Northumbria Research Link

Citation: Zhou, Tao, Wu, Tao, Zhang, Huailin, Wu, Qiang, Chen, Weidong, Ye, Chenwen and He, Xingdao (2019) Influence of light coupling configuration and alignment on the stability of HWG-based gas sensor system for real-time detection of exhaled carbon dioxide. IEEE Sensors Journal. ISSN 1530-437X (In Press)

Published by: IEEE

URL: https://doi.org/10.1109/JSEN.2019.2939555 < https://doi.org/10.1109/JSEN.2019.2939555 >

This version was downloaded from Northumbria Research Link: http://nrl.northumbria.ac.uk/40634/

Northumbria University has developed Northumbria Research Link (NRL) to enable users to access the University's research output. Copyright © and moral rights for items on NRL are retained by the individual author(s) and/or other copyright owners. Single copies of full items can be reproduced, displayed or performed, and given to third parties in any format or medium for personal research or study, educational, or not-for-profit purposes without prior permission or charge, provided the authors, title and full bibliographic details are given, as well as a hyperlink and/or URL to the original metadata page. The content must not be changed in any way. Full items must not be sold commercially in any format or medium without formal permission of the copyright holder. The full policy is available online: http://nrl.northumbria.ac.uk/policies.html

This document may differ from the final, published version of the research and has been made available online in accordance with publisher policies. To read and/or cite from the published version of the research, please visit the publisher's website (a subscription may be required.)





Influence of light coupling configuration and alignment on the stability of HWG-based gas sensor system for real-time detection of exhaled carbon dioxide

Tao Zhou, Tao Wu*, Huailin Zhang, Qiang Wu**, Weidong Chen, Chenwen Ye, and Xingdao He

59

60

1 37 Abstract—A mid-infrared tunable diode laser absorption 38 spectroscopy (TDLAS) gas sensor based on hollow waveguide 39 (HWG) gas cell for real-time exhaled carbon dioxide (eCO₂) $_{\Delta O}$ detection is reported. A 2.73 µm distributed feedback (DFB) laser 41 was used to target a strong CO₂ absorption line, and wavelength modulation spectroscopy (WMS) with the second harmonic 42 (WMS-2f) was used to retrieve the CO_2 concentration with high 43 sensitivity. The influence of different parameters, including 44 coupling configuration of HWG, laser-to-HWG and 45HWG-to-detector coupling alignment on the stability of the $_{46}$ HWG sensor is systematically studied. The HWG eCO₂ sensor 47 12 13 showed a fast response time of 2.7s, detection limit of 17 ppmv, and measurement precision of 20.9 ppmv with a 0.54 s temporal 48 14 resolution. The eCO₂ concentrations changed in breath cycles ⁴⁹ 15 16 were measured in real time. The Allan variance indicated that 50 17 the detection limit can reach 1.7 ppmv, corresponding to a 51 detection sensitivity of 1.3×10^{-8} cm⁻¹Hz^{-1/2}, as the integration time 52 18 increases to 26 s. This work demonstrates the performance 53 characteristics and merits of HWG eCO₂ sensor for exhaled 5319 20 54 21 breath analysis and potential detection for other exhaled gases. 55 22

23 Index Terms-tunable diode laser absorption spectroscopy, 56 24 hollow waveguide, distributed feedback laser, carbon dioxide 57 25 58

26

I. INTRODUCTION

REATH ANALYSIS can provide a non-destructive, 61 real-time disease diagnosis and metabolic state 62 29 monitoring, and hence plays a very important role in the field 63 30 of medical diagnostics. Human breathing gases contain several 64 31 kinds of gases, such as N₂, O₂, CO₂, H₂O with a relatively high 65 32 concentrations accounting for more than 99% of the total 66 33 content, and hundreds of other kinds of breathing gases, such 67 34 as acetone, methane, ammonia, carbon monoxide etc. in the 68 35 concentration levels varies from parts per million by volume 69 36 (ppmv) to parts per trillion by volume (pptv) [1]. Some of 70 71

Tao Wu is with the Key Laboratory of Nondestructive Test (Ministry of Education) of Nanchang Hangkong University, Nanchang 330063, China. 75 76 (e-mail: wutccnu@nchu.edu.cn).

