https://doi.org/10.31925/farmacia.2024.5.13 **ORIGINAL ARTICLE**

NON-DESTRUCTIVE ANALYSIS OF BARIUM SULPHATE TABLETS BY NEAR-INFRARED SPECTROSCOPY

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Abstract

A novel formulation of barium sulphate tablets was developed to replace the commercial radiopaque markers, since the commercial products are quite expensive and there is a restriction access for Thai patients. The quantitative determination of barium sulphate according to the United State Pharmacopoeia is performed using a gravimetric method which requires tedious sample preparation steps. In this study, fast and non-destructive analysis of barium sulphate tablets by benchtop and portable near infrared spectrometry (NIR) combined with chemometrics approach was developed and compared with reliable inductively coupled plasma–optical emission spectrometry (ICP-OES). Partial least square regression (PLSR) was the chemometrics tool selected in this study. The optimum PLSR model for benchtop NIR was obtained from standard normal variate (SNV) and orthogonal signal correction (OSC) pretreated NIR spectral data with 1 latent factor, R^2 Pearson for prediction was 0.9727, root mean square error of prediction (RMSEP) and bias were 3.7265 and 0.6614. While the best model for portable NIR was also obtained from SNV and OSC pretreated NIR spectral data with 2 latent factors, R^2 Pearson for prediction was 0.9371, RMSEP and bias were 5.6147 and -0.2604. The assay results of benchtop and portable NIR were not significantly different from ICP-OES.

Rezumat

Ulterior obținerii unei formulări cu sulfat de bariu sub formă de comprimate, menită să înlocuiască markerii comerciali actuali de radioopacitate, determinarea cantitativă a API a fost realizată conform printr-o metodă rapidă și nedistructivă de spectrometrie *benchtop* în infraroșu apropiat (NIR), combinată cu abordarea chemometrică și a fost comparată cu spectrometria de emisie optică cu plasmă cuplată inductiv (ICP-OES). Regresia parțială a celor mai mici pătrate (PLSR) a fost instrumentul chemometric selectat în acest studiu. Modelul PLSR optim pentru NIR de *benchtop* a fost obținut din date spectrale NIR cu variații normale standard (SNV) și corecție a semnalului ortogonal (OSC) cu 1 factor latent, factorul R2 Pearson pentru predicție fiind regăsit 0,9727, eroarea pătrată medie a predicției (RMSEP) și bias au fost calculate 3,7265 și respective 0,6614. Cel mai bun model pentru NIR portabil a fost, de asemenea, obținut din datele spectrale NIR pretratate SNV și OSC, dar cu 2 factori latenți, factorul R2 Pearson pentru predicție a fost 0,9371, RMSEP și bias-ul au fost 5,6147 și respectiv -0,2604. Rezultatele testului NIR de *benchtop* portabil nu au fost semnificativ diferite de cele obținute prin intermediul ICP-OES.

Keywords: barium sulphate, near infrared spectrometry, partial least square regression, chemometrics

Introduction

Radiocontrast agents are substances used to enhance the visibility of internal structures in X-ray-based imaging techniques such as computed tomography (contrast CT), projectional radiography and fluoroscopy. The physicians can select the therapeutic option for patients with severe constipation who otherwise have negative GI evaluations [1-3].

In Thailand, commercial radiopaque markers are quite expensive and must be imported only, therefore it is a restriction access for Thai patients. For this reason, inventing an equivalent drug product as prototype to replace the commercial products is challenging.

Barium sulphate ($BaSO_4$) is normally used as a contrast agent in diagnostic X-ray procedures called radiopaque contrast media. It works by coating the oesophagus, stomach or intestine with a material that is not absorbed into the body so the diseased or damaged areas can be clearly seen by X-ray examination or CT scan. Because of this property, the inexpensive barium sulphate product has been developed to replace commercial radiopaque markers [3-4].

Assay is an important quality control attribute for pharmaceutical products. The assay method for barium sulphate tablets existing in the USP 2023 is gravimetric analysis which requires complicated sample preparation

and long time consuming [5]. This study was conducted for development of non-destructive analysis of barium sulphate tablets based on near-infrared spectroscopy and combined with chemometric method.

