High sensitivity measurement of NO, NO_2 and NH_3 using MIR-QCL and time division multiplexing WMS technology

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ABSTRACT

A compact system based on mid-infrared quantum cascade laser(QCL) operated in room temperature was developed for the simultaneous monitoring of NO, NO_2 and NH_3 in the air. Laser beams of three QCLs with central wavelength located at 1900 cm-1, 1600 cm-1, 1103.4 cm-1 were coupled to pass through the 60m long gas cell together. With the technology of time division multiplexing, wavelength modulation spectroscopy(WMS) signals of three lasers can be detected at adjacent scan process. The real-time second harmonic analysis was implemented to achieve simultaneous detection of NO, NO_2 and NH_3. A minimum detection limit(MDL) of 0.2ppb for NO, 0.12ppb for NO_2 and 0.1ppb for NH_3 with an optimum integration time around 100 seconds can be achieved for this setup. An ambient monitoring of three gasses during 5hours was performed to inspect the local air quality.

Keywords: Mid-infrared; absorption spectroscopy; Quantum cascade laser; real-time monitoring; Time divide multiplexing; Wavelength modulation

1. INTRODUCTION

As the precursors of secondary fine particulate matters, NO, NO_2 and NH_3 in the air play an important role in the formation of haze. Despite their low atmospheric concentrations, NO and NO_2 represent an important factor regarding air quality given their contribution to local ozone production[1]. And the NO_X will promote the acid rain, cause soil acidification, affect the growth of plants[2] . At levels higher than 1ppm in air, NO_2 and NH_3 can cause severe damage to human respiration systems[3]. Providing excess nitrogen input to ecosystems, Ammonia can have harmful effects on ecosystems and

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biodiversity through influencing acidity of natural waters and soils[4]. Hence, continuous and in situ sensing at trace level is necessary especially in the application of environmental monitoring.

Wavelength modulation spectroscopy[5-8], combined with second harmonic detection, is able to improve detection limits substantially and monitor various gases with high resolution. Generally, multi-pass cell with better performance can improve the sensitivity and stability of the measurement. A robust extractive cell optically stable at the process temperature and showing fast response for ammonia slip measurement was developed[9]. To avoid interference of other nature, such as overlapping absorption features or pressure broadening effects, a detailed investigation of the simulated absorption spectra of NO and NO_2 was performed in the range of 1600 and 1900cm^{-1}[10]. Since NO, NO_2 and NH_3 have fundamental absorption in mid-infrared wave band, gas detection at ppb level can be achieved with QCLs. A quantum cascade-laser-based atmospheric ammonia sensor for high-sensitivity was demonstrated, which provided the capabilities for improved gas-phase NH_3 sensing with a noise equivalent limit of 0.15ppbv[11]. Fluctuations of NO and NO_2 during 12hours in the field was investigated with high measurement rates, good linearity in a large concentration range and necessary sensitivity[12]. However, because of the strong absorption characteristics of NO_X and NH_3, extractive closed-path systems may suffer from slow response times as well as inaccurate results.

In the following sections, we introduced a QCL-based instrument for monitoring NO, NO_2 and NH3 in the open air. In contrast to closed-path systems, nonintrusive open-path design of gas cell minimizes challenges and provides fast response times. Three absorption lines located at 1900 cm-1, 1600 cm-1, 1103.4 cm-1 were selected, where NO, NO_2 , NH_3 have their fundamental ro-vibrational modes and the line strength are two order stronger than those in near-infrared absorption area. Application of time division multiplexing technology enables the combination of three QCLs, and realizes simultaneous NO, NO_2 and NH_3 detection at ppb level.

2. INSTRUMENT DESIGN

The schematic diagram of the open-path sensor is shown in Fig. 1. In order to eliminate the interference by other gas species in the air and to meet the requirements of detecting limit, three absorption lines located at 1900 cm-1, 1600 cm-1 and 1103.4 cm-1 were selected respectively for NO, NO_2 and NH_3. Quantum cascade lasers (Alpes Lasers), controlled by low-noise drivers (Wavelength Electronics, PLD1250) and precise temperature controllers (Wavelength Electronics, PTC10K-CH), were installed on the surface of peltier devices with excellent heat dissipation. Green indication light was used to guide optical path adjustment.

