A New Method for High Precision Measurement of Ultra-low Concentration SO₂

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Keywords: Coal-fired power plant, Sulfur dioxide, DOAS, Fast Fourier Transform

Abstract: In order to achieve ultra-low emission online monitoring with higher accuracy, the paper demonstrates a new method of low concentration SO_2 measurement based on DOAS and fast Fourier transform. Wavelet domain denoising was applied according to the characteristics of noise of raw spectrum. To reduce spectral leakage, the fast Fourier transform with Hanning window is used to extract the broad-band component of optical density. This method is a new differential absorption spectrum analysis method, which can be well fit the slow varying part of the original spectrum. When concentration ranges from 3 to 31ppm, the relative error of retrieved result is under 2%, and in many cases even lower than 1%. Experiment results indicate that the method in this work has high accuracy and linearity.

1. Introduction

Environmental pollution, especially air pollution, has always been a hot issue of international concern. In 2014, an ultra-low emission reform plan was issued to restrict SO_2 emission standard to $35mg/m^3$ for coal-fired power plant [1]. The test procedures for CEMS was also officially implemented in March 2018, providing more detailed and stringent specifications for ultra-low emission online monitoring system. Therefore, online monitoring of pollutant emissions has become an essential technical basis. Only measurements with higher accuracy and faster response can be used to facilitate the necessary adjustments.

With advantages of unique advantages such as simple instrument structure, high measurement accuracy and sensitivity, and relatively low cost, DOAS measurement is widely used in the monitoring of gas emissions from power sources such as power plants, chemical plants, and cement plants [2]. In order to achieve ultra-low emission online monitoring with higher accuracy, the paper proposes a new method of low concentration SO_2 measurement based on traditional DOAS and fast Fourier transform. The focus of the work presented here was to obtain the differential absorption cross section using fast Fourier transform, and retrieve the concentration of the sample SO_2 gas. The paper analyzed the accuracy of the measurement.

2. Theory

DOAS. Among those optical technologies for gas concentration measuring, differential optical absorption spectroscopy (DOAS) has proved to be one of the most powerful methods to measure a wide variety of trace gases [3, 4, 5]. The technique was first used by U. Platt and D. Perner in the late 70s [6, 7]. DOAS technique relies on Beer-Lamberts Law, see equation 1.

$$I(\lambda) = I_0(\lambda)e^{-L \cdot \sigma(\lambda) \cdot c} \tag{1}$$

Where $I(\lambda)$ is the measured intensity, $I_0(\lambda)$ is the reference intensity emitted by the lamp, L is the length of the optical path, c and $\sigma(\lambda)$ are the concentration and the wavelength-dependent absorption cross section of the species. The dimensionless quantity $L\sigma(\lambda)c$ is often referred to as the optical density, denoted A.

In atmospheric conditions Rayleigh and Mie scattering also contribute to the radiation extinction. By scattering light away from the line of sight these phenomena act like absorption processes, although they are actually not. Considering the general fact, the absorption cross section of a given molecular species can be rewritten as the sum of two terms:

$$\sigma(\lambda) = \sigma_0(\lambda) + \sigma'(\lambda) \tag{2}$$

Where $\sigma_0(\lambda)$ represents the slow variation of the cross section with wavelength (the broad-band component), which is due to Rayleigh and Mie scattering and other disturbances. And $\sigma'(\lambda)$ represents the rapid variation due to an absorption band. The differential absorbance can be defined:

$$A'(\lambda) = \ln \frac{I_0'(\lambda)}{I(\lambda)} = \sigma'(\lambda) \cdot c \cdot L \tag{3}$$

Thus, the concentration can be calculated from equation 3 with the $\sigma'(\lambda)$ taken from the literature or measured in the laboratory and $A'(\lambda)$ by a suitable fitting.

Fast Fourier Transform. To obtain differential optical density $A'(\lambda)$ from optical density, the general method is using fifth order polynomial fitting to divide the broad-band component. In this paper, fast Fourier transform (FFT) is chosen. FFT decomposes a signal into sine waves of different amplitudes and frequencies [8]. It converts a time domain signal into a frequency domain signal. The frequency information of the spectral can be obtained by the Fourier transform, thereby extracting the slowly variation component.

When performing FFT, the signal needs to be cut off. In the case of non-periodic truncation, spectral leakage occurs, and the window function can be used to reduce leakage (but not eliminate leakage unless it is an infinitely long rectangular window) [9]. In engineering applications, five kinds of windows are commonly used: Rectangular Window, Hanning Window, Hamming Window, Blackman Window, and Blackman-harris Window. Each window function has its own applicable condition. In this paper, the purpose is to focus more on frequency points than on energy. In this case, there is a need to choose a window function with a narrow main lobe. The Hanning window is a good choice.

