

## Rapid Differentiation of Commercially-Available Soy Sauces using Near-Infrared Spectroscopy

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### ABSTRACT

*Near-infrared (NIR) spectroscopy was used to differentiate between four leading brands of soy sauce in the Philippines; the local brands included Datu Puti (DP), Marca Piña (MP), and Silver Swan (SS). A naturally-brewed imported brand, Kikkoman (KK), was used for comparison. Spectral data of soy sauce samples were acquired in absorbance mode from 900 nm to 1700 nm. First- (1D) and second- (2D) derivative transforms of preprocessed spectral data were analysed by a combination of principal component analysis (PCA) – linear discriminant analysis (LDA), and by partial least squares regression (PLSR). Spectral data with no derivative (ND) transformation was analysed for comparison. Preprocessing methods included mean scatter correction (MSC), Savitzky-Golay (SG) smoothing, and standard normal variate (SNV); these were used in different combinations to determine the best treatment. PCA-LDA results showed that the MSC-SG-ND treatment gave the best result overall with 97.6% of samples classified correctly, and 96.9% of variability explained by two principal components. For PLSR, data preprocessed using SNV-SG-2D transformation gave the best results after cross-validation, with a 9-factor model with root mean square error (RMSE) and coefficient of determination ( $R^2$ ) of 0.114 and 0.989, respectively. Using an independent set of soy sauce samples, the PLSR model was able to correctly identify 100% of DP, KK and MP; however, all SS samples were misclassified as DP or MP. This underscores the need for extensive sampling to build up a spectral library of soy sauce from different brands and sources; this will enable rapid testing of products for authenticity, quality and safety.*

**Keywords:** NIR spectroscopy; spectral fingerprint; soy sauce; differentiation; chemometrics

**Abbreviations:** 1D – 1st order differentiation; 2D – 2nd order differentiation; AIC – Akaike information criterion; LDA – linear discriminant analysis; MC – mean centering; MSC – multiplicative scatter correction; ND – no differentiation; NIR – near-infrared; PCA – principal component analysis; PLSR – partial least squares regression; RMSE – root mean square error; SG – Savitzky-Golay; SNV – standard normal variate; VIP – variable of importance for projection

### INTRODUCTION

Soy sauce is a popular food condiment produced by fermenting soybean with other ingredients such as wheat, rice, brine solution and fermenting culture of

fungi for 6-8 months (Fukushima, 2004; Liu, 2015). During fermentation, proteins, carbohydrates and other components of soybeans and wheat are converted to peptides, amino acids, sugars, alcohols, and other low molecule compounds that define the soy sauce's aroma and unique taste (a combination

of tartness, sweetness, and saltiness) (Sanchez, 2008; Lee, 2015). The reaction between sugars and amino acids produces the brown hue of soy sauce (Liu, 2012).

Soy sauce can also be produced by acid hydrolysis of vegetable protein (acid-HVP) for 12 to 16 hours (Gao *et al.*, 2015). During acid-HVP, proteins and carbohydrates from defatted soybeans and wheat gluten, respectively, are chemically digested with hydrochloric acid and sodium hydroxide (Sano *et al.*, 2007). However, soy sauce produced by acid-HVP contain carcinogens such as 3-monochloro-1,2-propanediol (3-MCPD) and 1,3-dichloropropanol (1,3-DCP) (Baer *et al.*, 2009). International food standards specify a maximum limit of 0.4 mg kg<sup>-1</sup> for 3-MCPD (Codex Alimentarius, 2015) with the Philippine government imposing this limit in June 2012 (DOH-FDA, 2011). Other compounds such as dark humins, levulinic acid, formic acid, dimethyl sulfide, hydrogen sulfide and furfurals that cause unnatural flavors and strong off-odor are present (Liu, 2012; Fukushima, 2004). Moreover, some essential amino acids are degraded during chemical hydrolysis resulting in a less nutritious product (Gao *et al.*, 2015; Zhu *et al.*, 2009).

