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COMPACT NEAR-INFRARED SPECTROMETER FOR QUANTITATIVE DETERMINATION OF WOOD COMPOSITION[**]

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A compact desktop near-infrared spectrometer with near-infrared spectrum acquisition software was developed based on fixed grating type fiber optic spectrometer with MEMS technology. The light source stability, baseline stability, instrument signal-to-noise ratio, and dark current drift are four important indicators for the performance test and evaluation of the spectral system. The test results show that the light source reaches a stable state after being warmed up for 2 s. The standard deviation of 100 %T line of 1200–1550 nm instrument is less than 0.0003, and the signal-to-noise ratio is 3000:1. The dark current relative standard deviation fluctuates between 0.0019 and 0.0035. Based on 88 samples of the crushed material of lumber for wood cellulose and lignin contents, the quantitative calibration model was established using multiple scatter correction spectra pretreatment method set up after the correction model of cellulose and lignin. Root mean square errors of calibration set of cellulose and lignin are 0.6096 and 0.9572%, respectively. Root mean square errors of prediction set of cellulose and lignin are 1.2884 and 1.7712% respectively. The experimental results show that the developed small NIR spectrometer has a stable working state, and the prediction results for cellulose and lignin content based on the calibration model for powdery wood samples verify that the small NIR spectrometer has a high detection accuracy and can be used in the rapid detection of common materials.

Keywords: *compact near-infrared spectrometer, stoichiometry, calibration model, cellulose, lignin.*

МАЛОГАБАРИТНЫЙ СПЕКТРОМЕТР БЛИЖНЕГО ИНФРАКРАСНОГО ДИАПАЗОНА ДЛЯ КОЛИЧЕСТВЕННОГО ОПРЕДЕЛЕНИЯ СОСТАВА ДРЕВЕСИНЫ

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Малогабаритный настольный спектрометр ближнего ИК-диапазона с автоматической регистрацией спектра разработан на основе волоконно-оптического спектрометра с неподвижной дифракционной решеткой с использованием микроэлектронных и микромеханических технологий. Стабильность источника света и базовой линии, отношение сигнал/шум прибора и дрейф темнового тока — важные показатели проверки работоспособности спектральной системы. Результаты

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эксперимента показывают, что источник света достигает стабильного состояния после прогрева в течение 2 с. Стандартное отклонение линии 100% пропускания прибора в диапазоне 1200—1550 нм составляет <0.0003, отношение сигнал/шум 3000:1. Относительное стандартное отклонение темнового тока 0.0019—0.0035. Количественная калибровочная модель содержания древесной целлюлозы и лигнина разработана на основе 88 образцов измельченных пиломатериалов с помощью корреционной модели целлюлозы и лигнина, а также последующего учета поправок на многократное рассеяние. Среднеквадратичные ошибки калибровки по целлюлозе и лигнину 0.6096 и 0.9572%, предсказанного содержания целлюлозы и лигнина 1.2884 и 1.7712%. Разработанный компактный спектрометр ближнего ИК-диапазона имеет стабильные рабочие характеристики. Основанные на калибровочной модели порошкообразных образцов древесины результаты прогнозирования содержания целлюлозы и лигнина подтверждают, что описываемый спектрометр обладает высокой точностью и может быть использован для быстрого обнаружения отдельных компонентов смеси веществ.

Ключевые слова: *малогабаритный спектрометр ближнего инфракрасного диапазона, стехиометрия, калибровочная модель, целлюлоза, лигнин.*

Introduction. Near infrared spectroscopy is an efficient and rapid modern analytical technology, which integrates the latest research achievements of computer technology, spectroscopy, chemometrics [1, 2] and other disciplines. It has been increasingly applied in many fields with its unique advantages [3]. The near infrared spectrum belongs to molecular vibration spectrum, which is generated by anharmonic energy vibration of covalent chemical bonds. It is the doubling and combination frequency of the molecular vibration and comes from the absorption of C–H, O–H, N–H and other chemical bonds [4]. According to the Lambert–Beer absorption law, if the composition content of a sample changes, its NIR characteristics will also change. According to the different spectral characteristic information, the NIR spectrum can be used for qualitative and quantitative analysis of samples. As a fast and efficient nondestructive testing technology, NIR is widely used in agricultural production, food processing, and the pharmaceutical industry [5–7]. With the rapid development of NIR spectroscopy, micro NIR spectrometer has become the focus of analysis and research [8, 9]. The development of miniature NIR spectrometer includes the design of spectral detection system and detection software [10, 11]. In this study, a fixed grating fiber near-infrared spectrometer based on MEMS technology was used.

