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Application of near- and mid-infrared spectroscopy combined with chemometrics for discrimination and authentication of herbal products: A review

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ABSTRACT

Herbal medicines along with its preparations have been commonly used as preventive and promotive agents around the world, especially in developing countries. Motivated by economic profits, the high-priced value of herbal medicines may be substituted or adulterated with less expensive ones; therefore, the authentication methods must be developed to overcome the adulteration practices. Due to their properties as fingerprint analytical techniques, near-infrared (NIR) and mid-infrared (MIR) spectroscopies offered fast and reliable techniques for authentication of herbal medicine. The data generated during authentication of herbal medicines were complex and difficult to be interpreted; therefore, the statistical approach called chemometrics has been used to treat data. The objective of the present review was to highlight the updates on the application of NIR and MIR spectroscopies and chemometrics techniques (discrimination, classification, and quantification) for discrimination and authentication of herbal medicine.

INTRODUCTION

Herbal medicine is the most widely used complementary and alternative medicine therapies throughout the world (Joos *et al*., 2012). Herb is part or whole of plants used for medicinal and therapeutic applications. Herbal medicines typically consisted of plants or plant extracts containing some active constituents, which frequently work synergistically (Folashade *et al*., 2012). Chemical constituents having some medicinal benefits are referred as active ingredients or active principles, such as curcuminoid present in Curcuma species. The presence and levels of active components depend on several factors, including plant species, time and season of harvesting, soil types, and other environmental conditions (Heinrich, 2015). Currently, over 80% of the world population use herbal medicines as preventive and promotive agents either in developing or developed countries (Barnes, 2003). As a consequence, the increased use of the herbal product has also driven to some actions of adulteration and abuse of the herbal products, leading to consumers and producers disappointment, and in some instances, the abuse and adulteration can cause health problems (Bodeker *et al*., 2005).

The discrimination and authenticity of herbal products are emerging issues (Georgiev *et al*., 1999), especially in countries which develop alternative medicines as primary health care such as China, India, Germany, and Indonesia (Liang *et al*., 2004). Herbal authentication is mainly related to improper labeling and economic adulteration. Motivated by economic profits, high-quality herbal medicines may be adulterated with lower quality herbals having less expensive price to defraud the consumer. The adulteration practice also involved the substitution, either in part or whole of expensive herbal components with cheaper and inferior herbal products. An authentic herbal product can be defined as herbal that complies

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with the description or labeling provided by the producers, which included plants composition, its geographic region of origin, and the variety or species of ingredients (Jordan *et al*., 2010).

Han *et al*. (2016) have reported adulteration practices in Chinese Herbal Medicines. Using DNA barcode database of traditional Chinese Medicine (TCM), 1,436 samples representing 295 medicinal species from seven primary TCM markets in China have been investigated. Of the 1,260 samples, approximately 4.2% of herbal medicines were identified to be adulterated. Some herbal components such as Ginseng Radix et Rhizoma, Radix Rubi Parvifolii, Dalbergiae odoriferae Lignum, Acori Tatarinowii Rhizoma, Inulae Flos, Lonicerae Japonicae Flos, Acanthopanacis Cortex, and Bupleuri Radix are among target of adulteration. The survey also reported that adulterants were present in the Chinese market. In order to assure the quality of labeled herbal medicines, it is essential to establish the methods to identify its authenticity either by checking the composition of herbal ingredient or monitoring batch-to-batch reproducibility (Kulkarni *et al*., 2014).

DISCRIMINATION AND AUTHENTICATION TESTING

Several methods have been used for identification, discrimination, and authentication of herbal ingredients, including macroscopic and microscopic evaluation, simple wet chemical tests such as color or precipitation, and application of some sophisticated instruments like spectrophotometer, real-time polymerase chain reaction, and chromatographs (especially in thin layer chromatography, gas chromatography, and high-performance liquid chromatography) (Kamboj, 2012). During last years, a new strategy for herbal medicine discrimination and authentication has been introduced by applying analysis of targeted compounds (classical approach) and non-targeted analysis by fingerprint profiling and metabolomics approach (Riedl *et al*., 2015). In the classical approach, authenticity testing was based on the analysis of specific marker compounds which are indicative for certain herbal products. For example, curcuminoid was determined using validated analytical method that can be used for identification of Curcuma species. The addition of *Curcuma longa* with other herbal materials would decrease curcuminoid content and could be used as an indicator of adulteration practice (Lestari *et al*., 2017). Targeted analysis has its own advantage and disadvantages. The advantages of this approach are high sensitivity, high selectivity, and simple data analysis, while its disadvantage included that high efforts are being put on the validation of the analytical method to ensure the validity of method, time-consuming, typically involving extensive sample preparation and multiple analysis, and only known compounds can be detected (Esslinger *et al*., 2014). Chromatographic based-methods are ideal methods for analysis of targeted compounds due to its capability to provide good separation among analytes present in herbal medicines (Daszykowski and Walczak, 2006).

In fingerprinting approaches, many compounds or features are used for authentication by investigating response profiles and then comparing the profiles between authentic and adulterated herbal medicines. Spectroscopic including near- and mid-infrared, nuclear magnetic resonance (NMR), and chromatographic methods were commonly used for profiling patterns between authentic and adulterated herbal medicines (Rafi *et al*., 2015). Metabolomics is described as the study of small molecules and metabolites based on comprehensive chemical analysis with the aim to detect as many substances as possible. NMR spectroscopy and chromatographic techniques combined with mass spectrometer detectors such as gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectroscopy (LC-MS) were widely used for metabolomics study (Markley *et al*., 2017; Savorani *et al*., 2013). Non-targeted analyses have advantages of high-throughput approach, simple or no sample preparation, and allowing detection of unexpected additives/deviations, and they also have main disadvantage of the need of sample databases and multivariate modeling (Esslinger *et al*., 2014).