3. Experiment Description

The experimental setup is shown in Figure 1. The choice of the light source and spectrometer is determined by the spectral region to be investigated. A high-pressure 25W deuterium lamp (Ocean Optics D-2000) was used as a UV light source. The grating spectrometer had a spectral range of 200 ~ 400nm and a resolution of 0.1nm. Based on mass flow controller, the gas supply system (GAINWAY GW-5000) was used to generate sample gas of different concentrations and pumped the sample gas into the absorption cell with a flux of 0.6 liter per minute regulated by a controlling valve. The gas absorption cell used was custom made and based on the White multiple foldback structure for a stable optical path. And it also has sensor probe connector for temperature and pressure measuring.
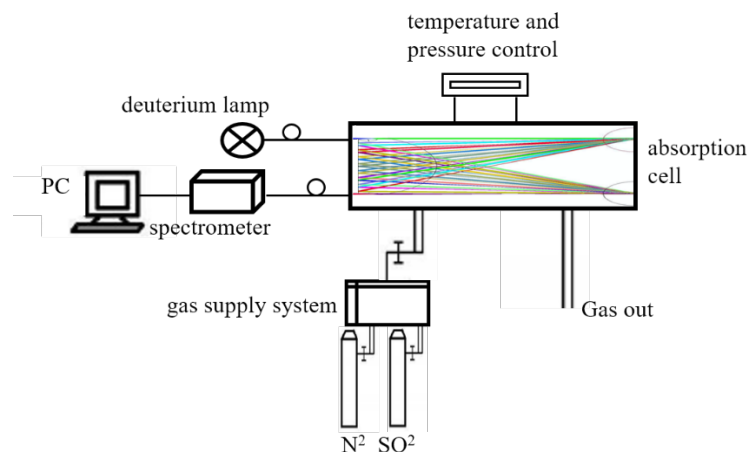
Figure 1. Experimental setup

In the experiment, nitrogen was used as the dilution gas. The standard gas and nitrogen used are national first-class standard gases. All the experiments were conducted in the same environment (308K, 101.33kPa). The integration time of the spectrometer was set to 100ms.

The experimental procedure was as follows: after the preheating of the light source, the dark noise and reference spectrum were recorded with the cell filled with only N_2. Then SO_2 of preset concentration was introduced in the absorption cell with a flux of 0.6 liter per minute. Until the gas filled the chamber evenly, recording the emission spectrum.

4. Method and Results

SO_2 has two absorption bands in the UV wavelength from 200 to 240nm and from 280 to 320nm. The change of absorption spectrum around 300nm is strong, and to avoid the possible interference of other gases, the spectral region from 291 to 312nm was selected to investigate.

Spectrometers inevitably have some noise, due to mechanical vibration, Random motion of electrons, and so on. The simplest and most straightforward way to improve the signal-to-noise ratio (SNR) in low-absorbance measurement applications is to increase the average number of measurements. So, the experiment used 50 times of scans to average, compromised with the time of spectrum acquiring. Considering the dark noise of each pixel of the CCD detector in the spectrometer is different, the noise features of intensity spectrum can be directly subtracted. Based on the dark noise recorded, a five-order polynomial is fitted and subtracted, and the residual difference was used to be subtracted from raw spectrum acquired later, see Figure 2.
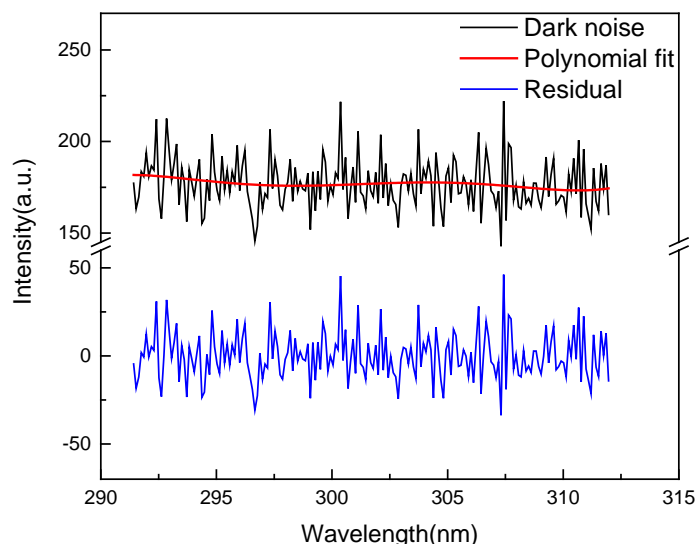