In the experiment three 50Hz-frequency time division multiplexing sawtooth signals accompanied with a 30kHz-frequency sinusoidal signal were used to modulate lasers' injection current. The ramp and modulation signals were generated by a Data Acquisition Device (NI-USB 6363) with a resolution of 16 bits. Three QCLs were multiplexed using beamsplitters, and coupled into a 25cm long reference gas cell equipped with wedged CaF2 windows before injected into

the 60m long open-path multi-pass cell. Compared with plane mirrors, wedged mirrors can effectively remove optical interference. Since the 60m long multi-pass cell was directly exposed to the air, a short path cell was essential for calibration purpose. As was shown, while examining the response of the system at different concentration of gas samples, mirror 1 and mirror 2 were placed behind the reference cell and reflected laser beams to the detector without passing through multi-pass cell. For an open-path setup, this design minimized deviations of calibration brought by NO, NO2 and NH3 with background concentration at ppb level in the air.

When calibration was finished, mirror 1 and mirror 2 were removed. The output beams from the multi-pass cell were focused on a room-temperature MCT photodiode (Vigo, PVI-2TE) by an off-axis parabolic mirror and precise adjustment was made to optimize the detector signal. Data acquisition of the electric signals was performed using the DAQ card (NI-USB 6363) with a sampling rate of 2MHz. The original spectral signal was averaged for 50 times to enhance signal to noise ratio. In operation, digital lock-in processing of the acquired data can be performed within one sawtooth wave cycle, which leads to a response time of 1s.