Benchtop and portable near-infrared spectroscopes combined with chemometrics approaches have been used for non-destructive analysis of active pharmaceutical contents in various pharmaceutical dosage forms [6-12]. However, almost those active pharmaceutical ingredients are organic molecules which can be strongly absorbed near infrared radiation and resulting to clear and strong NIR absorption bands. For our best knowledge, chemometric-assisted near-infrared spectroscopy for quantitative determination of inorganic active pharmaceutical ingredient such as barium sulphate, has not been demonstrated. This study is the first application of NIR combined with chemometrics for quantitative analysis of inorganic pharmaceutical ingredient in tablets. Analysis methods were carried out with benchtop and portable NIR instruments. Partial least square regression (PLSR) was selected as the chemometrics tool for this study [13-15]. In addition, inductive couple plasma optical emission spectroscopy (ICP-OES) method was also developed and validated for using as the reference method for chemometric method development.

Materials and Methods

Two kinds of tablets were used in the study, 100 core tablets containing 0 - 90% barium sulphate and 30 coated tablets containing 50% barium sulphate. The overall 130 tablets were firstly collected their NIR spectra with portable NIR, benchtop NIR and finally, measured the actual barium sulphate content in each tablet by ICP-OES. The NIR spectra from portable and benchtop NIR were subjected to the chemometrics program to build up PLSR models for quantitative determination of barium sulphate by using the actual concentrations from ICP-OES as the reference values. PLSR models were constructed from original and pretreated NIR data.

Chemicals and instruments

Barium (ICP standard) was taken from Agilent (Agilent Technologies, CA, USA). Analytical grade sulfuric acid, 98% and nitric acid, 65% were purchased from RCI Labscan (Bangkok, Thailand). The Agilent 5800 ICP-OES (Agilent Technologies, CA, USA) was used to measure barium sulphate content through the study. NIRFlex 500 (Buchi, Switzerland) and MicroNIR (Viavi Solutions, Scottsdale, AZ, USA) were utilized for measurement of barium sulphate tablets.

Barium sulphate tablets formulation

The wet granulation method was used to prepare barium sulphate core tablets with varying strengths (0 - 90% weight ratio), as detailed in Table I. A dry mix of barium sulphate and microcrystalline cellulose underwent blending process before mixing with the binder solution until a damp mass was achieved. The binder solution was prepared by dissolving PVP K30 in ethanol. Subsequently, the damp mass was sieved through no. 14, and the obtained granules were dried for 1 hour before passing through sieve no. 18. The granules were then mixed with magnesium stearate and compressed using a single punch tableting machine, resulting in tablets with a diameter of 6 mm and an average weight of 100 mg for all formulations. The prepared core tablets underwent sampling and characterization for hardness, friability, disintegration time and weight variation to ensure compliance with the USP standard. For the film coating of 50% weight ratio tablets, tablets were coated with the in-housed coating mixture in the film coating machine.

Table I

Formulation of barium sulphate tablets

Composition (mg/tablet)	Formulation									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Barium sulphate	0.00	10.00	20.00	30.00	40.00	50.00	60.00	70.00	80.00	90.00
Microcrystalline cellulose	96.50	86.50	76.50	66.50	56.50	46.50	36.50	26.50	16.50	6.50
PVP K30	3.00									
95%EtOH	q.s.									
Mg stearate	0.50									
Total	100.00									

ICP-OES method and method validation

The ICP-OES instrument conditions were set as follow, the viewing mode was radial, read time was 5 seconds, RF power was 1.2 KW, stabilization time was 15 seconds, viewing height was 8 mm, nebulizer flow was 0.7 L/min, plasma flow was 12 L/min and auxiliary flow was 1 L/min.

Preparation of Standard Curve for ICP-OES

Standard solutions at the concentrations of 10, 50, 100, 150 and 200 ng/mL were prepared by diluting the stock standard solution with ultra-pure water. The stock standard solution concentration of 12.5 µg/mL was diluted to achieve the desired concentrations.

Linearity

The linearity of the analytical method was studied by plotting a calibration curve of the standard substances in the concentration range of 10 - 200 ng/mL. The linearity was assessed using the R^2 value obtained from regression analysis.