Qiang Wu is with the Department of Physics and Electrical Engineering, 77 Northumbria University, Newcastle upon Tyne, U.K. (e-mail: 78 giang.wu@northumbria.ac.uk).

these respiratory gases have been proven to be useful as biomarkers for metabolic monitoring and disease diagnosis [2]. The changes in exhaled CO_2 (eCO₂) concentration as well as the end-tidal CO₂ concentration is important for some early disease diagnosis and physiological monitoring of the human body [3], while eCO_2 analysis requires high sensitivity/stability, excellent selectivity and well-designed breath sampling systems.

Laser absorption spectroscopy has been widely used in gas detection and plays an important role in industrial process analysis, environmental pollution monitoring, scientific research and other fields [4]. Due to its medical interest, in recent years a variety of spectroscopy techniques have been developed to detect CO₂ and ¹³CO₂/¹²CO₂ isotopic ratio in exhaled breath. Non-dispersive infrared spectroscopy (NDIR) is commonly used for the detection of eCO₂ [5]-[7]. NDIR measures the gas concentrations by detecting the infrared light attenuation using a photo detector. Commercial NDIR CO₂ capnographs work very well with high target gas selectivity and do not need frequent calibration, however, it usually possesses low sensitivity and faces interference from water vapor and hydrocarbons. Beyond that method, high finesse optical cavity based absorption spectroscopy, such as cavity ring-down spectroscopy (CRDS) [8] and integrated cavity output spectroscopy (ICOS) [9], and tunable diode laser absorption spectroscopy (TDLAS) with a multi-pass cell have also been widely used for eCO₂ detection [10], [11]. The use of high finesse optical cavity and multi-pass cell significantly increases the absorption path length and improves the detection sensitivity. However, these conventional systems have disadvantages of rigid requirement of precision optical light alignment, high cost, large physical size and especially large volume (usually larger than 100 ml) resulting in unsuitable for real time exhaled gas measurement [9], [12]. Hollow waveguide (HWG) possesses a low volume and an extended optical path length that gives absorption spectroscopy a fast response time and high sensitivity with lower cost [13], [14]. Several authors have reported the use of HWG gas cells in absorption spectroscopy using TDLAS or Fourier transform infrared spectroscopy (FTIR). Xiong et al. [15] designed an HWG based CO₂ sensor for capnography using direct absorption spectroscopy. Kim et al. [16]

This work is supported by the Key Research and Development Program of 72Jiangxi Province, China (20171BBG70003, 20192BBH80019), the Ministry 73 of Human Resources and Social Security of China.

established a gas sensor with an HWG combined with an FTIR
 spectrometer for CO₂ and CH₄ detection.

3 All present studies are mainly focused on the improving coupling efficiency of laser to HWG [17], [18]. However ⁵⁰ 4 stability is a significant parameter for an HWG-based sensor ⁵¹ 5 system, which is mainly limited by temperature drifts, 52 6 7 mechanical vibrations, and moving fringes in background 53 8 spectra, and usually described by the Allan variance. However, 9 the investigation of the effect of laser-to-HWG and 10 HWG-to-detector coupling alignment on stability of 54 HWG-based sensor system is missing in the previous 11 literatures. In this paper, a mid-infrared HWG eCO₂ sensor 12 employing a 1 m long HWG was developed for real-time eCO_{2 55} 13 14 detection. Second harmonic (WMS-2f)wavelength 15 modulation spectroscopy (WMS) was applied for eCO₂ detection. A systematic study of the influence of sensor system 57 16 parameters, including coupling configuration of HWG, 58 17 18 laser-to-HWG and HWG-to-detector coupling alignment on 59 the stability of the HWG sensor was performed. Our study $_{60}$ 19 20 shows that, Laser-to-HWG and HWG-to-detector coupling 21 alignment play more important role to the stability of the sensor system, which provides a new guide for improving 61 22 23 stability of the system. Finally, real time experiment for eCO₂ 24 was conducted to evaluate the performance of HWG eCO₂ 25 sensor for medical requirement. 62

