Evaluation of pH of curry soup containing coconut milk by near infrared spectroscopy

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Abstract. The pH is the important parameters to characterize the food deterioration and an indicative of food spoilage. The aim of this research was to apply the near infrared (NIR) spectroscopy to evaluate pH of curry soup containing coconut milk. The soup samples from mixing tank, water content adjusted tank, UHT pipe and laminated containers in the production line were collected. There were also the pH adjusted samples where the curry was made from the same recipe but increasing placed time for 2, 4 and 6 hr after 0 hr. There are 73 samples in total. The sample was scanned with FT-NIR spectrometer. A prediction model for pH was established using NIR spectral data in conjunction with partial least squares regression, which was validated using leave one out cross validation and test set validation. After validated by unknown samples, the leave one out cross validation model showed better prediction performance. The best model developed using first derivative spectra in 9403.8-7498.3, 6102-5446.3 and 4605.4-4242.9 cm⁻¹ provided an coefficient of determination ($r^2$), root mean square error of cross validation (RMSECV), bias and ratio of performance to interquartile (RPIQ) of 0.73, 0.28, 0.01 and 1.89. The model was usable for screening and some other “approximate” calibrations. The model could be improved for further development of robust model using more natural samples in evaluation of pH in the curry soup.

1. Introduction
The pH is one of the important parameters to characterize the food deterioration. It is an indicative of food spoilage and can indicate to the consumer any food quality changes [1]. There were some researchers studied the relationship between the pH of food and its deterioration, for example, fresh noodle [2], chicken sausage [3], fish [1,4], fresh pork burger [5] and cane juice [6]. Fish is among the most consumed foods in the world and is very prone to microbial spoilage, which cause an increase in the pH of fish, due to an increase in volatile nitrogen bases concentration levels [4]. In case of sausage, the low pH value is a positive character in sausage production because microorganism growth is reduced in low pH conditions [7]. Therefore, shelf life of the product will increase with low pH values [3]. However, from the study of Korkeala et al. (1987) [8] above the level of $10^9$ lactobacilli/g in vacuum-packed cooked ring sausages a sharp decrease in pH from 6.3 down to approximately 5.4, was observed. The biocide-treated juice retained its initial pH over 71 hr and in strong contrast, after 71 hr the untreated juice had markedly lower pH.

Coconut milk is used in traditional tropical Asian food including curry soup. In order to preserve coconut milk, heat treatment is required [9]. Seow and Gwee (1997) [10] describe that pasteurization involves heating the milk to temperature of 72 °C for 20 min whereas Arumughan et al. (1993) [11] indicated that ultra-high temperature (UHT) treatment of coconut milk requires heating the milk at 121
°C for 20 min. The drastic heat treatment is required because raw coconut milk is a low-acid liquid food, with a pH of around 6.2 [12]. In curry soup containing coconut milk industry, the already mixed sample of the soup has been collected for pH measurement. The pH specification for Green curry and Red curry is 5.4-6.4, that of Panang curry is 5.2-6.2 and that of Massaman curry is 5.1-6.1.

The near infrared (NIR) spectroscopy, a rapid, accurate and environmental friendly method for quantifying the constituents and quality parameters of agricultural product and food, has been used both in research and industry. It was used to evaluate the pH of some food for acidity such as tomato juice [13], white vinegars [14], apple wine [15], yogurt [16] and loquats [17]. There has been no report about pH measurement using NIR spectroscopy for food deterioration. Therefore, this research paper aims to report the application of near infrared spectroscopy on evaluation of pH of curry soup for the industrial purpose.

2. Materials and Methods

2.1. Samples
The Green curry soup, Massaman curry soup and Panang curry soup from mixing tank, water content adjusted tank, ultra high temperature (UHT) pipe and laminated containers were collected. The Green curry soup samples were collected in the process line on 18-Sep-14, 03, 07-Nov-14, 09-Dec-14, 08 and 15-Jan-15. The Massaman curry soup samples were collected on 20, 24-Nov-14, 31-Jan-15, 12-Feb-15 and 18-Mar-15 and Panang curry on 04, 06-Sep-14, 30-Oct-14, 16 and 22-Jan-15. The 8-10 samples were collected each day. There was no sample of Red curry soup from the process line. There were also the pH adjusted samples where the curry was made from the same recipe but increasing placed time of 2, 4 and 6 hr from 0 hr. The dates for adjusting recipe was 12, 24, 19-Dec-14 and 14-Jan-15 for Green curry soup and 14 and 24-Oct-14 for Red curry soup and 13 and 18-Feb-15 for Massaman curry soup and 23 and 30-Jan-15 for Panang curry soup. The adjusted samples were 2-3 samples per level of each curry. There are 73 samples in total. After collecting a sample from the processing line, or pH adjusting, the sample of 200 ml were subjected immediately to homogenization (T25 digital ULTRA-TURRAX, IKA, Germany) at 2500 rpm for 3 minutes before NIR scanning.

