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Non-destructive analysis of glycyrrhizin in Ummaruekvati dispensatory Thai traditional medicine

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ABSTRACT

Ummaruekvati is an antitussive traditional medicine. It contains licorice as the main ingredient and the major chemical component is glycyrrhizin. The conventional method for quantitative analysis of glycyrrhizin content in licorice is by high-performance liquid chromatography, which is destructive of the sample, time consuming, high cost, and has many steps in the sample preparation process. In this study, a rapid and non-destructive near-infrared spectroscopy (NIR) method was applied for quantitative analysis of glycyrrhizin content in Ummaruekvati dispensatories. A partial least squares chemometric method with various data pre-treatments was performed to establish the calibration model. The best calibration model was obtained using baseline correction over the wavelengths of 1000–2500 nm with four principle components. It showed a high coefficient of determination (R^2 = 0.9392), low root mean squared error of cross-validation (RMSECV = 0.0532), and low standard error of calibration (SEC = 0.0516). The average predicted results of glycyrrhizin content in five tested Ummaruekvati dispensatories were 91.74% with the percentage of relative standard deviation of 11.49. The results showed that non-destructive NIR spectroscopic analysis combined with chemometrics can be used for routine quality control of glycyrrhizin content in Ummaruekvati dispensatories with advantages of reduced time with no sample preparation or sample loss.

Keywords: Chemometrics, licorice, near-infrared spectroscopy, partial least squares, quantitative analysis, Ummaruekvati dispensatory

INTRODUCTION

Ummaruekvati is a Thai Traditional Medicine listed in Thailand National List of Essential Medicines as an antitussive drug.[1] It is composed of six herbs; licorice (50%), terminalia gall (KN, 10%), cumin seeds (TN, 10%), coriander seeds (LN, 10%), emblic myrobalan (PN, 10%), and belleric myrobalan (SN, 10%). The main ingredient is licorice which has been used as a medicinal herb in China for many years[2] and is ranked as the second most prescribed herb in China after ginseng.[3] The efficacy and quality of licorice raw material differs widely not only according to the different plant parts used but also to the geographic area of cultivation, harvest time, and growing conditions. All of these factors can result in large quality variations even after implementing restricted material selection procedures.[4] The quality of raw licorice herb products is generally assessed by visual inspection which is somewhat subjective and biased. The Chinese Pharmacopoeia specifies that licorice powder must contain glycyrrhizin not less than 2.0%.[5] Therefore, the glycyrrhizin content should be measured to guarantee the quality of Ummaruekvati dispensatory.

Conventional analysis of glycyrrhizin content in licorice is by high-performance liquid chromatography (HPLC) due to its good specificity, accuracy, precision, and quantification parameters.[6] However, the disadvantages of HPLC are the many steps of sample preparation, the destruction of samples, the time taken to perform the analysis, and the high cost.[6] In recent years, several non-destructive analyses, which do not destroy or damage the sample being tested, have been employed to solve these problems and to meet the requirements of high-throughput analysis.[7-10] Vibrational spectroscopic technology such as near-infrared spectroscopy

(NIR) has been integrated with chemometrics to provide a rapid and powerful analytical tool for the non-destructive analysis of herbal medicines.[11-14] Peerapattana *et al*.[15] quantitatively analyzed alpha-mangostin in hydrophilic ointment using NIR. They also used NIRs for quantitative analysis of alpha-mangostin in mangosteen pericarp powder and capsule.[16] Zhang and Ye[17] had review the chemical analysis of the Chinese herbal medicine Gan-Coa (licorice). NIR was one of the analytical methods reported in that paper. Chen and Sorensen[18] employed NIRs to determine the content of glycyrrhizic acid in licorice. This method showed similar precision and accuracy to HPLC. Wang *et al*.[6] developed a rapid, non-destructive, and real-time method for the determination of glycyrrhizic acid in Glycyrrhiza uralensis using fiber-optic NIR spectroscopy. It was also used for the classification of licorice samples according to their growing conditions, geography areas, and plant part.[19] There were many reports of using NIRs for quantitative analysis the active pharmaceutical ingredient in herbal medicine.[20] Chemometrics are used to interpret NIR spectra as the absorption peaks are broad and overlap, making single wavelength calibration impossible. Here, we report the establishment of a calibration model for quantitative analysis of glycyrrhizin content in Ummaruekvati dispensatory using NIR spectroscopy in combination with chemometrics. For verification, the obtained model was used to predict the glycyrrhizin content of both internal and external sample data sets and compared with the HPLC reference method. The qualitative classification of licorice samples from different sources was also established.