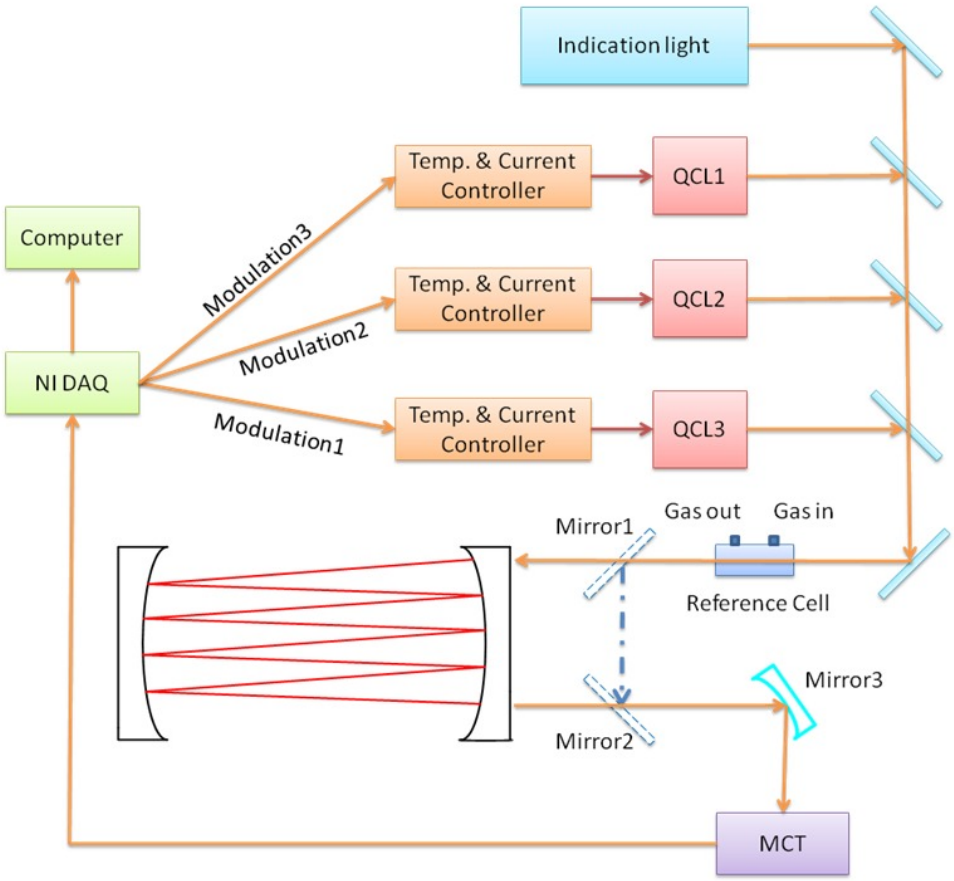

Fig. 1 Instrument setup

3. EXPERIMENTAL RESULT AND DISCUSSION

3.1 Calibration

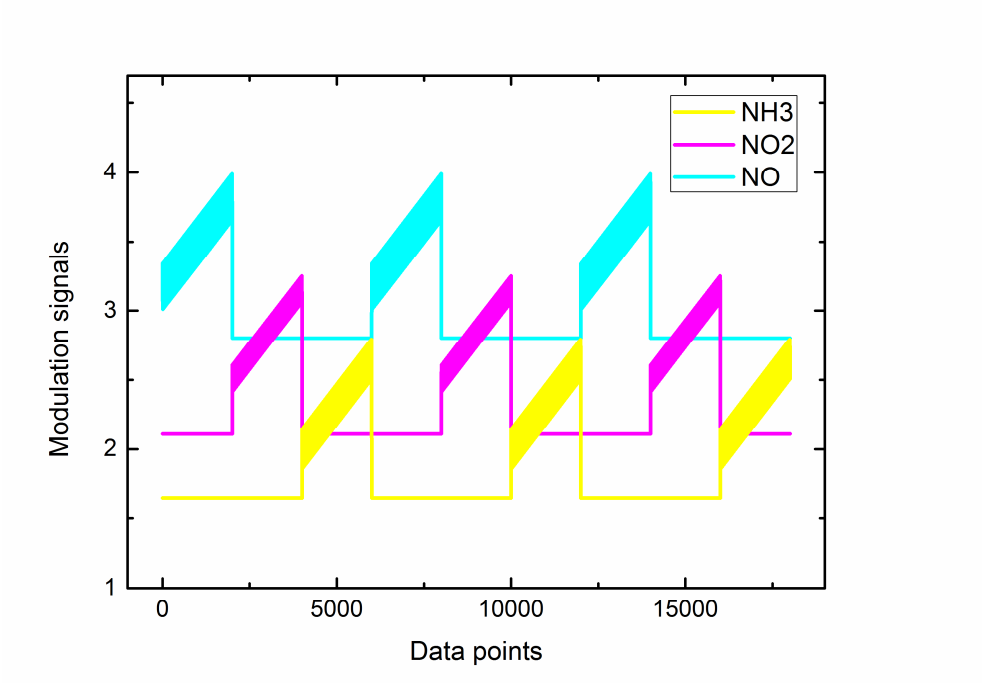

Fig. 2 Time division multiplexing signals

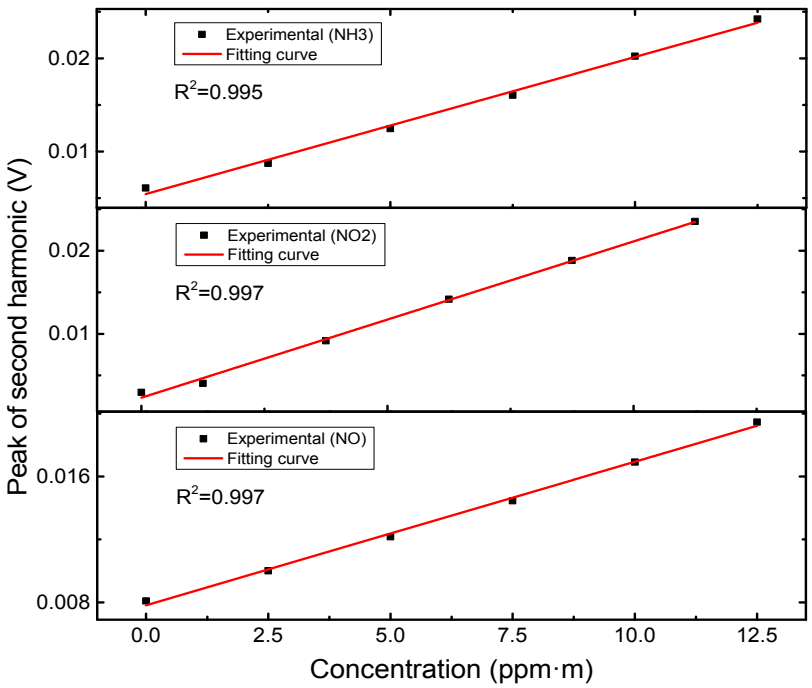

Fig. 3 Calibration curve

Tests at different modulation parameters were conducted to ensure a smooth base line as well as an optimum signal to noise ratio. Time division multiplexing signals generated by the instrument at adjacent scan process was depicted in Fig. 2. The sweep frequency was 50 Hz and the modulation frequency was 30 kHz. A relative high modulation frequency was selected to eliminate the adverse effect of atmospheric turbulence in the air. While QCLs were not on working state, the bias current was set smaller than threshold current to remove the interference of emitting light. Time division multiplexing technology decreased the average light-emitting time of QCLs as well as the produced heat and improved the thermal stability in a long period. While the tuning range and frequency response of QCLs differed from each other, the modulation signals of QCLs aimed at different gases were distinctive.

