Study on Measurement Lower Limit of DOAS System Based on kalman Filter

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Abstract. Differential Optical Absorption Spectroscopy (DOAS) technique put forward by Platt in 1970s has been widely applied to the measurement of atmospheric trace gas. The key procedures in the retrieval algorithm are the separation of the absorption cross section into two parts and the solution of linear equations about concentration with the least-squares method. However, the above procedures can’t be effectively applied to the monitoring of low concentration gases at short light path length. Here, an improved inversion algorithm based on kalman filter is applied to the optimal estimation of gas concentration instead of applying the least squares. Thus, it is not necessary to select specific wavelengths and subtraction of background spectroscopy. The concentration is treated as the state variable and is calculated with linear recursion. Research on experiment of quantitative measurement for SO₂ show that the accuracy of inversion is greatly improved with kalman filter at low ratio of signal to noise and the measurement lower limit is less than 28.6mg/m³ at a light path length of 0.5 m. Zero drift of the DOAS system based on the improved algorithm is less than 2.9mg/m³. It is also found that dynamic measurement range can be broadened by combining traditional DOAS algorithm with the improved algorithm by setting an appropriate threshold for the differential optical density.

1. INTRODUCTION
In the past decades, Differential Optical Absorption Spectroscopy (DOAS) has been widely used for monitoring of trace gases (Platt et al., 1979; Platt et al., 1988; Platt et al., 1984; Plane et al., 1992) in the stratosphere or troposphere. It was platt et al. who first (Platt et al., 1979) started to utilize the differential absorption for tropospheric gas composition measurement simultaneously without disturbing the chemical behaviors of substances to be investigated. The most straightforward
atmospheric molecules to detect with DOAS are SO2, NO2 and O3 (Plane et al., 1992; Axelsson et al., 1990; Platt et al., 1980) in the u.v./visible. In the tropospheric application, the light from a broad band xenon lamp is transmitted through the atmosphere for distances up to several kilometers. After the light is received, the measurement spectrum is matched to the spectral absorption of known molecules applying the least-squares fitting to derive gas concentrations. A new and interesting application (Mellqvist et al., 1996) of the DOAS technique is to be used for the in-situ detection of flue gases across the stack. However, it is very difficult to be used for the monitoring of low concentration flue gas or for the flue gas mixed with dust particles of high concentration at so short light path length with traditional DOAS technique. In the present article, an improved DOAS algorithm based on kalman filter was investigated and developed to greatly improve the accuracy and sensitivity at short light path length. Different from the traditional DOAS algorithm, the kalman filter applied linear recursion at all wavelengths in a certain wavelength region. The improved DOAS technique can be used to lower the detection limit. Also, if it is combined with traditional DOAS by setting an appropriate threshold for the differential optical density, then it can be used to enlarge the dynamic measurement range.

2. FUNDAMENTAL PRINCIPLE OF DOAS AND RETRIEVAL ALGORITHM

2.1 Fundamental Principle of DOAS

DOAS technique utilizes the configuration of differential absorption in the selected wavelength region to eliminate the interference of other gases and dust particles. The basic principle of DOAS is based on the Lambert-Beer law and the model can be expressed as follows:

\[ I(\lambda, L) = I_0(\lambda, L) \exp[-L \cdot C \cdot \sigma(\lambda, T, P)] \]  

(1)

![Fig. 1 Schematic of Lambert-Beer law](image)

In the actual measurement, the pollutant gases to be measured usually coexist with other gases and dust particles. So the attenuation after the light is transmitted through the absorber includes the absorption of gas molecules and dust particles as well as the scattering of them.