The ability to rapidly manufacture a cheap alternative to naturally fermented soy sauce has resulted in fraudulent practices such as mislabelling acid-hydrolysed product as pure fermented soy sauce (Sano *et al.*, 2007) or mixing brine solution, monosodium glutamate, and dark soy sauce in suitable ratios (Natcha & Panmanas, 2014). A report by the non-profit organization Food & Water Watch (FWW) shows that China's food safety system suffers from major deficiencies that have allowed manufacturers to produce adulterated, unsafe or contaminated products such as milk powder, seafood and honey. Among the scandals is a report of imitation soy sauce containing hair clippings (Tang and Babich, 2014); more recently, family-owned companies in Tianjin were discovered to have been manufacturing fake condiments (including soy sauce) for up to 10 years using unsafe ingredients and practices (CNN Philippines, 2017). However, despite the numerous food scandals periodically originating from this country, many food processors now find that China is too important

to abandon as a source of ingredients and raw material (Zhang and Xue, 2016; FWW, 2011).

High-performance liquid chromatography (Zhu *et al.*, 2009) fluorescence resonance energy transfer (Gao *et al.*, 2015), and liquid chromatography coupled with mass spectrometry (Sano *et al.*, 2007) have been used to differentiate between purely fermented and chemically synthesized soy sauce. However, these methods require extensive sample preparation, chemical reagents and buffers, specialized training and costly instruments. Near-infrared (NIR) spectroscopy can potentially detect adulteration of soy sauce (Natcha and Panmanas, 2014), and differentiate between soy sauce made from whole or defatted soybean (Kinoshita *et al.*, 1998; Iizuka and Aishama, 1999). NIR spectroscopy is also rapid, requires minimal sample preparation, and can be operated with minimal training once a suitable and robust calibration model has been developed. This method can provide a rapid way of differentiating between various soy sauce products manufactured under different methods. The general objective of the study was to develop a NIR spectroscopy method to differentiate between locally manufactured soy sauce products in the Philippines with reference to an imported brand considered as naturally fermented soy sauce. However, the study was limited to selected local brands and focuses on soy sauce samples in plastic packs. Results of the study could then be used as a basis for later development of a portable instrument for market surveillance.

## METHODOLOGY

### Sampling Scheme and Sample Preparation

Samples of soy sauce of various brands were obtained from six different markets and department stores (designated as A, B, C, D, E and F) in the municipality of Los Baños, Laguna province. Three popular brands of soy sauce manufactured in the Philippines were used for the study: Datu Puti (DP), Marca Piña (MP) and Silver Swan (SS). The imported Kikkoman (KK) brand was considered as a purely fermented product (Kikkoman, 2014) and used for comparison. For DP, MP and SS, three 10-mL replicate samples were taken from each pack;

for KK, five 5-mL replicate samples were obtained (Table 1). All pouches were stored at room temperature ( $\approx 25^\circ\text{C}$ ). Samples were passed through Whatman filter paper to remove any suspended solids prior to spectra acquisition. These samples served as a training set for developing models for predicting brands of soy sauce.

A separate set of soy sauce samples (3 packs per brand) was purchased from one market to serve as a prediction set. Three 10-mL samples were extracted from each pack for spectral data acquisition.

### Spectral Data Acquisition

All components of the NIR spectra acquisition system were manufactured by Ocean Optics (Florida, USA). Spectra were acquired in absorbance mode using a NIRQuest 512 spectrometer with a useable wavelength range of 900-1700 nm. A tungsten-halogen lamp (HL-2000) was used as the light source. Spectrasuite software (2011 release, Ocean Optics, Florida, USA) was used for instrument control and data recording; the following settings were used: integration time = 15 ms, scans to average = 30, boxcar width = 5 nm. A reference spectrum was recorded using distilled water in a quartz cuvette (10-mm path length) as a blank solution; this served to subtract the contribution of water to the spectral signature. Dark spectrum was recorded with the spectrometer filter slot blocked to prevent the entry of light. Data acquisition was performed at room temperature ( $\approx 25^\circ\text{C}$ ) at all times.

