RESEARCH ON WAVELENGTH CALIBRATION OF LINEAR-CCD REMOTE RAMAN SPECTROMETER. Xiaoyu Wang[1], Ping Liu[1], Xiaobin Qi[1], Changqing Liu[1], Yanqing Xin[1], Ayang Xiao[1] and Zongcheng Ling[1*] [1]Shandong Provincial Key Laboratory of Optical Astronomy and Solar-Terrestrial Environment, Institute of Space Sciences, Shandong University, Weihai, Shandong, 264209, China. (zcling@sdu.edu.cn)

Introduction: The accuracy of wavelength measurement is the core performance index of linear-CCD remote Raman spectrometer, and the error of wavelength measurement will directly affect the accuracy of various qualitative and quantitative analyzes using spectral data [1-3]. The wavelength measurement error of linear-CCD remote Raman spectrometer comes from two aspects: the hardware characteristics of the instrument and the calibration process of the instrument. The hardware performance of the instrument determines the upper limit of the measurement accuracy, while the accuracy of the calibration model determines the lower limit of the measurement accuracy.

At present, the key issues in wavelength calibration include model selection, algorithm selection, calibration point selection, and the influence and control of measurement errors [4]. Restricted by the influence of various factors in the wavelength calibration process and the dependence on the Raman spectrometer hardware system parameters, although the research focus of different literature is different, the model form of linear-CCD remote Raman spectrometer wavelength calibration equation can be divided into two categories: 1) Parameter estimation model based on optical principle equations [5], and 2) power polynomial fitting model based on function approximation theory [6]. The latter model is more common in practical applications. The least-square algorithm is one of the commonly used methods of the calibration equation, and the coefficients of the solution model are optimized according to the analysis results of the fitting residuals [7].

The wavelength calibration equation is the mapping function of linear-CCD remote Raman spectrometer to realize the wavelength measurement, and the algorithm parameters involved in the process of determining the calibration equation also determine the calibration accuracy of the wavelength. Therefore, the influence and control of the precision in the wavelength calibration process of linear-CCD remote spectrometer need to be further studied. In this work, the Gauss-Lorentz function is used to optimize the shape of the calibration spectrum to obtain the exact value of each peak position. The mapping relationship between pixel and wavelength was established by a polynomial fitting equation, and the spectral data before and after calibration were compared to evaluate the influence of the calibration equation on wavelength accuracy. In addition, the calibration process and method proposed in this paper are simple and convenient, which can provide a reference for the calibration of linear-CCD remote Raman spectrometer systems.

Instrumentation: We built a coaxial remote Raman system at Shandong University by using Nd:YAG Q-switched laser, intensification charge-coupled device (ICCD) spectrometer and a Cassegrain telescope, as shown in Figure 1. Its detection range is 256-3982 cm^{-1}, and the resolution is about 3.6 cm^{-1}@0.1 mm slit width. In order to evaluate the accuracy of wavelength measurement, the wavelength calibration experiment was carried out.

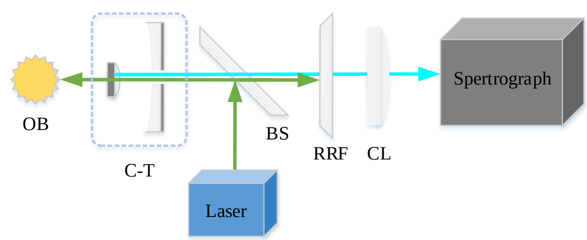

Figure 1: Optical diagram of Remote Raman Spectrometer. The labels in the figure are as follows: BS=beam splitter, RRF=Rayleigh rejection filter, CL=collimating lens, CT=Cassegrain telescope, OB= objective.