NO, NO_2 and NH_3 samples were injected into the reference cell to record the response of the sensor system at different concentration of gas samples. Mirror 1 and mirror 2 were placed behind the reference cell to reflect beams directly to the detector. Due to the strong absorption characteristics of NO_X and NH_3, gas flows of each concentration were maintained for fifteen minutes to acquire stable 2f signals. Experimental data during the last five minutes were recorded so as to obtain accurate instrumental response. Peak values of 2f signals were calculated and good linear relationships between gas concentration and peak values in a large scope was observed in Fig. 3.

3.2 Allan deviation

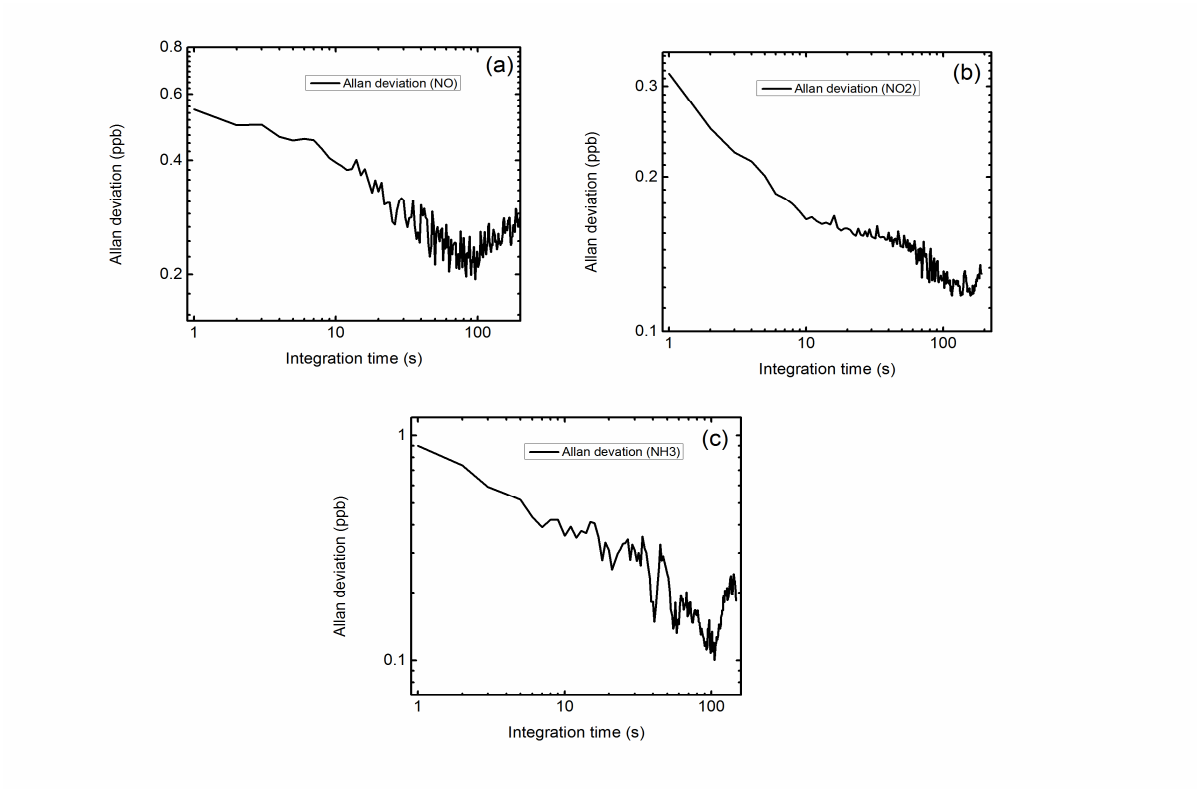

Fig. 4 Allan deviation plots for NO(a), NO_2(b) and NH_3(c)

Pure gas flow of N_2 during an extend period of time was used to investigate the minimum detection limit(MDL) of three gases. To remove negative effects derived from concentration fluctuations in the ambient air, combined laser beams did not pass through the multi-pass cell during the test. Allan variance analysis[13-15] was performed for different periods and the results were depicted in Fig.4 showing the precision on gas measurements as a function of the integration time of the original signals. As was presented, The MDL of 0.2ppb for NO, 0.12ppb for NO_2 and 0.1ppb for NH_3 with an optimum integration time around 100 seconds can be achieved for this setup. The optimum integration time for different QCLs almost coincided owing to the similar setup for them, including same drivers, shared reference cell and detector. The plots demonstrated a 1Hz precision of 0.55, 0.34 and 0.9ppb for NO, NO_2 and NH_3 respectively. The deviation of 1Hz precision was mainly derived from different line strength as well as distinctive frequency response. While the concentration of NO, NO_2 and NH_3 in the air fluctuated at ppb level, this instrument was suitable for environmental monitoring with a response time of 1s.