Each sample replicate was scanned twice; hence, 180 NIR spectra were obtained for each brand (Table 1), giving a total of 720 spectra to form the training set. Similarly, for the separate prediction set, 18 NIR spectra were recorded for each brand, or a total of 72 spectra. Data at the opposite ends of the operating range of the spectrometer were discarded 50 nm from the minimum and maximum wavelengths to eliminate spectral noise. The training set of 720 spectra was randomly divided to form a

**Table 1. Sampling scheme for soy sauce by brand for the training set\***

BRAND (PACK SIZE)	NUMBER OF SAMPLE PACKS		REPLICATE SAMPLES PER PACK (X)	TOTAL NUMBER OF SPECTRA (W)
	Per Market (Z)	Total (Y)		
Datu Puti (200 mL)	5	30	3	180
Marca Pina (220 mL)	5	30	3	180
Silver Swan (200 mL)	5	30	3	180
Kikkoman (100 mL)	3	18	5	180
Grand Total				720

\* $Y = (Z) \cdot (6 \text{ markets}); W = (Y) \cdot (X) \cdot (2 \text{ scans per replicate})$

**Table 2. Combinations of data preprocessing and pretreatment methods using ParLeS ver. 3.1**

TREATMENT NUMBER	TRANSFORMATION COMBINATIONS <sup>Z</sup>
1	No transformation
2	MSC – SG – ND
3	MSC – SG – 1D
4	MSC – SG – 2D
5	SNV – SG – ND
6	SNV – SG – 1D
7	SNV – SG – 2D

<sup>Z</sup>Abbreviations: 1D – first derivative; 2D – second derivative, MSC – mean scatter correction; ND – no derivative; SG – Savitzky-Golay; SNV – standard normal variate

calibration set (120 samples per brand) and validation set (60 samples per brand).

### Preprocessing and Pretreatment of Spectral Data

ParLeS version 3.1 (Viscarra-Rossel, 2007) was used to preprocess and pretreat the NIR spectra of each sample as shown in Table 2. These procedures serve to smooth out the spectral curve, scale the spectra, eliminate scattering effects, and identify peaks and valleys that correspond to wavelengths that contribute significantly to correct prediction. All spectra were scaled using mean centering.

### Principal Component Analysis and Linear Discriminant Analysis of Pretreated NIR Spectra

Principal component analysis (PCA) and linear discriminant analysis (LDA) were used to generate