The fingerprint and metabolomics approaches have been applied for quality control of herbal medicines. Fingerprinting and metabolomics in herbal authentication represents the characteristic patterns of the components using certain analytical methods (Razmovski-Naumovski *et al*., 2010). The data generated during non-targeted approach (fingerprint profiling and metabolomics) are usually huge and complex and difficult to be interpreted; therefore, an advance statistical evaluation known as chemometrics was used (Small, 2006). Owing to its properties such as fingerprint nature which allow to make fingerprinting profile of herbal components, near-IR (NIR) and mid-IR (MIR) spectroscopies have been widely used for discrimination and authentication of herbal components (Rohman *et al*., 2014).

INFRARED SPECTROSCOPY

Infrared (IR) spectroscopy has been defined as the interaction between electromagnetic radiations in the infrared region with samples. This spectroscopy measures the vibrational energy levels in a compound. Each chemical bond has a unique vibrational energy level (Bunaciu *et al*., 2015). The IR electromagnetic radiation was divided into three regions, namely, NIR with wavenumbers range of 14,000–4,000 cm^{-1} (corresponding to wavelength of 800–2,500 nm), MIR at 4,000–400 cm^{-1} (2,500–50,000 nm), and far IR at wavenumbers of 400–50 cm^{-1} (50–1,000 μm). NIR and MIR spectroscopies were commonly used for confirmation (identification), qualitative and quantitative analyses of herbal medicines and pharmaceutical products, and offered an alternative to wet-chemical techniques (Lohumi *et al*., 2015).

NIR and MIR spectroscopies have gained popularity in identification and authentication analysis due to several advantages, namely, its rapidness with respect to fast acquisition, non-destructive analytical technique meaning that samples analyzed by IR spectroscopy can be analyzed using other instrumental technique like chromatography, low cost, ease in sample preparation with minimal sample treatment, and can be applied for analysis of liquid, semi-solid, and solid samples. The fast-growing application of IR spectroscopy was also supported by the advancement in computer and software technology, especially in chemometrics (Mazivila and Olivieri, 2018). However, IR spectroscopy also has its own disadvantages due to the nature of spectra and environment condition. The physical state of evaluated samples and the testing environment could influence IR spectra, which make the interpretation of spectra more complicated. In addition, spectra obtained are frequently complex which make the extraction of relevant information difficult. Fortunately, the statistical software known as chemometrics could facilitate these problems. IR spectroscopy and chemometrics are complementary methods and widely applied for authentication of several fields covered in pharmaceutical products, namely, drugs (Mazivila and Olivieri, 2018), cosmetics (Rohman and Man, 2009), herbal products (Rohman *et al*., 2014), as well as food sectors, including fats and oils (Baeten and Aparicio, 2000), honey (Mehryar and Esmaiili, 2011), and meat (Schmutzler *et al*., 2015).

CHEMOMETRICS

Chemometrics is defined as the application of mathematics and statistics to treat chemical data (Gemperline, 2006) and is considered as part of analytical chemistry sciences. Chemometrics can help analytical chemists to deal with all steps of analytical procedures, starting from the experimental design and optimization through extraction of chemical information and final decision (Daszykowski and Walczak, 2006). Chemical data typically include properties and values of numerous compounds as determined by instrumental methods and having various sources of variance. Accordingly, the statistical evaluation of such data should use one or more multivariate data statistics (chemometrics). Multivariate statistics allows the simultaneous analysis of several independent variables (factors) against several dependent variables or responses (Granato *et al*., 2018).

The most common types of chemometrics used in NIR and MIR spectroscopies for discrimination and authentication of herbal medicines include:

- Spectral processing using derivatization (first and second derivatives), standard normal variate (SNV), multiplicative scattering correction (MSC), filtering, wavelet transformations (WT), feature selection, and folding-unfolding. The main objective for data pre-processing is improving the accuracy and robustness of subsequent classification or quantitative analyses, improving interpretability of data by transforming raw data into an understandable format, detecting and removing of outliers, and reducing the dimensionality of the data (Lasch, 2012). The first and second derivatives can eliminate baseline variations among samples analyzed significantly and enhance the small spectral differences. MSC was capable of correcting light scattering, additive, and multiplicative spectral effects. SNV is a mathematical transformation method normally applied to the log ($1/R$) spectra to minimize slope variation and to correct for scatter effect. WT enables infrared spectrum to be analyzed as the sum of wavelet functions with different spatial and frequency properties (Lai *et al*., 2011).
- Classification and discrimination techniques, either supervised or unsupervised pattern recognition techniques. The chemometrics of linear discriminant analysis (LDA), partial least square-discriminant analysis (PLS-DA), and orthogonal projection to latent structures-discriminant analysis (OPLS-DA) are supervised, while principal component analysis (PCA), soft independent modeling of class analogy (SIMCA), cluster analysis (CA), artificial neural networks (ANN), multivariate analysis of variance, and canonical variate analysis (CVA) are considered as unsupervised pattern recognition (Rohman *et al*., 2016).
- Multivariate calibrations intended to facilitate quantitative analysis of target analytes, including stepwise multiple linear regression (SMLR), principle component analysis (PCR), PLS, and modified PLS (Singh *et al*., 2013).

Figure 1 exhibited the scheme of general steps during the application of chemometrics methods to treat NIR and MIR spectra data to assess the discrimination and authentication of herbal medicine products, including spectral treatment, classification, and quantification (Nunes, 2014).