Figure 2. Dark noise and polynomial fit

The noise caused by other environmental factors, such as solid particle scattering and Gaussian white noise, cannot be directly eliminated by subtracting the dark noise. It will bring a large error to the calculation of the SO_2 absorption cross section. In this paper, wavelet transform is chosen for the further denoise processing [10]. By comparing the inversion precision under different denoising parameters and selecting the optimal parameters, the wavelet base is selected as db9 and the decomposition layer is 4 layers. The de-noising effect is shown in Figure 3.
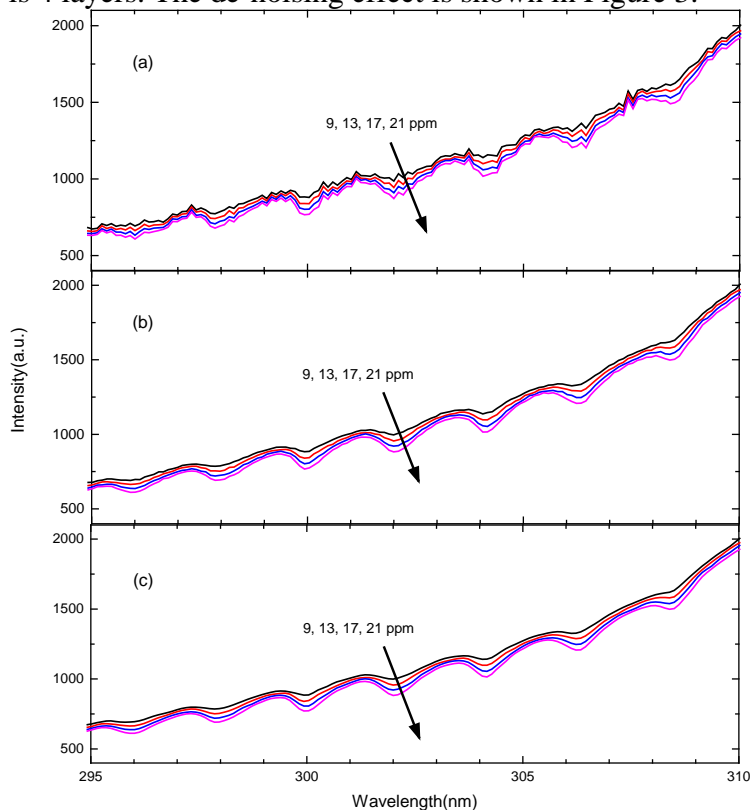

Figure 3. Intensity spectrums: (a) raw spectrum, (b) after dark noise subtraction, (c) after wavelet denoising

After de-noising process, the optical density is evaluated according to equation 2. Then, fast Fourier transform is used to extract the broad-band component of optical density. Before performing a fast Fourier transform, there's a need to interpolate the data points to $N=2^L$ (L is a natural number). When performing FFT, signal's non-periodic truncation leads to spectral leakage. So, the Hanning window is used on the optical density.
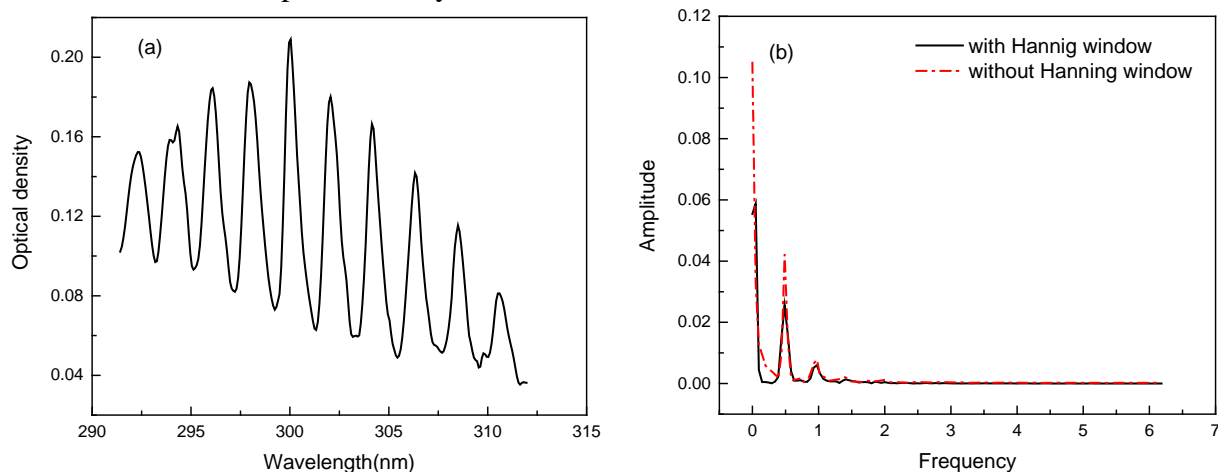

Figure 4. (a) Optical density in 291 ~ 312nm, (b) FFT frequency spectrogram of optical density

