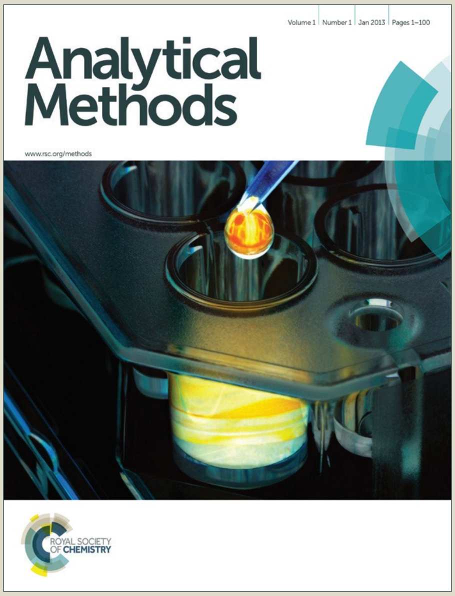
Analytical Methods



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A novel approach to discriminate *Lycium barbarum* from Zhongning area using FT-IR spectroscopy and chemometrics

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Abstract: An increasing number of fake and inferior *Lycium barbarum* fruits from Zhongning production area appear in the market due to large demand of consumers. Present study was focused on the classification and identification of Zhongning *Lycium barbarum* (ZNL) from different production areas using Fourier transform infrared (FT-IR) spectroscopy coupled with chemometrics. Results revealed that the spectral region between 1909-1311 cm^{-1} was found to be feasible for both classification and identification of ZNL. FT-IR in combination with discriminant analysis (DA) and soft independent modeling of class analogy were used for classification and identification of ZNL among different *Lycium* production areas in China, and FT-IR coupled with DA can classify and identify ZNL from the other production areas successfully. The recognition rates of the calibration and validation sets were 94.0 % and 100 %, respectively. In conclusion, the proposed method is a useful tool to identify ZNL among different *Lycium* production areas in China.

Introduction

Lycium barbarum L., known as Chinese wolfberry or Goji, is a kind of multi-branched shrub that belongs to *Solanaceae*. Its chemical constituents, which are commonly used in herbal medicine and tonic applications, have been extensively studied and found to contain polysaccharide-protein, polysaccharides, flavonoids, vitamins and zeaxanthin[1-4]. Therefore, *L. barbarum* has numerous biological activities for potential pharmaceutical interest, including immune-regulatory, antitumor, anti-fatigue, and antioxidant properties; it also reduces neuronal damage and blood-retinal barrier disruption[5-8]. Geographical origin is one of the most important quality parameters for many foods, because climate, soil, and cultivation methods cause differences in the chemical composition of plants[9]. In China, the most popular *Lycium* ecotype currently growing is in Zhongning County, Ningxia Hui Autonomous Region, China. Zhongning *Lycium barbarum* (ZNL) with its unique geography and suitable climate features, always produces high quality. The main features of *Lycium* are its large fruit size, nice color and high contents of polysaccharide, flavonoid, and trace elements, resulting in its high price in traditional medicine and international markets. Moreover, given the aforementioned features, ZNL is attracting increasing attention, which leads to its great need in the field of pharmacy and functional foods. At present, with the increasing demand for *Lycium*, the ZNL market is saturated with fake and inferior *Lycium*, and the specific differential detection method of *Lycium* is rarely reported. Therefore, simple and efficient methods to meet the demand are of urgent need.