Currently, there are a number of user-friendly chemometrics software packages which are free or commercially available to carry out statistical calculations of complex data. Each software has its own advantages and features. Unscrambler®, SIMCA® SIRIUS®, and Pirouette® offered standard methods of multivariate statistical analysis, such as classification with PCA and SIMCA and multivariate calibration with PCR, PLS, and SMLR, but there is a few capacity for writing personal programs. On the other hand, Minitab® and Matlab® are routinely designed to facilitate the writing of personal programs, while Grams® 32 is particularly useful for calibration modeling during quantitative analysis rather than for the exploration of a data matrix and classification by different pattern recognition techniques (Gad *et al*., 2013; Rodionova and Pomerantsev, 2006). Currently, Chemoface, a user-friendly and free interface software is used for chemometrics analysis (Nunes *et al*., 2012).

AUTHENTICATION OF HERBAL MEDICINE USING NEAR INFRARED SPECTROSCOPY

Near-infrared (NIR) spectroscopy is a fast and non-destructive analytical technique which provides chemical and physical information of samples (Roggo *et al*., 2007). The combination of NIR spectroscopy and multivariate data analysis offered many interesting perspectives either qualitative or quantitative analyses, which shows the authentication of herbal medicines (Reich, 2005). The American Society of Testing and Materials has defined NIR spectroscopy as the interaction between samples and electromagnetic radiation in the NIR region, corresponding to the wavelength of 780–2,526 nm, located between visible light and MIR region (Wang and Yu, 2015). The most prominent peaks of NIR absorption originated from the overtones and combinations of the fundamental vibrations appeared in MIR peaks related to functional groups containing hydrogen bonds such as –O–H, –S–H, –C–H, and –N–H (Jamrógiewicz, 2012). Table 1 shows the application of NIR spectroscopy for authentication of herbal medicines.

Discrimination and spectral fingerprinting of *Wolfiporia cocos* (F.A. Wolf) Ryvarden & Gilb, one of the traditional Chinese medicine, have been performed with NIR spectroscopy and PCA. The identification and discrimination of *W. cocos* based on its geographical origin are one of the acceptance prerequisites for its worldwide recognition because the therapeutic effect of *W. cocos* depends on its chemical components. The active compounds contained in *W. cocos* revealed difference due to geographical origins. Hence, authentication based on geographical origins was very essential. The powder of samples was subjected to NIR spectrophotometer at wavenumbers 10,000–4,000 cm^{-1} using 64 scanning and resolution of 4 cm^{-1}. NIR spectra of *W. cocos* were pre-treated with Norris, mean centering, standardization, and the second derivative, successively. After optimizing spectral

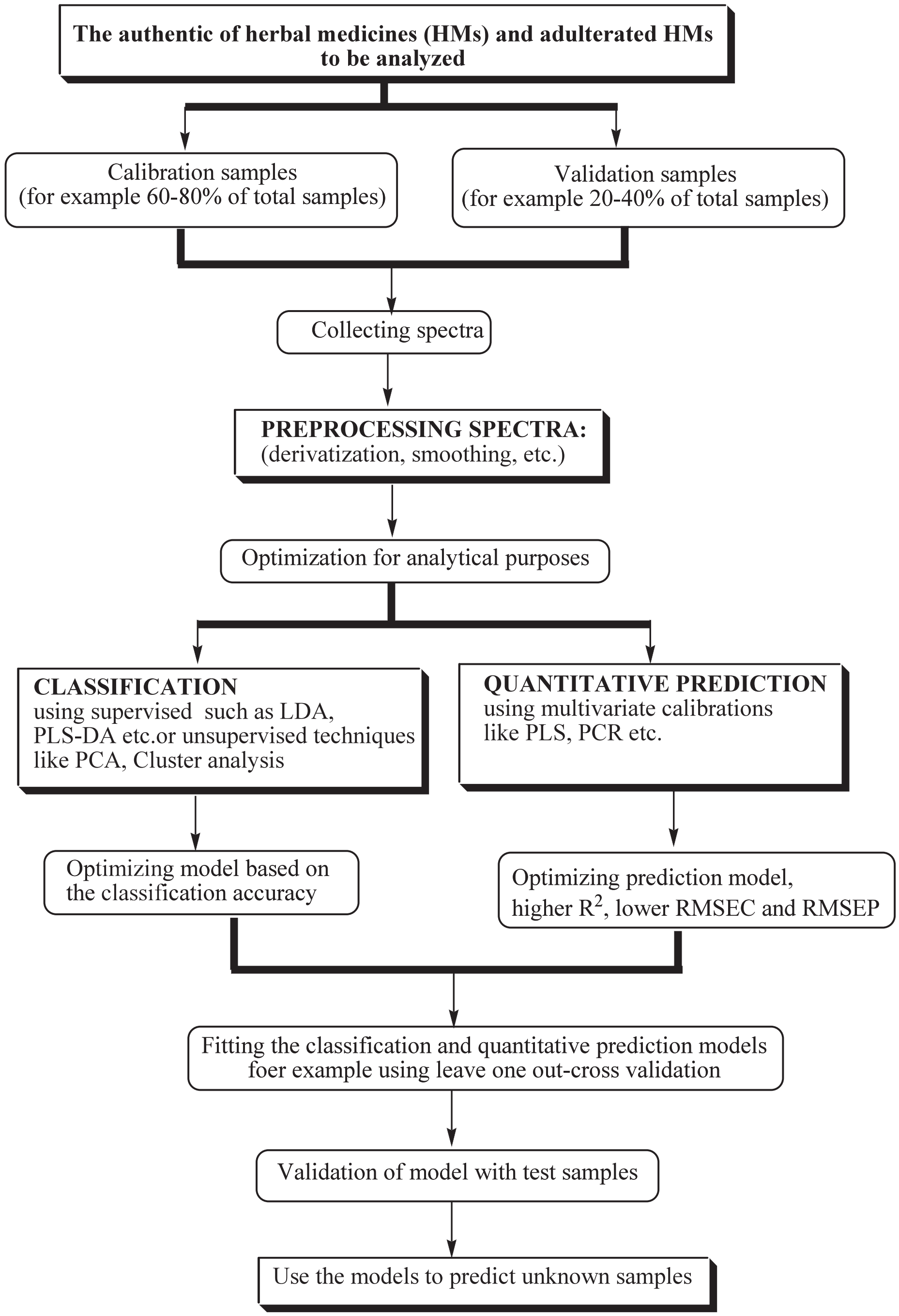

Figure 1. The general steps involved in the application of chemometrics methods to treat near- and mid-infrared spectra data to assess the authentication of herbal medicine products [adapted from Gad *et al.* (2013)].