MATERIALS AND METHODS

Plant Materials

All plant materials were purchased from herbal drug stores in Bangkok and Sakon Nakhon, Thailand, between January and June 2017 and identified by Dr. Prathan Luecha. Licorice root powders were bought from Wetchapong (Bangkok, G01), Jaogreumper (Bangkok, G02), Hua Cheaw (Bangkok, G03), Tai An Jarn (Bangkok, G04), and E-Sae (Bangkok, G05). Terminalia gall (KN, Jaogreumper), cumin seeds (TN, E-Sae), coriander seeds (LN, Bom Bae Panitch, Bangkok), emblic myrobalan (PN, Tai An Jarn), and belleric myrobalan (SN, local market, Sakon Nakhon) were bought in the form of dried material. All ingredients were tested for their physical and chemical properties according to the methods described in the Thai Herbal Pharmacopoeia.[21] Each herb was milled with a grinder and passed through 80 mesh sieve (pore size 177 μm) before use.

Sample Preparation for Calibration Model and Internal Validation Data

To create a robust calibration model, an appropriate experimental design has to be implemented.[22] The D-optimal design (Design-Expert® Version 9, Stat-Ease, USA) was used to design the composition of the mixtures. The range of each herb was ± 50% of the target concentration. The six herbs were mixed according to the ratios, as shown in Table 1. All ingredients were put in a plastic bottle with 15 metal balls (diameter 4 mm) as a mixing aid. The bottle was mixed for 20 min on a Y-shaped blender (Model: PA, Type: 15, LM Machinery, USA). The batch size of each mixture was 30 g. For the calibration set, only licorice from Hua Cheaw (G03) was used due to the limitations of licorice raw materials.

Table 1: Composition of each formulation (in percent) created by Design-Expert® Software

Run	Licorice	KN (%)	TN (%)	LN (%)	PN (%)	SN (%)
	G03 (%)					
1	54	11	11	5	14	5
2	48	5	12	5	15	15
3	42	15	7	15	6	15
4	34	15	15	12	15	9
5	62	5	6	5	7	15
6	53	11	15	11	5	5
7	41	10	12	10	13	15
8	44	5	6	15	15	15
9	75	5	5	5	5	5
10	59	15	6	9	6	5
11	63	5	5	10	11	6
12	50	15	5	5	12	12
13	63	5	5	10	11	6
14	65	5	5	15	5	5
15	68	5	11	5	7	5
16	61	5	11	10	5	8
17	54	5	6	15	10	11
18	51	14	12	5	5	12
19	55	5	15	5	10	10
20	60	10	5	10	5	11
21	45	11	10	15	9	9
22	45	5	15	15	15	5
23	45	15	15	5	12	8
24	56	5	7	5	15	11
25	49	11	5	15	15	5
26	45	5	15	15	5	15
27	49	15	5	10	5	15

Sample preparation for prediction data

Five Ummaruekvati dispensatories (W01, W02, W03, W04, and W05) were prepared by mixing licorice from the five commercial suppliers (G01, G02, G03, G04, and G05, 50%) with five herb powders (KN, TN, LN, PN, and SN, 10% each). The source of licorice was varied because it is the major component of the formula and different sources may show different glycyrrhizin content.[6]

Calibrated standard glycyrrhizin curve

The glycyrrhizin content was measured using Agilent gradient HPLC. The analysis was performed on a TSKgel® ODS-80Ts

HPLC C18 (octadecyl) column (L× I.D. 25 cm × 4.6 mm, 5 μm particle size) with UV/Vis detector at 237 nm. The elution was carried out with acetonitrile as mobile phase A and 0.05% phosphoric acid as mobile phase B at a flow rate of 1 mL/min. The elution gradient of HPLC mobile phase followed the Chinese pharmacopoeia [Table 2].[5] The sample injection volume was 10 μL. The analysis time was 40 min.