Fourier transform infrared (FT-IR) spectroscopy combined with chemometrics has been widely used in many scientific studies. It is a direct, reliable, and fast method that makes it possible to simultaneously obtain specific information about different parameters, mainly in the 3000–400 cm^{-1} region, because bands are associated with the vibrations of functional groups of the molecules[10-12]. The associated bands of proteins, fats, lactose, and lactic acid are well known and have been described in milk and cheese[13-16]. Currently, in the field of *Lycium* classification, different *Lycium* species are usually distinguished through micro-section, observation, and analysis by professionals. Such methods are highly subjective and undeterministic. Some works used FT-IR, second derivative IR spectra and 2D correlation infrared spectroscopy for the distinction of eight *Lycium* species and obtained acceptable results[17-18]. The discrimination of Goji's geographical origin through non-targeted liquid to quadruple time-of-flight mass spectrometry also obtained good results[19]. However, such methods had some disadvantages, such as complex, tedious and hard operation. Moreover, FT-IR spectroscopy combined with multivariate analysis has been used as a rapid and reliable method to determine the cultivation ages and cultivars of ginseng[20-22]. Some researchers also conducted FT-IR spectroscopy with multivariate techniques to discriminate and classify red, blue, and green spray paints, and results proved the method's effectivity[23–25]. FT-IR spectroscopy has also been successfully used in the classification and discrimination of living matters[26-30].

This study was conducted to identify the cultivation region and quality of ZNL. A total of 149 samples were obtained, and different spectral pretreatments were conducted. Various spectral regions were chosen, and different chemometric methods were applied to achieve ZNL classification from other regions. This study aimed to provide a new trend and perspective for ZNL discrimination and quality evaluation.

Material and method

Samples

Mature wolfberries (*L. barbarum*) were obtained from Ningxia Chinese Lycium Group Company, including ZNL (Ningxia, China) and non-Zhongning *Lycium* (NZNL), which came from other regions of Ningxia, Xinjiang, Qinghai, Gansu, China

Reference samples were prepared by removing all foreign matters, cut into pieces with scissors, and desiccated by heated air combined with vacuum drying for 12 and 8 h, respectively. Finally, the dried samples were evenly milled and passed through a 60 mesh sieve to obtain the final samples.

Analytical protocol

A Bruker VERTEX 70 series FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) was used for this study. Moreover, high-speed universal grinder (Tianjin Taisite Instrument Co., Ltd.) and vacuum drying oven (Dalian Eilite Instrument Co., Ltd.) were used in this work. Transmission FT-IR spectra were taken though KBr pellets, in which the ratio of KBr to sample was 100:1 (w/w). The measurement parameters were as follows: 150 × 150mm window size, 4.0cm^{-1} resolution, 32 co-added spectra, and 4000–400cm^{-1} range. Each sample was measured three times. The average of the three spectra obtained from the same sample was used in subsequent analyses.

Data processing

Data covering the FT-IR wavelength region (4000–400cm^{-1}) were collected, and models were developed and validated using this complete range along with a number of subsets. Each spectrum was an ensemble average of three scans collected from the cell. The spectra of 149 samples were pretreated through normalization to correct the measurement variation. Each spectrum was aligned to the baseline using an instrumentation software before converting the spectra into JCAMP-DX format. The most accurate models were developed using the wavelength range of 1909-1311cm^{-1}, and only these models were discussed further in this study.

Software

All statistical treatments were performed using Unscrambler X10.1(CAMO, Norway) and TQ Analyst 8.3.125 (Thermo Scientific, USA). The commercial database software used included OMNIC 7.3 (Thermo Scientific, USA) and OPUS 5.5(Bruker, Germany).

Data analysis

Visual grouping

The samples were randomized and divided into two groups: a calibration group that consisted of 111 of the samples and a validation group that consisted of the remaining sample of 38. Sample assignment to each group was performed by selecting every sample as a member of the calibration group and the remaining samples were assigned to the validation group. Random selection did not generate equal-sized groups.

Soft independent modeling of class analogy (SIMCA)

SIMCA is based on making a PCA model for each class in the training set. Unknown samples were then compared with the class models and assigned to classes according to their proximity to the training samples. It is also known as a supervised pattern recognition method as the individual PCA models define classification rules. In the case of all classification methods, making a SIMCA model needed a training stage and a test stage. SIMCA modeling requires building one PCA model for each class which describes the structure of that class as well as possible. The optimal number of PCs should be chosen for each model separately, according to a suitable validation procedure. Before developing a SIMCA model, it is helpful to determine if the data being considered exhibit any tendency to cluster by the classes. Before using the models to predict class membership for new samples, one should also evaluate the model specificity, i.e. whether the classes overlap or are sufficiently distant from each other. Specific tools, such as model distance and modeling power are available for this purpose. The discrimination power of SIMCA was based on the largest possible distance among classes.

