A new toxic and harmful gas analyzer based on DOAS technology

Zhengyang Yuan¹, Jiayong Zhou¹, Xinyin Qian²*, Shizhong Wang¹, Juntao Zhao¹ and Hongqi Shi¹

¹ Wuhan Second Ship Design and Research Institute, 430205, Wuhan, China
² Huazhong University of Science and Technology, Audit Office, 430074, Wuhan, China
2017210195@hust.edu.cn

Abstract: This paper introduces a new type of toxic and harmful gas analyzer based on DOAS (differential optical absorption spectroscopy) technology. Combined with the least square method, it can monitor H2S, NH3, SO2, NO2 and CH3SH online at the same time, and the prescribed minimum is as low as 0.1ppb, the detection breadth and accuracy are higher than those of the current common DOAS instruments.

1. Introduction
Ecological change and environmental pollution have become important issues of global concern [1]. The pollutants discharged during the chemical industry production have characteristics such as many kinds, large quantities and high toxicity, which easily lead to environmental emergencies, thus seriously affecting the ecological environment and endangering human health. Therefore, the rapid and real-time monitoring of multi-component atmospheric trace components has become the key research direction in the field of environmental monitoring [2]. In recent years, the on-line monitoring technology of environmental pollution based on DOAS principle has developed rapidly and has been widely used in flue gas monitoring, toxic and harmful gas monitoring, as well as some other fields.

This paper will introduce a new type of toxic and harmful gas online monitoring system based on DOAS technology, focusing on its working principle and concentration inversion process, and analyzing the equipment performance combined with outside test.

2. The principle of DOAS technology
The theoretical basis of differential optical absorption spectroscopy is Lambert-Beer Law, and it can be described as follows: after a parallel monochromatic light $I_0(\lambda)$ passes through the sample absorption cell filled with gas, its light intensity will be attenuated to $I(\lambda)$ because of the absorption and dispersion of gas molecules [3]. That is:

$$I(\lambda) = I_0(\lambda) \cdot \exp \{-L[\sum_{i=1}^{n} \sigma_i(\lambda)]c_i\}$$

In the formula, $I_0(\lambda)$ represents the incident light intensity, $I(\lambda)$ represents the emergent light intensity, $L$ represents the optical path, $c_i$ represents the concentration of the i-th gas, and $\sigma_i(\lambda)$ represents the absorption cross section of the i-th gas at wavelength $\lambda$.

In fact, when the light beam passes through the gas to be measured, it will not only produce...
absorption with gas molecules, but also produce Rayleigh scattering, Mie scattering and Raman scattering, in which Rayleigh scattering and Raman scattering are caused by gas molecules, while Mie scattering is caused by aerosol particles or dust [4]. Fig.1 shows the interaction between light and gas.

![Figure 1. Schematic diagram of interaction between light and gas](image)

At this point, the Lambert-Beer law is revised as follows:

\[
I(\lambda) = I_0(\lambda) \exp \left\{ -L \sum_{i=1}^{n} \sigma_i(\lambda) c_i + \varepsilon_R(\lambda) + \varepsilon_M(\lambda) \right\}
\]

In the basic algorithm of DOAS technology, the gas absorption cross section consists of two parts:

\[
\sigma_i(\lambda) = \sigma_{i, \text{slow}}(\lambda) + \sigma_{i, \text{rapid}}(\lambda)
\]

In the formula, \(\sigma_i(\lambda)\) can be measured in the laboratory or obtained from known databases or literature, \(\sigma_{i, \text{slow}}(\lambda)\) is the part that changes slowly with wavelength, \(\sigma_{i, \text{rapid}}(\lambda)\) is the part that changes rapidly with wavelength. The extinction effect caused by particle scattering and other factors changes slowly with wavelength, so the gas absorption is only related to the rapid change \(\sigma_{i, \text{rapid}}(\lambda)\), and the differential optical thickness can be expressed as:

\[
OD' = \ln \frac{I_0'(\lambda)}{I'(\lambda)} = L \sum_{i=1}^{n} \sigma_{i, \text{rapid}}(\lambda) c_i
\]

In the formula, \(\sigma_{i, \text{rapid}}(\lambda)\) is the differential absorption cross section, \(OD\) (optical density) represents the reference optical density at wavelength \(\lambda\), and \(OD'\) can be derived from \(OD\).

Since \(L\) is known, and \(\sigma_{i, \text{rapid}}(\lambda)\) can be deduced from \(OD\) and \(\sigma_i(\lambda)\), then the concentration of a certain molecule can be calculated.

3. The specific algorithm of this DOAS system
This DOAS system monitors H\(_2\)S, NH\(_3\), SO\(_2\), NO\(_2\) and CH\(_3\)SH at the same time, and considers the interference of O\(_3\) and CH\(_2\)O. The way to eliminate the interference of these two gases is to bring them into the concentration inversion process, that is, to treat them as the gas to be measured for concentration inversion. And at this point, there are 7 kinds of gases to be measured.