Standard glycyrrhizin (TCI, Japan) was accurately weighed and dissolved in 70% ethanol in a volumetric flask to produce 200 μg/ml of standard stock solution. Then, aliquots of the standard stock solution were diluted to 5, 10, 50, and 100 μg/ml. The standard glycyrrhizin solutions were filtered through a syringe filter (0.45 μm) and glycyrrhizin contents were measured using HPLC according to the same conditions. The calibrated standard curve between peak area and glycyrrhizin concentration was plotted. The correlation of the HPLC peak area and glycyrrhizin concentration was calculated.

This HPLC analytical method was validated in terms of precision by injection of standard glycyrrhizin at five different concentrations (5, 10, 50, 100, and 200 μg/ml) in the same day for repeatability (within-day precision) and in different day for intermediate precision (between-day precision). The results were calculated for percentage of relative standard deviation (%RSD) and the value should not over 10%.[23] Accuracy of method was determined using three different concentrations (15, 75, and 150 μg/ml) of glycyrrhizin and the results were calculated for glycyrrhizin concentration. The concentrations were calculated for percentage of recovery (%recovery) and the value of each concentration should not lower than 90.0%.[23]

Determination of glycyrrhizin content by HPLC

A 0.2 g aliquot of licorice powder from each commercial supplier (G01, G02, G03, G04, and G05) was transferred to a 100 mL stopper conical flask. The volume was adjusted to 100 mL with 70% ethanol and the solution was ultrasonicated (power 250 W, frequency 40 kHz) for 30 min with continual replenishment of solvent. The samples were then filtered through syringe filter (0.45 μm) into small glass vials.[5] Each sample was analyzed for 5 times using the validated HPLC method. The amount of glycyrrhizin was calculated by comparison with the calibrated standard glycyrrhizin curve.

Table 2: Ratio of solvents A and B for eluting gradient of HPLC mobile phase[5]

Time (min)	Solvent A (acetonitrile)	Solvent B (0.05% phosphoric acid)
0	19	81
8	19	81
15	25	75
25	40	60
35	50	50
36	100	0
40	19	81

NIR spectroscopic measurement

NIR diffuse reflectance spectroscopy (Model: Xds Rapid Content Analyzer Xm-1100 Series, FOSS Analytical AB, Sweden) was used in this study. An aliquot (0.8 g) of each sample from the calibration set, the prediction set, the five commercial licorice sources (G01, G02, G03, G04, and G05), and the KN, TN, LN, PN, and SN powders was individually filled into glass vials (1.8 cm diameter and 2.5 cm height). The NIR spectrum was obtained by an average of 32 scans in the wavelength range of 1000–2500 nm (or wave number of 4000–10,000 cm^{-1}). Each sample was measured for 15 spectra with eight spectra randomly selected to be used in the calibration data set. The remaining seven spectra were used as the validation data set. The vials were randomly shaken 3 times before each measurement.

Data preprocessing and multivariate analysis

Principal component analysis (PCA) and partial least squares regression (PLS) were used to analyze the obtained data (Unscrambler® X version 10.2, CAMO Software, USA) with a maximum number of seven factors. The data preprocessing was done to remove background information and noise. This could improve the multivariate regression and provide better end models.[24-26] Three data pre-processing methods were applied; multiplicative scattering correction (MSC), baseline correction (BC), and MSC plus first derivative (MSC+1^{st}), to reduce multicollinearity and the baseline offset arising from scattering effects, thus enhancing the information related to chemical constituents.[27] The best model was selected in terms of the required number of factors (also called principal components, PCs), determination coefficient (R^2), root mean square error of cross-validation (RMSECV), and standard error of calibration (SEC).[28] The best calibration model was determined to minimize the RMSECV by the leave-one-out cross-validation method in the PLS software.