2.2 Retrieval Algorithm

Though the Mie and Rayleigh scattering caused by dust particles and gases don’t belong to absorption process in equation (1), diffused light derived from them can not be detected by the detector. So the Mie and Raileigh scattering can be equally viewed as the absorption process. In equation (1), the absorption cross section was separated into two parts which included the rapid part \( \sigma_i \) varying rapidly with wavelength and the slow part \( \sigma_s \) showing a general slope with wavelength. As a result, \( \sigma_i \) was
expressed as:

\[ \sigma_i = \sigma_i' + \sigma_i'' \]  

(2)

If equation (2) is put in equation (1), then the calculation model can be written as equation (3):

\[
I(\lambda, L) = I_0(\lambda, L)\exp\left[-\sum_i c_i \cdot \sigma_i(\lambda, T, P) + \epsilon_0(\lambda, L)\right] \cdot L = \sum_i c_i \cdot \sigma_i(\lambda, T, P) \cdot L
\]

(3)

In equation (3), defining \( I_0(\lambda, L) = I_0(\lambda, L)\exp[-(\sum_i c_i \cdot \sigma_i(\lambda, T, P) + \epsilon_0(\lambda, L)) \cdot L] \), it denotes the absorption without any differential absorption and the slow features are derived by fitting a low-order polynomial (1st-6th order) (Mellqvist et al., 1996), \( I_p \), to the recorded spectrum, then equation (3) is modified as:

\[
D'(\lambda) = \ln \frac{I_0(\lambda)}{I(\lambda)} = \ln \frac{I_0(\lambda)}{I(\lambda)} = \sum_i c_i \cdot \sigma_i(\lambda, T, P) \cdot L
\]

(4)

After that, some featured points are chose to form the equations about concentrations:

\[
D'(\lambda_i) = \ln \frac{I_0(\lambda_i)}{I(\lambda_i)} = \left[ C_1 \cdot \sigma_1(\lambda_i) + C_2 \cdot \sigma_2(\lambda_i) + \cdots + C_n \cdot \sigma_n(\lambda_i) \right]
\]

\[
D'(\lambda_2) = \ln \frac{I_0(\lambda_2)}{I(\lambda_2)} = \left[ C_1 \cdot \sigma_1(\lambda_2) + C_2 \cdot \sigma_2(\lambda_2) + \cdots + C_n \cdot \sigma_n(\lambda_2) \right]
\]

\[
D'(\lambda_3) = \ln \frac{I_0(\lambda_3)}{I(\lambda_3)} = \left[ C_1 \cdot \sigma_1(\lambda_3) + C_2 \cdot \sigma_2(\lambda_3) + \cdots + C_n \cdot \sigma_n(\lambda_3) \right]
\]

\[
D'(\lambda_n) = \ln \frac{I_0(\lambda_n)}{I(\lambda_n)} = \left[ C_1 \cdot \sigma_1(\lambda_n) + C_2 \cdot \sigma_2(\lambda_n) + \cdots + C_n \cdot \sigma_n(\lambda_n) \right]
\]

(5)

2.3 Retrieval Algorithm of DOAS Based on Kalman Filter

Here, the improved DOAS algorithm based on kalman filter was put forward. It can be applied to compensate for the deficiency of traditional DOAS at short light path length. Good results could also be achieved even under the strong background spectrum and severe overlapping of spectrum lines. Compared to the traditional DOAS algorithm, the DOAS based on kalman filter performed linear recursion i.e. the concentration was derived from the previous calculated results and current observed values at every wavelength in a continuous wavelength region. The kalman filter can be described with two equations which are state equation and measurement equation respectively introduced by Van Veen et al (Veen et al., 1990; Veen et al., 1991; Veen et al., 1993).

State equation:

\[ C(k) = IC(k-1) \]

(6)

measurement equation:

\[ x(k) = S^T(k)C(k) + n(k) \]

(7)

Where, the concentration is treated as the state variable denoted by \( C(k) \) and it is a constant not varying
with wavelength. $I$ is the transfer matrix of state between $C(k)$ and $C(k-1)$. Measurement value $x(k)$ is a scalar denoting the differential optical density at wavelength $\lambda_k$. $S^T(k)$ is the transpose of the vector of sensitivity coefficients composed of differential absorption cross sections. $n(k)$ is the white measurement noise with a mean value of zero.

3. EXPERIMENTAL SYSTEM
A schematic of the setup is shown in Figure 2. In the system, the impulse and short arc xenon lamp was selected as the light source which can supply the continuous and broad band spectrum between 200 and 1100 nm. The resolution of the fiber spectrometer is 0.4 nm. The system is separated into two parts: the upper part in the dashed frame was used for obtaining the mixture of different component concentration and the lower part below it was the optical setup which was also the main body used for measurement.