Accuracy

The accuracy of the ICP-OES method was studied using the spiked standard approach. Three concentrations

of the samples (80 - 120% of target concentration) were prepared by spiking standard barium sulphate into the placebo, three replicates were performed for each concentration. The samples were then digested and diluted using the same method as the preparation of tablet dosage forms. The analysis was carried out using ICP-OES, and the accuracy was expressed as the % recovery according to the following formula:

$$\% \text{ Recovery} = \frac{\text{Amount standard added}}{\text{Amount standard found}} \times 100 \quad \text{(Eq.1)}$$

Precision

Both repeatability and intermediate precision were studied. For repeatability, 10 samples were assayed in the same day, and the results were expressed as the % RSD. For intermediate precision, the experiment was repeated on another day with the same procedure as repeatability.

Sample preparation for ICP-OES measurement

One tablet was placed in a beaker, and 5 mL of nitric acid was added. Heat was applied using a hot plate until it dissolved. Then, 15 mL of sulfuric acid was added, and heating continued until a clear solution was obtained. The solution was cooled and transferred to a 25 mL volumetric flask. The volume was adjusted with sulfuric acid and diluted with ultra-pure water to achieve a concentration of barium sulphate within the range of the standard curve.

Portable NIR measurement

A tablet was placed on the reflectance standard and was measured by the portable NIR (MicroNIR) on the upper side with diffuse reflectance mode. The NIR spectrum was scanned between 1000 and 1680 nm and the total measured data points were 125. All NIR spectral data were collected and transferred to the Unscrambler® program for PLSR construction. One hundred non-coated tablets containing 0 - 90% of barium sulphate (0, 10, 20, 30, 40, 50, 60, 70, 80 and 90%), 10 tablets for each concentration and 30 coated tablets of 50% barium sulphate were individual collected their NIR spectrum.

Benchtop NIR measurement

The same tablets from portable NIR were recorded NIR spectra in benchtop NIR (NIRFlex 500) with tablet add-on tool using diffuse reflectance mode. The spectra were scanned and recorded from 1000 - 2500 nm, the total measured data points were 1501.

PLSR model development and validation

NIR spectra from portable and benchtop instruments were imported to the Unscrambler program (Aspen Tech, MA, USA) for PLSR modelling. Total 130 spectra were collected from each instrument; 90 spectra (70 spectra from 0 - 90% of barium sulphate core tablets, 7 spectra for each concentration and 20 spectra from the coated tablets of 50% barium sulphate) were used as calibration samples and the remaining 40 spectra (30 spectra from 0 - 90% of barium sulphate core tablets, 3 spectra for each concentration and 10 spectra from the coated tablets of 50% barium sulphate) were kept as the external validation samples. PLSR models were constructed from the original and pre-treated NIR spectral data. The optimal PLSR model was selected from a model that can provide the best model parameters. The highest R^2-model calibration, the highest R^2 Pearson for prediction of external validation samples, the lowest root mean square error of prediction (RMSEP, Eq.2) and bias (Eq. 3) were selection criteria for the optimal model.

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{n}} \quad \text{(Eq. 2)}$$

$$\text{Bias} = \frac{(y_{ref} - y_{pred})}{y_{ref}} \quad \text{(Eq. 3)}$$

where, y_i and $\hat{y}_i$ are the reference and predicted values for sample i from the validation set, respectively, and n is the number of samples in the validation set.

Results and Discussion

Measurement of barium sulphate by ICP-OES and method validation

Sample preparation procedure and ICP-OES conditions were optimized for barium sulphate tablet. The successive sample preparation procedure and the optimum ICP-OES condition was described in Experimental section. The final procedure and optimum method were validated for linearity, accuracy and precision. All method validation results were acceptable as shown in Table II. These results were supported that the optimal ICP-OES method was able to use for the intended purpose.