2.2. Near infrared scanning on sample
Each sample was transferred into a quartz cup (diameter 64 mm and long 50 mm) and was scanned through quartz under the cup by an FT-NIR spectrometer (MPA, Bruker, Ettlingen, Germany) in diffuse reflection mode at a wavenumber between 12,500-3,600 cm⁻¹ with a nominal resolution of 16 cm⁻¹ resolution. All experiments were performed at room temperature (25±1 °C). Each sample was scanned in duplicate. All scan results were recorded in absorption mode (log 1/R). The duplicate spectra of each sample were averaged before further analysis.

2.3. Analysis of pH of curry soup
After scanning, the sample was measured for pH by pH-meter (HI 8521, HANNA instrument, Rhode Island, USA) equipped with a glass electrode by using buffer pH 7.00 and buffer pH 4.00 as calibration standard. Each sample was measured in triplicates.

2.4. Repeatability and maximum coefficient of determination
The precision of reference test of pH of curry soup was determined using the repeatability value (Rep). The repeatability is calculated by the standard deviation of the farthest different of the triplicate. Then the maximum coefficient of determination (R_max²) was calculated following Dardenne (2009) [18] using the equation (1).

$$R_{\text{Max}}^2 = \frac{SD_y^2 - Rep^2}{SD_y^2}$$ (1)
Where, SD_y is the standard deviation of pH value of calibration set. According to Dardenne (2009) the maximum $R^2$ could get with no error in the spectra or the model. He indicated that sometimes, SD_y and Rep was sufficient to give up NIR model development: it means a range too narrow and/or a reference method not sufficiently precise.

2.5 Spectrum pre-treatment and NIR spectroscopy model establishment

The NIR spectroscopic models for predicting the pH of curry soup were developed by partial least squares (PLS) regression. The OPUS, v.7.0.129 multivariate analysis software package (Bruker, Ettlingen, Germany) was used in both spectrum pre-treatment and model development. The NIR spectra used for model development were pre-treated in the following way; no pre-treatment, constant offset elimination, straight line subtraction, vector normalization (SNV), min-max normalization, multiplicative scatter correction (MSC), first derivatives (17 points segment), second derivatives (17 points segment), first derivatives+straight line subtraction, first derivatives+SNV and first derivatives+MSC. The modeling was two types including the leave one out cross validation model where total samples were used and test set validation model where 50% of samples were used for calibration and another 50% was used for validation. The optimum model was selected from a combination of a number of PLS factors, spectral pre-treated method and wave number ranges based on the lowest root mean squared error in cross (leave one out) validation (RMSECV). After that the model was validated and the coefficient of determination ($r^2$), root mean squared error in prediction (RMSEP), ratio of performance to interquartile (RPIQ) for skew distribution data set and the prediction bias were calculated. For skewed distributions, the ratio of standard error of validation to the standard deviation (RPD) is not acceptable for standardizing the SEP with respect to the population spread [19]. To calculate the RPIQ index, the SD (standard deviation of the prediction set) was replaced by the interquartile (Q3-Q1) where Q3 and Q1 was the value below which 75% and 25%, respectively, of the samples were found [19].

3. Results and Discussion

Figure 1 shows the average spectra of 4 curry soup.

![Figure 1. Average spectra of Green curry, Red curry, Panang curry and Massaman curry.](image-url)
The number of samples, minimum (Min), maximum (Max), mean and standard deviation (SD) of pH of curry soup sample sets are shown in Table 1. The repeatability of pH reference test for Green, Red, Massaman and Panang curry soup were 0.00, 0.00, 0.01 and 0.01. Therefore, the average repeatability was 0.01 and the $R^2_{Max}$ was 1.0 indicated that the NIR spectroscopic model should be potentially developed further.

Table 1. Number of samples, minimum (Min), maximum (Max), mean and standard deviation (SD) of pH of curry soup samples of calibration set and prediction set.

| Sample set       | No. Samples | Mean | Max  | Min  | SD  |
|------------------|-------------|------|------|------|-----|
| Total            | 73          | 5.66 | 6.16 | 3.98 | 0.54|
| Calibration set  | 37          | 5.69 | 6.15 | 3.98 | 0.53|
| Validation set   | 36          | 5.64 | 6.16 | 4.08 | 0.56|

The optimum model was selected if the model provided best prediction performance which was minimum RMSECV. Table 2 shows the statistics of prediction of pH of curry soup by optimum PLS models. The optimum model for pH of curry soup of leave one out cross validation was developed using 10 PLS factors in the range of 9403.8-7498.3, 6102-5446.3 and 4605-4242.9 cm$^{-1}$ that was pre-treated by the first derivative (17 Pts.) methods. This model showed the $r^2$, RMSECV, bias and RPIQ of 0.73, 0.28, 0.01 and 1.89, respectively. The optimum model for pH of curry soup of test set validation was developed using 10 PLS factors in the range of 9403.8-5446.3 cm$^{-1}$ that was pre-treated by the straight-line subtraction methods. This model showed the $r^2$, RMSEP, bias and RPIQ of 0.75, 0.28, 0.03 and 1.91, respectively. It was worth noting that Williams (2010) [20] has indicated that an $r^2$ of 0.66-0.81 implies that a model was usable for screening and some other “approximate” calibrations. This result was similar to the prediction of pH of Mediterranean buffalo milk [21] by Fourier-transform mid-infrared spectroscopy which provided the $r^2$ of 0.76 where the averaged pH was 6.66. In case of Brown Swiss milk samples, De Marchi et al. (2009) [22] reported the application of mid-infrared spectroscopy models developed for pH could discriminate between high and low values ($r^2 = 0.59$ to 0.62). There was no report on NIR spectroscopy for prediction of pH of coconut milk or animal milk and its product.

