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Feasibility of detecting soybean oil adulteration with chicken fat by using NIR spectroscopy combined with chemometrics analysis

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Abstract

Adulteration of edible oil is one of the major concerns in the food industry. We report our result of feasibility study using NIR Spectroscopy and chemometrics analysis for detection of chicken fat adulteration in soybean oil. NIR spectra measurements were conducted on pure soybean oils and adulterated samples by varying the concentration of chicken fat (1 to 50% v/v in soybean oil). The chemometrics analysis for classification and quantification of soybean oil adulterated samples was then conducted using Soft Independent Modelling of Class Analogy (SIMCA) model and Partially Least Square (PLS) model at the wavelength range of 1350 -2230nm. The SIMCA model was able to classify correctly between pure and adulterated sample. PLS calibration gives good results between predicted and measured data in both calibration and test data with R^2 value more than 0.98. Overall, the result is encouraging given that the adulteration down to 1% was successfully quantified with root mean square error of 0.4033.

Keywords: food adulteration, NIR spectroscopy, chemometrics analysis, soybean oil

INTRODUCTION

Soybean oil is one of the vegetable oils that widely used and become popular due to the high concentration of unsaturated fatty acid. It contains 61% polyunsaturated fatty acid, 25% monounsaturated fatty acid and only 15% saturated fatty acid. Therefore soybean oil is one of the edible oils that have been subjected to adulteration by animal fat which covers under the authenticity issue. Generally, the authenticity issues comprises of adulteration, mislabeling, and characterization and misleading origin.

Adulteration of animal fat into vegetable oil happens due to the purpose of improving the oil stability, enhancement of food flavor and reducing the cost and price of the product. Adulteration for reducing oil price is related to economic reason which is done by replacing the higher value products with lower grade, cheaper, and more easily available substitutes (Gunstone, 2011; Rohman and Che Man, 2012). For example, the adulteration of animal fat in sunflower oil happen in fried food industry to increase the stability of the oil because higher polyunsaturated oil undergo faster oxidation that contributes to off flavor product (Marikkar et al., 2012). Thus, the adulteration mentioned will improved the frying quality of the oil but affect the fried food's flavor.

Although there is no epidemiologic studies about the relation between type of cooking oil used with cardiovascular disease, there is a suggestion that the myocardial infraction risk can be reduce by replacing palm oil with a polyunsaturated nonhydrogenated vegetable oil (Kabagambe et al., 2005). There were more than 20000 people became ill in the Spanish Toxic Oil Syndrome in year 1981 due to ingestion of rapeseed oil adulteration. The studies found that the France rapeseed oil was denatured with aniline, then mixed with other oils before selling in 5 litre containers as pure olive oil in Spain (Posada De La Paz et al., 1996).

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In terms of religious concern, some religions forbid the presence of animal fats in consumer goods including foods, cosmetics, and pharmaceuticals. In example, Muslims and Hindus are prohibited to consume any part from pig and cow respectively. As for vegetarians, adulteration with animal source is very much undesired.

Therefore, it is necessary to find a reliable method to detect the vegetable oil adulteration. Some techniques such as high- performance liquid chromatographic (HPLC)(Marikkar et al., 2005), Gas chromatography with flame ionization detector (GC- FID) (Dahimi et al., 2013), differential scanning calorimetry (DSC) (Marikkar et al., 2012) and Fourier Transform Infrared Spectroscopy (FTIR) (Che Man and Mirghani, 2001) have been successfully applied to detect and identify adulterants in food. NIR spectroscopy coupled with chemometrics analysis has emerged as an attractive alternative technique for adulteration detection. The interests in NIR spectroscopy lies in its advantages of straightforward and speedy characterization of samples (Ng et al., 2007). The continuous methodologies in NIR spectroscopy implemented able to record and provide spectra quickly with no pretreatment. The molecular bonds: O-H, C-H, C-O, and N-H are subject to vibrational energy changes when irradiated by NIR frequencies which determine the frequency at which it absorbs NIR energy (Cen and He, 2007). Thus, NIR absorptions are based on overtones and combinations of fundamental vibrations of the investigated molecule. Compared to FTIR, the NIR spectroscopy deals with only the overtones of the primary spectrum and their combinations and as such need helps from statistical analysis, normally termed as chemometrics analysis.