Materials and methods. *Basic composition of spectrometer.* NIR spectroscopy instruments are generally composed of miniature light source, spectrometer, sample carrier, detector and control device, and data processing software system (Fig. 1). The core component of the small NIR spectrometer is a fixed grating fiber near-infrared spectrometer based on MEMS technology. The spectrometer is integrated with fixed grating, InGaAs detector, A/D conversion, and other electronic circuits. Small near infrared instruments use halogen tungsten lamp as external light source. Through two light source modules (*1*), the near-infrared light from the light source irradiates the sample cup (*7*). The diffuse light produced by the materials in sample cup (*7*) gathers together via condensing lens (*3*) and then enters to the optical fiber via small a type fiber interface. Through optical fiber coupling, the diffuse light goes into the fixed grating fiber NIR spectrometer

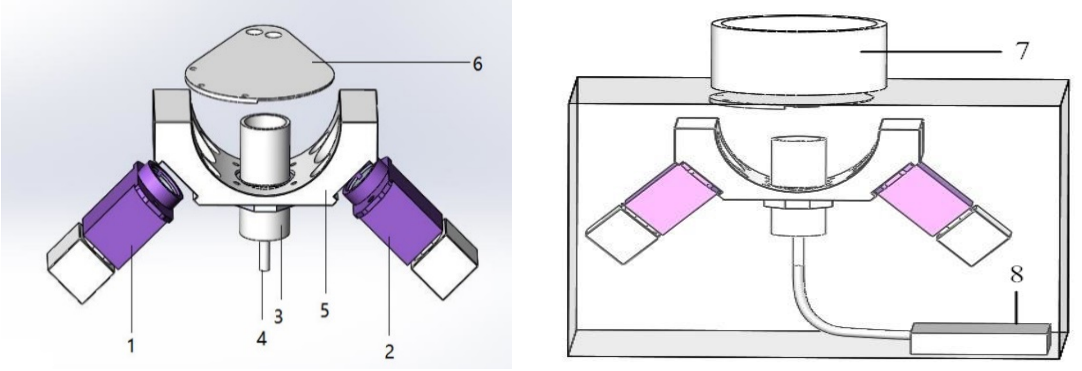

Fig. 1. Schematic diagram of the small near infrared spectrum detection system: 1, 2 – light source module, 3 – condensing lens, 4 – small A type interface, 5 – base, 6 – gold-plated reflecting plate, 7 – sample pool, 8 – fixed grating fiber near-infrared spectrometer.

and is finally transformed into numerical signal input to the computer by the internal *A*/*D* conversion [12]. For ease of use, the instrument is integrated with gold-plated reflector plate (*6*) as a reference; At the same time, in order to improve the accuracy and stability of wavelength, the instrument is also integrated with a standard material calibration device, which is convenient for wavelength calibration at any time.

Main performance test of NIR spectrometer. Since the core components used in the miniature NIR spectroscopy are integrated with the fixed grating fiber NIR spectrometer based on MEMS technology, some important technical parameters are determined by the core components themselves. Table 1 lists the main technical parameters of the fixed grating fiber NIR spectrometer. After the instrument is integrated, stability of the light source energy distribution, the signal noise ratio of the instrument, the baseline stability, and the dark current and other parameters should be tested to verify the working state of the instrument.