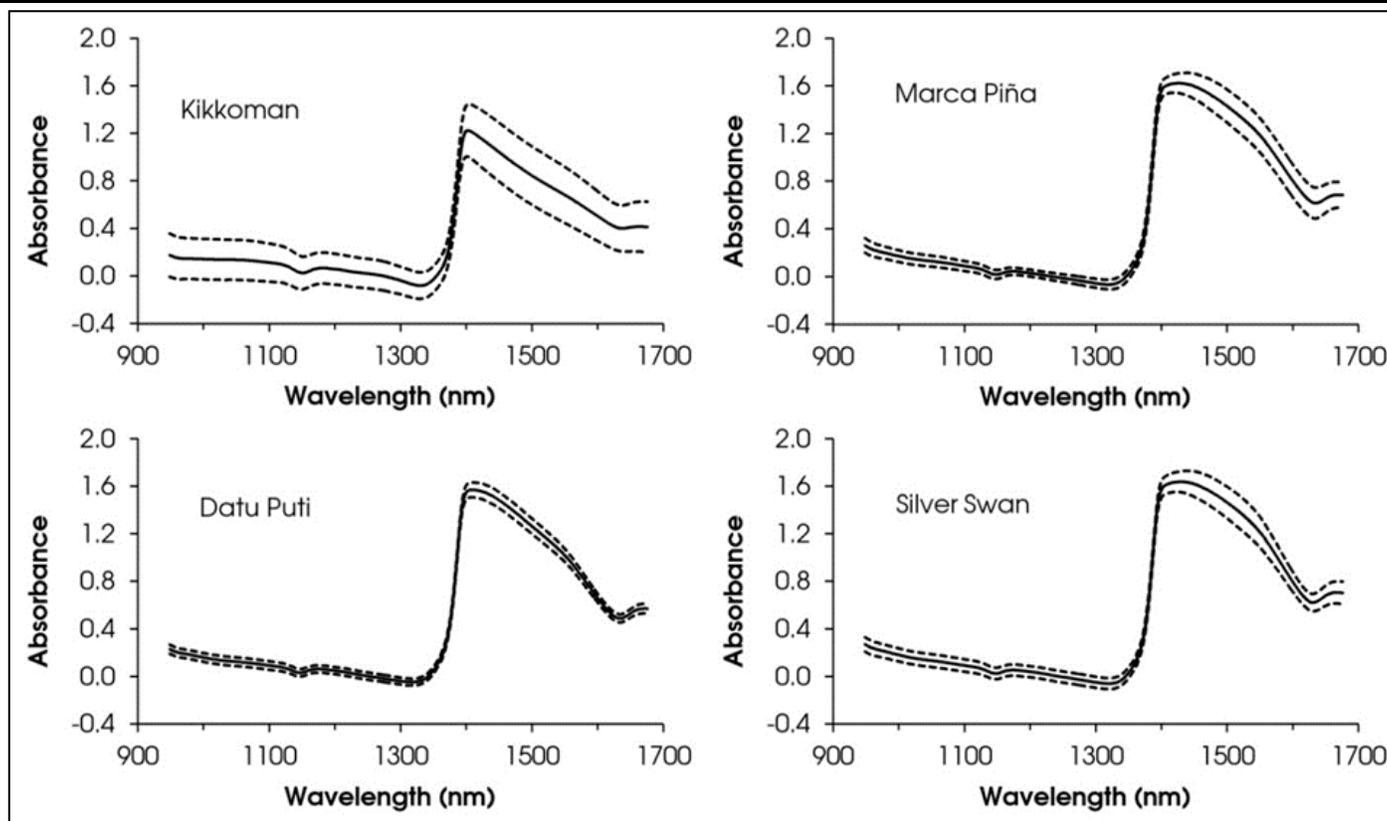


Figure 1. NIR spectral fingerprint of popular brands of soy sauce available in the Philippines. Solid lines represent the average spectral profile of 180 sample spectra for each brand; dotted lines denote the 95% confidence interval.

mathematical models to classify soy sauce samples according to brand. ParLeS ver. 3.1 (Viscarra-Rossel, 2007) was used to perform PCA, while the XLSTAT add-in for Microsoft Excel 2013 was used for LDA.

PCA was performed for a maximum of 10 principal components. LDA was subsequently performed using the scores for the first principal components derived from PCA that explain at least 95% of the variability in the NIR spectral data. Classification of samples was made using the LDA models of all combinations of pretreatment methods.

### Partial Least Squares Regression

Partial least squares regression (PLSR) was performed using ParLeS ver. 3.1 (Viscarra-Rossel 2007) to form regression models to predict the brand of a sample of soy sauce. Numerical values were assigned to each brand (to serve as a dummy

variable) as follows: DP = 1, MP = 2, SS = 3, KK = 4. The optimal number of factors in the regression model was determined using leave-one-out cross-validation up to a maximum of 30 PLSR factors using the calibration data set. Only treatment combinations (shown in Table 5) with a low number of PLSR factors and high  $R^2$  values were considered for further validation and prediction.

## RESULTS AND DISCUSSION

### Spectral Fingerprinting of Soy Sauce Brands

The mean NIR spectral profile of each soy sauce brand as a function of wavelength is shown in Figure 1. From the visual inspection of the profiles, in Figure 1, no obvious differences between brands can be observed. All brands have a strong absorption band near 1400 nm, with Kikkoman soy sauce having the sharpest peak. Absorption at 1170 nm to 1180 nm are mainly related to the C–H stretch

second overtone of sugars and alkenes. The NIR absorption at 1660 nm, on the other hand, are mainly due to the C–H stretch first overtone of compounds having methylene group (–CH<sub>2</sub>). Lastly, the strongest absorption in 1400 nm can be associated with the O–H stretch, first overtone in phenols and alcohols (Workman & Weyer, 2008; Shenk *et al.*, 2008). First- and second-derivative spectra also showed no obvious differences between brands (data not shown). However, the 95% confidence intervals for KK spectra were greater compared to the three local brands (Figure 1), possibly indicating a greater variation in components of the naturally fermented brand.