RESULTS AND DISCUSSION

Determination of glycyrrhizin content by HPLC

The results from HPLC analytical method validation showed %RSD of repeatability and intermediate precision were in the range of 0.12–4.22 and 0.18–2.79%, respectively. For the accuracy, %recovery of three different concentrations was in the range of 98.49–98.75 which follows the International Council for Harmonization guidelines.[23]

The HPLC chromatogram of licorice (G03) is shown in Figure 1. The retention time of the glycyrrhizin peak in this chromatogram (36.857 minutes) was similar to that for the standard glycyrrhizin solution (data not shown). The standard calibration curve of glycyrrhizin concentration (in the range of 5–200 μg/ml) and the HPLC peak area was plotted, and each concentration was measured 5 times. The plot showed a linear relationship with y = 4.7185x - 13.727, where y is the peak area and x is the glycyrrhizin concentration (μg/ml) and the R-square value was 0.9998. This relationship was used to calculate the content of glycyrrhizin (%) in the five different commercial sources of licorice root. The glycyrrhizin content in licorice root

was 2.29, 2.23, 2.35, 3.43, and 2.78% for G01, G02, G03, G04, and G05, respectively. All commercial licorices had glycyrrhizin content higher than 2%, which means that all licorices met the Chinese Pharmacopoeia requirement.[5] It is noticeable that the licorice from G04 source contained the highest amount of glycyrrhizin (3.43%). The glycyrrhizin content in Ummaruekvati dispensatories was 1.15, 1.11, 1.17, 1.72, and 1.39% for W01, W02, W03, W04, and W05, respectively.

NIR spectroscopic analysis

The NIR spectra of 10 single herbs (five commercial licorices G01-G05, KN, TN, LN, PN, and SN) and all mixtures (27 mixtures in the calibration set and the five dispensatories W01–W05) are shown in Figure 2a and 2b, respectively. The chromatograms of 10 single herbs [Figure 2a] had broad and overlapping peaks. The chromatograms of all mixtures [Figure 2b] showed little observable difference and individual samples could not be clearly separated. The chemometrics or multivariate data analysis tool was then applied to retrieve the differential data. The PLS model was used to establish the relationship between glycyrrhizin content measured by HPLC and predicted by NIR. It was found to be a linear relationship with the correlation coefficient (R^2) values of the validation data set close to 1.0 [Table 3 and Figure 3].

Since NIR spectra also reflect the physical properties of the samples (sample particle size, layer thickness, and density), several data pre-treatments were used to eliminate these confounding factors and establish the best calibration model. The results presented in Table 3 show that all data pre-treatments (no pre-treatment, MSC, BC, and MSC+1st) provided acceptable results using four factors. The R^2 values of validation were all higher than 0.92 (indicating that the PLS model is usable in most applications including quality assurance.[29]) In addition, RMSECV values were low and bias values in the validation sets were less than 0.6 x SEC, indicating no systematic error between the calibration and validation sets.[30] Thus, all calibration models were used to predict the glycyrrhizin content in the Ummaruekvati dispensatory external samples (W01–W05).