treatment, the wavenumbers of 7,501.74–4,088.35 cm^{-1} were finally used for discrimination and classification. PCA using these wavenumbers could discriminate *W. cocos* between poriae cutis and the inner part of the sclerotia of *W. cocos* in the pattern space of PCA (Yuan *et al*., 2018).

Authentication of *Picea abies* L. Karst seed from five seed lots in Sweden, Finland, Poland, and Lithuania has been carried out using NIR reflectance spectra at a wavelength of 780–2,500 nm using a resolution of 0.5 nm (Farhadi *et al*., 2017). Classification model of samples was performed using OPLS-DA. The model performance was validated using two test sets, namely, internal validation using 600 seeds and external validation using 1,158 seeds. In internal validation, the same seed lots were included during modeling, while in external validation, seed lots were excluded. OPLS-DA model could correctly classify 99% of Swedish, Finnish, and Polish seeds and 97% of Lithuanian seeds in internal validation, while during external validation, OPLS-DA model could correctly classify of Swedish, Finnish, Lithuanian, and Polish seeds with accuracy levels of 81%, 96%, 98%, and 93% of seeds according to their respective classes, respectively. The mean classification accuracy was 99% and 95% for the internal and external test set, respectively.

Table 1. The application of NIR spectroscopy for authentication of herbal medicines.

Samples	Issues	Measurement conditions-chemometrics	Chemometrics	Results	References
Echinacea species	Identification of *Echinacea angustifolia* root, *E. purpurea* root, *E. purpurea* tops, *E. purpurea* seed and *E. pallida* root, as well as adulterated *E. angustifolia* root	Wavenumbers of 12,000–4,000 cm^{-1} using 25 scanning at a resolution of 8 cm^{-1}.	SIMCA for classifica tion. Near-infrared (NIR) spectra were pre-processed using noise weighting, MSC normalization, and derivatization.	This model was capable of properly identifying authentic and adulterated Echinacea samples.	(Neal-Kababick and Flora, 2010)
	Identification of *Echinacea purpurea* and its authentication with *E. angustifolia, E. pallida*, or *Parthenium integrifolium*.	Wavenumbers of 10,000–4,000 cm^{-1} using 25 scanning at a resolution of 8 cm^{-1}.	NIR spectra were subjected to SNV and derivatization. PCA was used for classification	A total of 10% of *E. purpurea* (authentic samples) and 0% of false samples were misidentified. The adulteration of 10% can be detected.	(Laasonen *et al*., 2002)
Fritillaria	Rapid discrimination of seven different Fritillaria samples based on their total alkaloids	NIR spectra were acquired at 12,000–3,700 cm^{-1} using 32 scanning and resolution of 4 cm^{-1}.	NIR spectra were subjected to Min–Max normalization, MSC, Vector normalization method, and First derivative Subtraction. PLS was used for quantitative analysis.	PLS at wavenumbers of 4,165.8–6,082.8 cm^{-1} using eight components was successfully used for quantification of alkaloids (Peiminine and Sipeimine) to discriminate *Fritillaria ussuriensis* and other Fritillaria.	(Meng *et al*., 2015)
Picea abies L. Karst	Authentication of *Picea abies* L. Karst seed from five seed lots in Sweden, Finland, Poland, and Lithuania	Near-infrared spectra (NIRS) at a wavelength of 780–2,500 nm using a resolution of 0.5 nm	PCA was used for outlier identification. OPLS-DA was used for classification among seeds	OPLS-DA could classify seeds according to its origin with accuracy levels of 99% and 95% during internal and external validations.	(Farhadi *et al*., 2017)
Paeoniae Radix	Differentiation of geographical origin of Paeoniae Radix by quantifying main components	NIR diffuse reflectance spectra at 10,000–4,000 cm^{-1} using 32 scans and resolution of 16 cm^{-1}	NIR spectra were preprocessed using MSC and derivatization. PCA for classification, while PCR and PLS were used for quantification	PCA could classify Paeoniae Radix according to a different origin. Paeoniflorin, albiflorin, and benzoylalbiflorin could be quantified with high R^2 and low RMSEC and RMSEP	(Luo *et al*., 2008)
Radix scutellariae	Classification of geographical origins of *Radix scutellariae* samples	NIR diffuse reflectance spectra at 10,000–4,000 cm^{-1} using 64 scans and resolution of 16 cm^{-1}. Spectra were pretreated with SNV, Savitzky–Golay filter, and second derivative	DA and PLS-DA were used for classification of Radix scutellariae samples. PLSR was used for quantification of flavonoids	DA and PLS-DA could classify *Radix scutellariae* samples. Baicalin, wogonoside, baicalein, and wogonin were quantified using PLSR with acceptable accuracy and precision.	(Li *et al*., 2011)
Radix puerariae	Differentiation of two *Radix puerariae*, *Pueraria lobata,* and *Pueraria thomsonii* by determining puerarin, daidzin, and total isoflavonoid	NIR spectra 1,100–2,500 nm with a resolution of 0.5 nm and 32 scanning	Spectra were pretreated with second derivative. LDA and SIMCA for classification and PLS for quantification of puerarin, daidzin, and total isoflavonoid	LDA and SIMCA could successfully classify Radix Puerariae into two different clusters corresponding to the two species. PLS can predate analytes with R = 0.970 (puerarin), R = 0.939 (daidzin), and R = 0.969 (total isoflavonoid)	(Lang *et al*., 2015)
Angelicae gigantis Radix	Classification of *A. gigantis* Radix samples based on NIR spectra and specific marker of Decursin	NIR spectra were pretreated with second derivative	SIMCA	SIMCA at a wavelength of 540–1,680 nm could classify Korean and Chinese A. gigantis Radix samples	(Woo *et al*., 2005)
Salvia miltiorrhiza	Classification of cultivated or wild *S. miltiorrhiza* from different origins	NIR diffuse reflectance spectra at 10,000–4,000 cm^{-1} using 32 scans and resolution of 2 cm^{-1}.	NIR spectra were pre-treated with Savitzky–Golay method and second derivative spectra	PLS-DA and SIMCA could classify cultivated or wild *S. miltiorrhiza* from different origins	(Zhu *et al*., 2018)