**Table 3.** Percentage of correct classification of soy sauce samples by brand using linear discriminant analysis of principal component scores

TREATMENT NUMBER	TRANSFORMATION AND PRE-PROCESSING COMBINATIONS <sup>z</sup>	% CLASSIFICATION BY BRAND				% CORRECT CLASSIFICATION
		DP	KK	MP	SS	
1	No transformation	98.3	100.0	82.8	42.2	80.8
2	MSC – SG – ND	100.0	100.0	96.7	93.9	97.6
3	MSC – SG – 1D	100.0	100.0	62.2	93.9	89.0
4	MSC – SG – 2D	100.0	55.0	72.2	80.6	76.9
5	SNV – SG – ND	100.0	100.0	96.7	93.9	97.6
6	SNV – SG – 1D	100.0	100.0	62.2	92.8	88.8
7	SNV – SG – 2D	0.0	7.8	52.8	61.7	30.6

<sup>z</sup>Abbreviations: 1D – first derivative; 2D – second derivative, DP – Datu Puti, KK – Kikkoman, MP – Marca Piña, MSC – mean scatter correction; ND – no derivative; SG – Savitzky-Golay; SNV – standard normal variate, SS – Silver Swan

### Discriminant Analysis

The preprocessing and transformation treatments for spectral data produced PCA models that accounted for more than 90% of variation; results of

