DETECTION OF VOLATILE OIL CONTENT OF SINGLE-GRAIN ZANTHOXYLUM SEED BASED ON NIR

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Abstract: A NIR model was established to predict the volatile oil content of single particle red Zanthoxylum seed in this paper. With the characteristic of irregular surface, A single Zanthoxylum seed will reflect the great difference in response to spectrum signals the entire spectrum detection and exceptional sample rejection method were employed before model optimization. As a result, the NIR model for predicting the content of volatile oil were built up by 74 red Zanthoxylum seed and results indicated: the NIR model of the single grain Zanthoxylum seed had good stability and predictability (RSD<10%,RSD>3). Results of this paper suggested that NIR could be used as a quick and convenient method for predicting the volatile oil content of Zanthoxylum seed, which is useful for breeding and the quality evaluation of it.

Key words: NIR, Zanthoxylum seed, Model Optimization

1. INTRODUCTION

Zanthoxylum is economic cultivars in many countries of Asia in people's daily life. It is not only an important spice but also has great medicinal value. The volatile oil content of Zanthoxylum seed is one of important purchase

standards，as well as deep processing，sale and breeding. At present, the detection method of volatile oil is very time-consuming (at least five to six hours per sample) based on the existing GB "Zanthoxylum" (SB/T10040-92) and "Zanthoxylum grade quality" (LYT1652-2005). It is difficult to detect the quality of Zanthoxylum for each sample need to do pre-processing and consumption of chemical. It also has brought great inconvenience in market circulation links, breeding and other requirements for nondestructive testing. So how fast, and how to make non-destructive testing on Zanthoxylum quality is an urgent problem to solve.

NIR spectroscopy technology has been well developed recently in China because this technology is quick, no chemical-consuming and nondestructive. NIR is gradually applied in the field of food and agriculture. The technology has good performance especially for on-line detection and locale detection. Duan S. Q. (Duan et al, 1996) used infrared spectroscopy, i.e. atomic absorption spectrometry and elemental analysis methods to identify the organic component and inorganic elements of Zanthoxylum. Lin P. Y. (Lin et al, 2003) used ATR-Fourier Transform Spectrometry, with cluster analysis method to identify Zanthoxylum herbs. However, there is no report in the literature that the Zanthoxylum seed volatile oil was detected rapidly and non-destructive with NIR.

Establishing a fast and non-destructive detective method has important significance to promote the Zanthoxylum breeding, deeply products and quality detection. It also has practical value to establish an effective system of quality assessment and quality standards. NIR model is established to predict the volatile oil content of single particle red Zanthoxylum seed in this paper. The authors discuss the practicality and feasibility of this method as a new, fast, and non-destructive green detection.

2. MATERIALS AND METHODS

2.1 Experimental design

The sample set is composed of single particle red Zanthoxylum seeds of 74 groups. They are collected from farmer's trade wholesale market of Chongqing, CaiYuanBa and BeiPei, some of which are purchased from several big supermarkets of Chongqing. The Zanthoxylum seed volatile oil density scope is 1.1937-3.4304(ml/100mg). The volatile oil content is obtained by food scientific institute of SouthWest University according to GB.

2.2 Instruments and spectral data

Near infrared spectra were collected on the Zanthoxylum seed sample set by diffuse reflectance from 12500 cm^{-1} to 4000cm^{-1}, Resolution is 4cm^{-1} , scanning 64 times each samples by the Fourier near-infrared spectroscope MATRIX-I spectrometer (the diffuse reflection integral ball appendix; the PbS detector) (BRUKE Corp Germany). Figure 1 shows original NIR spectrum curves.

