Research on laser water vapor concentration detection technology in the air-sea flux observation

Ke-ke ZHANG1, a, Xue-yong ZHENG2, b, Shi-zhe CHEN1, c, Xiao-zheng WAN1, d, Ji-ming ZHANG1, e, Qiang ZHAO1, f, Bo WANG1, g, Liang QI1, h

1Institute of Oceanographic Instrumentation, Qilu University of Technology (Shandong Academy of Sciences), Qingdao, Shandong 266061, China
2Qingdao Kernel Spectrum Technology Co., Ltd, Qingdao, Shandong 266043, China

18661475909@163.com, bflykernel@126.com, chcszom@163.com, d18661817997@163.com, ejimingzhangwld@163.com, fzqhero9494@163.com, gbob80.wang@hotmail.com, h563498491@qq.com

Abstract. In the observation of water vapor flux at air-sea interface, the collection frequency of water vapor concentration is more than 10 Hz. High-speed and high-precision measurement of water vapor concentration is an urgent problem to be solved in the observation of water vapor flux at air-sea interface. The ratio of the peak-peak value of second harmonic to the average value of first harmonic is used to measure water vapor concentration based on tunable diode laser absorption spectroscopy. The sensitivity of laser water vapor concentration detection equipment caused by marine salt fog and dust is reduced through precise optical design, and the water vapor concentration at the air-sea interface is calculated using a binary polynomial fitting algorithm. The response frequency of the laser water vapor concentration analyzer is 40 Hz. The water vapor concentration values from the laser water vapor concentration analyzer and LI-7500 CO₂/H₂O gas analyzer are collected synchronously in real time using LabVIEW software. The comparison results show that they have good consistency in the trend and response speed of water vapor concentration, and the measurement deviation of water vapor concentration is within ±1%. The experimental results show that it can meet the needs of high-speed, high-precision measurement of water vapor concentration in the air-sea interface water vapor flux observation.

1. Introduction

Air-sea interface flux is an important parameter for describing the interaction between the atmospheric boundary layer and the surface layer of the ocean. Water vapor flux at air-sea interface is the exchange of water vapor between the ocean and the atmosphere. Water vapor flux is closely related to ocean salinity change, atmospheric water vapor content, ocean and land precipitation and so on. High-speed and high-precision measurement of water vapor concentration is very important for the observation of water vapor flux at air-sea interface. Tunable diode laser absorption spectroscopy (TDLAS) is a gas measurement technology based on molecular absorption spectroscopy. It has the advantages of high sensitivity, high precision and fast response[1-3]. Domestic research institutes represented by Anhui Institute of Optics and Precision Machinery, Chinese Academy of Sciences have made some achievements in measuring water vapor concentration by tunable diode laser absorption spectroscopy. Yanan Cao studied water vapor concentration in a closed glass container using tunable diode laser
absorption spectroscopy[4]. Ying He measured water vapor concentration in large-scale area using tunable diode laser absorption spectroscopy, and compared it with the measurement data of LI-7500 gas analyzer in the same site vorticity correlation observation system[5]. Wei Nie carried out the measurement of water vapor absorption spectrum parameters at low temperature based on TDLAS technology[6].

Although many scholars have made a lot of fruitful research on the measurement of water vapor concentration using TDALS technology, this technique has not been applied to air-sea flux observation. At present, non-dispersive infrared spectroscopy (NDIR) is used in the field of water vapor flux measurement. In this paper, TDLAS technology is applied to the laser water vapor concentration measurement of air-sea flux observation, and a high-speed and high-precision laser water vapor concentration detection equipment is developed to replace expensive imported products. It is of great significance to improve the level of marine monitoring and marine scientific research in China.

2. Detection Principle

Tunable diode laser absorption spectroscopy is a gas measurement technology based on the theory of molecular absorption spectroscopy. When a laser beam passes through the measured gas, if the laser emission spectrum is overlapped with the gas absorption spectrum, the output light intensity will be weakened by the absorption of the gas, and the Bill-Lambert law is satisfied between the input light intensity and the output light intensity.

When narrow-band light passes a gas cell, the transmitted intensity \( I(v) \) at a specific optical frequency \( v \) is given by Beer-Lambert law[7-8]:

\[
I(v) = I \cdot \exp \left[ -\alpha(v)CL \right].
\]

where \( I \) is the incident intensity; \( I(v) \) is the output intensity; \( v \) is the laser frequency; \( \alpha(v) \) is the absorption coefficient; \( C \) is the gas concentration; \( L \) is the length of the gas cell.