For the mixed gas of 7 components, at wavelength \(\lambda\), there is:

\[
D'_\lambda = \sigma'_1 c_1 L + \sigma'_2 c_2 L + \cdots + \sigma'_7 c_7 L
\]

In the formula, \(D'_\lambda\) is the light absorbance of the mixed gas at wavelength \(\lambda\), \(\sigma'_i\) is the differential absorption cross section of the i-th gas, and \(c_i\) is the concentration of the i-th gas.

Due to the influence of system noise, while only one selected wavelength may lead to fluctuation greatly, we choose several different wavelengths and get a system of equations [5]:

---

NEMD 2021
IOP Conf. Series: Earth and Environmental Science 702 (2021) 012051
doi:10.1088/1755-1315/702/1/012051
The equation can be described as: the dependent variable (matrix D) depends on 7 independent variables (differential absorption cross section matrix $\sigma$). It is known that the total number of samples is $m$ ($m \geq 7$), and it is needed to solve the regression coefficient $c_i$ (i.e. gas concentration). Obviously this is a multiple linear regression model, and $c_i$ is the regression coefficient to be calculated.

The least square method can make full use of the measured data when inverting the concentration of the gas to be measured [6]. Moreover, the slow change of the spectrum, Rayleigh scattering and Mie scattering can be easily eliminated by polynomial fitting method [7]. Therefore, this system adopts the least square method for linear regression fitting, and the 7-element fitting function is:

$$y = f(a_1x_1, a_2x_2, \ldots, a_7x_7)$$

The residual sum of squares is used to describe the deviation degree between all observed values and regression lines:

$$Q = \sum_{i=1}^{m} \left[ y_i - f(a_1x_{1i}, a_2x_{2i}, \ldots, a_7x_{7i}) \right]^2$$

In the formula, $(y_i, x_{1i}, x_{2i}, \ldots, x_{ni})$ is the value of each sample point in $m$ samples. When finding the best fitting line, it is necessary to minimize the sum of squares $Q$ of residuals. Combined with the calculus median solution method, there are:

$$\begin{align*}
\sum_{i=1}^{m} y_i - a_1 \sum_{i=1}^{m} x_{1i}^2 - a_2 \sum_{i=1}^{m} x_{1i}x_{2i} - \ldots - a_7 \sum_{i=1}^{m} x_{1i}x_{7i} &= 0 \\
\sum_{i=1}^{m} y_i - a_2 \sum_{i=1}^{m} x_{2i}^2 - a_1 \sum_{i=1}^{m} x_{2i}x_{1i} - \ldots - a_7 \sum_{i=1}^{m} x_{2i}x_{7i} &= 0 \\
&\vdots \\
\sum_{i=1}^{m} y_i - a_7 \sum_{i=1}^{m} x_{7i}^2 - a_2 \sum_{i=1}^{m} x_{7i}x_{1i} - \ldots - a_6 \sum_{i=1}^{m} x_{7i}x_{6} &= 0
\end{align*}$$

The regression coefficient can be obtained by solving the equations.

The greatest advantage of the least square method is that it can simultaneously deduce the concentrations of various gases to be measured. It is just based on this algorithm that this DOAS system can simultaneously deduce the concentrations of 7 gases.

4. General System Information

This DOAS system mainly includes (1) ultraviolet light source, (2) White pool, (3) optical fiber spectrometer and (4) CCD detector.

4.1. Ultraviolet light source

The light source module is mainly composed of deuterium and lens group. Deuterium lamp has a strong emission spectrum in the range of ultraviolet 200~300 band, and many toxic gases have strong absorption in ultraviolet band, as shown in Figure 2.
The biconvex lens in the experiment can turn the light produced by deuterium lamp into parallel light.

4.2. Multiple reflection pool
The general multi-reflection cells are White type and Herriott type. White pool is suitable for both ordinary light source and laser light source, and Herriott pool is only suitable for laser light source. This system monitors 5 toxic gases and 2 interfering gases at the same time, which involves a wide range of wavelength. Therefore, the White pool is selected as the multiple reflection pool of this system, and its structure is as follows:

4.3. Optical fiber spectrometer
The optical fiber spectrometer uses optical fiber as signal coupler to couple the measured light into spectrometer for special analysis, and its basic configuration includes a grating, a slit and a detector. The light is transmitted to the entrance slit of the spectrometer through optical fiber and then projected onto the collimating objective lens, and then forms a parallel light beam to enter the optical grating, where dispersion occurs. Images are formed at the exit slit through the focusing mirror, thus obtaining spectra arranged in wavelength order. The schematic diagram of spectrometer structure is shown in
4.4 CCD detector

CCD (Charge Coupled Device) is a kind of photoelectric imaging device, which can obtain the information of the whole spectrum band at the same time, especially suitable for the detection of wideband spectrum, without mechanical scanning device.