Fig. 2 Schematic of experimental system for measuring concentration of flue gas
1 xenon lamp; 2 optical fibre; 3, 7 collimating lens; 4 measurement cell; 5 equipment of controlling temperature; 6 heating belt; 8 spectrometer; 9 pc; 10 high purity nitrogen; 11 aerosol generator; 12 dust collector; 13 vacuum pump; 14 K-type thermocouple; 15 pressure gauge; 16 analytical instrument for flue gas; 17 device for absorbing exhaust gas; 18 preheating pipe; 19 mixing pipe; 20 flowmeter; 21 standard gas;

Measurement of SO$_2$ was performed in this paper at room temperature and atmospheric pressure. The measurement cell shown in Figure 2 was cylindrical with a length of 0.5 m and a diameter of 0.06 m. Two fused quartz windows were attached to each side of the cell sealed with graphite. In order to conveniently add dust particles in the gases, a separate dust cell with the same length and diameter was put before the measurement cell in the light path. The light was transmitted through the dust cell first and then was transmitted through the measurement cell. The effect is the same as that of the coexistence of gases and dust particles in the measurement cell, which can be derived from equation (8).
\[ I(\lambda, L) = I_0(\lambda, L) \exp\left[\left(-\sum \sigma_i(\lambda, T, P) + \varepsilon_1(\lambda) + \varepsilon_2(\lambda)\right) \lambda L\right] A(\lambda) \]

\[ = I_0(\lambda, L) \exp\left[\left(-\varepsilon_1(\lambda) + \varepsilon_2(\lambda)\right) \lambda L\right] A(\lambda) \exp\left[-\sum \sigma_i(\lambda, T, P) \lambda L\right] A_2(\lambda) \]  

\[ = I_1(\lambda, L) \exp\left[-\sum \sigma_i(\lambda, T, P) \lambda L\right] A_2(\lambda) \]  

(8)

In order to obtain the uniform mixture of different component before entering the measurement cell, standard gases and pure nitrogen gas were flowed into flowmeters according to volume ratio. Then the mixture was flowed into the pre-heating pipe with a length of 7 m and a diameter of 0.06 m. After that, the mixture was divided into two parts: one passed through the flue gas analyzer for monitoring the concentration and the other passed through the measurement cell, finally both entered the bottle for absorbing exhaust gases. The work flow of the measurement part is described as below: Firstly, the light emitted by xenon lamp entered the dust cell after it was collimated by lens 2, then the light entered the measurement cell, finally the light was focused on the optical fiber connected with spectrometer. Dust particles in the dust cell were supplied uniformly by the aerosol generator which utilized the density difference between dust particle and copper powder. They were fluidized by high pressure industrial nitrogen just like fluidized bed in a cylindrical container and were mixed according to mass ratio. The particle number concentration could be monitored by ELPI (electrical low-pressure impactor) as well as the mass concentration, shown in Figure 3 a and b respectively. The unit of l/h denotes the flux of industrial nitrogen and percentage denotes the mass ratio of dust particles to copper powders.

4. EXPERIMENTAL RESULTS AND ANALYSIS

The experiment was performed when gases were flowed through the measurement cell with different algorithms. The concentration inversion of SO₂ was performed between 290 and 310 nm. The desired gas concentration was achieved by diluting high concentration gas with pure nitrogen in the volume ratio, simultaneously, the concentration was monitored by a commercial analytical instrument for the flue gas. The traditional DOAS and the DOAS based on kalman filter were marked as DOAS¹ and DOAS² respectively. All the experiments were performed at the light path length of 0.5 m.

4.1 Comparison of SO₂ Concentration Measurement with Different Algorithms
The relative errors based on different retrieval algorithms are shown in Figure 4. The solid line denotes the relative errors derived from DOAS\textsuperscript{1} corresponding to the value listed in the left y-axis and the dashed line denotes the relative errors derived from DOAS\textsuperscript{2} corresponding to the value listed in the right y-axis. The value at the bottom of Figure 4 denotes the concentration and the upper value is the maximum differential optical density corresponding to the concentration.