The laser driving circuit is composed of a DC drive signal, a low-frequency triangular wave signal and a high-frequency sine wave signal. Because of the influence of the intensity modulation in the process of wavelength modulation[9], the laser power can be represented as:

\[
I = I_0 \left( 1 + p_{\Omega}\gamma x - p_{\omega}m\cos\omega t \right).
\]

where \( I_0 \) is the incident intensity; \( \gamma \) is the half width at half maximum (HWHM); \( m \) is the width-normalized frequency modulation amplitude; \( p_{\Omega} \) and \( p_{\omega} \) describe the laser power variations as a function of the optical frequency originated from the low frequency triangle-wave modulation and the high frequency cosine modulation. According to Eq.2 and Eq.1, it is obtained that:

\[
I(v) = I_0 \left( 1 + p_{\Omega}\gamma x - p_{\omega}m\cos\omega t \right) \exp \left[ -\alpha(v)CL \right].
\]

Considering the nonlinearity of the intensity modulation, the odd harmonic component and the high-order harmonic component are introduced into the second harmonic, which can distort the second harmonic[10]. The second harmonic signal is asymmetric[11], and the peak-peak value of the second harmonic can be expressed as:

\[
V_{2,PP} = \frac{2S_{2,\text{max}} - S_{2,\text{min1}} - S_{2,\text{min2}}}{2} \propto I_0CL.
\]

where \( S_{2,\text{max}} \) is the peak value of the second harmonics; \( S_{2,\text{min1}} \) and \( S_{2,\text{min2}} \) are the two valley values of the second harmonics respectively.

According to Eq.4, the peak-peak value of the second harmonic is directly proportional to the water vapor concentration and it can be used to measure the water vapor concentration. However, such factors as dust, window pollution and laser power attenuation change will change the transmittance, and then affect the peak-peak value of the second harmonics. When the transmittance of the system changes, in order to eliminate the influence of the change of the transmittance on the instrument linearity, an
influencing factor that synchronously changes with the peak-peak of the second harmonic needs to be found.

According to reference[12], the first harmonic signal is singularly symmetric. According to Eq.3, the average value of the first harmonic can be expressed as:

\[ V_{\text{aver}} = I_0 P_{\omega} \sqrt{\gamma} \]  \hspace{1cm} (5)

The average value of the first harmonic is proportional to the light intensity \( I_0 \), and it has nothing to do with the water vapor concentration to be measured. The ratio of the peak-peak value of the second harmonic to the average value of the first harmonic can be expressed as:

\[ S_{\text{out}} = \frac{V_{2pp}}{V_{\text{aver}}} \propto CL. \]  \hspace{1cm} (6)

According to Eq.6, the ratio of the peak-peak value of second harmonic to the average value of first harmonic is proportional to the measured water vapor concentration and the length of absorption path, which can be used to measure water vapor concentration.

The second harmonic peak-peak value and the first harmonic average value come from the high frequency modulation sine wave, which are completely synchronized with the light intensity change, the dark current, the circuit and so on. The ratio of the two is not related to the light intensity and the transmittance attenuation, which can be used to eliminate the influence of laser output intensity fluctuation and window contamination on water vapor concentration measurement.

3. System Design
The principle block diagram of TDLAS water vapor concentration detection is shown in Fig. 1. According to HITRAN 2016 molecular spectroscopy database[13], there is a strong absorption line of water molecules near 1392 nm, and it can be used to detect water vapor concentration. The vertical cavity surface emitting laser (VCSEL) operating at 1392 nm is used as the light source.
Laser is the core device of the laser water vapor concentration analyzer. The stability of the working current and temperature of the laser is very important for the core components[14]. The current drive of the laser consists of DC, low-frequency triangular wave and high-frequency sinusoidal wave. The temperature control circuit and current drive circuit control the diode laser to emit the laser. The tunable laser generates spectral absorption in the open gas cell. Then the photoelectric detector is used to convert the absorbed signal. After photoelectric conversion, the signal is band-pass filtered. The second harmonic peak-peak signal and the first harmonic average signal are obtained by using phase-locked amplification technology. A temperature probe is set in the absorption gas cell to correct the temperature of the detected harmonic signal. The temperature data and harmonic signals are fed into the data processing unit, and the water vapor concentration is calculated according to the fitting equation.

In the measurement of water vapor flux, the collection frequency of water vapor concentration should be above 10 Hz[15-16], which requires a higher response frequency of laser water vapor...
concentration analyzer. The frequency of low frequency triangular wave scanning signal and high frequency sinusoidal wave modulation signal are 40 Hz and 30 kHz respectively. Fig. 2 shows triangular wave signal and second harmonic wave signal. Data acquisition is carried out along the descending edge of triangular wave. Data processing is completed at the rising edge of triangular wave. The response frequency of laser water vapor concentration analyzer is 40 Hz, which can meet the needs of high dynamic measurement of water vapor flux at air-sea interface.