Table II

Method validation results of ICP-OES method

Method validation parameters	Results
Linearity (Equation, R^2)	
Day 1	$y = 368x - 1315$, $R^2 = 1$
Day 2	$y = 370x - 656$, $R^2 = 0.9984$
Day 3	$y = 365x - 1411$, $R^2 = 0.9968$
Accuracy (% Recoveries at 80%, 100%, 120% of the target concentration)	
Day 1	101.05%, 101.69%, 101.85%
Day 2	101.75%, 101.46%, 101.84%
Precision (% RSD of 10 determinations)	
Repeatability	0.91%
Intermediate precision	1.16%

Measurement of NIR spectra of barium sulphate tablets

NIR spectrum of barium sulphate exhibits the absorption band around 5000 - 6000 cm^{-1} which is the overtone of sulphate (-S=O) functional group [16]. However, the excipients in tablet formulation can provide the NIR signal in this wavelength region. For this reason, the changing of NIR spectra of 0 - 90% barium sulphate between 5000 and 6000 cm^{-1} was not the absolute contribution from the different of barium sulphate contents only. To solve this problem, multivariate analysis method based on principle component analysis (PCA) was employed in order to extract the useful spectral data which corresponded to barium sulphate from the whole spectral data. In this study, partial least square regression (PLSR) was chosen for the development of quantitative model for barium sulphate in tablet dosage form. Because this algorithm contains PCA process in both spectral data and concentration matrices [17]. Not only the original spectral data, but also the pretreated spectral data with standard normal variate (SNV), orthogonal signal correction (OSC), multiplicative scatter correction (MSC), detrending and Savizky-Golay 1° derivative algorithms were further used for PLSR modelling.

Development of PLSR models from benchtop NIR for quantitative determination of barium sulphate

For benchtop NIR, 6 PLSR models were constructed from the NIR spectrum of benchtop NIR using original data and the pretreated data. The results of all models were presented in Table III. It was found that the optimum model is the one created from SNV and OSC pretreated data, with a latent factor of 1, an R^2 model value of 0.9551. Applying the optimum model to a validation set of 39 samples, the highest value of R^2 Pearson value at 0.9727 and the lowest RMSEP of 3.7265 was obtained. These results implied that benchtop NIR had the potential for the quantitative determination of barium sulphate in tablet dosage form with good method linearity and appropriate accuracy. The plots of successive model were displayed in Figure 1. In addition, both core and coated tablets were utilized in calibration and validation samples. The PLSR methodology is a powerful tool for the multivariate calibration of the various samples with different formulas of excipients resulting to the calibration model which is able to determine amount of interest compound in such samples.

Table III

Constructed PLSR models with model parameters

Benchtop NIR						
Data pretreatment*	**Factors**	**R^2 model**	**RMSEC**	**R^2 Pearson**	**RMSEP**	**Bias**
Original	8	0.9509	5.0392	0.9288	6.1004	1.6073
1° Derivative	5	0.9628	4.3872	0.9534	4.7928	0.1992
OSC	3	0.9456	5.3024	0.9353	5.9498	1.7352
Detrending	7	0.9468	5.2453	0.9385	5.8542	1.9930
SNV+MSC	5	0.9315	5.9510	0.9198	6.3588	0.9611
SNV+OSC	1	0.9551	4.8174	0.9727	3.7265	0.6614
Portable NIR						
Data pretreatment*	**Factors**	**R^2 model**	**RMSEC**	**R^2 Pearson**	**RMSEP**	**Bias**
Original	6	0.9770	3.5553	0.9330	5.8213	-0.6665
1° Derivative	4	0.9345	5.9944	0.8730	8.1844	-1.5738
Detrending	7	0.9844	2.9246	0.8271	9.4277	-1.2632
SNV+OSC	2	0.9710	3.9901	0.9371	5.6147	-0.2604
OSC	1	0.9536	5.0445	0.9293	5.9951	-0.7785

* OSC = Orthogonal signal correction, SNV = Standard normal variate, MSC = Multiplicative scatter correction, RMSEC = Root Mean Square of Calibration

As described above, the sulphate (SO_4^{2-}) functional group can interact with near-infrared radiation, resulting to the NIR signal in the range of 5000 - 6000 cm^{-1}. The registered spectrum showed the comparing of NIR spectra between tablets with 0% (blue line) and 50% of barium sulphate (orange line) revealed that the intensities of the NIR spectrum in the 5000 - 6000 cm^{-1} range increased with the concentration of barium sulphate in the tablet. However, the elevation intensities did not solely come from barium sulphate but also from other excipients in the tablets (spectrum of 0% barium sulphate).