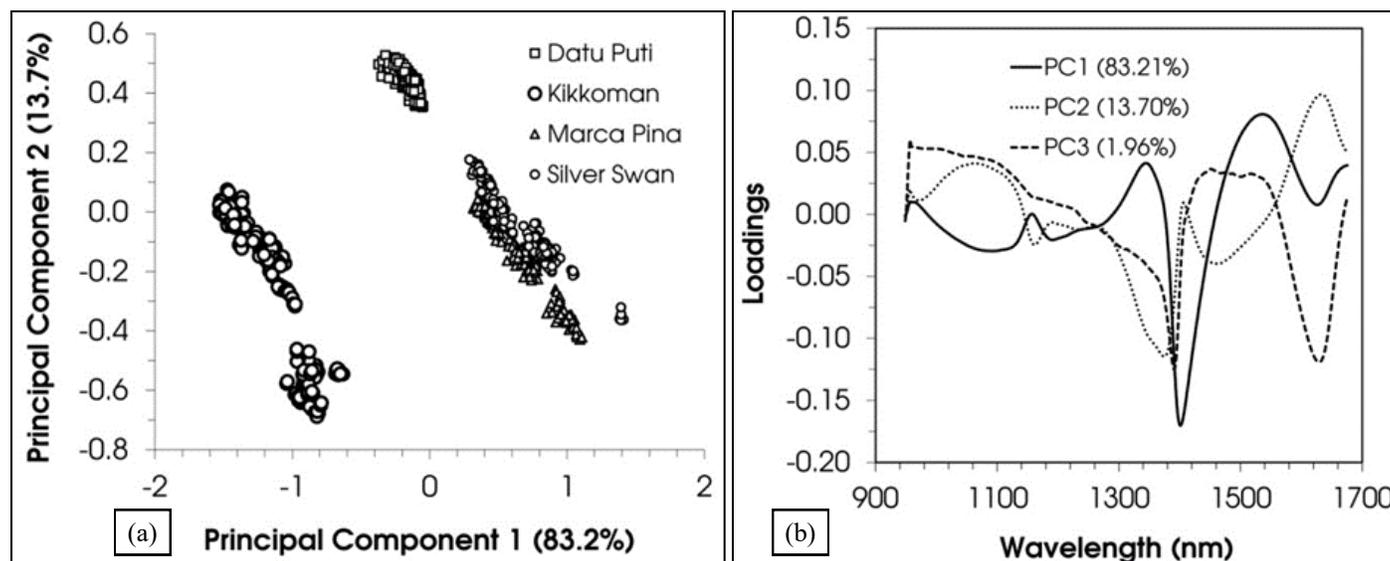


Figure 2. Results of principal component analysis for differentiation between soy sauce brands using Treatment 2 (mean scatter correction, Savitzky-Golay smoothing, and no differentiation): (a) score plots of the first two principal components (PC); (b) loading scores for PC 1, 2 and 3 versus wavelength.

Table 4. Absorption bands and functional groups of NIR wavelengths<sup>z</sup> with high loadings in the first three principal components of PCA.

WAVELENGTH (nm)	NIR ABSORPTION BAND	FUNCTIONAL GROUP
1350, 1380, 1400, 1460, 1545	C–H combination	Hydrocarbons Sugars
1400	O–H stretch, first overtone	Phenols (2-methoxy phenol) Alcohols (methanol, ethanol)
1460	N–H stretch, first overtone	Secondary amine
1545	O–H-stretch, C–H stretch, first overtone	Carboxylic acid (acetic acid, propanoic acid, benzoic acid); Sugars
1630, 1640	C–H stretch, first overtone	Alkenes, other compounds containing C–H aromatic groups

<sup>z</sup>Source: Workman & Weyer, 2008; Shenk *et al.*, 2008; Yokotsuka, 1986

Table 5. Performance of data preprocessing treatments using partial least squares regression with leave-one-out cross-validation for predicting soy sauce brands.

TREATMENT NO.	TRANSFORMATION COMBINATIONS <sup>z</sup>	CROSS-VALIDATION RESULTS <sup>z</sup>			
		No. of Factors	RMSE	R <sup>2</sup>	AIC
1	No transformation	16	0.071	0.996	-1239
2	MSC – SG – ND	16	0.075	0.996	-1214
3	MSC – SG – 1D	11	0.075	0.995	-1219
4	MSC – SG – 2D	9	0.115	0.989	-1022
5	SNV – SG – ND	16	0.069	0.996	-1254
6	SNV – SG – 1D	11	0.075	0.995	-1221
7	SNV – SG – 2D	9	0.114	0.989	-1022

<sup>z</sup>Abbreviations: 1D – first derivative; 2D – second derivative; AIC – Akaike Information Criterion; MSC – mean scatter correction; ND – no derivative; RMSE – root mean square error; SG – Savitzky-Golay; SNV – standard normal variate

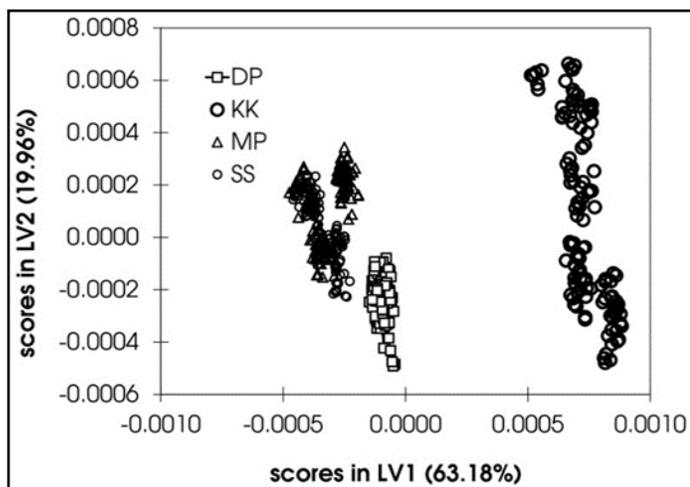


Figure 3. Score plot of partial least squares regression using a 9-factor model of NIR spectral data subjected to standard normal variate, Savitzky-Golay smoothing, and 2nd derivative differentiation.