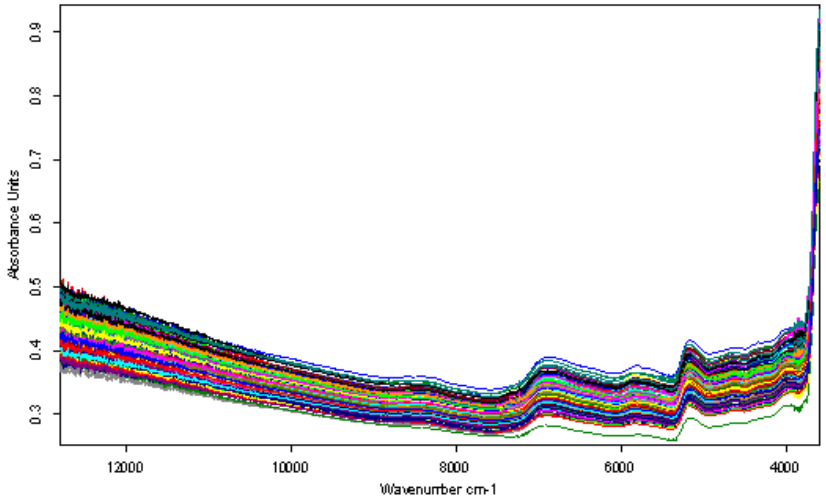

Fig1:74 unit original NIR spectrum of single red Zanthoxylum seed

2.3 Evaluation parameters of Near-Infrared model

To check the model if forecast ability and the usability, two evaluation parameters were used: one is relative standard deviation RSD(Lu et al,2000)and another relative analysis error RPD(Lu et al,2000;Yan et al,2005). RSD indicates the prediction ability of the model,and if RSD<10% ,it means that the model can be applicable in actual detection. While RPD index shows that if the model is stable and predictive. If RPD>3, the model has the high steady capability predictive ability (D.Cozzoline et al, 2004).

3. RESULTS AND DISCUSSION

3.1 Selection of sample

The spectrum of a single Zanthoxylum seed is different from one seed to another in one sample. In this experiment, each scanned spectrum curve as a sample was processed. Figure 2 shows original NIR spectrum curves of three particles from the same sample. And the total number of primitive spectrum is 222. In the experiment, the effect of the spectrum difference on the model influence is bigger than the density difference. Here first primitive sample centralism outlier samples 22 are elimated based on the F statistics significance examination method. We selected 140 samples as the training set. The testing set is made up of the other 60 samples. The classifier is based on Kennard-Stone (R W Kennard et al,1969;Lu et al,2004) method .

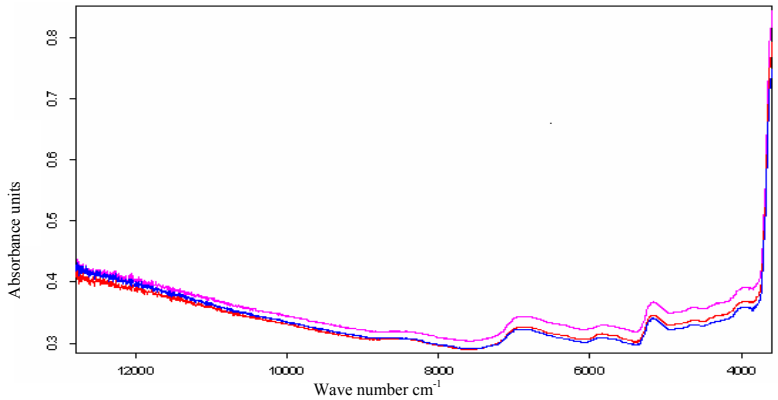

Fig 2: spectrum picked up three particles from the same sample

3.2 Elimation of outlier samples

The sample is red single particle Zanthoxylum seed. Its irregular surface can make the scanning spectrum inaccurate. Therefore, in order to establish a good NIR model of single particle Zanthoxylum seed, it is necessary to reject the unusual sample and model optimization.

The so-called unusual sample refers to the sample with big error of density value or the spectrum data, the common solvent used in rejection unusual sample: method based on the forecast density residual error, restructuring spectrum residual error, principal components score cluster analysis, as well as the release lever value and the student T-test and so on (Wang H W,1999;Wang D J et al,2004;Xu et al,2000).