As can be seen in Figure 4, in the FFT frequency spectrogram without Hanning window, the main lobe width is stretched out. Based on the Fourier spectrum, by intercept the low frequency part taken by the inverse Fourier transform can be obtained in the slowly varying part of the absorbance. After several comparative experimental studies, the interception threshold was chosen to be 0.35. After the splitting of the optical density into a 'slowly' and 'rapidly' varying part, differential optical density is obtained. According to equation 4, differential absorption cross section can be evaluated from the known concentration. As shown in Figure 5(a), the deviation of the differential optical density of SO_2 in different concentration is distinctly small.
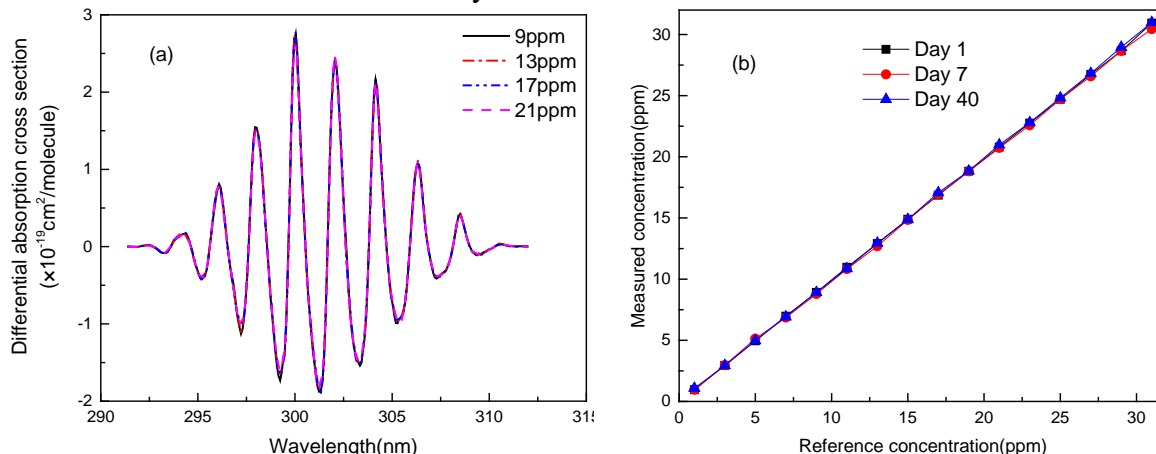

Figure 5. (a) Differential absorption cross section of SO_2 in different concentration, (b) Comparison between reference and measured concentration

The standard library of SO_2 differential absorption cross section is established by calculating on a set of known concentrations SO_2 gas through the above process. The process of concentration inversion: first calculate the differential absorbance of the unknown concentration gas, and then fit the standard differential absorption cross section by least squares method to calculate the concentration [11]. This experiment also uses nonlinear compensation to obtain more accurate results.

To evaluate the algorithm performance of this method, the whole procedure was tested for SO_2 of different concentration, ranging from 3 to 31ppm. And the test was carried out at different intervals. The concentration measurement results are presented in Figure 5(b). Even after 40 days, the concentration retrieved by the method in this work still have high accuracy and linearity. The relative error is less than 2%, and in many cases even less than 1%.

Table.1. Measured concentration and relative error

Reference concentration (ppm)	Day 1		Day 7		Day 40	
	Measured concentration (ppm)	Relative error	Measured concentration (ppm)	Relative error	Measured concentration (ppm)	Relative error
3	2.95	-1.52%	3.01	0.46%	2.96	-1.43%
5	4.95	-1.00%	4.91	-1.78%	4.97	-0.56%
9	8.91	-0.99%	8.94	-0.66%	8.91	-1.04%
13	12.91	-0.73%	12.96	-0.31%	12.95	-0.37%
17	16.86	-0.80%	16.78	-1.30%	17.07	0.40%
21	20.80	-0.94%	20.78	-1.03%	20.98	-0.11%

5. Conclusion

The fast Fourier transform signal processing method is used to analyze the absorption spectrum of the SO_2 gas, and the slow absorption is obtained by inverse Fourier transform in the low frequency

portion of the intercepted transformed spectrum, thereby obtaining a differential absorption spectrum of the gas. In this method, the key point is the selection of the inverse Fourier transform segment. In the differential absorption spectroscopy, the method has a good effect in removing the peak and improving the signal-to-noise ratio, so that the inverse gas concentration is more accurate, which is a new spectral analysis method in the differential absorption spectroscopy. Based on the dark noise recorded, polynomial is fitted and subtracted, and the residual difference was used to be subtracted from raw spectrum. And wavelet transform is chosen for the further denoise processing.

In this work, the optical length and volume of the absorption cell are 700cm, 0.5L respectively. The spectral region from 291 to 312nm was selected to investigate. All the experiments were conducted in the same environment (308K, 101.33kPa). The concentration retrieved by the method in this work still have high accuracy and linearity. The relative error is less than 2%, and in many cases even less than 1%.

Acknowledgments

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