26 II. WM

II. WMS METHOD

63

The application of WMS in TDLAS can effectively improve ⁶⁴ 27 28 the detection sensitivity and has been widely used in the measurement of absorption spectroscopy [19]. In WMS-2 f^{65} 29 30 method, the injection current of the DFB laser is modulated by 66 the sawtooth wave superimposed with a high-frequency 67 31 sinusoidal signal. The frequency (wavelength) v(t) and ⁶⁸ 32 intensity $I_0(t)$ of the laser are also modulated accordingly 33 70 34 [20]. 71

$$v(t) = \overline{v} + a\cos(2\pi f t) \tag{1)72}$$

36
$$I_{0}(t) = \overline{I_{0}} \Big[1 + i_{0} \cos(2\pi ft + \psi_{1}) + i_{2} \cos(2 \cdot 2\pi ft + \psi_{2}) \Big] \begin{array}{c} 73\\74\\(2) 75 \end{array}$$

38 Where \overline{v} is the average laser frequency (wavelength); *a* and 76 39 *f* are the amplitude of wavelength modulation and modulation 77 40 frequency, respectively; $\overline{I_0}$ is the average laser intensity; i_0 78 41 and i_2 are the Fourier coefficients of the linear and non-linear $\frac{79}{80}$ 42 intensity modulations; ψ_1 and ψ_2 are the phase shift of the 81 43 linear and non-linear intensity modulations, respectively. For 82 44 weak absorption ($\alpha(v) < 0.05$), the absorption can be 45 expanded into the Fourier cosine.

46
$$\alpha[\overline{\nu} + a\cos(2\pi ft)] = -\sum_{k=0}^{\infty} H_k(\overline{\nu}, a)\cos(k \cdot 2\pi ft) \quad (3)$$

47 Here, H_k is the k_{th} harmonic component of the absorbance α .

48
$$H_k(\overline{\nu},a) = -\frac{1}{2\pi} \int_{-\pi}^{\pi} \alpha \left(\overline{\nu} + a\cos\theta\right) d\theta, k = 0$$
(4)

$$H_{k}\left(\overline{\nu},a\right) = -\frac{1}{\pi} \int_{-\pi}^{\pi} \alpha \left(\overline{\nu} + a\cos\theta\right) \cos k\theta d\theta, k \ge 1$$
 (5)

For the WMS-2f detection, a reference signal with a frequency of 2f is sent to the lock-in amplifier, and the X-channel of the modulation signal (the in-phase signal) can be expressed as follows.

$$X_{2f} = \frac{G\overline{I}_0}{2} \left[H_2 + \frac{i_0}{2} (H_1 + H_3) \cos \psi_1 + i_2 \left(1 + H_0 + \frac{H_4}{2} \cos \psi_2 \right) \right]$$
(6)

Here *G* account for the optical-electrical gain of the detection system. Usually, i_2 is much smaller than i_0 . For an isolated transition, the odd term of the Fourier coefficient at the center of the spectrum line is zero. The relationship between the peak value $X_{2f}(\overline{v})$ of the WMS-2*f* signal and the mole fraction *x* of the target gas can be calculated as.

$$X_{2f}(\overline{\nu}) \approx \frac{GI_0}{2} H_2(\overline{\nu})$$

= $-\frac{G\overline{I}_0 PSxL}{2\pi} \int_{-\pi}^{\pi} \phi(\overline{\nu} + a\cos\theta) \cdot \cos 2\theta \cdot d\theta$ (7)

Where *P* and *L* are the total gas pressure and the effective optical path length, respectively. *S* and ϕ are the line strength and line shape function, respectively.

III. LINE SELECTION

According to the HITRAN database [21], CO₂ has strong absorption lines in the mid-infrared region. For the eCO₂ detection, the main interfering gas is H₂O. Apart from H₂O, the concentrations of other potential interference in breathing gases are 10⁴-10¹⁰ times smaller than that of eCO₂, which make their influence negligible. To eliminate the interference from H₂O, the CO₂ absorption line was selected at 3661.637 cm^{-1} with a line strength of 7.135 \times 10⁻²² $cm^{-1}/(molecule \cdot cm^{-2})$, which has no overlap with that of H₂O. Fig. 1 shows the simulation of the absorption spectrum of 5% H₂O and 5% CO₂ for wavenumber range from 3657.57 cm⁻¹ to 3665.95 cm⁻¹ at a pressure of 270 torr and a temperature of 296 K. The inset of Fig. 1 shows the selected absorption line at 3661.637 cm⁻¹. It is worth noting that the choice of absorption line also considers the characteristics of the laser. The stronger absorption line at 3663.851cm⁻¹ has not been selected, because it is out of the wavelength tuning range of the laser used in our experiments.