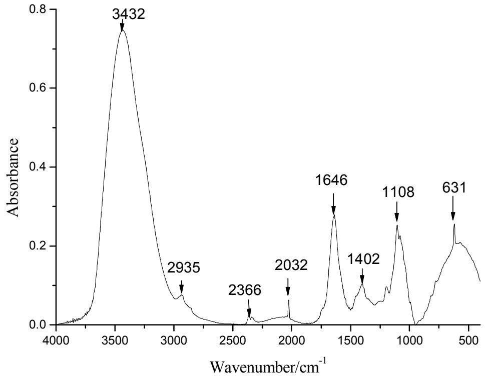
Discriminant analysis (DA)

DA is a classification method of TQ Analyst software. Different spectral pretreatment methods, including a constant, peak or normalize ratio (A/b=k*c), multiplicative signal correction (MSC), Standard Normal Variate (SNV), Norris derivative filter, and Savitzky–Golay (SG) filter) were selected to produce better results. The Savitzky-Golay filter is a type of filter. The method essentially performs a local polynomial regression (of degree k) on a distribution (of at least k+1 equally spaced points) to determine the smoothed value for each point. Methods are also provided for calculating the first up to the fifth derivatives. The samples were classified, and the spectral information of the samples was imported. To make a robust and available discriminate model, different spectral pretreatment method were applied, and the analysis spectral regions and various principal component (PC) numbers were changed. The value was either decided by the highest recognition rate or the lowest error rate.

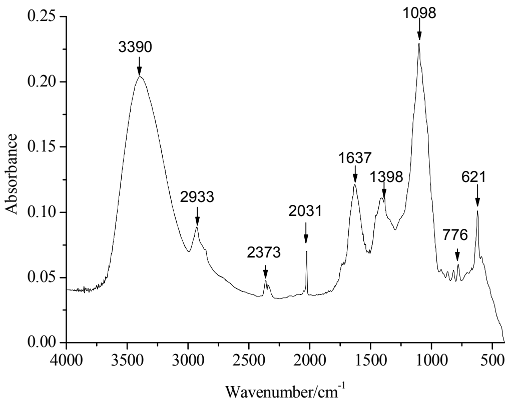
Results and discussion

Spectral analysis

The chemical compounds of *Lycium* are polysaccharides, organic acids, steroids, peptides, flavonoids, and trace elements. Fig. 1 shows the FT-IR spectra of the two kinds of typical *Lycium* samples at room temperature.



(a) Original spectrum of the ZNL sample



(b) Original spectrum of the NZNL sample

Fig 1. Original spectra of the two typical *Lycium* (a) and (b)

As shown in Fig. 1, several characteristics could be extracted, such as the strongest peak at 3390cm^{-1} belonging to the stretching vibration of O-H groups, and the peak at 2925 cm^{-1} assigned to the stretching vibration of -CH_2 groups. Furthermore, the peak at 1626 cm^{-1} was mostly ascribed to the stretching vibration of C=O groups in the volatile oils and other compounds embodying carbonyl group, and the stronger peaks in 1600-1000 cm^{-1} were mainly attributed to the stretching vibration of C-O and C=O, which displayed the characteristic absorption bands of polysaccharides and glycosides.

Although the spectra of the two kinds of *Lycium* species were rather similar, some differences in the shape or intensity were observed. The absorbance peak of *Lycium* was extremely different under the range of 1800–1000 cm$^{−1}$. In particular, the characteristic band at 1108 cm^{-1} was from the ZNL sample, while characteristic band at 1098 cm^{-1} was from the NZNL sample. Therefore, we could create a robust classification model of *Lycium* under the spectra range of 1800–1000 cm$^{−1}$.

Effective wavenumber (EW) selection

EW selection can simplify the model, and improve the forecasting capacity and robustness of the calibration models to eliminate of collinear variables[31]. The value of X-loading weights was employed in the EW selection method and it was estimated using the PCA model.