3.3 Ambient monitoring

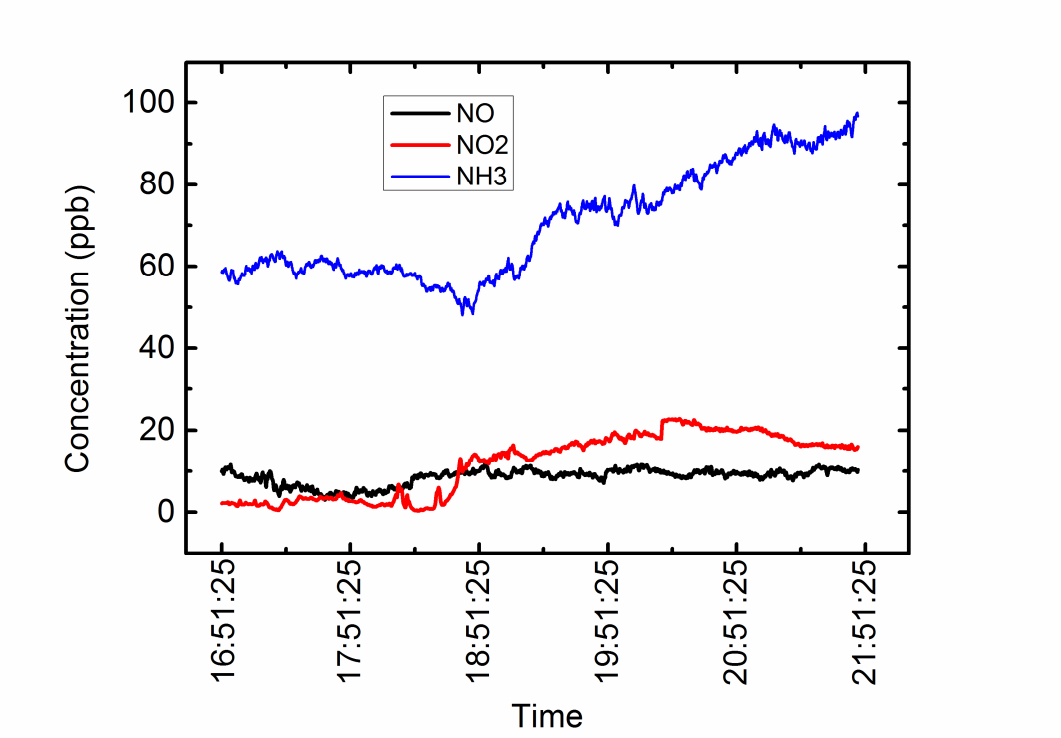

Fig. 5 Ambient monitoring of NO, NO_2 and NH_3

A continuous monitoring of NO, NO_2 and NH_3 during 5hours in the open air was depicted in Fig.5. Measuring site was in the countryside distant from urban area, where the air quality was excellent. Additional on-site work including re-calibration was performed to minimize the influence of temperature disparities between day and night. As was shown, the concentration of three gases increased since the sunset at about half past sixteen. This was mainly due to the impact of meteorological conditions. In the daytime, environmental temperature increases with sun esposure, which leads to a stronger atmosphereic turbulence. As a consequence of the enchanced atmospheric diffusion capacity, concentration of the

pollutants during the day was less than that of night[16]. Since the NO_X was mainly generated by automobile exhaust[17] and measuring site was far away from pollution sources, a low concentration level of NO and NO_2 was observed. During the test, ammonia concentration was remained around 60ppb in the daytime and reached up to 95ppb at night. While agricultural activities were the major source of NH3 discharges, a relative high concentration level was reasonable in the countryside.