² Fig. 1. The simulation of the absorption spectrum of 5% H_2O and 5% CO₂ at 3 270 torr and 296 K. The inset shows the selected absorption line at 3661.637 4 cm⁻¹.

IV. EXPERIMENT SETUP

5

6 The eCO_2 sensor based on HWG is shown in Fig. 2(a). A 7 DFB laser (Nanoplus GmbH, Germany) with a center wavelength of 2.73 μ m and a maximum output power of 11.2 $_{52}$ 8 9 mW was used as an optical source. The laser was packaged in 10 a TO-5 can with integrated Peltier and temperature sensor, which attached to an aluminum heatsink to remove heat 11 12 dissipated from Peltier and the laser. A laser controller (ILX 13 Lightwave, LDC-3724C, USA) was used to control the current 14 and temperature of the laser diode. The current of the laser was 15 set to 148.39 mA, and the operating temperature of the laser 16 was set and controlled at 30 °C. High-frequency sine wave (1.7 kHz) generated by a lock-in amplifier (Stanford Research 17 18 System, SR830, USA) and a sawtooth wave (20 Hz) generated 19 by a function generator were superimposed by an adder, and 20 then sent to the modulation current port of the laser controller 53 for performing WMS. The laser beam was collimated by a 21 22 collimating lens and coupled through an aperture diaphragm into a 1 m long and 1 mm inner diameter HWG (Polymicro 56 23 24 Technologies, HWEA10001600, USA) gas cell with the 57 25 volume of 0.78 cm³, which was much smaller than that of the conventional multi-pass gas cell. The HWG fiber was firstly 58 26 inserted into a fiber ferrule, and then inserted into the slot in 59 27 the gas chamber and sealed with a layer of silicone rubber $\frac{60}{10}$ 28 outside the chamber as shown in Fig. 2(b). The light output $\frac{61}{2}$ 29 from the HWG cell was detected by a photodetector (VIGO $\frac{62}{22}$ 30 System S.A., PVI-4TE-10.6, USA). The lock-in amplifier $^{0.5}_{64}$ 31 demodulated the output signal of the photodetector to obtain $\frac{1}{65}$ 32 the WMS-2f signals, which was then acquired by a data $\frac{66}{66}$ 33 acquisition card (ADlink, DAQ-2010, China) and further 67 34 processed by a self-developed LabWindows program. The 68 35 36 modulation parameters, such as modulation amplitude, 69 37 modulation frequency, reference phase, time constant of 70 38 lock-in amplifier, and laser scanning frequency, and gas 71 39 pressure in the HWG were optimized by obtaining maximum 72 40 detection WMS-2f signal. In order to reduce the CO_273 41 interference from the air, the laser and the photodetector were 74 42 placed very close to the HWG cell. For exhaled CO₂75 76

43 measurement, most breathing gas exhaled through a 44 mouthpiece was vented to the atmosphere through the small 45 gap between breath sampler and breath tube, while a part of the sample was continuously drawn to the HWG cell through 46 breath tube by a vacuum pump (DIVAC, 1.2 L, Germany). A 47 48 mass flow controller (MFC, MKS Instruments, USA) and a pressure controller (MKS Instruments, 640B, USA) were used 49 to control constant gas flow rate and stable pressure in the 50 51 HWG cell.



Fig. 2. Schematic of the experimental setup (a) and the optical fiber splice (b).

V. THE COUPLING PATTERN OF LASER BEAM TO HWG AND ITS EFFECT ON SYSTEM SNR AND STABILITY

The coupling configuration between the laser beam and the HWG can be achieved in a focusing coupling configuration or in a direct coupling configuration (incident directly into the HWG). Here, the focusing coupling configuration and the direct coupling configuration are both studied. The influence of the laser spot size (modulated by an aperture diaphragm) on direct coupling configuration is considered. The stability of the system for these two coupling mode is explored. The relation between stability time and SNR of direct coupling configuration is investigated.