As we can see, the measurement error of the traditional DOAS algorithm varies from 0% to 228.6% for the concentration of SO\textsubscript{2} in the range of 20 to 12889 mg/m\textsuperscript{3}. When the concentration of SO\textsubscript{2} is less than 326 mg/m\textsuperscript{3}, the relative error of the traditional algorithm varies between 5.3% and 228.6%. Contrarily, on the same experimental conditions, the maximum relative error of the improved algorithm approximates to 30% and 10% respectively. Over the concentration of SO\textsubscript{2} from 326 to 7877 mg/m\textsuperscript{3}, the relative error is less than 8% for the traditional algorithm, and less than 19% for the improved algorithm. When the SO\textsubscript{2} concentration exceeds 7877 mg/m\textsuperscript{3}, the errors increase gradually for both the traditional algorithm and the improved algorithm and are more than 10%. This reason may be that the Lambert-Beer law is not suitable for the absorption measurement of high concentration gas. Therefore, it is necessary that the linearity correction to the law must be adopted when measuring the gas with relatively high concentration. It is noteworthy that a symbol $OD^\text{m}_m$ defined as the maximum value of the differential optical density is listed in Figure 4. Since the performances of different algorithms are greatly different when $OD^\text{m}_m$ changes, two values of $OD^\text{m}_m$, 0.0481 and 0.9272 corresponding to the SO\textsubscript{2} concentration of 326 mg/m\textsuperscript{3} and 7877 mg/m\textsuperscript{3} respectively, are selected as the threshold of $OD^\text{m}_m$. So it is suggested that the measurement of gas concentration should be performed in three different areas by judging $OD^\text{m}_m$. Consequently, if $OD^\text{m}_m$ is less than 0.0481, the improved algorithm is adopted and if $OD^\text{m}_m$ is between 0.0481 and 0.9272, the traditional algorithm is selected. When $OD^\text{m}_m$ is more than 0.9272, the traditional algorithm is superior to the improved algorithms. Furthermore, from the above analysis of experimental results, the dynamic measurement range of SO\textsubscript{2} concentration may be broaden by the combination of the traditional DOAS algorithm with the improved algorithm in DOAS system.
4.2 Comparison of SO₂ Concentration Measurement Results with The Interference of NO

Table 1 shows the comparison of SO₂ concentration measurement results with the interference of standard 1304 mg/m³ NO at a flux of 3l/min based on different algorithms of DOAS. Judging from the $OD_m^i$, the concentrations listed in Table 1 belong to the second area. It is proved once again that the calculation results from the traditional algorithm are generally superior to that from the improved algorithm in the defined second area. As can be seen, although the measurement of SO₂ is interfered by NO, the maximum relative error of the calculation results is less than 9% applying the traditional DOAS algorithm.

Table 1 Calculation results and errors based on three different algorithms

| Real value (mg/m³) | DOAS¹ error (mg/m³) % | DOAS² error (mg/m³) % | $OD_m^i$ |
|------------------|-----------------------|-----------------------|---------|
| 1483             | 1604                  | 8.1                   | 1627    | 9.6 | 0.1987 |
| 1796             | 1842                  | 2.5                   | 1836    | 2.2 | 0.2218 |
| 2099             | 2214                  | 5.4                   | 2231    | 6.3 | 0.2722 |
| 2534             | 2637                  | 4.1                   | 2646    | 4.4 | 0.3185 |
| 3177             | 3366                  | 5.9                   | 3361    | 5.8 | 0.4078 |
5. ZERO DRIFT CALIBRATION OF THE DOAS SYSTEM

The repetitive experiments of calibrating the zero drift for SO\textsubscript{2} were also carried out at the same light path length. The dust cell in the light path is full of high concentration dust particles which lead to the distribution of transmittance light intensity shown in Figure 5. It can be seen that after the light is transmitted through the dust cell and measurement cell, few light will enter the spectrometer. Table 2 lists the calibrating results of repetitive experiments. The zero drift from the traditional algorithm reaches about 57.2 mg/m\textsuperscript{3}, however, the value presented by the improved algorithm is less than 2.86 mg/m\textsuperscript{3}. So the improved algorithm can be used for the measurement of extremely low concentration gas including the calibration of zero drift.