Continued

Samples	Issues	Measurement conditions-chemometrics	Chemometrics	Results	References
Genera Protium and Crepidospermum	Identification of plant species of genera Protium and Repidospermum from different origins	NIR spectra at 1,000–2,500 nm using 16 scans with a resolution of 8 cm^{-1}.	LDA	LDA using variables of absorbance values at 1,667–2,500 nm could discriminate species at different developmental stages and the adult stage.	(Lang *et al*., 2015)
Lonicerae japonicae Flos	Classification and identification of *L. japonicae* Flos from different origins	NIR spectra at 10,000–4,000 cm^{-1} using 4 cm^{-1} resolution	PCA was used for classification and multivariate calibrations (PCR, PLS, and MLR) were used for quantification	PCA could classify *L. Japonicae* Flos from different origins based on main active components which include neochlorogenic acid, chloro- genic acid, caffeic acid, as quantified using PCR	(Li *et al*., 2013)
Glycyrrhizi uralensis Fisch (licorice)	Authentication of licorice samples according to their parts, growing conditions, and geographic areas	Fiber optic diffuse reflectance NIRS spectroscopy 10,000–4,000 cm^{-1} using 16 cm^{-1} resolution and 150 scanning.	PCA and SMICA for classification, PLS was used for quantification	PCA could classify licorice samples originated from different geographic areas of Gansu and Inner Mongolia provinces and from different growing conditions. PLS at 4,300–7,100 cm^{-1} could predict glycyrrhizic acid, chemical marker in licorice.	(Wang *et al*., 2007)
Rhei Radix et Rhizoma	Authentication of Rhei Radix Rhizoma based on its origin, mainly based on levels of main components (chrysophanol, aloe-emodin, rhein, emodin, and physcion)	NIR spectra were recorded at 12,000–4,000 cm^{-1} with a resolution of 8 cm^{-1} and 64 scanning at 25°C	NIR spectra were pre-processed with Savitzky-Golay smoothing, MSC, and three combinations methods. Quantification of main components was assayed using NIR spectrometer combined with PLS and ANN	Quantification using PLS was more suitable for analysis of chrysophanol, aloe-emodin, emodin, and physcion whereas ANN was better for rhein. For the optimal NIR models chrysophanol, aloe-emodin, rhein, emodin, and physcion, the correlation coefficients of calibration were 0.9916, 0.9762, 0.9839, 0.9794, and 0.9800, respectively	(Jintao *et al*., 2018)
Fructus forsythiae	Differentiation of *Fructus forsythiae* according to geographic areas	NIRS at 12,000–4,000 cm^{-1} with a resolution of 4 cm^{-1} and 32 scanning	NIR spectra were subjected to second derivative and Norris smoothing. Classification was performed using LDA and CA	Using absorbance values at 11,000–4,100 cm^{-1} as variables, seven principle components were used, and LDA could classify Fructus forsythiae with the correct accuracy of internal cross-validation identification was 96.99%	(Bai *et al*., 2012)
Fructus Lycii	Discrimination of Fructus Lycii of four different geographic regions from Ningxia, Inner Mongolia, Hebei, and Sinkiang of China	NIR spectra were measured at 12,500–3,600 cm^{-1}, and the spectra were obtained by averaging 64 scans, with a resolution of 8 cm^{-1}	NIR spectra were subjected to derivatization	Two dimensional (2D) synchronous and asynchronous spectra at 4,950–5,700 cm^{-1} could discriminate among samples from different geographic regions.	(Lu *et al*., 2008)
Rhizoma Corydalis	Classification of Rhizoma Corydalis according to their geographical origin	NIRS at 1,000–2,500 nm range with a resolution of 2 nm (the spectra were sampled at 751 wavelengths)	Spectra were preprocessed with the first and second derivative, MSC, SNV, and wavelet transform. Classification modeling was carried out using LS-SVM, RBF-ANN, PLS-DA and KNN	LS-SVM, RBF-ANN, PLS-DA, and KNN performed reasonably classification among Rhizoma Corydalis from different origins. There are no significant differences ($p > 0.05$) and LS-SVM offered he best classification with an accuracy level over 95%.	(Lai *et al*., 2011)
Ephedra plants	Classification and discrimination of Ephedra genus (*E. sinica*, *E. intermedia*, and *E. equisetina*)	NIRS in diffuse reflec tance mode were acquired from 37 pulverized samples at 10,000 and 4,000 cm^{-1}, averaging 64 scans at resolution 4 cm^{-1}	NIR spectra were subjected to first and second derivative, MSC, SNV, as well as smoothing and Norris smoothing. Classification was performed with DA, SOM, and BP-ANN.	Three Ephedra plants could be differentiated and classified based on two habitats. DA model could classify with an accuracy level of 84.2%–91.9%, SOM and BP-ANN models have accuracy levels of 93.3%–100.0%.	(Fan *et al*., 2010)