5% CO₂ was continuously pumped into the HWG cell, and the pressure in the cell was controlled at 270 torr. In the focusing coupling configuration, the laser beam is focused into the center of the HWG inlet by a lens with a focal length of 50mm. In the direct coupling configuration, the aperture size of the aperture diaphragm was sequentially set to 0.7 mm, 1 mm, 1.5 mm, 2 mm, 2.3 mm, where 0.7 mm is the minimum aperture that can be set by the aperture diaphragm used in our experiment, and 2.3 mm is the actual size of the laser beam.

The WMS-2f signals for focusing coupling and direct 1 2 coupling with different spot sizes were recorded and shown in 3 Fig. 3. It can be seen that the SNR for focusing coupling is 4 highest. For direct coupling configuration, as the spot size 5 decreases, the SNR decreases, this is due to a gradual 6 reduction of the laser power. Fig. 4 shows the Allan variance 7 obtained by measuring WMS-2f signals. It can be clearly seen 8 that, although the focusing coupling has highest SNR, the 9 system stability for focusing coupling is worse (with higher 10 variance limit) than that of direct coupling with 1 mm spot. As 11 the spot diameter decreases from 2.3mm to 0.7mm, the system 12 stability time for direct coupling is increased from 6 s to 57 s, 13 which is possibly due to the fact that smaller aperture and acceptance angle collects center of the laser beam which has 28 14 15 better laser beam quality illuminated to the HWG, resulting in $\overline{29}$ small fiber model noise. However, the smaller aperture results 3016 in smaller SNR (as shown in Fig. 5), which is not conducive to 31 17 improving the detection sensitivity (As the aperture is 32 18 gradually reduced, the detection sensitivity is reduced from 33 19 7.9×10^{-6} cm⁻¹Hz^{-1/2} to 1.8×10^{-6} cm⁻¹Hz^{-1/2}). Here, direct ³⁴ 20 coupling with the aperture of 1 mm reaches a compromise 35 21 36 22 between good SNR and long stability time.



Fig. 3. The WMS-2*f* signals for focusing coupling and direct coupling withdifferent spot sizes.



Fig. 4. The Allan variance obtained by measured WMS-2f signals.



Fig. 5. The relation between stability time and SNR of the system as the spot diameter changes.

For direct outcoupling, possible parallel optical surfaces interference caused by focusing lens is avoided. To study the effect of partial collection of light from the fiber on system stability, the distance between the output of HWG and the detector was varied between -200µm and 200µm based on initial distance of 4cm. An optimal detector displacement distance Δz was found at -40µm (Fig. 6). It is noted that this optimal value obtained in the experiments is for our setup only. The detector is suggested to be placed as close as possible to the fiber end to collect all the light coming from the fiber end for any HWG-based setup. The influence of incoupling (position of the laser) on system stability was also investigated. The lateral displacement Δr between the center of laser beam and the center axis of HWG was varied from 0 to 120µm in 40µm steps. We found the laser at the central position given longest stability time (Fig. 7).

37

38 39

40

41

42

43

44

45

46

47

48





Fig. 6. (a) The Allan variance for WMS-2*f* signals at varied displacement 3 distance of detector; (b) Stability time versus detector displacement distance.



Fig. 7. (a) The Allan variance for WMS-2f signals at varied displacement 52
distance of laser; (b) Stability time versus laser lateral displacement distance.
53
54