In this paper we elimate the unusual samples through software OPUS6.0 (BRUKER Corp.). After unusual samples rejection, the training sample set is 116 integers, and the test sample set is 37.

3.3 Model calibration

Conventional spectrum denoising methods and their combination are used in this experimental, and PLS is the most popular linear calibration method in NIR quantitative analysis. We use software OPUS6.0 to pretreatment the spectrum and optimize the model. Figure 3 shows the spectrum after pretreatment.

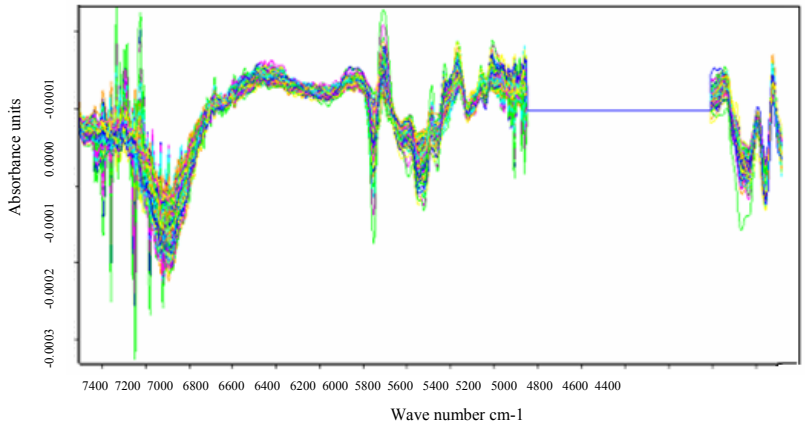

Fig 3 first derivative + MSC spectrum after wave pretreatment

pretreatment of spectrum the first derivative and MSC ,methods were applied to make pretreatment of spectrum , and the scope of spectra is adopted from 4601.6 cm^{-1} to 4248.7 cm^{-1}, and from 7500.2 cm^{-1} to 5448.2 cm^{-1}; the number of principal component is 7; Root Mean Square Error of Estimation is 0.209; Coefficient of determination is 0.9049. The relationship of target value and the prediction value of training set are shown in Figure 4. It shows that a good linear relationship was obtained between the chemical analysis curve and the NIR predictive curve.

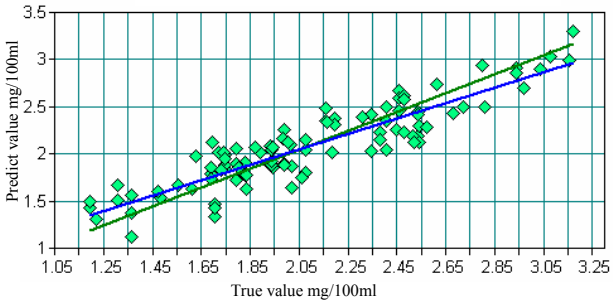

Fig 4:model Prediction analysis on target value of training Set

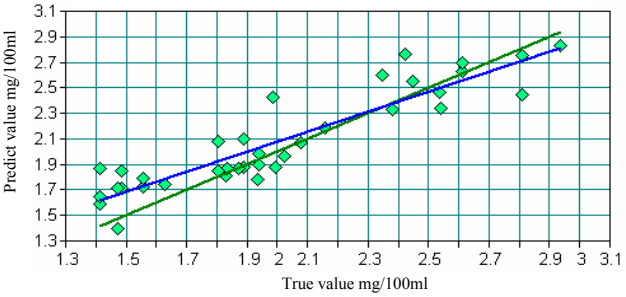

Fig 5: model Prediction analysis on target value of testing set

Use the above model to predict the test samples. The decision coefficient is 0.9136 and root mean square error of estimation is 0.197. The relationship of true value and the predict value of test set are shown in Figure 5. It shows that there is a good linear relationship between the chemical analysis and the NIR predictive value.

