Research on Laser Absorption Spectrum Detection Technology for CO$_2$ and NH$_3$ Regional Emission

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Abstract. High-sensitivity emission monitoring of CO$_2$ and NH$_3$ in farmland region is very important for analyzing environment and climate change. The on-line detection technology was studied based on open-path tunable diode laser absorption spectroscopy technology (OP-TDLAS). The detection spectrum of open path was extracted to realize accurate concentration inversion by designing the multi-line fitting algorithm. The system detection stability was evaluated by Allan variance that the detection limit of NH$_3$ and CO$_2$ were about 0.048 µL/L and 4.31 µL/L respectively. The detection experiment was carried out in farmland of north Anhui to prove that both of the fertilization and straw returning to the field were the emission source of CO$_2$ and NH$_3$ from soil. The growth effect of the former was slower but higher than that of fertilization. This stable spectrum detection method can obtain large-scale concentration results and clear emission rules, which provide technical support for the environment-friendly agriculture.

Introduction

In recent years, our country has adopted straw returning to the field$^{[1,2]}$ which has changed the physical and chemical properties of the soil in a certain extent and even increased the possibility of CO$_2$ and NH$_3$ emission from the soil. Therefore, CO$_2$ and NH$_3$ emission data in large-scale farmland need obtain by effective and stable detection method to assess its impact on the atmospheric environment, which has become an urgent problem in agriculture and environmental fields$^{[3,4]}$.

Gas monitoring in farmland ecosystem usually adopts box method$^{[5]}$, micrometeorology method$^{[6-7]}$ and so on. These methods mainly study local soil emissions which are vulnerable to environmental factors, and the requirements to underlying surface and atmospheric stability are high. In recent years, open-path tunable diode laser absorption spectroscopy (OP-TDLAS) technology has been gradually applied for large-scale monitoring. This technology$^{[8,9]}$ continuously measures the gas without sampling and pretreatment. It is more effective to monitor adsorbed gases (such as NH$_3$). Moreover, it has the advantage of fast detection$^{[10]}$ and high sensitivity combined with long optical path technology. Flesch et al. (2007) measured methane volatilization in pasture based on TDLAS technology to verify its measurement accuracy. Todd et al. (2015) carried out ammonia emission monitoring in dairy farmland, and the volatilization rate obtained was 304g·head$^{-1}$·d$^{-1}$. Anning Zhu et al. (2012) carried out ammonia emission monitoring before and after nitrogen fertilizer application in Huang-Huai-Hai farmland with TDLAS and BLS technology to obtain the emission rule.

At present, there are few reports on effective extraction of characteristic absorption spectrum and improvement of detection stability in open-path detection. In this paper, the multi-line fitting
The algorithm was designed to realize spectrum detection. Allan variance analysis was carried out to determine the measurement stability, and the OP-TDLAS system was used to monitor CO$_2$ and NH$_3$ regional Emission in farmland.

**Basic Principles**

According to Lambert-Beer’s law, the monochromatic laser with the laser emitting frequency $\nu$ and initial light intensity $I_0$ passes through an absorption medium with certain length of $L$, and the relationship between laser received intensity $I_v(\nu)$ and absorbance $A(\nu)$ is expressed as:

$$A(\nu) = \ln \frac{I_0}{I_v(\nu)} = k(\nu)L$$

(1)

$k(\nu)$ is the spectral absorption coefficient of a single gas at a single transition:

$$k_v = S(T) \phi(\nu) P x$$

(2)

where $S(T)$ is the line strength, $P$ is the pressure, $x$ is the gas concentration, $\phi(\nu)$ is a normalized linear function. By integrating formula (2), the gas concentration is expressed as:

$$x = \frac{A}{S(T)PL}$$

(3)

The wavelength range of spectral transition was tuned to retrieve the gas concentration from the transition absorbance results when the temperature, line strength and pressure are known.

**Detection System and Technology**

**System Design**

The OP-TDLAS system structure is shown in Fig. 1. The DFB lasers are used as light sources to monitor NH$_3$ absorption line at 6528.8 cm$^{-1}$ and CO$_2$ absorption line at 6336.3 cm$^{-1}$ respectively. The beam combiner couples the two time-division scanned laser beams and divided them into three beams. One beam passed a reference cell filled with standard gases, and the other two beams transmitted to the open optical system consisting of the telescope and retro-reflector. The two optical systems used to measure respectively the gases absorption spectrum of background path and downwind path for quantitatively inverting the concentration.

![Figure 1. System structure.](image-url)
averaged. (2) The characteristic absorption spectrum was extracted by deducting background and normalizing. (3) The invalid signals of low correlation with the standard spectrum were rejected. (4) The integral absorbance was obtained with line profile fitting. Especially to gas spectrum with multiple absorption peaks, multi-line profile fitting is performed with the number, position and line width of the absorption line, as shown in Fig. 2(a). (5) The target gas concentration was inverted according to the measured temperature and pressure and the line strength from Hitran database.