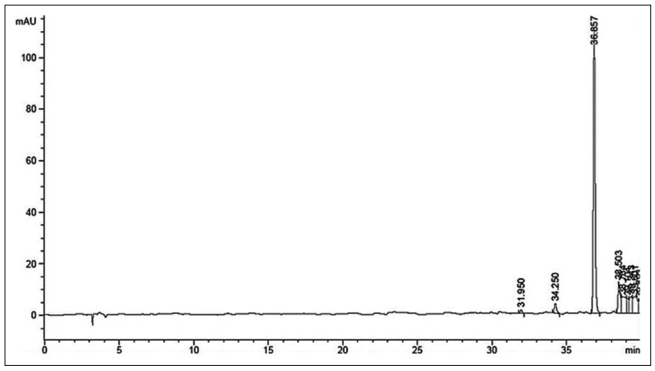

Figure 1: High-performance liquid chromatography chromatogram of licorice

NIR predicted glycyrrhizin content

External samples of Ummaruekvati dispensatories (W01–W05) were used to evaluate the model's predictability. The percent predictability was calculated from the ratio of NIR predicted to HPLC measured glycyrrhizin content multiplied by 100. Thus, the percentage reflects the fit of the model. The percent predictabilities of all four models (no pre-treatment, MSC, BC, and MSC+1st) are shown in Table 4. For all models, the percent glycyrrhizin predictability was the highest for the W03 dispensatory and the lowest for the W04 dispensatory. The high percentage predictabilities for the W03 dispensatory are likely to be due to the make-up of the calibration model data set. There was only one source of licorice (G03) used for creating the samples for calibration data set. This calibration set was then used to predict the glycyrrhizin content of all five Ummaruekvati dispensatories (W01, W02, W03, W04, and W05), which contained five different sources of licorice (G01, G02, G03, G04, and G05, respectively). Therefore, the predictive ability of the model will be higher for W03 as the variation that is expected from source of licorice (G03) was already included in the calibration model.[22] The lowest percent predictability of glycyrrhizin in W04 is likely to be due to the high glycyrrhizin concentration of G04 (1.72%), which was higher than the range of glycyrrhizin concentrations used to prepare the calibration model (0.5–1.5%), meaning that the results needed to be interpreted outside the validated range.[22] The residual predictive deviation (RPD) is defined as the ratio of the standard deviation of the validation data set to the RMSECV.[31] An RPD of this model was 2.35. A value between 2 and 2.5 indicates that coarse quantitative predictions are possible.

The MSC + 1st data pre-treatment model showed the highest R^2 values of calibration and validation, and the lowest SEC, RMSECV, and bias values. However, the average percent

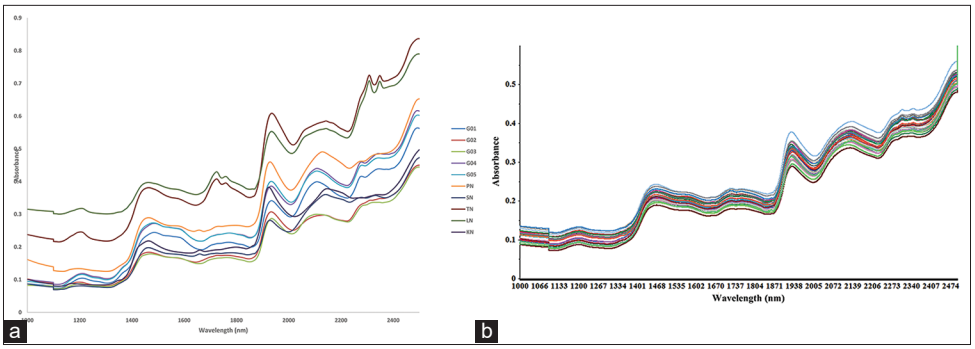

Figure 2: The near-infrared spectra of (a) 10 single herbs (five licorices and KN, TN, LN, PN, and SN) and (b) all 27 powder mixtures in calibration set

Table 3: Summary of calibration and validation results from PLS analysis

Pre-treatment	Factors	Calibration		Validation		Bias	SEC × 0.6
		R^2	SEC	R^2	RMSECV		
None	4	0.9392	0.0529	0.9345	0.0549	0.0003	0.0317
MSC	4	0.9414	0.0519	0.9378	0.0537	−0.0002	0.0311
BC	4	0.9422	0.0516	0.9392	0.0532	0.0002	0.0310
MSC + 1st	4	0.9610	0.0423	0.9582	0.0438	−0.0004	0.0254

Table 4: The percentage predictability of glycyrrhizin contents in five Ummaruekvati dispensatories from each pre-treatment model

Ummaruekvati dispensatories	None		MSC		BC		MSC+1st	
	Predictability (%)	%RSD	Predictability (%)	%RSD	Predictability (%)	%RSD	Predictability (%)	%RSD
W01	89.01	1.7632	96.95	0.5708	98.23	2.6551	86.90	0.5042
W02	91.56	2.1188	71.73	1.2406	90.19	3.1368	66.01	1.2508
W03	94.79	3.547	99.62	1.2522	105.26	6.6889	89.46	0.4533
W04	70.92	2.7401	70.45	2.0362	77.65	7.6237	63.97	1.0562
W05	80.53	1.5454	89.03	0.7865	87.39	1.8861	76.68	0.4353
Average	85.36		85.56		91.74		76.60	
%RSD	11.31		16.10		11.49		15.21	