Ultraviolet light emitted by deuterium lamp light source is collimated by collimating mirror and then enters into White pool. After filtering (removing smoke and dust particles, etc.), the gas in the environment is also sucked into the White pool. When ultraviolet light passes through the gas to be measured, it will interact with the gas to be measured. The optical path (i.e. the total length of ultraviolet light passing through the gas to be measured) of ultraviolet light is greatly increased after being reflected by the mirror in the White pool for many times, and the detection limit is also increased according to Lambert-Beer Law. After passing through the White pool, the ultraviolet light is collimated by the lens, coupled by the optical fiber and then enters the optical fiber spectrometer. Through the dispersion of the grating, the spectrum is formed and then reaches the CCD detector. The CCD detector converts the received optical signal into electrical signal, and then digitalizes it and stores it in the memory for data processing. Finally, the upper computer uses DOAS algorithm to invert the data to obtain the gas concentration.

The working principle diagram of the DOAS system is shown in Fig. 5.
In the process of data analysis and processing, the hardware and software average filtering technology is used to reduce the influence of the slow change of light source intensity with time on the measurements results.

The main idea of the DOAS system technology is shown in Fig. 6.
5. Monitoring performance of outfield experiment

In the outfield test, the sampling mode of continuously collecting gas is selected to ensure the real-time monitoring of the system. The experiment environment temperature is 7°C, humidity is 60%, and the working AC voltage is 220V, while its frequency is 50Hz. In this experiment, the average calculation is performed every 600 times, the integration time is set to 24ms each time, the optical path of White pool is 6.3 meters, and the concentration inversion time is about 3~5 seconds. The 2 interfering gases participate in the calculation but do not display the results, and the concentration values of the 5 gases to be measured are renovated every 19 seconds. Mercury lamp is applied for calibration in the test, and the corresponding relationship between characteristic spectral lines and channels is shown in Fig. 7.
Seen from Fig. 8, the gas concentrations retrieved by this DOAS system combined with the least square method are H2S 0.1ppb, NH3 0.9ppb, SO2 0.8ppb, NO2 282.8ppb and CH3SH 1.4ppb. Therefore, this system can be used for real-time, on-line and non-contact high-sensitivity measurement of trace toxic and harmful gases.

![Figure 8. Concentration display diagram](image)

6. Outlook
The online monitoring technology of environmental pollution and environmental safety based on optical and spectral technology is developing rapidly at present, and its application width and depth are still expanding. This DOAS system can monitor 5 kinds of toxic and harmful gases at the same time, which can be measured in real-time, on-line and non-contact, and the detection limit reaches 0.1 ppb. It is very suitable for gas monitoring in chemical parks, coal-fired power plants and other areas, and has great application prospects in industry. Moreover, based on the characteristics of the least square method, the types of gases detected by this DOAS system can be further expanded.

References
[1] Intergovernmental panel on climate change, climate change 2007, the physical science, technical summary of the working group report [R]. New York: Cambridge University Press, 2007.
[2] LIU Wenqing, CHEN Zhenyi, et al. On-line Monitoring Technology and Applications for Air Pollution and Environmental Safety [J]. JOURNAL OF ATMOSPHERIC AND ENVIRONMENTAL OPTICS, 2015, 10(2): 82-91.
[3] J Mellqvist, H Axelsson, and A Rosen. DOAS for Flue Gas Monitoring-III. In-situ Monitoring of Sulfur Dioxide, Nitrogen Monoxide and Ammonia [J]. Quant. Spectros. Transfer. 1996, 56(2): 225~240.
[4] F. A. Videla, D. C. Schinca, and J. O. Tocho. Alternative Method for Concentration Retrieval in Differential Optical Absorption Spectroscopy Atmospheric-Gas Pollutant Measurements. Appl. Opt. 2003, 42(18): 3653~3661.
[5] Shi Xiang. Study on on-line system for monitoring concentrations of SO2 and NO in flue gas with differential optical absorption spectroscopy technique [D]. Chongqing University, 2014.
[6] HAN Fangfang, ZHANG Xiaoling, SUN Yongyue, et al. UV Differential Algorithm Used for Vehicle Tail-Gas Determination [J]. CHINESE JOURNAL OF SENSORS AND ACTUATORS, 2011, 24(9): 1238-1241.
[7] SHAO Litang. Inversion algorithm of differential optical absorption spectroscopy to measurement low concentration of polluted gas under short light path [J]. *Proceedings of the CSEE*, 2008, 28(23): 65-69.