4. CONCLUSION

By applying time division multiplexing technology to WMS, an instrument monitoring NO, NO_2, and NH_3 simultaneously in the air was demonstrated. To realize gas detection at ppb level, QCLs with central wavelength located at mid-infrared area were selected, where the target gases have their stronger absorption lines. Time division multiplexing technology decreased the average light-emitting time of QCLs as well as the produced heat and improved the thermal stability in a long period. An excellent liner instrumental response at different concentration of gas samples was recorded in a large scope. With an optimum integration time around 100s, the MDL for three gases was less than 0.2ppb. A real-time and in-situ detecting of NO, NO_2 and NH_3 was performed during five hours in the country. The variation trend coincided well with local meteorological condition and geography condition. Above all, this detecting system is suitable for real-time NO, NO_2 and NH_3 monitoring in the air with quick response, excellent stability and low MDL.

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REFERENCES

[1] Klein A., Witzel O., Ebert V. , "Rapid, Time-Division Multiplexed, Direct Absorption- and Wavelength Modulation-Spectroscopy," Sensors, 14(11), 21497-21531(2014).

[2] Yang X. T., Xie W. Q., Yuan Z., G., "Research on the NO concentration of marine diesel emission by tunable diode laser absorption spectroscopy technique," Optik-International Journal for Light and Electron, 2016(127), 3788-3791(2016).

[3] Yavari F., Castillo E., Gullapalli., et al, "High sensitivity detection of NO_2 and NH_3 in air using chemical vapor deposition grown grapheme," Applied Physics Letters, 100(20), 201320(2012).

[4] Andrea P., David B., H., Christine F. B., et al, "Metrology for ammonia in ambient – concept and first result of the EMRP project MetNH_3," International Congress of Metrology, 07003(2015).

[5] Fernholz T., Teichert H., Ebert V., "Digital, phase-sensitive detection for in situ diode-laser spectroscopy under rapidly changing transmission conditions" Appl. Phys. B, 75(2), 229-236(2002).

[6] Andersson M., Persson L., Svensson T., "Flexible lock-in detection system based on synchronized computer plug-in boards applied in sensitive gas spectroscopy," Review of Scientific Instruments, 78(11), 113107.1-113107.7(2007).

[7] Mei L., Svanberg S., "Wavelength modulation spectroscopy-digital detection of gas absorption harmonics based on Fourier analysis," Appl. Opt., 54(9), 2234-2243(2015)
[8] Miller D. J., "Interactive comment on "Open-path, quantum cascade laser-based sensor for hign resolution atmospheric ammonia measurements" by D. J. Miller," Atmos. Meas. Tech. Discuss, 6(7005), 3128-3136(2013).
[9] Panella B., Maas D., Brandle., Hubert., "Highly sensitive tunable diode laser absorption spectroscopy for process and emission monitoring," Renewable Energy and the Environmental Congress, EW1A3, 2013.
[10] Tuzson B., Zeyer K., Steinbacher N., et al, "Selective measurements of NO, NO_2 and NO_Y in the free troposphere using quantum cascade laser spectroscopy," Atmos. Meas. Tech. 2013(6) 927-936(2013).
[11] Miller D. J., Sun K., Tao L., "Open-path quantum cascade-laser-based sensor for high-resolution atmospheric ammonia measurements," Atmos. Meas. Tech. 2014(7), 81-93(2014).
[12] Jagerska J., Jouy P., Tuzson B., et al, "Simultaneous measurement of NO and NO_2 by dual-wavelemgth quantum cascade laser spectroscopy," Optics express, 23(2), 1512-1522(2015)
[13] Werle P., Mucke R., Slemr F., "The limits of signal averaging in atmospheric trace-gas monitoring by tunable diode-laser absorption spectroscopy," Appl. Phys. B, 1993(57), 131-139(1993).
[14] Sanchez N., P., Yu Y., Dong L., et al "Detection of hydrogen peroxide based on long-path absorption spectroscopy using a CW EC-QCL," Proc. SPIE 9755, 081-087 (2016).
[15] Pakmanesh N., Cristescu S. N., Ghorbanzadeh A., "Quantum cascade laser-based sensors for the detection of exhaled carbon monoxide," Appl. Phys. B, 2016(122), 1-9(2016)
[16] Zhang H., Liu G. J., Mei J. M., et al, "Observation study on concentration diurnal variation of atmospheric pollutants in Tongling city," Journal of USTC, 44(8), 679-687(2014).
[17] Su Z. H., Ma Z. W., "Variation of atmospheric environment in Guiyang and the correlation between pollution status and emission load in recent year," Advanced in Geosciences, 6(2), 129-135(2016).