9 VI. INVESTIGATION OF RESPONSE TIME AND 10 CONCENTRATION CALIBRATION

11 The response time of the HWG eCO_2 sensor was investigated as shown in Fig. 8. Two mass flow controllers 12 13 controlled the flow rate of pure CO₂ gas (CO₂ \geq 99.999%) and 14 pure nitrogen gas ($N_2 \ge 99.999\%$) respectively. Five different 15 samples of CO₂ with concentrations varying from 0 to 6.3% 16 were prepared by changing the flow rates of two mass flow controllers while maintaining a constant gas flow rate of 6.7 17 ml/s through the HWG cell. The pressure in the HWG cell was 18 19 controlled to be 270 torr for obtaining WMS-2f signal. In the beginning, the HWG cell was full of pure nitrogen. Then, at 40 55 20 21 s, the diluted CO₂ gas samples were filled into the HWG cell. 22 The duration time of each concentration level gas sample was

approximately 30 s to ensure that the measured signal was in a 23 24 stable state. At the end of the measurement, pure nitrogen was 25 again filled into the HWG cell. There was no significant drift 26 found during the measurement period by the nitrogen signal 27 levels. As shown in the insert of Fig. 8, the response time τ_r (10 28 - 90%) of the concentration levels in rising and falling process 29 was about 2.7 s and 2.2 s, respectively, while the delay time τ_d (0 - 10%) was approximately in the same time of 0.6 s [22]. 30 31 Due to the smaller volume of the HWG than the traditional gas 32 cell ($\tau_r \sim 5$ min) [12], the response time τ_r is much faster 33 compared to the traditional gas cell with the similar gas flow 34 rate. It is worth noting that the response time τ_r here also 35 included the time for gas mixing time in the HWG cell, the actual response time of the HWG sensor was less than 2.7 s.



Fig. 8. Continuous measurements for different CO2 concentration levels.

37 38

39 40

41

42

43

44

45

46

47

48

49

50

51

In order to obtain the relationship between WMS-2*f* peak values and CO₂ concentrations, CO₂ samples were prepared by using pure CO₂ gas and 3000 ppmv standard CO₂ gas diluted with pure N₂, and the continuous measurements for different CO₂ concentration samples were performed and averaged 5 times with a 100 ms acquisition time. Fig. 9(a) shows the WMS-2*f* signals at different CO₂ concentrations with a 0.5 s temporal resolution. A linear relationship between WMS-2*f* peak values and CO₂ concentrations was observed as shown in Fig. 9(b). Fig. 9(b) shows the fit curve have a good linearity for CO₂ concentrations. The error bars of the WMS-2*f* peak values were in the order of 10⁻³, which cannot be clearly seen in Fig. 9(b).





34 35

36

37

38

39

40

41

42

43

44

45

56

57

58

59

60

61

62

63

64

65 66

69

70

71

1 2 3 46 Fig. 9. The calibration results of CO_2 concentrations. (a) The WMS-2f signals 47 at different CO₂ concentrations; (b) Relationship between measured WMS-2f 4 peak values and different CO2 concentrations.

VII. MEASUREMENT PRECISION

5

6 The measurement precision of the HWG eCO₂ sensor can be 7 analyzed by Gaussian distribution [23]. 300ppmv diluted CO₂ 8 gas sample was used as reference gas and pumped into the 9 HWG cell. The gas pressure and flow rate were maintained at 10 270 torr and 6.7 ml/s, respectively. 600 measured data points 11 were successively recorded and averaged 5 times corresponding to 0.54 s temporal resolution, as shown in Fig. 12 13 10(a). A histogram plot of CO_2 concentration deviation which 14 is fitted by a Gaussian profile is shown in Fig. 10(b). The measurement precision can be determined by the half width at $\frac{1}{48}$ 15 16 half maximum (HWHM) of the Gaussian profile. It indicates $\frac{1}{49}$ 17 that the measurement precision was 20.9 ppmv with 0.54 s 50 18 temporal resolution. The corresponding average concentration 19 value was 297 ± 20.9 ppmv. The measurement precision was 51 20 mainly limited by random noise and etalon fringes 52 21 superimposed on the WMS-2f signals. In addition, the small 53 jitter of the HWG would lead to instability of the WMS-2f 54 22 23 signals, which also affected the measurement precision. 55



24 25 26 Fig. 10. (a) 600 measured data points were successively recorded and 67 averaged 5 times corresponding 0.54 s temporal resolution; (b) A histogram 68 27 plot of CO₂ concentration deviation which is fitted by a Gaussian profile.