For this reason, chemometrics methods are necessary to separate the signal of barium sulphate from other excipients and create a model for quantitative analysis. In this study, several data pretreatment algorithms including standard normal variate (SNV), orthogonal signal correction (OSC), multiplicative scatter correction (MSC), detrending and Savizky-Golay 1st derivative were applied to obtain the optimum prediction model [18-19]. For benchtop NIR spectra of barium sulphate, using the data pretreatment methods could enhance the useful signal to obtain the better quantity prediction models. From Figure 2, comparing the score plots of PLSR models for the original data with data that underwent both SNV and OSC data pretreatment, it can be observed that the data showed improve concentration clustering with data pretreatment.

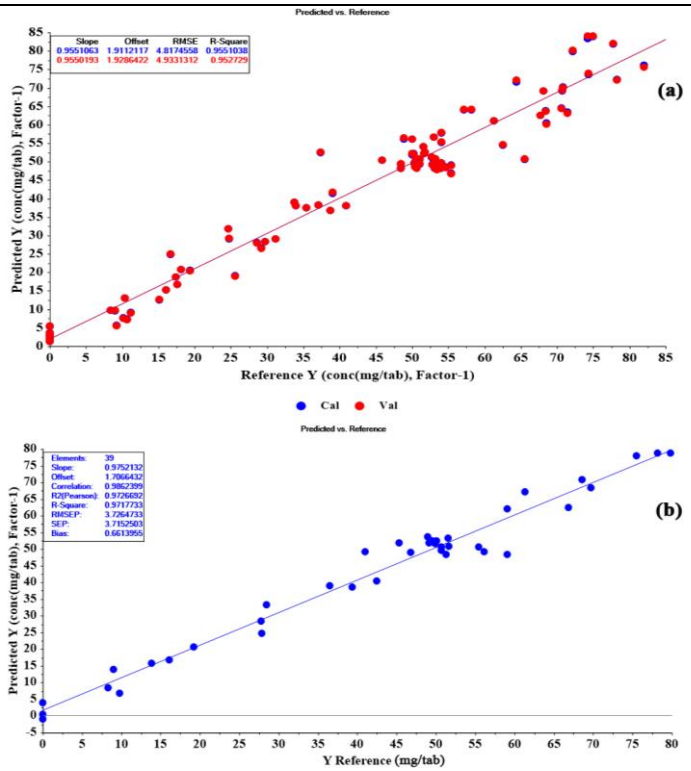

Figure 1.

(a) Calibration and internal validation curves of the optimum PLSR model of benchtop NIR and (b) the plot of the predicted barium sulphate values from the optimum PLSR model vs. reference values obtained from ICP-OES

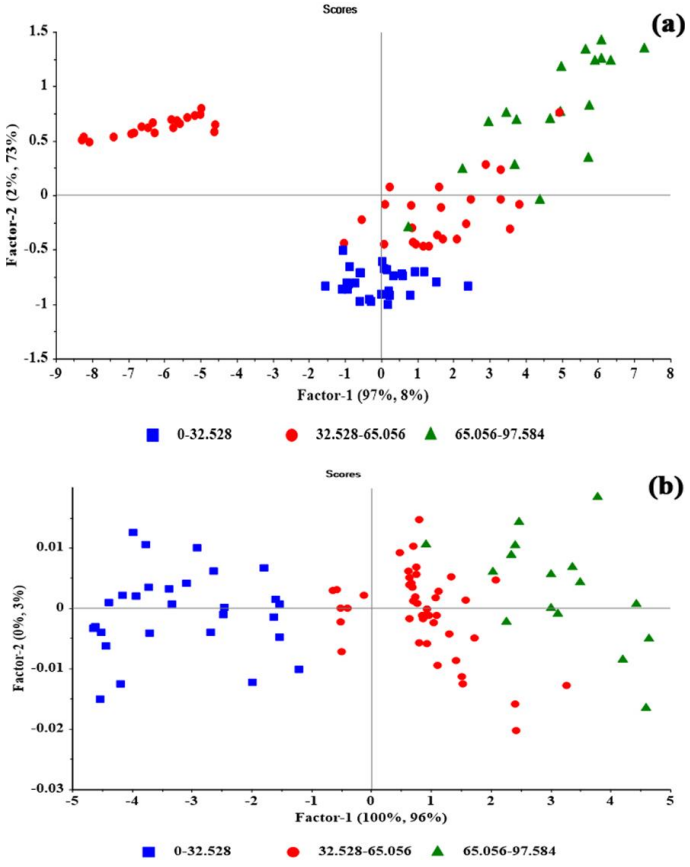

Figure 2.

