique could simplify sample preparation and reduce the preparation time from 45 min to only 20 min, as shown in Figure 2.

The efficiencies of each solvent (75% methanol, 100% methanol, and boiling water) for DESIR sample preparation were compared and investigated by the FT-NIR spectrometer. A total of 29 samples for both calibration and validation procedures were carried out using the leave-one-out cross-validation method. Figures of merit are shown in Table 1.

Original spectra of DESIR samples prepared by 75% methanol, 100% methanol, and boiling water as solvents are shown in Figure 3. The spectrum of sample is derived from the unification of all component spectra and is unique as a human fingerprint. It was found that spectral patterns from filtrates extracted by all solvents were similar, indicating the resemblance of their composition. From Figure 3, the prominent peak at 5235 cm$^{-1}$ in all three spectra was identified as the absorption of GMF, and weak peaks at around 7353 and 6803 cm$^{-1}$ arise from GMF as well, as shown in Figure 3.
A weak peak at 4460 cm\(^{-1}\) related to amino acids is attributed to the N–H stretching and NH\(_3^+\) deformed vibration.\(^{12}\) The peak at 4460 was found in the spectrum of histamine powder measured in the wavenumber range of 3500–7000 cm\(^{-1}\), as shown in Figure 4.

Comparison of the calibration equations was done based on the lowest standard error of cross-validation (SECV) and the highest coefficient of determination (\(r^2\)). Table 2 shows the results of calibration equations developed from DESIR samples extracted by 75% methanol, 100% methanol, and boiling water solvents.

From Table 2, the best calibration equation is achieved from boiled water as a solvent with the lowest SECV of 2.33 ppm. The second one is 75% methanol (SECV = 2.64 ppm) and the last one is 100% methanol (SECV = 3.07 ppm). This result did not support the hypothesis that increasing the solvent concentration can enhance the extraction yield\(^{16}\) as an equation developed from 100% methanol as a solvent had a bigger error. The reason for the error might be that 100% methanol affects the pH value that was not suitable for histamine extraction in tissues of tuna fish sample.\(^{8,28}\)

Consequently, 75% methanol and boiling water would be used to extract histamine for experiment 2.

**Experiment 2: Development of Calibration Equations for Determination of Histamine Content in Tuna Fish.** From experiment 1, 75% methanol and boiling water were used as solvents for analysis in this part. To obtain the stability of equation for determination of histamine in tuna fish samples, adding more samples and increasing variance were performed. Calibration equations were built from the calibration set, and their accuracies were tested by the validation set. The calibration set should be designed to cover all possible variations. The distribution of histamine in calibration and validation sets is shown in Figure 5. Optimal quantitative PLS models were built from trial and error for consideration of the wavenumber region, number of factors, and pretreatment of spectra. The results obtained by optimization are summarized in Table 3. The number of factors that gave the lowest errors for the equations of 75% methanol and boiling water solvents were 5 and 4, respectively, which were acceptable. As the results of wavenumber selection, the variables in the ranges about 6804–6094.3 and 5454–4242.9 cm\(^{-1}\) were selected for models of 75% methanol and boiling water solvents. Regression coefficient plots of both 75% methanol and boiling water solvents showed the major wavelengths needed to predict histamine (Figure 6). The peaks of the both regression coefficient plots at 4456 and 4463 cm\(^{-1}\) were observed, which are related to the absorption band of histamine at 4460 cm\(^{-1}\) shown in Figure 4.

![Figure 3. Original spectra of DESIR samples prepared by different solvents compared to the GMF spectrum.](image)

![Figure 4. Original spectrum of histamine in the range of 3500–7000 cm\(^{-1}\).](image)

![Figure 5. Histogram showing the frequency distribution of histamine content in calibration and validation sets.](image)

| solvent         | \(r^2\) | SEC\(^a\) (ppm) | SECV\(^b\) (ppm) | bias (ppm) | paired \(t\)-test |
|-----------------|--------|-----------------|-----------------|------------|-----------------|
| 75% methanol    | 0.81   | 0.25            | 2.64            | 0.20       | 0.41\(^d\)      |
| 100% methanol   | 0.66   | 0.59            | 3.07            | 0.08       | 0.14\(^d\)      |
| Boiling water   | 0.84   | 0.85            | 2.33            | 0.13       | 0.30\(^d\)      |

\(^{a}\)Coefficient of determination. \(^{b}\)Standard error of calibration (SEC). \(^{c}\)Standard error of cross-validation (SECV). \(^{d}\)No significant difference between actual and NIR predicted histamine contents at 95% confidence interval.
prepared with 75% methanol as the solvent showed the SEP of 3.18 ppm and RPD of 1.66. The SEL or standard error of duplicates analyzed by the reference method (fluorometric method, AOAC 977.13) for histamine content analysis was 0.33 ppm, as calculated by eq 1. Comparison between SEP and SEL showed that the error from DESIR and NIR techniques (SEP) was rather higher. Therefore, the application of DESIR and NIR methods to detect the histamine content was not suitable for process control but suitable for a rapid, simple, and cheap method for screening analysis.