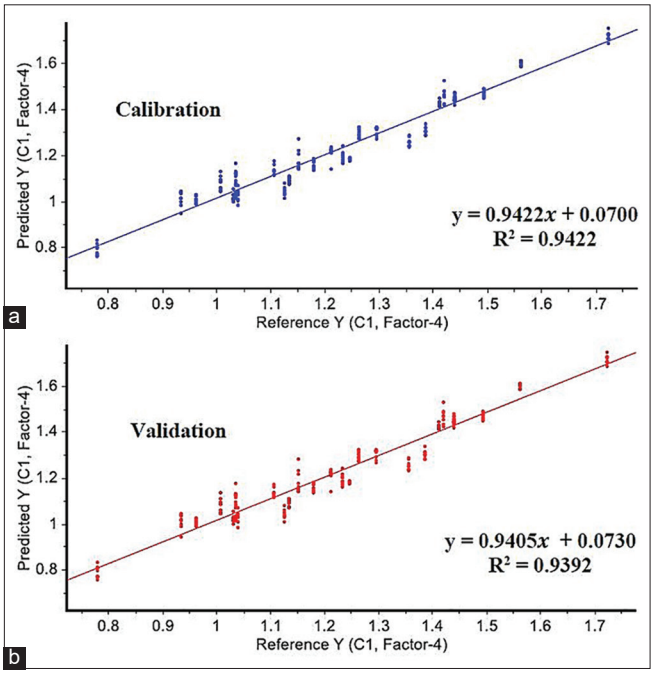

Figure 3: Relationship between the measured and predicted glycyrrhizin concentration in Ummaruekvati powder mixtures (BC pre-treatment) (a) calibration and (b) validation (internal samples).

predictability of the MSC + 1st model was the lowest of the tested models [Table 4]. The percent predictability was highest using the BC data pre-treatment model. This indicates that the better model is impossible to state from only relative measures such as correlation, instead, an absolute measure has to be used.[22] For the average percent predictability [%AP, Table 4], the no pre-treatment and MSC treatment models were both around 85%AP, the baseline treatment model (BC) was 91%AP, and the MSC + 1st treatment model was 76%AP. In this situation, we recommend using the BC treatment to predict external data.

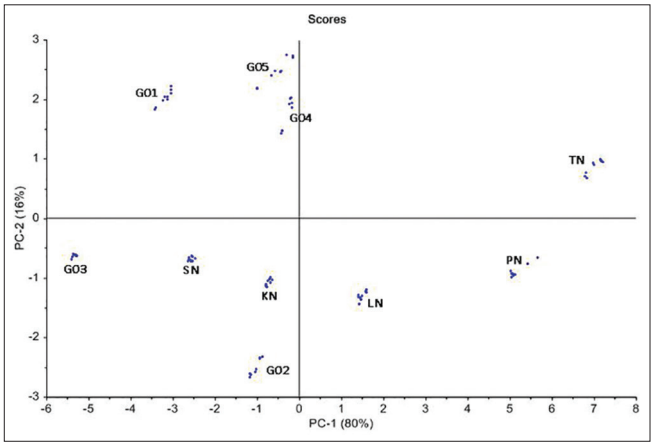

Figure 4: Scatter plot of PCA of five licorices (G01, G02, G03, G04, and G05), and other five herbs (BC pre-treatment) composed in the Ummaruekvati dispensatory; that is, KN, TN, LN, PN, and SN (PC = 2).