To the best of our knowledge, despite the many reported publications, there are no published results regarding the use of NIR spectroscopy for analysis of chicken fat in soybean oil. Therefore, in this work, chemometrics analysis is developed to detect the presence of chicken fat in soybean oil using NIR spectroscopy. We conduct an experiment to acquire NIR spectral data of pure chicken fat, pure soybean oil and of soybean oil adulterated with chicken fat. The spectra data were analyzed with chemometrics analysis using Matlab R2013a software for classification and quantification. With the objective of investigating the feasibility of detecting soybean oil adulterated with chicken fat from the pure one, this article is organized as follows. The next section describes the experimental setup. The result is discussed in section three. Section four conclude and suggest future works.

MATERIALS AND METHODS

Sample preparation

The soybean oil and adipose tissues of chicken were obtained from local market in Selangor, Malaysia. The chicken fat was prepared by rendering the adipose tissue of chicken in the oven for 2 hours at 100°C. Next, the process continued with filtering method for separating the chicken fat with the non-melted adipose tissue which was conducted according to previously reported procedure by Rohman and Che Man (Rohman and Che Man, 2009). The sample preparation then proceeds with the adulteration of chicken fat into soybean oil by mixing them together into accurately calculated volume proportions. The calibration standards were prepared in different concentration range from 1% to 50% volume per volume (v/v). For storage, samples were stored in amber glass bottle filled with nitrogen gas blanket. The oils and fats were stored under refrigerated conditions at - 20°C and melted at 60°C in water bath prior to their use for spectra measurement.

NIR spectra measurement

All samples were analyzed using the DLPNIRscanEVM spectrometer from Texas Instrument which is equipped with cooled Indium Gallium Arsenide (InGaAs) detector. The schematic of the setup is depicted in Figure 1. The measurement was done using transmittance measurement mode with wavelength range from 1350 to 2450nm. The NIR spectra were scanned with digital resolution of 4 nm using custom scan as mode of operation. Each spectrum was obtained by an average of 3 scans. The reference spectral was recorded before measurement of each different concentration with the empty quartz cuvette. The

spectra measurement of adulterated sample was repeated three times with five samples for each concentration.

All of the spectra were recorded as absorbance values with respect to a reference baseline at each data point. After each measurement, the spectral data were downloaded from the DLPNIRscanEVM spectrometer in csv format and were pre-processed before proceeds for chemometrics analysis using MATLAB based software program.

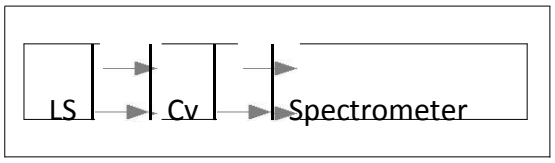

Figure 1. The schematic of the transmission setup consists of polychromatic light source (LS) and cuvette (Cv) for sample holder.

RESULTS AND DISCUSSION

Spectra features of NIR

The measurement for all concentration samples were done in wavelength region from 1350 to 2450nm. As can been seen in Figure 2, the clear different of spectra measurement can be observed in wavelength region between 2100 and 2200 nm due to the absorption band of fatty acids with the cis-double bonds. The cis-double bonds normally presence as in the cis-unsaturated fatty acids in the animal fat and vegetable oil (Ng et al., 2007). Soybean oil is known for its higher contains of unsaturated fatty acids compared to the saturated fatty acids. The NIR absorbance value is decreased as the concentration of chicken fat adulteration increased. Adding the chicken fat content will decrease the unsaturated fatty acids in the sample.

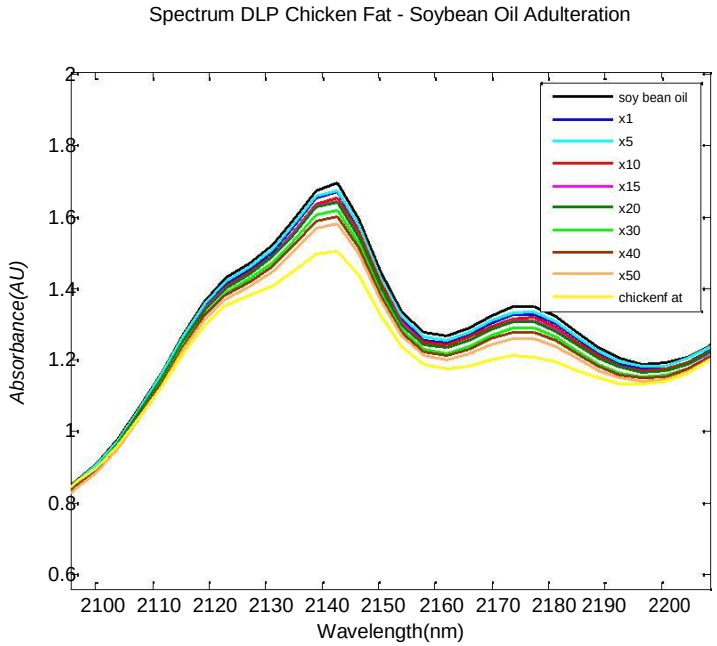

Figure 2. Plot of soybean oil, 1%-50% chicken fat in soybean oil and pure chicken fat.