Both boiling water and 75% methanol can extract histamine out of fish meat. Both calibrations demonstrated the capabilities of analysis by this technique. However, the errors from this analysis might be due to the extraction procedure for the reason that solvent used in the DESIR technique not only extract the substance interested but also other compounds that can dissolve in methanol and boiled water. Therefore, these undesirable compounds might interfere with the absorption of histamine in the samples.

The error from this analysis is expressed with SEP. A comparison of SEP from two equations calculated by eqs 2 and 3 was performed. R^2 between two sets of prediction errors was 0.15 (Figure 8). From Table 4, the interval of lower limit (0.73) and upper limit (1.61) covered 1, indicating that SEP from two equations was not significantly different at the 95% confidence interval. Thus, the calibration result developed from 75% methanol as the solvent was reasonable as well as the one developed from boiling water. Furthermore, for routine analysis, the performance of calibration equations has to be evaluated according to ISO 12099, which was calculated from eqs 4−9, and is shown in Table 5.

Table 3. Calibration Equation Results Developed by Partial Least Squares (PLS) Regression

| solvent          | pretreatment | calibration set | validation set | factors | region (cm\(^{-1}\)) |
|------------------|--------------|-----------------|----------------|---------|----------------------|
| 75% methanol     | SNV          | \(R^2\) | SEC\(^a\) ppm | \(r^2\) | SEP\(^b\) ppm | bias (ppm) | RPD\(^c\) |  |
|                  | 0.76         | 2.66            | 0.63           |         | 3.18                | 0.16       | 1.66       | 5 | 6804−6094.3, 5454−4242.9 |
|                  | 1st + SNV    | 0.79            | 3.31           | 0.72    | 3.44                | 0.30       | 1.54       | 4 | 5454−4597.7   |
|                  | MSC          | 0.86            | 2.77           | 0.71    | 3.47                | 0.21       | 1.52       | 4 | 7506−4242.9   |
| boiled water     | SNV          | 0.79            | 2.45           | 0.69    | 2.94                | 0.10       | 1.80       | 4 | 6804−6094.3, 5454−4242.9 |
|                  | MSC          | 0.88            | 2.52           | 0.79    | 3.06                | 0.41       | 1.73       | 4 | 9403.7−4242.9 |
|                  | 2\(^{nd}\)   | 0.81            | 3.14           | 0.78    | 3.12                | 0.44       | 1.70       | 4 | 7506−6094.3, 5454−4242.9 |

\(^a\) Standard error of calibration (SEC). \(^b\) Standard error of prediction (SEP). \(^c\) Ratio of SEP to standard deviation of the reference method value.
From ISO 12099, bias values obtained from both equations (bias = 0.16 and 0.10 ppm for 75% methanol and boiling water, respectively) were lower than bias confidence limits (\(T_b\) for 75% methanol = ±1.09 ppm and \(T_b\) for boiled water = ±1.01 ppm), verifying that NIR predicted and reference values were not different in the statistical significance. The slope test of both 75% methanol and boiling water solvents calculated by eq 6 were \(t_{obs} = 0.00\), which were less than \(t_{(1-\alpha/2)} = 2.03\), indicating that the slopes were not different from 1 at the 95% confidence interval. Moreover, SEP = 3.18 and 2.94 ppm (for 75% methanol and boiling water, respectively) were lower than bias (bias = 0.16 and 0.10 ppm for 75% methanol and boiling water solvents) calculated by \(t_{obs}\). SEP = 3.18 and 2.94 ppm (for 75% methanol = 1.09 ppm and boiling water = 1.01 ppm), verifying that SEP could be accepted. The results showed that the NIR predicted values obtained from both solvents were not significantly different from the actual values at the 95% confidence interval.

### CONCLUSIONS

A rapid and simple method, DESIR, considerably improves NIR applications involving detection in the ppm level. The potential of this technique was exhibited in calibration results. A good trend for the technique that applies NIR and DESIR for screening and rapid determination is observed, even though this method is not sufficiently developed as compared to the AOAC method. Extraction by boiling water is more cost-saving than 75% methanol because no chemical is required. Boiling water therefore has advantage over 75% methanol for long-term analysis by the NIR technique. In the future study, the accuracy of histamine determination by NIR may be improved by developing a preconcentration process or trying other solvents that might be more effective to extract only histamine to reduce the interference of other components in NIR absorption.

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**Notes**

The authors declare no competing financial interest.

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