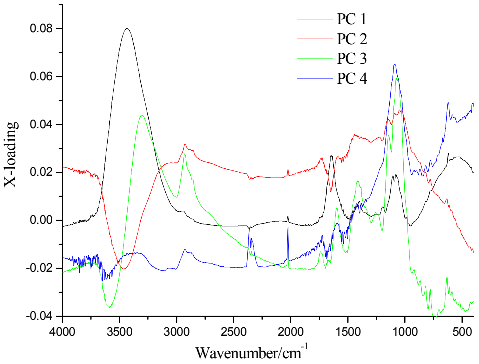
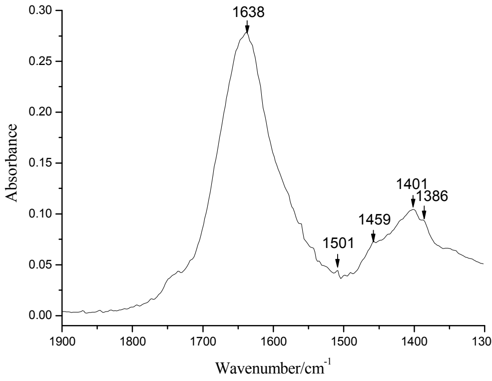
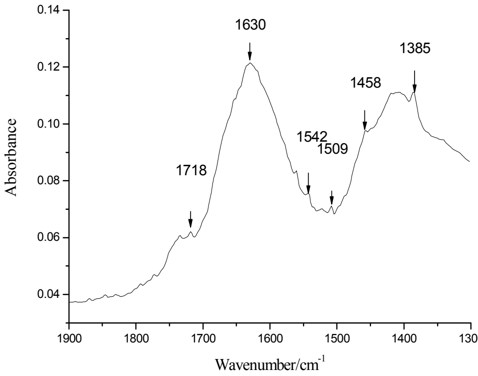


Fig. 2 Effective wavenumber selection using X-loading weight

The X-loading weights of the first four PCs by PCA are shown in Fig. 2. The loading weights showed how much each wavenumber contributed to the response variation. Wave numbers with large loading weight values are important for the PCA model. The spectral regions of X-loading weights with absolute values of over 0.02 were used for modeling. As shown in Fig. 2, the spectral regions of 3700-3100 and 1800-900 cm^{-1}showed higher loading weight and contributed more to the robustness of the identification model. Compared with the PCA model obtained with full spectra, the X-loading weight methods considerably improved the performance of the model. Excellent performance was obtained from the PCA model with EWs selected using the X-loading weight method. PCA is a kind of data dimension reduction technique of multivariate statistical analysis. PC is the result of the original variable reorganization, replacing the original variables involved in the modeling, reduced the workload of the analysis process. Selected a suitable PCs value, when the cumulative contribution rate of PC was greater than 85%, we can think it is enough to response the information of original variables, the corresponding value is the number of PCs. According to the PCA analysis, we found that the value of 3 PC is perfect, with the cumulative contribution rate of 90%, selected for further research. Most of the peaks that appeared in the regions of 3700-3100cm^{-1} belonged to the vibration of O-H bond, including stretching vibration, deviational vibration and bending vibration. All those molecular movements made a small difference among various *Lycium* samples. Nevertheless, simple and effective identification pre-analysis was conducted. According to the pre-analysis results and the X-loading weight values, the spectra of 1909-1311cm^{-1} was chosen for in-depth and detailed analysis.



(a) Characteristic spectrum of the ZNL sample



(b) Characteristic spectrum of the NZNL sample

Fig. 3 Characteristic spectra of two typical *Lycium* samples (a) and (b)

Fig. 3 compiles the characteristic FT-IR spectra of *Lycium* from different production areas under room temperature. As shown in Fig. 3, the typical part of 1900-1300cm^{-1} was chosen. Detailed peak positions of the typical samples are also illustrated in Fig. 3.