Chemometrics

In chemometrics, the classification is used to sort the samples into individual classes depends with the numerical values of variables. This feasibility study will use a two class classification as to separate the pure sample and adulterated sample. For chemometrics analysis, the spectra measurement range used is between 1350 and 2240nm. The model used to classify the pure and adulterated sample was constructed by using a supervised technique

namely Soft Independent Modelling of Class Analogy (SIMCA). In SIMCA, a class is modeled by means of principle component and employed to classify the samples into their specific group. For this study, the principal component is 12. As per Figure 3 below, the pure soybean oil and adulterated oils are 100% correctly classified.

```
How many PC do you want to retain?   12
How many PC do you want to retain?   12
-----------------------------------------
             Actual Classes
-------------1--------2-----
Predicted|
  Classes|
_________|_________________
       1 |    15.0 |    0.0
       2 |    0.0 |    120.0
-----------------------------------------
-----------------------------------------
             Actual Classes
-------------1--------2-----
    TP |   15.00 |   120.00
    FP |   0.00 |   0.00
    FN |   0.00 |   0.00
    TN |   120.00 |   15.00
Preci. |   1.00 |   1.00
Sensi. |   1.00 |   1.00
Speci. |   1.00 |   1.00
-----------------------------------------
Model Accuracy is 1.00
-----------------------------------------
```

Figure 3. Classification result from SIMCA.

For chemometrics analysis, the quantification of the soybean oil in the adulterated oil samples was performed using Partial Least Squares (PLS) model. For chemometrics evaluation, the samples of all adulteration oils were divided into a calibration and test set. Therefore the measured data is divided into 70% for calibration set and 30% for test using Kennard Stone algorithm. From PLS, the correlation of determination (R^2) of calibration set R^2C and test set or prediction R^2P for chicken fat adulterated in soybean oil is 0.9996 and 0.9994 respectively. Meanwhile, the RMSEC and RMSEP is 0.3434 and 0.4033 respectively. The small value of RMSEP indicated that the PLS model able to estimate the lower percentage of chicken fat adulteration. Moreover, the test plot is overlapping with the calibration plot as in Figure 4. This showed that the test set be able to fit correctly with the calibration data.

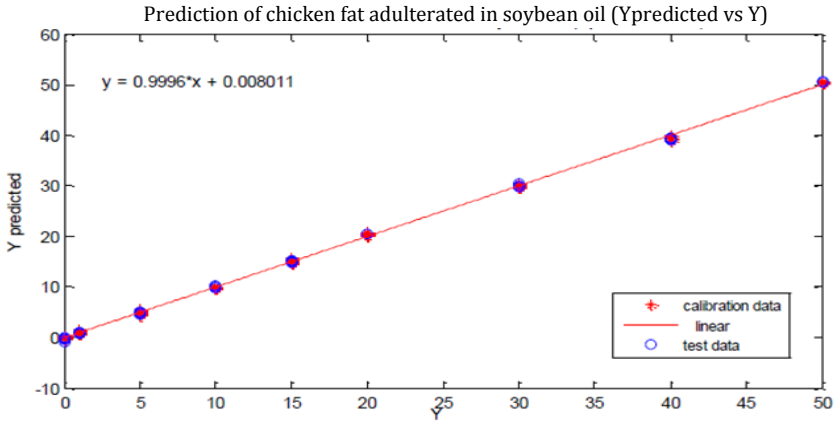

Figure 4. Prediction of actual value of adulterant (chicken fat) and NIR predicted value.

CONCLUSIONS

The following conclusions can be drawn from the study:

- It has been shown in this work that it is feasible to use the NIR spectroscopy combined with chemometrics analysis to detect chicken fat adulteration in soybean oil with above 1% adulteration.
- The pure soybean oil and adulterated sample is correctly classified. The result can be

improved further if one were to use a spectrometer with better resolution but the fact that the size of the present setup is small gives advantage in for example on-site screening of edible oil adulteration .

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