TABLE 1. Main Technical Parameters of Fixed Grating Fiber Near-Infrared Spectrometer

Parameter	Specifications
Spectral range	900–1700 nm
Spectral resolution	<16 nm FWHM/8.2 nm Pixel
Spectral accuracy	2 nm (typ.)
Reproducibility	≤0.1 nm
Signal to noise ratio (16 bits ADC)	≥ 5,000 at $T_{\text{integration}} = 2$ ms
Operating temperature	0 to +40°C
Detector array	InGaAs, 128 elements
Dimensions	69.3×39.6×13.6 mm
Weight	45 g
Connectors	USB 2.0 (micro B socket)
Power requirements	Via USB or external 5V
Power consumption	1.5 W

Stability of light source energy. The stability of light source energy refers to the time when the light power becomes stable after the light source is turned on. The light source instrument is composed of Welch Allyn halogen lamps for the company's 997418-21 (rated power 3.500 V/0.430 A). Under the condition of room temperature at 26°C, the power output of the halogen tungsten lamp source with a current change is adjusted by the DP832A regulated power supply. When the voltage of the rated light energy reaches 100%, the time required for the light energy to be detected (1.116 V/0.272 A) in this state is to stabilize the light energy distribution. Other parameters of the instrument are set as follows: wavelength range ~900–1700 nm, integral time 10 ms, scanning interval 500 ms, and scanning times 16; the sample and reference are replaced by air, continuous scanning reference is maintained, the light source is kept on for 2 min during the detection process, and the light source is turned off after the test is introduced. The above steps are repeated every 10 min, and repeat five times for each group with the same scanning number to obtain a total of 15 sets of data.

TABLE 2. Light Source Minimum and Maximum Deviation Values when the Light Source is Stable

Wavelength point	Mean	RSD	Relative range
Minimum (905 nm)	2 303.50	0.0093	0.5538
Maximum (1627 nm)	33 081.78	0.0089	0.7123

Since the energy of the light source will fluctuate after the light source is just turned on, the average spectral data of 16 scans from 0.5 to 5 s are taken at a time interval of 0.5 s to detect the time required for energy stability of the light source. The specific spectrum is shown in Fig. 2. It can be seen from the figure that the energy distribution tends to be stable after the light source works for 2 s (the fourth curve). Table 2 shows the mean value and energy deviation statistics at the minimum and maximum values of spectral energy when the light source is stable.

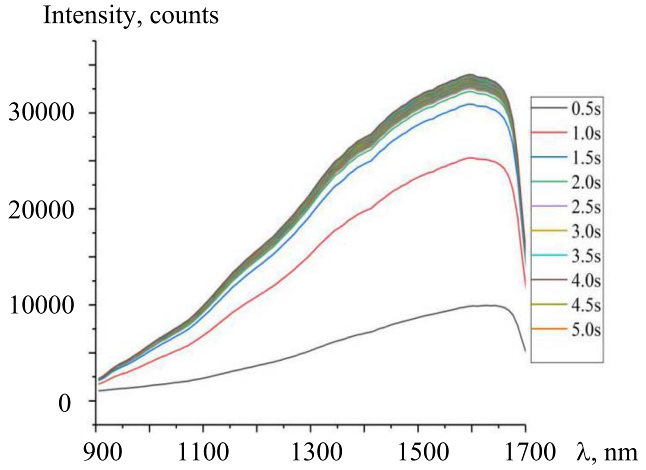

Fig. 2. Energy spectrum of the light source 0.5–5 s after applying the voltage.

Stability of spectral baseline. The stability of baseline is another important indicator of the stability of the NIR spectrometer, which affects the accuracy of measurement. The stability of baseline (100% *T*-line) is defined as the extent to which the instrument has drifted relative to the baseline obtained from the value of reference scan. The stability of baseline can be evaluated using the relative standard deviation of the 100% *T*-line of the instrument and measured several times in a row over a period of time. Test conditions are as follows: 1) room temperature is 26°C; 2) instrument uses 20 min light preheat; 3) light source is maintained in the normal-on state; 4) light energy is in a full range of 20, 50, and 80% of three kinds of states such as testing; 5) wavelength ranges from 900 to 1 700 nm; 6) integration time is 10 ms; 7) scanning frequency is set to 16, 64 2 class; 8) sample and reference are used instead of air; 9) one spectrum is saved every 10 min; 10) spectrum including 1 article is reference spectra and 1 the sample spectra; 11) continuous scanning is 7 h. After each change of instrument parameter setting, the dark current is retested. Each parameter combination has 42 spectral data and a total of 6 groups. The statistical data of baseline drift test under different parameters are shown in Table 3.