Fig. 2  Sampling frequency of laser water vapor concentration analyzer

Fig. 3  Second harmonic signals at different water vapor concentrations

Fig. 3 shows the second harmonic signal collected under different water vapor concentration. The peak-peak value of the second harmonic is proportional to the water vapor concentration. The system can effectively suppress the influence of light intensity fluctuation, optical lens window pollution and other factors on the measurement of water vapor concentration by the ratio of the peak-peak value of the second harmonic to the average value of the first harmonic.

4. Data Fitting

For water vapor concentration measurement using TDLAS harmonic detection method, the change of temperature and water vapor concentration will cause the change of line strength and line broadening of water vapor absorption spectrum. Therefore, the influence of temperature and water vapor concentration on the measured value of water vapor concentration should be considered in the process of measuring water vapor concentration at air-sea interface[17].

Water vapor concentration calibration experiment was carried out by using temperature and humidity standard box and high precision cold mirror dew point meter. By controlling temperature and relative humidity in temperature and humidity standard box, temperature and water vapor concentration were changed. When the temperature and relative humidity in the temperature and humidity standard box are stable, the temperature and water vapor concentration measured by the cold mirror dew point analyzer are recorded, and the temperature and AD values of the laser water vapor concentration analyzer are also recorded. Using matlab cftool function to fit binary polynomial data, the fitting curve is shown in Fig. 4. The fitting equation is as follows:

\[
C = p_1 + p_2 \cdot x + p_3 \cdot y + p_4 \cdot x^2 + p_5 \cdot x \cdot y + p_6 \cdot y^2 + p_7 \cdot x^2 \cdot y + p_8 \cdot x \cdot y^2 + p_9 \cdot y^3 + p_{10} \cdot x^2 \cdot y^2 + p_{11} \cdot x \cdot y^3 + p_{12} \cdot y^4 + p_{13} \cdot x^2 \cdot y^3 + p_{14} \cdot x \cdot y^4 + p_{15} \cdot y^5
\]

where \( p_1 = -1202; \ p_2 = -36.73; \ p_3 = 6.82; \ p_4 = -1.677; \ p_5 = 0.1413; \ p_6 = 0.003138; \ p_7 = 0.004002; \ p_8 = 0.000112; \ p_9 = 1.323e-06; \ p_{10} = -6.676e-07; \ p_{11} = 2.623e-08; \ p_{12} = -3.588e-10; \ p_{13} = 1.673e-11; \ p_{14} = -1.675e-12; \ p_{15} = 2.601e-14; \) \( x \) is temperature; \( y \) is AD value; \( C \) is water vapor concentration.
The coefficient R-square of the fitting function is 1, Adjusted R-square is 1, RMSE is 54.75, and the polynomial fitting effect is better. Laser water vapor concentration analyzer collects temperature and AD values in real time. The model can be used to retrieve water vapor concentration at air-sea interface.

5. Comparative Experiment
The LI-7500 series of LI-COR open-circuit CO₂/H₂O gas analyzer has been widely used in the field of global vorticity covariance carbon flux monitoring. LI-7500 uses non-dispersive infrared spectroscopy to measure the density of CO₂ and H₂O in the air. The comparative experiment was carried out between laser water vapor concentration analyzer and LI-7500, as shown in Fig. 5.

After fitting the data of laser water vapor analyzer, the equipment was compared with LI-7500 of LI-COR Company. Laser water vapor concentration analyzer and LI-7500 are placed in the temperature and humidity standard box at the same time. By changing the temperature and water vapor concentration, the laser water vapor concentration analyzer and LI-7500 water vapor concentration are collected synchronously in real time using LabVIEW software.
Fig. 6 shows the output values of laser water vapor analyzer and LI-7500 in the range of 0~130 mmol/mol. From the figure, it can be seen that the laser water vapor analyzer and LI-7500 have good consistency in the trend of water vapor concentration change and response speed and the measurement error of the two analyzers is less than ±1%.

6. Summary
In this paper, a prototype of laser water vapor concentration analyzer is developed based on tunable semiconductor laser absorption spectroscopy. The peak-peak value of the second harmonic and the average value of the first harmonic are used to measure the water vapor concentration at the air-sea interface. The influence of ocean salt fog and dust on the window is reduced through precise optical design. The water vapor concentration values of laser vapor analyzer and LI-7500 CO₂/H₂O gas analyzer are collected synchronously. The measurement results show that the deviation of water vapor concentration is less than ±1% in the whole range, and the response frequency of the device can reach 40 Hz. Laser water vapor concentration analyzer based on tunable diode laser absorption spectroscopy technology provides a new way for high-speed and high-precision measurement of water vapor concentration in air-sea interface flux.