|     | DOAS\textsuperscript{1} | DOAS\textsuperscript{2} |
|-----|-------------------------|-------------------------|
| SO\textsubscript{2} | (mg/m\textsuperscript{3}) | (mg/m\textsuperscript{3}) |
| 0   | 57.2                    | -0.09                   |

Fig. 5 Comparison of the original and transmitted light intensity

1#—original light intensity;
2#—transmitted light intensity with the existence of dust particles;

Table 2 zero drift with different algorithms for the concentration inversion of SO\textsubscript{2}
6. CONCLUSIONS
The improved DOAS algorithm based on kalman filter was investigated to perform the accurate measurement of SO$_2$ from flue gases. Experimental results obtained on a bench-scale rig show that the improved algorithm have a detection limit less than 28.6 mg/m$^3$ at the light path length of 0.5 m even if there exists the interference of other background gases and dust particles. Also, the zero drift of the DOAS system based on improved algorithm is less than 2.86 mg/m$^3$. It is also found that the accurate measurement of SO$_2$ can be carried out by applying the improved DOAS algorithm according to the maximum value of differential optical density. Therefore, two values of 0.0481 and 0.9272 were put forward as the threshold to decide which DOAS algorithm is adopted. Thus the measurement of flue gases is performed in three different areas according to $OD_m$. If $OD_m$ is less than 0.0481, then the improved algorithm is adopted and if $OD_m$ is between 0.0481 and 0.9272, the traditional DOAS algorithm is adopted. When $OD_m$ exceeds 0.9272, both the traditional and improved algorithm bring significant relative errors. Fortunately, the traditional least-square retrieval algorithm enables the accurate measurement of relatively high concentration gas at a relatively short light path length. Therefore, it is advisable that the improved algorithm combined with the least-square retrieval algorithm of DOAS are used, which greatly lowers the detection limit and broaden the dynamic measurement range of flue gas concentrations by setting an appropriate threshold for the maximum value of differential optical density.

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NOMENCLATURE

| Symbol | Description                                      | Unit          |
|--------|--------------------------------------------------|---------------|
| $\sigma_d$ | differential absorption cross section of gas molecule | cm$^2$/mole  |
| $\sigma_{ib}$ | a pseudo absorption cross section denoting the slow features of the molecular absorption | cm$^2$/mole |
| $D(\lambda)$ | the differential optical density at the wavelength of $\lambda$ |      |
| $I_0(\lambda)$ | the received light intensity excluding the differential absorption | counts    |
\( I_\mu(\lambda) \) a low-order polynomial denoting the slow features \[ \text{counts} \]

\( m \) the total number of discrete wavelength;

\( n \) the species of gases to be measured.

\( \lambda \) wavelength \[ \text{nm} \]

\( L \) light path length \[ \text{m} \]

\( T \) temperature \[ \text{K} \]

\( P \) pressure \[ \text{pa} \]

\( i \) the index of gases to be measured

\( I(\lambda, L) \) transmittance light intensity \[ \text{counts} \]

\( I_0(\lambda, L) \) original light intensity \[ \text{counts} \]

\( I_1(\lambda, L) \) light intensity received after light is transmitted through the dust cell \[ \text{counts} \]

\( A(\lambda) \) the attenuation caused by the system such as the lens and the spectrometer etc.

\( A_1(\lambda) \) the attenuation after the light is transmitted through the dust cell

\( A_2(\lambda) \) the attenuation caused by the measurement cell

\( C_i \) concentration of the \( i \)th gas \[ \text{mg/m}^3 \]

\( \sigma_i(\lambda, T, P) \) absorption cross section depending on temperature and pressure \[ \text{m}^2/\text{mole} \]

\( \varepsilon_R(\lambda) \) coefficient of Rayleigh scattering \[ \text{1/m} \]

\( \varepsilon_M(\lambda) \) coefficient of Mie scattering \[ \text{1/m} \]

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