TABLE 3. Statistics of Baseline Drift Tests under Different Parameters

Light source energy, %	Number of scans	Minimum light source energy (905 nm)		Maximum light source energy (1627 nm)	
		RSD	SNR Drift	RSD	SNR Drift
20	16	0.0128	0.0557	0.0004	0.0017
	64	0.0034	0.0168	0.0004	0.0016
50	16	0.0041	0.0174	0.0003	0.0013
	64	0.0014	0.0053	0.0008	0.0052
80	16	0.0030	0.0112	0.0002	0.0008
	64	0.0006	0.0024	0.0002	0.0007

With increase in light source energy, the measured relative standard deviation and the signal to noise ratio drift are both reduced. When the energy of the light source is 80%, it can be seen that the instrument reaches the optimal working state. As the number of scans increases, a better SNR can be obtained, so the measured relative standard deviation decreases.

Instrument signal-to-noise ratio. Signal noise ratio (SNR) is an important index of near-infrared spectroscopy instrument, which directly affects the accuracy of analysis results [13, 14]. At the rated voltage of the light source, the light source energy is 100%, the integration time is 10 ms, and the scanning times are set to 16. The peak-peak value of 100%*T* measured in the wavelength range of 900–1700 nm is shown in Fig. 3. Taking the wavelength range of 1200–1500 nm, the SNR is calculated to be 3000:1.

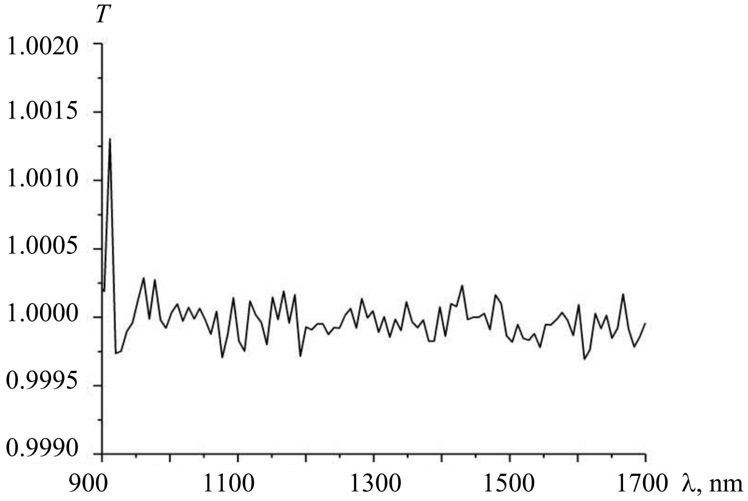

Fig. 3. *T* line with a wavelength of 900–1700 nm.

Dark current drift. At room temperature of 26°C, turn off the light source, set parameters of the instrument as follows: wavelength range of 900–1700 nm, integral time of 20 ms, and scanning times of 16 times. Turn on the instrument, detect the dark current once every 5 min, and continuously test for 3 h to obtain a total of 36 spectral data. Figure 4 shows the relative standard deviation distribution of dark current at different wavelength points under the detection conditions, and the relative standard deviation fluctuates between 0.0019 and 0.0035. The values of the dark current are different under different detection conditions, but the variation trend is the same.

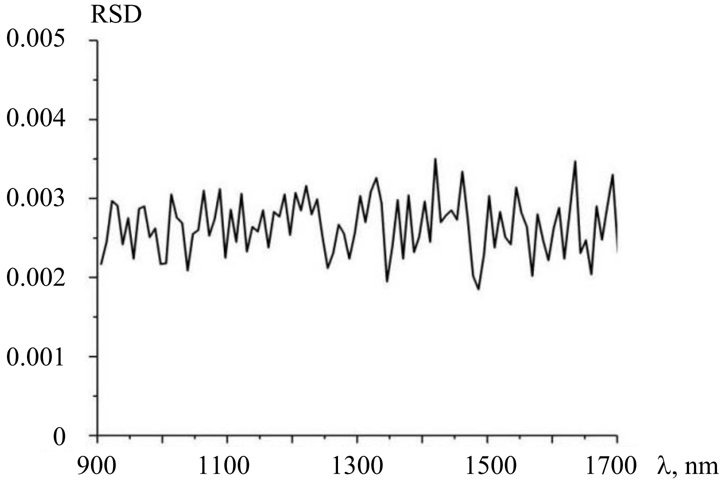

Fig. 4. Distribution of dark current relative standard deviation in 16 scans and 20 ms integral time continuous measurements.