In actual measurement, the absorption line of ammonia gas at $6528.8 \text{cm}^{-1}$ is the superposition of four spectral lines. The measurement error will be increase if single peak absorption fitting is used. Therefore, a multi-line fitting algorithm was designed and the residual error of fitting was within $\pm 1.5\%$, and the error of concentration inversion was decreased by 2.76%, as shown in Fig. 2(b).

![Figure 2. (a) Superposition absorbance signal by multi-line profile fitting (b) Residual error of multi-line profile fitting.](image)

**Detection Performance**

In actual measurement, the effective data integration time representing of system stability must be determined to reduce system random noise. The minimum occurrence time corresponds to the optimal integration time by Allen variance analysis. So, the actual data acquisition and average processing should be complete within this time, it can be expressed as formula (4):

$$\sigma_e^2(\tau_M) = \frac{1}{2} <(\bar{e}_i(\tau_M) - \bar{e}_i(\tau_M))^2> = \frac{1}{2(K-1)} \sum_{i=1}^{K-1} (\bar{e}_i(\tau_M) - \bar{e}_i(\tau_M))^2$$

where $K$ is the array length to obtain the sample variance, $\tau_M$ is the integration time. The slopes of Allen variance analysis represented different noise types.

Allen variance analysis was carried out with NH$_3$ and CO$_2$ monitoring, as shown in Fig. 3. In the range dominated by white noise, the Allen variance chart of 20 $\mu$ L/L ammonia monitoring results shows that the minimum with slope of -1 is 0.048 $\mu$ L/L represented the detection limit and the integration time is 9s. Similarly, the detection limit of 100 $\mu$ L/L CO$_2$ is about 4.31 $\mu$ L/L and the integration time is 8s.It can be seen that the drift affecting the OP-TDLAS system is not completely linear, the influence of 1/f noise and drift noise was dominant at measurement beginning, but too long integration time will affect the system sensitivity.
Experiment Results
The continuously monitoring of CO$_2$ and NH$_3$ in farmland in northern Anhui was carried out to study the gases emission rule. The optical systems are installed in the east-west direction as south wind prevails in this area. The monitoring height is 2.4m and path length is about 400m. Wheat straw was returned to the field on June 6$^{th}$, the base fertilizer was applied with corn sowing on June 10$^{th}$ and added fertilizer with rain after six days. The corn was harvested from September 30$^{th}$ to October 11$^{th}$.

NH$_3$ Monitoring Results
The monitoring results of ammonia in downwind direction are shown in Fig. 5(a). The background concentration path was about 0.08 $\mu$ L/L. Ammonia increased obviously after fertilization and decreased after two weeks. The maximum daily average concentration was 0.91 $\mu$ L/L during fertilization. Otherwise, the daily average concentration increased to the maximum of 1.7 $\mu$ L/L after wheat straw returning to the field because the wheat straw deteriorate in summer and ammonia emissions are affected by soil temperature and meteorological factors. It shows that fertilization and straw returning to the field both promote soil ammonia volatilization, but the effect of former was 1.34 times of that of latter. The daily trend of NH$_3$ emission is that the concentration rose to the maximum at noon, and then decreased to the minimum at night, as shown in Fig. 5(b).

CO$_2$ Monitoring Results
The monitoring results of CO$_2$ are shown in Fig. 6(a). In general, the CO$_2$ concentration increased gradually after fertilization because its emission by soil respiration increased from July to August due to rapid decomposition of wheat straw buried in soil at high temperature. In mid of October, the wheat didn’t grow up and the CO$_2$ concentration was close to the background value. During the experiment,
the minimum daily average concentration was 416 µL/L at the beginning, and the maximum was 532 µL/L after straw returning to the field.

Overall, straw returning to the field and fertilization are both the sources of CO2 volatilization. The potential increasing effect of the former is about 1.14 times of that of the latter. As the corn grows well after fertilization which enhances photosynthesis and respiration function, the concentration is lower at noon than that before fertilization, and it is higher at night. The average CO2 emission in summer is slightly higher than that in autumn because of sunshine and other meteorological factors.

Summary
The spectrum detection technology was studied with multi-line fitting algorithm designing to effectively extract absorption spectrum, and the error of concentration inversion was reduced by 2.76%. Through Allan variance analysis, the detection stability was determined. The monitoring of NH3 and CO2 in large-scale farmland in northern Anhui was carried out to obtain the gases emission rule: both of fertilization and straw returning to the field promote volatilization of NH3 and CO2 from the soil and they have typical daily variation trend. In the future, carbon and nitrogen emission flux of farmland can be measured with detection concentration and gas diffusion model, which provide technical support for the environmental-friendly agricultural.

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