Score plots of benchtop PLSR models of (a) original unpretreated spectral data model and (b) SNV and OSC pretreated spectral data

Development of PLSR models from portable NIR for quantitative determination of barium sulphate

Five PLSR models were developed from portable NIR spectral data (Table III). Same as benchtop NIR, the successive PLS R model of portable NIR was obtained from SNV and OSC data pretreatment with 2 latent factors. The R^2 of model was 0.9710, this value was confirmed for method linearity (Figure 3a). For model validation, the correlation coefficient in term of R^2 Pearson between the reference value (x-axis) and the determination results obtained from the model (y-axis) exhibited the R^2 value of 0.9371 (Figure 3b), this implied to the acceptable accuracy of PLSR model of portable NIR. The score plots of original NIR data PLSR model and SNV and OSC pretreated NIR data of the portable PLSR model were compared in Figure 4. The better data grouping by concentrations was found from SNV and OSC pretreated data compared with original NIR data model. Specificity of PLSR models from benchtop and portable NIR were expressed by statistical comparison with the results obtained from the reference method, ICP-OES. As shown in Table IV, the results of two methods were not significant different at 95% confidence interval.

Table IV

Statistic comparison of the results obtained from PLSR models and ICP-OES methods

Statistical evaluation	Spectroscopic method	
Comparison of variances (F-Test)	Benchtop NIR and ICP-OES	
	F-Experimental	F-Critical
	5.969	3.179
	Portable NIR and ICP-OES	
	F-Experimental	F-Critical
	1.102	1.717
Comparison of means (T-Test)	Benchtop NIR and ICP-OES	
	t-Experimental	t-Critical
	1.141	2.179
	Portable NIR and ICP-OES	
	t-Experimental	t-Critical
	0.052	1.992

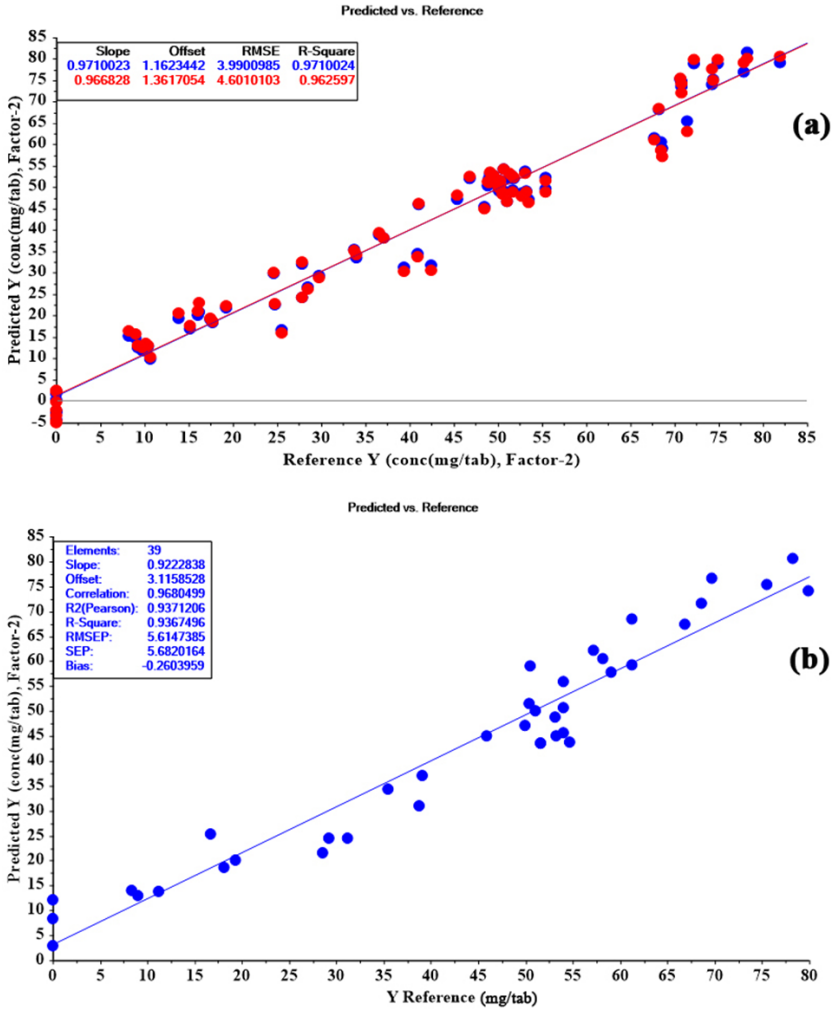

Figure 3.