Other indicators of NIR analyzer, including spectral resolution, wavelength accuracy, and wavelength reproducibility, are determined by the fixed grating fiber NIR spectrometer's core devices.

Introduction to spectrometer system software. The acquisition software can realize the real-time collection of spectral data of samples. Spectral measurement parameters, including integral time, average times, and delay time, can be set according to need, with single and continuous measurement modes. Under the condition of setting measurement parameters, manually turn on the switch controlling the light source, collect the dark current and background signal in turn, and store the data in the Dark and Reference folders [14]. After the reference is set, the spectrum is collected, and the resulting spectral data are stored in the Absorbance folder in CSV format.

The software of the stoichiometric method developed by our research group was used to preprocess and correct the spectrum.

Quantitative analysis of wood cellulose and lignin. Cellulose [15] and lignin [16] are the main components of wood. They are closely related to other properties of wood and the processing and utilization of wood [17]. They can be used to verify the results of research and the possibility of practical application of the near infrared spectrum instrument, to choose different wood samples as the research object, to establish a comprehensive quantitative calibration model of cellulose and lignin content [18, 19] by comparing the measured values of the prediction set sample to those obtained with the national standard method, to measure the error between the true value, and to verify the capabilities of the instrument [20].

Sample preparation. The samples used in this experiment were from the Institute of Forest Chemical Industry, Chinese Academy of Forestry, and a total of 88 samples, including *Pinusmassoniana Lamb*, *Cunninghamia lanceolate* Hook, *Eucalyptus robusta* Smith, *Populus*, and *Acacia confusa* Merr. All samples were milled and then bagged. The contents of cellulose and lignin were determined by GB/T 2677.10-1995 and GB/T 2677.8-1994. The sample of wood powder to be tested is treated with a benzene-alcohol mixture and then hydrolyzed with sulfuric acid with a mass fraction of 72%, and the obtained hydrolysis residue is the mass of lignin. When the pH 4–5, the wood sample from which the resin is extracted is treated with sodium chlorite to remove the lignin content, and the quantitative determination of the residue gives the total cellulose amount. The actual measured values were taken as the true values of the samples.

Spectral collection. The wood sample was placed in a diffuse reflection sample cup to collect NIR spectra. The detection parameters of the instrument were set as follows: ambient temperature 23–25°C, wavelength range 900–1700 nm, scanning times 5, and integration time 20 ms. After starting the instrument and preheating for 30 min, the NIR diffuse reflectance spectrum of the samples was scanned, and the average spectrum was taken after 3 times scanning for subsequent data processing. The NIR spectra of 88 wood samples are shown in Fig. 5.

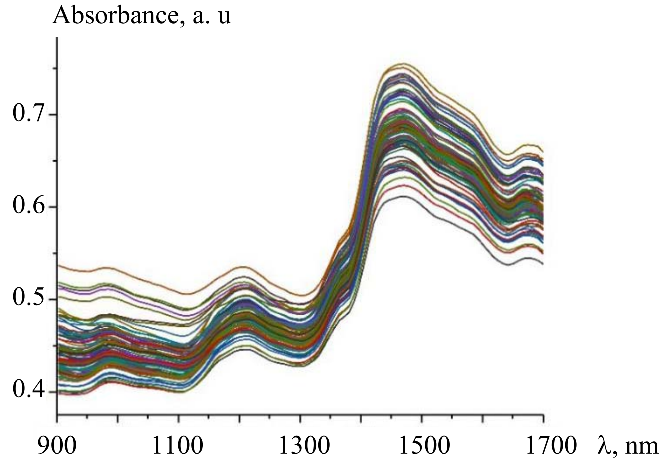

Fig. 5. Original NIR spectra of wood samples.