Continued

Samples	Issues	Measurement conditions-chemometrics	Chemometrics	Results	References
Pelargonium sidoides	Discrimination of *P. sidoides* and *P. reniforme* having similar toxonomic for authentication studies	NIRS at 10,000–4,000 cm^{-1}, using 32 scans.	The reflectance spectral data were converted to absorbance using log 1/*R* (*R* = reflectance). PCA and OPL-DA for discrimination and classification.	PCA exhibited distinguishable clusters between *P. reniforme* and *P. sidoides*, while OPS-DA showed distinct groupings *P. reniforme* and *P. sidoides* using seven main absorption peaks which contain putative biomarkers responsible for the discrimination of two species.	(Maree and Viljoen, 2011)
Peucedanum praeruptorum Dunn	Identification of peucedanum based on geographical growing areas	NIR spectra scanned at 8,500–3,500 cm^{-1}, 32 scanning, resolution 4 cm^{-1}, using air as background.	NIR spectra were pre-processed using Savitzky-Golay smoothing, derivativation, standard SNV, MSC, and autoscale. PCA, ANN, and PLS-DA were used for discrimination	ANN achieved 100% accuracy level for discrimination. PLSDA method achieved 100% identification rate using three latent variables. PCA was not able to classify Peucedanum from different georgaphical origins.	(Zhu and Chen, 2011)
Salvia miltiorrhiza Bge	Discrimination of *S. miltiorrhiza* from different origins	Each sample of *S. miltiorrhiza* was milled and passed through number 40 mesh sieve. NIR spectra were acquired 10,000–4,000 cm^{-1} at 4 cm^{-1} resolution by co-adding 32 scans.	Different pretreatments, including MSC and SNV were used. Inter val PLS (iPLS) was used for selection of the spectral region. DA used for discrimination.	DA could discriminate S. miltiorrhiza var. alba according to geographical origins among Taian, Laiwu, Rongcheng, and Guangrao classes.	(Duan *et al*., 2014)
Codonopsis pilosula	Discrmination of Codonopsis pilosula according to its geographical origin from Province Longxi, Tongwei, Changzhi, Linzhi, and Tibet Province	NIR reflectance diffuse spectra were recorded on the wavenumbers 12,000–4,000 cm^{-1}, from an average of 32 scans with 4 cm^{-1} resolution.	Spectra were pre-processed with SNV, first derivative, Savitzky–Golay algorithm smoothing. PCA was used to group samples. Random forests (RF) KNN were applied for classification models and predict the geographical origins of test samples.	RF offered excellent ability to discriminate C. pilosula with accuracy levels of classifications of up to 97% for the training set and 94% for the test set. Spectra treated with SNV + 1st derivative proved to be effective for removing effects which are not contributing to samples classification.	(Li *et al*., 2012)
Eleutherococcus senticosus	Discrimination of *E. senticosus* from other plants from other Araliaceae family	NIRS at 1,100–2,498 nm with a resolution of 2 nm and 64 scanning.	Spectra were pre-processed with SNV, first derivative, Savitzky–Golay algorithm smoothing. PLSDA and SIMCA were used for classification	SIMCA and PLSDA could classify *E. senticosus* with accuracy levels of 84% and 92%. It was possible to detect adulterations with about 5% foreign herbal material, depending on their closeness to the Araliaceae family.	(Lucio-Gutiérrez *et al*., 2011)
Hibiscus mutabilis L. and *Berberidis radix*	Rapid recognition of *H. mutabilis* and *Berberidis radix* through fingerprinting patterns.	NIRS were collected at the region of 10,000–4,000 cm^{-1} with 60 scanning and a resolution of 8 cm^{-1}.	PLSDA, PCA, and LDA for classification	PLSDA model showed good classification of samples according to different collection parts, collection time, and different origins or various species belonging to the same genera of herbal medicines.	(Fu *et al*., 2015)

BP-ANN = back-propagation artificial neural network; DA = discriminant analysis; HCA= hieratical cluster analysis; MSC = multiplicative scatter correction, SNV = standard normal variate correction, LS-SVM = least-squares support vector machines; RBF-ANN = radial basis function artificial neural networks; OPLS-DA = Orthogonal projection to latent structures discriminant analysis; PCA = principal component analysis; PLS-DA = partial least-squares discriminant analysis; KNN = K-nearest neighbors; SIMCA = Soft independent modelling of class analogy; SOM = self-organizing map; SVM-GS = support vector machines grid search.

Echinacea is one of the most popular herbals commonly used in dietary supplements and has an expensive price in the market, with immune-stimulatory and anti-inflammatory properties, especially the alleviation of cold symptoms (Tharun *et al*., 2017); therefore, the authentication of this plant is very essential. Several parts of this plant are used in the manufacturing of dietary supplement products, and NIR spectroscopy was used for identification of plant parts to comply with current good manufacturing practices (cGMPs). The differentiation of *Echinacea angustifolia* root, *E. purpurea* root, *E. purpurea* tops, and *E. purpurea* seed from various sources and *E. pallida* root from a single source, as well as adulterated *E. angustifolia* root were performed using NIR spectroscopy in combination with SIMCA (Neal-Kababick and Flora, 2010). Powdered samples (40 mesh) were placed in scintillation vials and scanned using reflectance NIR at wavenumbers of 12,000–4,000 cm^{-1} using 25 scanning at a resolution of 8 cm^{-1}. NIR spectra were subjected to data processing of noise weighting, MSC normalization, and spectral derivatization before being analyzed using SIMCA algorithm. SIMCA model was able to properly identify authentic and adulterated Echinacea materials. SIMCA using variables of absorbances on NIR spectra was also successfully used for classification of 48 herbal samples commonly used in food and pharmaceutical industries (Yang *et al*., 2013).