Calibration procedures: The procedures of wavelength calibration can be summarized in the following four steps:

1) Firstly, we should elect a suitable calibration lamp based on the wavelength range. This lamp will be placed at the target position of the detection system. Then, we should turn on the calibration lamp to preheat;

2) After collecting the spectral data of each standard lamp with the spectrometer, we should perform data preprocessing operations, including baseline removal and peak position fitting, to obtain the characteristic peak positions of the calibration lamp;

3) Select the wavelength and pixel number used in the modeling of the calibration equation;

4) Establish the relationship between the characteristic wavelengths of the standard spectrum and the pixel positions, and substitute the following equation of degree n to solve the polynomial coefficients a_0, a_1, a_2, a_3...a_n;

$$\lambda = a_0 + a_1 p + a_2 p^2 + a_3 p^3 \cdots + a_n p^n \quad (1)$$

Substitute the pixel positions into the fitting equation $\Lambda = f(P)$, and denote the obtained wavelength prediction value as $\hat{\lambda} = [\hat{\lambda}_1、\hat{\lambda}_2、…、\hat{\lambda}_n]$, and finally estimate the wavelength calibration accuracy by using the root-mean-square error (RMSE).

Result: Mercury, argon and neon lamps were used for the calibration of the spectrometer. After collecting the spectra of each standard lamp with the remote Raman spectrometer, we use the Gauss-Lorentz function to fit the emission lines of lamp to obtain their pixel locations. Their pixel number and the standard wavelength are respectively used as the input and output values of a multi-order fitting model using the least square method. Table 2 shows the modeling accuracy of calibration lamps under different number of fits. It can be seen that the calibration accuracy under different number of fits is similar and within 0.02 nm. With the increase of polynomial power, the fitting effect will be further optimized, but the effect of optimization is limited and will lead to overfitting. According to Occam's razor principle, as long as the residual level meets the requirements of the application, the number of fits should be chosen as low as possible. Therefore, the fourth-order fitting sum is selected as the power of the calibration equation, and the calibration equation is shown in Eq. (2). At this time, the calibration accuracy of the calibration equation is 0.017 nm.

$$y = -1.6 \times 10^{-13}x^4 + 6.1 \times 10^{-11}x^3 - 9.6 \times 10^{-8}x^2 + 2.0 \times 10^{-2}x^1 + 539.2 \quad (2)$$

Table 2: RMSE for calibration lights under different number of fits.

Calibration accuracy	Number of fits			
	Two	Three	Four	Five
RMSE(nm)	0.019	0.018	0.017	0.017

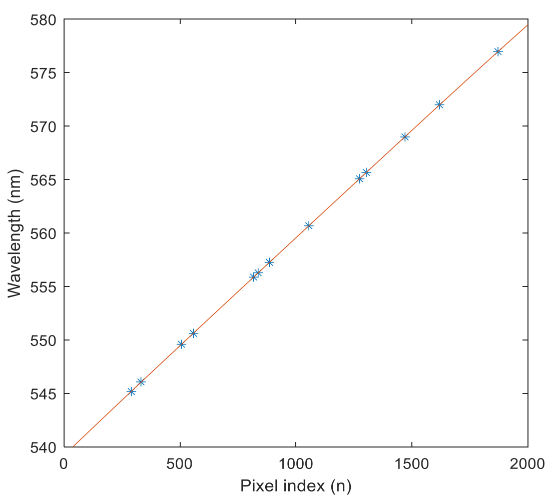

Figure 2: Relationship between detector response pixel and wavelength.

Conclusion: As a precision instrument, linear - CCD remote Raman spectrometer is susceptible to temperature, humidity, vibration and other factors, resulting in the reduction of wavelength accuracy, so it needs to be calibrated regularly. In this abstract, the Gauss-Lorentz function is used to fit the spectra of calibration lamps collected by the remote Raman spectrometer, and then the peak search method is used to accurately find the pixel positions corresponding to all characteristic spectral peaks. Then, a calibration equation for quartic polynomial fitting is established from the wavelength and the corresponding pixel number. Experimental results show that the established calibration model has high calibration accuracy.

The calibration process proposed in this paper is simple, and the calibration model has high calibration accuracy. The wavelength accuracy after calibration is better than that before calibration, which provides a reference for other wavelength calibrations of linear-CCD remote Raman spectrometers.

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