PCA

Qualitative differences between the five commercial sources of licorice (G01, G02, G03, G04, and G05) and the other herbs (KN, TN, LN, PN, and SN) are shown in the PCA plot (Figure 4). There was clear separation between each licorice and each herb that could be distinguished by the first two PCs [Figure 4], accounting for approximately 96.0% of the observed variance, suggesting the existence of distinctive differences in composition among them. Principal components (PCs) are considered as predictor variables than the optical data that are directly produced by NIR instruments. This is because these principal components represent true sources of variation of the spectra. They are sometimes called latent

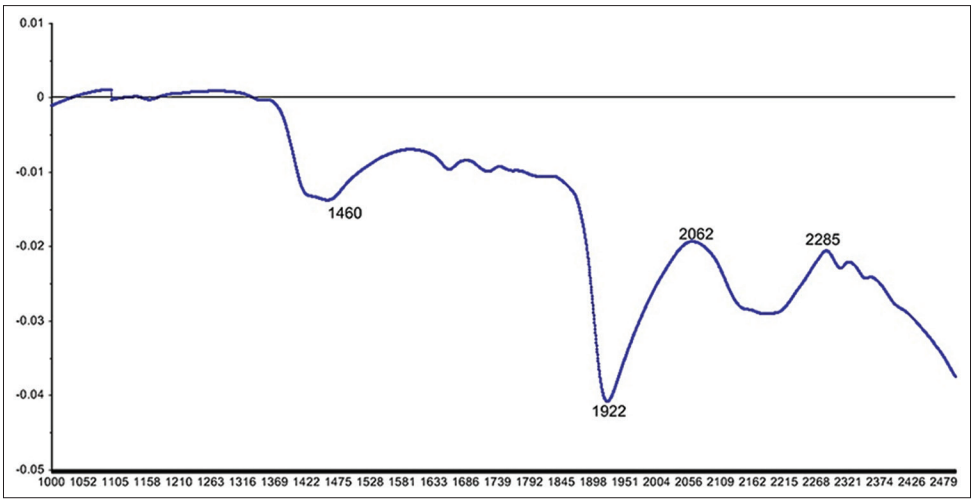

Figure 5: Regression vectors of near-infrared spectra from Ummaruekvati preparation (BC pre-treatment data)

variables as opposed to the direct variables that are actually measured.[31,32] Taken together, the percentage predictability and PCA results indicate that the samples used for creating the model should contain enough variety so that all expected sources of variance are expressed in the training data set. This will enable the model to accurately predict percentage glycyrrhizin from a variety of external samples.

The Regression Vectors of the Best Calibration Model

The regression vectors of the best calibration model (BC pre-treatment with four PCs) are shown in Figure 5. The major peaks were found at wavelengths 1460, 1922, 2062, and 2285 nm. The peak at 1460 nm represents N-H stretch first overtone, the peak at 1922 nm could be defined as C=O stretch second overtone. The other absorbance peaks could be defined as: N-H bend second overtone or N-H bend/N-H stretch combination (2062 nm), and C-H stretch/CH_2 deformation (2285 nm).[32] These results indicate that the BC pre-treatment with four PCs calibration model reflects the chemical information of the Ummaruekvati preparation.

CONCLUSION

A non-destructive NIR method for quantitative analysis of glycyrrhizin content in Ummaruekvati dispensatory was developed. The predicted results from a PLS method using four data pre-treatments were compared to obtain the best model. The best result was obtained using BC pre-treatment with four principle components and this was used for the modeling. The model validation was considered based on R^2, RMSECV, SEC, bias, and %AP values. The predicted results and reference values for glycyrrhizin content in five Ummaruekvati dispensatories were 1.1296% and 1.15% (W01), 1.0011% and 1.11% (W02), 1.2316% and 1.17% (W03), 1.3355% and 1.72% (W04), and 1.2147% and 1.39% (W05), respectively. An RPD of this model was 2.35 indicates that coarse quantitative predictions are possible. The W03 Ummaruekvati dispensatory had the highest percentage of predictability compared to the reference (105.26%) presumably because the W03 formulation had the same source of licorice (G03) as was used in the calibration set. Only licorice from Hua Cheaw (G03) was used due to the limitations of licorice raw materials. Thus, the variety and comprehensiveness of samples used in the calibration of the model should be considered to obtain more accurate data and increase predictability. In addition, if the number of samples is diverse and large enough, the validation by test set method should be done. This will make the model more accurate. Nevertheless, here, we demonstrated that NIR combined with chemometrics can be used for routine quality control of glycyrrhizin content in Ummaruekvati dispensatory with reduced time and no sample preparation or sample loss.

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