NIR spectroscopy combined with chemometrics of PLS-DA has been used for fast identification of three varieties of Chrysanthemum, namely, Dabaiju, Huju, and Xiaobaiju (Chen *et al*., 2014). A total of 139 Chrysanthemum samples were analyzed and divided randomly into a calibration set (92 samples) and prediction set (47 samples). NIR diffuse reflectance spectra of Chrysanthemum varieties were preprocessed using a first-order derivative (D1) and auto-scaling and then subjected to PLS-DA. Using absorbance values at wavenumbers of 10,000–4,000 cm^{-1}, PLS-DA could differentiate three Chrysanthemum varieties with accuracy rates of Dabaiju, Huju, and Xiaobaiju were of 97.60%, 96.65%, and 94.70%, respectively, in calibration sets and 95.16%, 86.11%, and 93.46% in validation (prediction) sets, respectively.

A rapid NIR spectroscopy coupled with multivariate calibration of PLS was used to discriminate Paeoniae Radix (dried root of *Paeonia lactiflora* Pallas, Family of Paeonaceae) in cultivation area of Hangshao, Boshao, and Chuanshao from different geographical origins in China. The different levels of active components (Paeoniflorin, albiflorin, and benzoylalbiflorin) contained in Paeoniae Radix as determined by HPLC-UV detection contribute to such discrimination. NIR spectra of samples were acquired at 10,000–4,000 cm^{-1} using 32 scanning at a resolution of 16 cm^{-1} and recorded as absorbance, using air as the background. The diffuse reflectance NIR spectra were subjected to several treatments, including MSC, first derivative, and Savitsky–Golay for correcting the scattering effect and eliminating the baseline shift to offer good correlation between results obtained with NIR spectroscopy and those obtained using HPLC-UV. The chemometrics of PCA can successfully classify Paeoniae Radix according to different cultivation area using the contents of paeoniflorin, albiflorin, and benzoylalbiflorin as variables (Luo *et al*., 2008).

AUTHENTICATION OF HERBAL MEDICINES USING MIR SPECTROSCOPY

Among infrared regions, MIR spectroscopy was the most commonly used technique for analytical purposes due to its fingerprint properties. The interaction between electromagnetic radiation in MIR regions with molecules can be analyzed in three different ways as emission, absorption, and reflection (Türker-Kaya and Huck, 2017). This interaction causes chemical bonds to vibrate at specific wavenumbers (frequencies), which depends on the mass of the constituent atoms, the molecule shape, and the stiffness of the bonds, according to Hooke's law (Baeten and Dardenne, 2002). The MIR region lies at wavenumbers of 4,000–400 cm^{-1}, which can be segmented into four regions, namely, 4,000–2,500 cm^{-1} (X-H stretching vibration), 2,500–2,000 cm^{-1} (the triple bond region), 2,000–1,500 cm^{-1} (the double bond region), and 1,500–400 cm^{-1} (the fingerprint region) (Karoui *et al*., 2010). The main advantages of MIR spectroscopy employed for discrimination and authentication of herbal medicines are found on sample preparations. Herbal medicines samples can be rapidly and directly tested to obtain a MIR spectrum because they are not separated or extracted and the procedure of sample preparation is nondestructive. The MIR spectrum fingerprint also contains the "whole" chemical information of all chemical compositions present in the herbal medicines (Sun *et al*., 2010). Table 2 listed the application of MIR spectroscopy in combination with chemometrics for authentication of herbal medicines.

Fourier Transform (FT) MIR Spectroscopy in combination with chemometrics has been developed as a rapid tool for classification of Baccharis species samples from the Atlantic Forest. For this purpose, 28 specimens were collected from different locations in Brazil. The samples were analyzed using FT-MIR spectrometer, using reflectance drift module at 4,000–400 cm^{-1}, 64 scans with a resolution of 4 cm^{-1}. MIR spectra data were subjected to pre-processing by normalization and auto-scaling. PCA was successfully used for the classification of samples into five groups, namely, *B. articulata, B. trimera, B. uncinella, B. organensis*, and *B. aracatubaensis* (Lourenço *et al*., 2015). FT-MIR spectroscopy combined with PCA using variables of absorbance values at fingerprint regions (2,000–400 cm^{-1}) was also successfully used for classification of five herbal medicines from different locations in India, namely, Arjuna (*Terminalia arjuna*), Aswagandha (*Withania somnifera*), Aawala (*Emblic myrobalan*), Vaasa (*Adhatoda vasica*), and Tulsi (*Ocimum sanctum*) (Singh *et al*., 2010).

Panax ginseng C.A. Meyer, one of the popular herbs commonly used for medicinal purposes, has been discriminated using FT-MIR spectroscopy combined with chemometrics of PCA and PLS-DA based on cultivation age (5 and 6 years) and parts (rhizome, tap root, and lateral root), while Partial least square regression (PLSR) was used to predict the ages and parts of ginseng samples based on PLS components numbers. Each FT-MIR spectrum of samples was collected in wavenumbers of 4,000–650 cm^{-1} with a resolution of 4 cm^{-1}. FT-MIR spectra were pre-processed differently using various normalization methods, including area normalization, minimum–maximum normalization, and vector normalization. Cross-validation using leave-one-out technique was used to minimize model overfitting and give the predictive capability of classification models. PLS-DA could discriminate ginseng into three parts (taproot, rhizome, and lateral root) and classify ginseng with 5- and 6-year cultivation ages. PLSR using two PLS components could predict the ages and parts of ginseng with a low root mean square error of prediction (RMSEP) value of 0.161 (Lee *et al*., 2017).