These FT-IR spectra showed their macro-fingerprints. Comparative and separate analyses were performed in the spectra of two typical samples. For example, the strongest peak at 1638 and 1630cm^{-1} was due to the bending of carbonyl. The absorbance values of these two sample types greatly differed, and various amounts of amino acid and polypeptide possibly exist in these samples. The peak at 1501 and 1509cm^{-1} belonged to the bending of –C-H groups in *Lycium,* whereas that at 1458 and 1459cm^{-1} was attributed to the bending vibration of methyl and methylene groups. Several kinds of amino acids might be present in these samples. The peak at 1386 and 1385cm^{-1} was due to the plane vibration of O-H groups in *Lycium*, phenolic acid compounds and carbohydrates. In the spectrum of ZNL sample, an absorbance peak was observed at 1401cm^{-1}, which was attributed to the bending vibration of methyl and methylene groups. This finding indicated the typical absorption of amino acids. The typical peak of NZNL sample was at 1542cm^{-1}, which was mainly attributed to the bending vibration of N-H groups and tretching vibration of C-N groups in protein amide II band. This peak displayed the characteristic absorptions of fatty acid and protein.

SIMCA

Upon analysis of the spectral region and considering the result of the SIMCA classification, a suitable spectral region was selected. Model and data processing were performed under this region. Various spectral pretreatment methods were applied to identify the ZNL in the typical production areas. All of the methods were verified by multivariate statistical analysis.

Table 1 Measurement of performance in the discrimination of *Lycium* samples of the calibration and validation groups using SIMCA

Spectral regions/cm^{-1}		Calibration				Validation			
1909–1311		No pretreatment	SNV	SG (9.4)	MSC	No pretreatment	SNV	SG (9.4)	MSC
Recognition rate/%	ZNL	55.56	90.60	83.76	52.99	58.12	85.47	82.91	52.99
	NZNL	53.13	87.5	84.37	46.88	53.13	81.25	81.25	56.25

A suitable value of three PCs was chosen for each class. The spectral region of the model was 1909–1311cm^{-1}. Different models were constructed using various data processing methods (No, SNV, SG 9.4, and MSC). Table 4 presents the classification rate of each model. The type of ZNL sample obtained a better classification regardless of the technique used, in which the type of NZNL sample was extremely confusing. The processing method of SNV and SG showed a better classification than that of MSC and No pretreatment. The SNV processing undoubtedly showed great significance in the identification of ZNL samples. As we all know, an applicable model at least meet the demands of recognition rate over 90%, and the further study should be performed without any hesitation.

DA

The DA method employed various spectral regions under the same pretreatment and various PCs or various pretreatments on the typical spectral region. An identification method was achieved according to the results of the model.

Table 2 Effect of different spectra without pretreatments on recognition rate of calibration and validation samples

Spectral regions/cm^{-1}	PC numbers	Calibration set/%		Validation set/%	
		ZNL	NZNL	ZNL	NZNL
3999–410	10	74.70	81.82	85.71	70
3780–2980	10	73.49	86.36	78.57	70
2980–2100	10	78.31	81.82	82.14	80
2560–1760	10	81.93	77.27	85.71	80
2100–1120	10	89.16	86.36	92.86	90
1300–960	10	86.75	81.82	85.71	80
1909–1311	10	93.98	90.91	100	100
920–410	10	86.75	86.36	92.86	80
1240–660	10	81.93	81.82	85.71	90
3999–410	10	74.70	81.82	85.71	70

The numbers of the ZNL calibration and validation sets were 83 and 28, respectively, and the remaining number of samples was the number of NZNL. Different spectra were purposefully selected without any pretreatments. Various spectral regions obviously resulted in various recognition rates of the calibration and validation sets. As shown in Table 2, in order to find a suitable spectral region, a constant value of 10 PCs was chosen for each treatment, different spectra exerted tiny effects on the recognition rate of the validation set. A perfect result of 100 % was achieved in the range of 2560-1760 cm^{1}. Various spectral regions exerted a great influence on the calibration set compared with the validation set. Only one spectral region had a recognition rate over 90% for both samples, and the recognition rates under the range of 1909-1311 cm^{1} were 93.98% and 90.91%. These results were due to the fact that the two samples exhibited different feature absorbance peaks in the range of 1909-1311 cm^{-1}.