Results and discussion. *Establishment and verification of calibration model.* For 88 samples, the Kennard–Stone [21] method was used to determine 61 samples as the calibration set and 27 samples as the prediction set for model validation. In addition to the chemical information of the samples, the spectrum also includes some other irrelevant information and noise such as electrical noise, background, sample stray light, etc. So, when the calibration model is set up, the spectra pretreatment should be properly applied to raw spectral data in order to reduce the influence of noise on model precision. The preprocessing method is multiple scatter correction [22], which uses the PLS [23] method to establish the overall correction model of cellulose and lignin content. The root mean square error of calibration (RMSEC), root mean square error of predication (RMSEP), and correlation coefficient R were used as indicators to evaluate the performance of the quantitative analysis model for cellulose and lignin content. In the spectrum range of 900–1700 nm, the PLS calibration model was established by using principal component number 10 and left-one method cross-validation. The relevant information of the model and the statistical data of the prediction effect are shown in Table 4. Figure 6 shows the distribution of the measured value and the true value of PLS model of integrated cellulose content. There is no significant difference between the predicted value and the true value of each parameter.

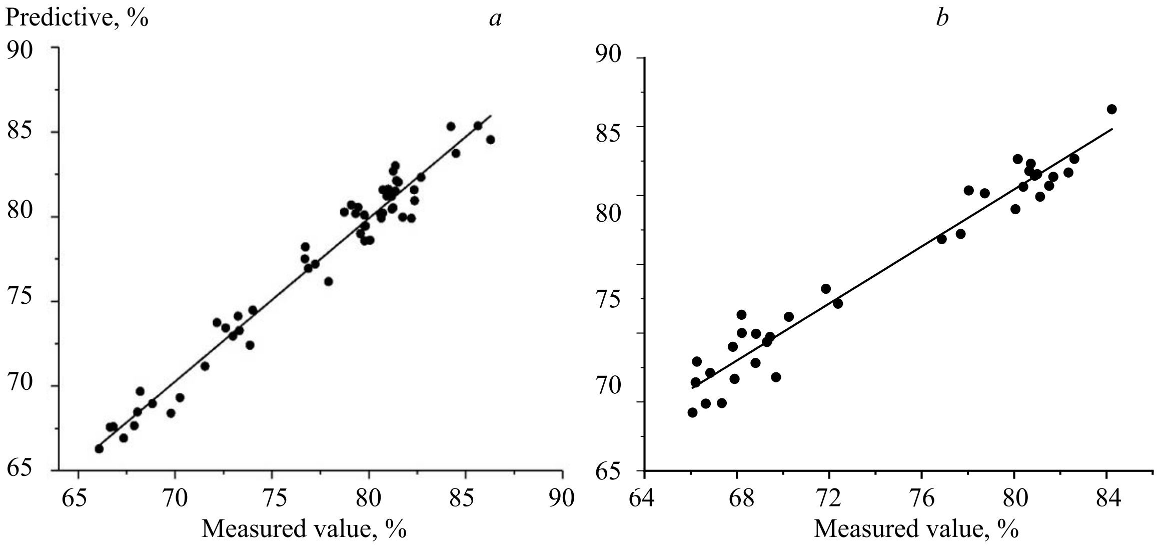

Fig. 6. The PLS model predicts the results of a) calibration set and b) validation set.

TABLE 4. PLS Modeling Results of Two Indicators

Index	Principal component	RMSEC, %	R_C	RMSEP, %	R_P
Cellulose	10	0.6096	0.9834	1.2884	0.9801
Lignin	10	0.9572	0.9605	1.7712	0.9545

Conclusions. The stability of the light source, baseline stability, signal to noise ratio, and dark current drift were tested. The results show that the performance of the fixed grating fiber near-infrared spectrometer based on MEMS technology is stable. The content of cellulose and lignin in wood was taken as the measurement index, and the calibration model was established by using PLS. RMSEC, RMSEP, R_c, and R_P of cellulose were 0.6096, 1.2884, 0.9834, and 0.9801, respectively; RMSEC, RMSEP, R_c, and R_P of lignin were 0.9572, 1.7712, 0.9605, and 0.9545%, respectively. The results show that the small NIR system can be used to determine the content of cellulose and lignin in wood, which provides a good reference for the development and design of small NIR instrument.

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