a) Calibration and internal validation curves of the optimum PLSR model of portable NIR and (b) the plot of the predicted barium sulphate values from the optimum PLSR model vs. reference values obtained from ICP-OES

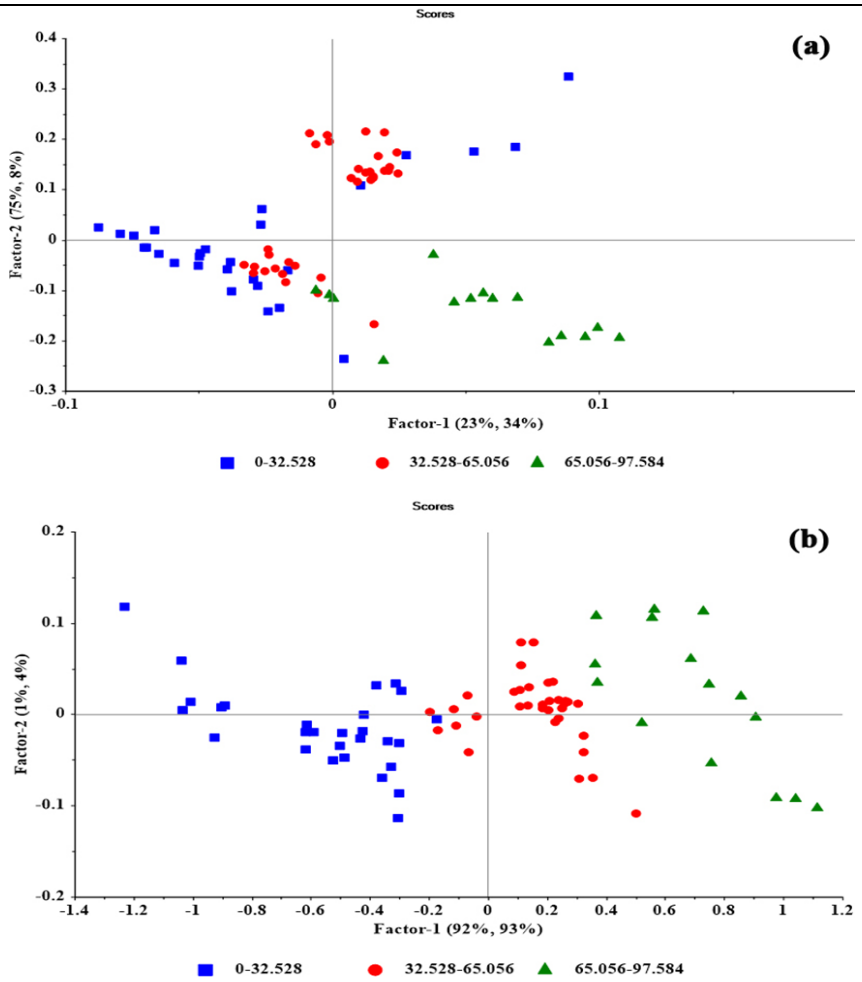

Figure 4.
Score plots of portable PLSR models of (a) original unpretreated spectral data model and (b) SNV and OSC pretreated spectral data

Conclusions

In summary, PLSR models for quantitative determination of barium sulphate in tablets were successfully developed from benchtop and portable NIR spectral data. Since barium sulphate is an inorganic substance which provides weak NIR signal, data pretreatment was necessary for enhancing NIR signal relevant to the sulphate functional group and resulting to the dramatic increasing of PLSR models prediction ability. This study demonstrated that the determination results of barium sulphate obtained from non-destructive and fast instruments, benchtop and portable NIR, were not statistical significantly different from the direct method, ICP-OES.

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Conflict of interest

The authors declare no conflict of interest.

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