Table 3 Effect of different PCs without pretreatments on the recognition rate of calibration and validation samples

Spectral regions/cm^{-1}	PC numbers	Calibration set/%		Validation set/%	
		ZNL	NZNL	ZNL	NZNL
1909-1311	4	51.81	78.57	68.42	90
1909-1311	5	66.26	71.43	78.95	80
1909-1311	6	69.88	78.57	78.95	100
1909-1311	7	79.52	82.14	86.84	100
1909-1311	8	77.11	82.14	84.21	100
1909-1311	9	75.9	82.14	84.21	100
1909-1311	10	93.98	90.91	100	100
1909-1311	11	87.95	89.29	100	100
1909-1311	12	87.95	89.29	100	100
1909-1311	13	87.95	89.29	97.37	100

Under the analysis of different spectral interval, considering that the PC numbers contributed to the classification of the samples, a constant value of 10 PCs was chosen for each treatment. From the Table 3, it's tempting to conclude that the PCs of 10 perfected for the deeper DA classification research. Further analysis of the results showed that different spectral interval had the same conclusion, the value of 10 PCs was an appropriate identification conditions.

Table 4 Effect of different spectral pretreatments on the recognition rate of calibration and validation samples

Spectral regions/cm^{-1}	Spectral pretreatment	Calibration set/%		Validation set/%	
		ZNL	NZNL	ZNL	NZNL
1909-1311	SNV	87.95	86.36	92.86	80
1909-1311	SNV+SG(7.3)	84.34	86.36	96.43	90
1909-1311	SG. (7.3)	79.51	87.95	100	100
1909-1311	MSC+SG. (7.3)	80.72	81.81	89.29	100
1909-1311	MSC	84.34	86.36	96.43	90
1909-1311	MSC+N (7.3)	81.93	81.81	85.71	90
1909-1311	Norris (7.3)	83.13	86.36	85.71	100
1909-1311	SNV+Norris (7.3)	85.54	77.27	92.86	90
1909-1311	SG (9.4)	86.75	89.29	96.43	80
1909-1311	Norris (9.4)	83.13	90.91	89.28	80
1909-1311	SNV+Norris (9.4)	81.93	86.36	96.43	90
1909-1311	MSC+Norris (9.4)	87.95	90.91	89.29	100

To reduce the scattering effects and compare the *Lycium* samples, the spectral region of the FT-IR (1909–1311 cm^{-1})

was subjected to different pretreatments (i.e., normalization, first and second derivative, SG, and Norris. Only the best classification results for the spectral region are presented in the present study (Table 4). Different pretreatments of the spectral region led to a small fluctuation on the recognition rate of the calibration set. The original spectrum is available and valuable. The optimal reference set was obtained by iteratively adding and removing reference samples until the recognition error and the uncorrected number of external estimates were minimized or more precisely balanced. Finally, the no-pretreatment of the spectral region at 1909–1311 cm^{-1} was regarded as the best choice. Under this condition, the recognition rates of the calibration set were 93.98% and 90.91%, whereas those of the validation set were 100% and 100%.

Conclusions

FT-IR combined with discrimination technique is a powerful tool for *Lycium* sample discrimination. Two methods were tested on different *Lycium* produces areas and good results were obtained. DA is an excellent methodology for ZNL discrimination, because it is a rapid technique that does not need a chemical reagent. The optimal identification results of the recognition rates of the ZNL and NZNL calibration set were 93.98% and 90.91%, respectively, whereas the ZNL and NZNL validation set were 100% and 100%, respectively. DA can meet the requirements of simple, feasible, and ordinary data processing with common software. Therefore, a simple, rapid, and reliable overall discrimination of ZNL cultivar was obtained at a low cost, which might be applied for rapid classification of ZNL *Lycium* cultivar. However, this study presented some limitations, and further work is necessary to obtain more robust classification rules with consideration for regional and time variability. Nevertheless, this study achieved a powerful and practical identification method for ZNL and provided a new trend and perspective for quality evaluation and breed discrimination.

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