Table 2. Statistics of prediction of pH of 4 curry soup (Green curry soup, Red curry soup, Massaman curry soup and Panang curry) by PLS models

| Validation method | No. Factor | Wavenumber (cm$^{-1}$) | Pretreatment               | Calibration                | Validation               |
|-------------------|------------|------------------------|----------------------------|-----------------------------|--------------------------|
|                   |            | 9403.8-7498.3, 6102-5446.3 and 4605-4242.9 | First derivative (17 Pts.) | $r^2$, RMSECV, bias and RPIQ | $r^2$, RMSEP/| RMSECV, Bias |
| Leave one out      | 10         | (1063-1334, 1639-1836 and 2171-2357 nm) |                            | 0.86, 0.21, 0.73, 0.28, 1.89 | 0.18, 0.75, 0.28, 1.91 |
| validation         |            |                        |                            |                             |                          |
| Test set validation| 10         | 9403.8-5446.3 (1063-1836 nm) | Straight line subtraction  | 0.90, 0.18, 0.75, 0.28, 1.91 | 0.03                     |

Figure 2 and 3 shows the scatter plots of pH measured by reference method (pH meter) and predicted by NIR spectroscopy of leave one out cross validation model and test set validation model, respectively.
Table 3 shows the true and predicted pH of 12 unknown samples of four curry soups by PLS models validated by a leave one out cross validation and test set validation. The prediction result of pH in the validation by test set samples model and the leave one out cross validation model were similar. The trend line of the models had the slope and offset far from the target line.

Table 4 shows the statistics result of prediction model performance for unknown samples. The model validated by leave one out cross validation model provided better prediction performance that the test set validation model with higher accuracy (less RMSEP and bias), higher precision (less standard error of prediction (SEP). The prediction was not good with unknown samples which might be because the calibration model contained less of samples of future samples. The model should be updated year by year.
Table 3. The comparison of true and predicted pH of unknown samples of four curry soups (Green curry soup, Red curry soup, Massaman curry soup and Panang curry soup) by PLS models validated by a leave-one-out validation and test set validation.

| No. | Curry Samples | True (%) | Model validated by leave-one-out validation | Model validated by test set validation |
|-----|---------------|----------|--------------------------------------------|----------------------------------------|
|     |               |          | Prediction (%) | Prediction (%) | Prediction (%) | Prediction (%) |
| 1   | Green         | 6.02     | 6.68           | 5.38           |                |                |
| 2   | Green         | 6.13     | 6.98           | 5.7            |                |                |
| 3   | Green         | 6.1      | 5.84           | 5.49           |                |                |
| 4   | Red curry     | 5.68     | 6.11           | 5.23           |                |                |
| 5   | Red curry     | 5.66     | 5.86           | 5.73           |                |                |
| 6   | Red curry     | 5.67     | 5.88           | 5.43           |                |                |
| 7   | Massaman      | 5.88     | 5.6            | 4.64           |                |                |
| 8   | Massaman      | 5.87     | 4.98           | 5.21           |                |                |
| 9   | Massaman      | 5.88     | 5.38           | 5.28           |                |                |
| 10  | Panang        | 5.66     | 5.7            | 4.93           |                |                |
| 11  | Panang        | 5.64     | 5.52           | 4.82           |                |                |
| 12  | Panang        | 5.64     | 5.83           | 4.9            |                |                |

Table 4. Statistics of prediction performance of leave-one-out validation and test set validation PLS models on unknown samples of four curry soups (Green curry soup, Red curry soup, Massaman curry soup and Panang curry soup)

| Model types         | Samples | RMSEP (%) | Bias (%) | SEP (%) |
|---------------------|---------|-----------|----------|---------|
| Leave-one-out validation | 12      | 0.602     | -0.0421  | 0.607   |
| Test set validation  | 12      | 0.824     | 0.59     | 0.582   |

RMSEP : root mean square error of prediction ; SEP : standard error of prediction ; RPD : ratio of standard error of validation to the standard deviation.

4. Conclusions
From the results presented in this study, NIR spectroscopy could be used as an alternative technique to evaluate of pH of curry soup since the model showed acceptable prediction accuracy. The predictive statistics suggested that these models were usable for screening and some other “approximate” calibrations of pH of curry soup containing coconut milk.

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