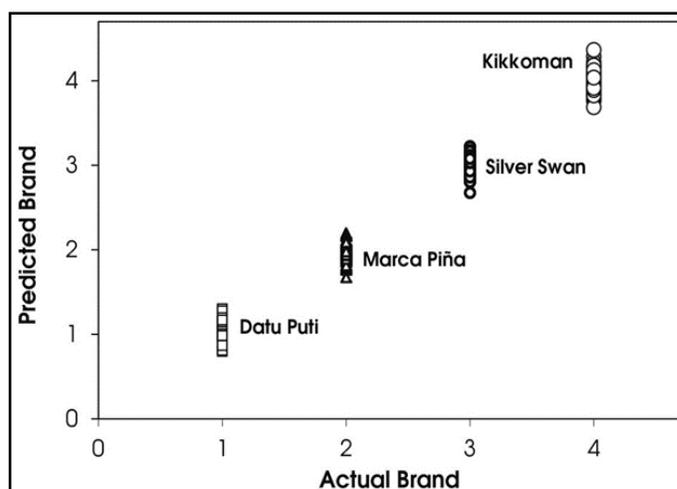


Figure 4. Performance of the partial least squares regression model using validation set of samples.

**Table 6. Identification of significant wavelengths based on performance of the partial least squares regression model of Treatment 7**

MEASURE OF PERFORMANCE	INTERPRETATION	WAVELENGTH BANDS WITH SIGNIFICANCE (nm)
Regression coefficients	Large absolute values (> 1000) indicate that a wavelength has a significant effect on prediction (Liu <i>et al.</i> , 2008; Mehmood <i>et al.</i> , 2012)	1130 – 1300 1400 – 1500 1650
Loading weights	Absolute value of loading weights > 0.04 indicate useful wavelengths (Liu <i>et al.</i> , 2008)	1400 – 1460 1500 – 1550
VIP	Indicates the contribution of each wavelength according to the variation explained by each latent variable or PLSR factor (Wold <i>et al.</i> , 2001; Mehmood <i>et al.</i> , 2012); wavelengths with VIP scores > 7.5 were considered significant	1400 – 1460 1500 – 1540

**Table 7. Validation results of the 9-factor partial least squares regression model of Treatment 7<sup>z</sup> for predicting soy sauce brand using the prediction set**

ACTUAL BRAND <sup>z</sup>	PREDICTED BRAND				TOTAL	% CORRECT CLASSIFICATION
	DP	KK	MP	SS		
DP	18	0	0	0	18	100.0%
KK	0	18	0	0	18	100.0%
MP	0	0	18	0	18	100.0%
SS	9	0	9	0	18	0.0%
Total	27	18	27	0	72	75.0%

<sup>z</sup>Treatment 7 used standard normal variate, Savitzky-Golay smoothing and 2<sup>nd</sup> derivative transformation of spectral data

<sup>y</sup>Abbreviations: DP – Datu Puti; KK – Kikkoman; MP – Marca Piña; SS – Silver Swan

subsequent LDA on PCA scores showed that using 1<sup>st</sup> and 2<sup>nd</sup> derivative transformation decreased the percentage of samples correctly classified according to brand (Table 3). The treatments with the highest percentage of correctly classified samples (97.6%) were Treatments 2 and 5 (combination of mean scatter correction or standard normal variate, with Savitzky- Golay smoothing and no differentiation). A plot of scores for the first two PCs of these treatments showed, however, that Treatment 2 gave the best classification results due to tighter clustering of samples according to brand (Figure 2a) and a slightly higher percentage (by 0.05%) of explained variation compared to Treatment 5. The first PC accounted for 83.2% of variation in NIR spectral data and represented the largest difference between brands. All KK and DP samples were correctly classified, while overlaps in the scores plot could account for the misclassification observed for MP and SS samples (Figure 2a).

The spectral loadings plotted against wavelength of the first three PCs are shown in Figure 2b. For each PC, wavelengths having large absolute loading values are considered to have a high contribution to the variability explained by the PCA model (Grootveld, 2014). The highest loadings for each PC were observed as follows:

PC1: 1350, 1400 and 1545 nm

PC2: 1380, 1460 and 1640 nm

PC3: 1390 and 1630 nm.