Two-dimensional (2D) correlation MIR spectroscopy (the measurement of MIR spectral changes due to time course) has been used for the authentication of *Lignosus* spp., medicinal mushroom used as a folk remedy, especially for clearing heat and moistening the lungs. *Lignosus rhinocerotis*, the most common species of Lignosus, was differentiated from different origins in Malaysia. The 2D-MIR spectra at the combined wavenumbers of 1,800–1,300 cm^{-1}, 1,300–900 cm^{-1}, and 900–400 cm^{-1} could be applied for differentiation of *Lignosus rhinocerotis* from different origins (Choong *et al*., 2014). 2D-MIR spectroscopy in combination with PCA using variables of absorbance values at 1,000–1,500 cm^{-1} could be successfully applied for differentiation of *Phyllagathis praetermissa* from *P. rotundifolia* (Tan *et al*., 2011).

FT-MIR spectroscopy in combination with multivariate analysis of PCA and CVA has been devoted for discrimination of *Curcuma longa* (turmeric), *Curcuma xanthorrhiza* (java turmeric), and *Zingiber cassumunar* (ginger) from different regions. The rhizomes of these plants had similar rhizome color and were used widely in herbal medicines. FTIR spectra in the MIR region (4,000–400 cm^{-1}) were subjected to SNV and first and second derivatives. PCA using variable of absorbances values at wavenumbers of 2,000–400 cm^{-1} could be used for

Table 2. The application of MIR spectroscopy in combination with chemometrics for authentication of herbal medicines*.

Issue	Wavenumbers used and spectral treatment	Chemometrics	Results	References
Discrimination of *Curcuma longa*, *Curcuma xanthorrhiza* and *Zingiber cassumunar* from different regions	MIR spectra 4,000–400 cm^{-1} were subjected to SNV and first and second derivative.	PCA and CVA for discrimination	PCA could be used for classification among samples evaluated. CVA gave better discrimination than PCA.	(Rohaeti *et al*., 2015)
Differentiation Phyllagathis praetermissa from P. rotundifolia.	2D-IR correlation MIR spectra at wavenumbers of 1,000–1,500 cm^{-1}	PCA	Two species could be differentiated and classified using PCA	(Tan *et al*., 2011)
Discrimination of wild Paris Polyphylla Smith var. yunnanensis from different origins	MIR at 4,000–650 cm^{-1}	PLS-DA and SVM-GS	PLS-DA and SVM-GS were capable of classifying samples of Paris Polyphylla from southeast and northwest districts with accuracy levels of 100% and with accuracy levels of. >87% for central of Yunnan regions.	(Wu *et al*., 2018)
Classification of *Dendrobium officinale* from different harvesting periods	4,000–550 cm^{-1}	Random forest model	Random forest model could classify *D. officinale* from different harvesting period with accuracy levels of 94.44% and 97.92% in calibration and validation set.	(Wang *et al*., 2018)
Authentication of *Orthosiphon stamineus* from different regions (white flowers and purple flowers)	1,800–800 cm^{-1} and the absorbance of FTIR spectra was normalized	PCA and SIMCA	Classification using SIMCA based on PCA model could classify samples with accuracy levels of 100% at 5% significance level	(Sim *et al*., 2004)
Discrimination between wild-grown *Ganoderma lucidum* and cultivated ones	MIR spectra at 4,000–450 cm^{-1} and subjected to SNV preprocessing	PCA and LDA	LDA could classify Wild-grown G. lucidum and cultivated ones with accuracy levels 98%.	(Zhu and Tan, 2015)
Discrimination of danshen, used for promoting coronary circulation in Chinese medicine, from different origins	MIR spectra at 4,000–400 cm^{-1} using a resolution of 4 cm^{-1}, with 16 scans. Spectra were pre-processed with MSC	PCA, SIMCA, and BP-ANN	Using SIMCA and PCA, 82% of the samples were discriminated correctly. BP-ANN could completely classify the origins of danshen.	(Li *et al*., 2006)
Discrimination of between *Boletus edulis* and *Boletus tomentipes* from different location origins	MIR spectra at wavenumbers The range of 1,800–400 cm^{-1} were used for discrimination.	HCA and PLSDA	HCA and PLS-DA could classify and discriminate *B. edulis* and *B. tomentipes* from different location origins	(Qi *et al*., 2017)
Discrimination *Hyocyamus niger* and *Peganum harmala* from other herbal samples.	MIR spectra 3,400–600 cm^{-1} were subjected to SNV.	K-means, HCA, PCA, and SOM	K-means, HCA, PCA, and SOM were able to discriminate two medicinal seeds, *H. niger* and *P. harmala* from other herbal samples	(Qi *et al*., 2017)

*See Table 1 for abbreviation used.

making the patterns of samples, groupings, similarities, and differences. These wavenumbers were preferred due to their capability to provide valuable information, which attributed to the chemical compounds present in the studied samples. Using the same variables, CVA gave better discrimination than PCA. Subsequently, the developed method could be used for the identification and discrimination of the three closely-related plant species (Rohaeti *et al*., 2015).

The quality of herbal medicines depends on the harvesting period and cultivated areas (geographical origins). FT-MIR using attenuated total reflectance (ATR) has been used for classification of *Dendrobium officinale*, a tonic herb commonly used in Traditional Chinese Medicine. MIR spectra at wavenumbers of 4,000–550 cm^{-1} were used as variables during classification modeling. Random forest model could classify *D. officinale* from different harvesting periods with accuracy levels of 94.44% and 97.92% in calibration and validation set (Wang *et al*., 2018), respectively.

CONCLUSION

NIR and MIR spectroscopies are fingerprint analytical techniques commonly used for discrimination and authentication of herbal medicines. Coupled with chemometrics of pattern recognitions, NIR and MIR spectra could be treated to be more easily interpreted for making a decision regarding the adulteration practices. The combination of NIR-MIR spectra and chemometrics offered rapid and powerful techniques for discrimination and authentication of herbal medicines.

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