In order to verify that the predictability and practicality of the model which predict the volatile oil content of the single red particle Zanthoxylum seed, the relative standard deviation (RSD)and the relative error (RPD) of the training sets and test sets are calculated and shown in table 1.

Table 1, Verification result of NIR mode*l*

Sample set	Sample number	R	RMSEE	RSD	RPD
Train set	116	0.9049	0.209	8.86%	3.17
Test set	47	0.9136	0.197	6.87%	3.21

From the table above, RSD of the training set and test sets is less than 10% and RPD is more than 3. It has a good calibration result，so the NIR model for forecast the volatile oil content of single particle red Zanthoxylum seed can be used for actual testing.

The experiment shows that the spectral data is not accurate because of the irregular surface of Zanthoxylum seed, so a large number of abnormal spectral data will appear. Therefore, if we do some pre-processing work before scanning spectral curve, such as changing Zanthoxylum seed into powder with Special equipment, or using a big sample cup while scanning, it can reduce the spectrum of differences, therefore reducing the abnormal sample. However, there are some drawbacks in pre-treatment work: on the one hand, the powder will make the samples destructed; on the other hand the powder will increase the detection time. It needs a certain number of samples by using big sample cup. Therefore, the suitable actual demand model can be established only according to the different application situation.

4. CONCLUSION

NIR models were established to predict the volatile oil content of single-particle red Zanthoxylum seed in this paper in order to enhance the breeding and the detection technology of the Zanthoxylum seed. As a result, the NIR model for predicting the content of volatile oil were built up by 74 red Zanthoxylum seed which buy from ChongQing and results indicated: the NIR model of the single grain Zanthoxylum seed had good stability and predictability (RSD<10%,RSD>3). Results of this paper suggested that NIR could be used as a quick and convenient method for predicting the volatile oil content of Zanthoxylum seed, which is useful for breeding and the quality evaluation of it.

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REFERENCES

D. Cozzolino, MJ Kwiatkowski, M. Parker, et al, Prediction of phenolic compounds in red wine fermentations by wisible and near infrared spectroscopy. Analytica Chimica Acta 513, 2004:73 ~ 80

Duan S Q, Gong M C Research on Zanthoxylum ingredient, Sichuan Chemical,1996, 4:34 - 36

Lin P Y, Tao C Y, Identification of genus Zanthoxlum by Fourier transform infrared spectrometry " Academic Journal of Second Military Medical University " 2003.9 -1029 to 1031

Lu W Z, Yuan H F, Xu G T, "Modern near-infrared spectral analysis technology". Beijing: China Light Industry Press, 2000

Lu Y J, Qu Y L ,Piao R G, The Algorithm of Eliminating the Similar Samples in the Process of Calibration and Prediction. Spectroscopy and spectral analysis,2004， 24（2）： 158~161

People's Republic of China forestry industry-standard "Zanthoxylum grade quality" (LYT1652-2005)

People's Republic of industry-standard "Zanthoxylum" (SB/T10040-92)

R W Kennard,L A Stone．Computer Aided Design of Experiments．Technometrics 11 (1969)： 137~148

Wang D J, Application of Near Infrared Spectroscopy Detection Technology to Agriculture and Food Analysis .Spectroscopy and spectral analysis, 2004 (04): 447 - 450

Wang H W, Partial least-squares regression method and its application. Beijing: National Defense Industry Press, 1999

Wu J Z Study on Quality Detection of Agricultural Products Based on Near Infrared Spectroscopy Technology, Doctoral dissertation 2006.6

Xu Guangtong, Hong-Fu Yuan, Wan-Zhen Lu. Development of Modern Near Infrared Spectroscopic Techniques and Its Applications. Spectroscopy and spectral analysis, 2000,20(02) :134 - 142

Yan Y L, Zhao L L Han D H, "Near-infrared spectral analysis foundation and application [M]. Beijing: China Light Industry Press, 2005