Acknowledgment
This project is supported by the national key research and development program of china (Grant No.2017YFC1403303), and the natural science foundation of shandong province (Grant Nos.ZR2017QD015, ZR2019MF022), and the shandong provincial key research and development program (Grant No. GG201703130110, 2019GHY112056).

References
[1] YANG Ya-han, LI Guo-lin, LI Xiao-peng, et al. Partial least squares algorithm application in TDLAS based trace H2S analyses in natural gas. Acta Photonica Sinica, Vol.46(2017), p.0230002
[2] ZHANG Ke-ke, YAN Xing-kui, ZHENG Xue-yong, et al. Research on laser humidity detection technology based on TDLAS. Optoelectronic technology, Vol.36(2016), p.23-27
[3] CHEN Hao, JU Yu, HAN Li, et al. Effects of temperature of laser shell on background signals for trace gas detection in TDLAS. Spectroscopy and spectral analysis, Vol.38(2018), p.1670-1674
[4] CAO Ya-nan, WANG Gui-shi, TAN Tu, et al. Concentration and pressure measurement of water vapor in sealed glass containers based on tunable diode laser absorption spectroscopy. Acta Photonica Sinica, Vol.65(2016), p.084202
[5] HE Ying, ZHANG Yu-jun, WANG Li-ming, et al. Study on large-scale regional laser detection methods for water vapor concentration. Spectroscopy and Spectral Analysis, Vol.33(2013), p.608-612.

[6] NIE Wei, KAN Rui-feng, XU Zhen-yu, et al. Measuring spectral parameters of water vapor at low temperature based on tunable diode laser absorption spectroscopy. Acta Photonica Sinica, Vol.66(2017), p.201421.

[7] WANG Di, NI Zi-yan, WANG Ming-ji, et al. Data processing of direct absorption spectroscopy for laser gas detection under modulated noise. Acta Photonica Sinica, Vol.48(2019), p.0307001.

[8] MO Xiao-bao, XUAN Liu, HUANG Zhi, et al. Study on Evaporation from a Free Water Surface Using Laser Absorption Spectroscopy. Chinese Journal of Lasers, Vol.42(2015), p.1015003.

[9] Schilt Stéphane, Thévenaz Luc and Robert Philippe. Wavelength modulation spectroscopy: combined frequency and intensity laser modulation. Applied Optics, Vol.42(2003), p.6728-6738.

[10] LI Han, LIU Jian-guo, HE Ya-bai, et al. Simulation and analysis of second-harmonic signal based on tunable diode laser absorption spectroscopy. Spectroscopy and Spectral Analysis, Vol.33(2013), p.881-885.

[11] Seyedali Hosseinzaeddine Salati and Alireza Khorsandi. Apodized 2f/1f wavelength modulation spectroscopy method for calibration-free trace detection of carbon monoxide in the near-infrared region: theory and experiment. Applied Physics B, Vol.116(2014), p.521-531.

[12] CAO Jia-nian, ZHANG Ke-ke and WANG Zhuo. New scheme of methane concentration detection with tunable diode laser absorption spectroscopy. Chinese Journal of Scientific Instrument, Vol.31(2010), p.2597-2602.

[13] I.E. Gordon, L.S. Rothman, C. Hill, et al. The HITRAN2016 molecular spectroscopic database[J]. J. Quant. Spectrosc. Radiat. Transfer, Vol.203(2017), p.3-69.

[14] YAN Wan-hong, ZHOU Yan-wen, YU Di, et al. Temperature control system of semiconductor device and application for infrared gas detection. Acta Photonica Sinica, Vol.48(2019), p.0312002.

[15] WANG You-heng, JING Yuan-shu, GUO Jian-xia, et al. Contrast research on flux correction methods for eddy-covariance measurement. Meteorological Science and Technology, 2011, Vol.39(2011), p.363-368.

[16] ZHAO Jia-yu, ZHANG Mi, XIAO Wei, et al. Greenhouse Gas Fluxes at Water-Air Interface in Small Pond Using Flux Gradient Method Based on Spectrum Analyzer. Environmental Science, Vol.38(2017), p.41-51.

[17] LI Zheng-jui, YAO Shun-chun, LU Wei-ye, et al. Study on temperature correction method of CO$_2$ measurement by TDLAS. Spectroscopy and Spectral Analysis, Vol.38(2018), p.2048-2053.