High loadings at these wavelengths may be attributed to major chemical constituents of soy sauce like alcohols, acids, and sugars (Table 4). These compounds, either singly or in combination with other components, have the strongest influence for discriminating between soy sauce brands.

### Partial Least Squares Regression

Table 5 shows the best results of PLSR analysis of transformed spectral data, where

up to 30 factors were tested. For selection of the best model, the number of PLSR factors must be as few as possible but must comprise all relevant information in the spectra; furthermore,  $R^2$  value must be as close to 1 as possible, while both RMSE and AIC values must be below (Nicolai *et al.*, 2007; Moghimi *et al.*, 2010; Viscarra Rossel, 2007). Based on these criteria, Treatment 7 (SNV-SG-2D) was selected for further validation.

A plot of the first two PLSR scores or latent variables (LV), designated as LV1 and LV2, clearly shows clustering according to brand (Figure 3). Clustering was more pronounced between KK samples and the three local brands. Among the local brands, DP samples could be clearly separated from MP and SS samples. The wider dispersion within the KK cluster could again be due to the natural brewing process used by the manufacturer. In comparison, the tight clustering observed for DP, MP and SS samples may be indicative of production through chemical hydrolysis, thus yielding products with definite and similar chemical composition regardless of processing batch (Ignacio, 1996).

### Selection of Effective Wavelengths

Wavelengths of significance can be identified through their regression coefficients, loading weights, and VIP values (Table 6); by combining these indicators, eleven wavelengths with the most significance were identified: 1402, 1407, 1413, 1420, 1426, 1431, 1505, 1514, 1519, 1524 and 1530 nm.

### Validation of the PLSR Model using Test Set of Samples

Using the best PLSR model on the validation set showed that this method could be used for classifying samples according to brand (Figure 4). Using a threshold value of  $\pm 0.5$  in the assessment of the predicted values for brand (DP: 0.5 – 1.5; MP: 1.5–2.5; SS: 2.5–3.5, and; KK: 3.5–4.5), the 9-factor PLSR model was able to correctly classify all soy sauce samples according to brand.

Final validation using the separate prediction set showed similar results for DP, KK and MP samples

(Table 7). The model, however, misclassified all SS samples as either DP or MP. Since the prediction set was composed of samples purchased one month after the training set, this could be due to large variations between the two batches of SS samples. The processing methods, ingredients, and conditions could be different between these particular batches of soy sauce, resulting in the misclassification. This emphasizes the need for more substantial sampling of soy sauce products with respect to manufacturing source to strengthen the PLSR model and improve its accuracy.

## SUMMARY AND CONCLUSION

The study showed that soy sauce brands could be separated according to their NIR spectral signatures through the use of combined principal component analysis (PCA) – linear discriminant analysis (LDA), or by partial least squares regression (PLSR) analysis. Wavelength regions with a high degree of contribution to the models were identified which are related to chemical components present in soy sauce. For PCA-LDA, the best classification was achieved using mean-centered spectral data that was pre-processed using mean scatter correction and Savitzky-Golay smoothing. For PLSR, the use of standard normal variate, Savitzky-Golay smoothing and 2<sup>nd</sup> derivative transformation on mean-centered data gave the best results for predicting soy sauce brand.

Results of the study could serve as a basis for the eventual development of a portable instrument for rapid testing of soy sauce products to detect adulteration, predict authenticity or test for safety. However, extensive sampling is needed to make regression models more robust and to build up a spectral library of different brands and sources of soy sauce.

## RECOMMENDATIONS

NIR spectroscopy was proven to be feasible in discriminating between locally manufactured soy sauces. It is recommended to study the effect of the type of packaging material in the spectral fingerprint of different soy sauce brands. A study to check the effect of storage duration and conditions on the

spectral fingerprint is also recommended. The application of NIR spectroscopy in determining soy sauces' chemical properties such as pH, salt, total solids, total nitrogen, amino acids, and the like can also be done.

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