28 VIII. CARBON DIOXIDE IN EXHALED BREATH

The eCO_2 was measured in real time from one healthy 7229 volunteer in our lab and the results recorded with 0.54 s 73 30 acquisition time are shown in Fig. 11. The pressure in the 74 31 HWG cell was controlled to be 270 torr, and the breathing gas 75 32 was introduced into the HWG cell by breath tube according to 76 33

the direction of gas passage shown in Fig. 2. During the inhalation, the environment air was pumped into HWG through the side-port of breath tube, and the CO₂ concentrations are stable and fluctuated around 360ppmv as shown in Fig. 11, hence the influence of ambient air on eCO2 detection can be negligible. In addition, the trends and values of concentration which are not affected by the breath rate changes were consistent with those in the literatures [24], [25]. It is noted that the response time τ_r of 3.7 s in this case is larger than that of 2.7 s described above. This is possibly due to the contribution of residual eCO₂ in long breath tube during exhalation. If the volume of breath tube is made smaller and the length of breath tube is shorter, the response time will be faster.



Fig. 11. Concentration dynamics of eCO2 in real time from one volunteer in our lab.

IX. DETECTION LIMIT

The signal averaging method is a simple but practical method for eliminating background white noise. If a signal is averaged N times, the white noise may be reduced by a factor of $N^{1/2}$, which can be estimated by Allan variance [26]. Allan variance can evaluate the stability of the measurement system as well as the detection limit. Allan deviation was performed on a constant concentration of 300ppmv diluted CO₂ sample which was pumped into HWG cell continuously, and Allan deviation (square root of variance) plot was shown in Fig. 12. The results shows that the Allan deviation decreases with the square root of the averaging time (shown in Fig. 12 as the red line of gradient = -0.5). The detection sensitivity was 17 ppmv with acquisition time of 0.54 s, corresponding to a detection sensitivity of 6.9×10⁻⁸ cm⁻¹Hz^{-1/2}, which indicates that the TDLAS sensor is applicable for clinical eCO₂ monitoring. The minimum in the Allan deviation plot at 26 s represents the optimum integration time. The detection limit can reach as low as 1.7 ppmv, corresponding to a detection sensitivity of 1.3×10^{-8} cm⁻¹Hz^{-1/2}, as the integration time increases to 26 s. Thereafter the Allan deviation moves into a drift dominated region where it starts to increase with increasing averaging time. Furthermore, the detection limit can be further improved by increasing HWG length, reducing hardware noise and fixing the HWG firmly to suppress the etalon signal. Table 1 shows the detection limit and other experimental parameters

obtained by using different methods to measure eCO₂. Though 20 1 2 direct absorption spectroscopy (DAS) used in ref. [10], [11], 21 [15] is calibration-free, the DAS is mainly limited by 1/f noise.22 3 The WMS uses a higher modulation frequency (~kHz) which 23 4 5 suppresses the 1/f noise effectively, which is verified in Table 24I that the absorbance sensitivity (independent of optical length 25 6 and related to stability of system) for WMA is usually higher 26 7 than that for DAS. It is noted that the absorption sensitivity of $_{27}$ 8 the HWG sensor can be improved significantly by adding two $_{28}$ 9 high reflectivity mirrors to both ends of the HWG to form a 29 10 high finesse resonant cavity, which effectively increases the 30 11 length of optical path [8].



13 14 15 16 17 18 Fig. 12. Allan deviation plot for measured 300ppmv CO₂ sample. TABLE I

12

DE	TECTION LIMIT AND OTHER EXPERIMENTAL PARAMETERS FOR ECO2
	DETECTION USING DIFFERENT METHODS

	Referen ce	Waveleng th (µm)	Pressu re (torr)	Optic al length (m)	Method	Detection limit/Absorba nce sensitivity	52 53 54 55
	[10]	4.91	380	26	TDLAS/ DAS (Multipass cell)	0.5%/~10 ⁻²	56 57 58 59
	[11]	2	760	0.025	TDLAS/ DAS (Single cell)	<300 ppmv/~10 ⁻⁴	60 61 62
	[15]	2.003	760	0.12	DAS (HWG cell)	10 ppmv/~10 ⁻⁵	63 64 65 66
	[27]	1.575	150	40	TDLAS/ WMS (Multipass cell)	100 ppmv/~10 ⁻⁴	67 68 69 70 71
	[28]	4.7	100	4	WMS (Multipa ss cell)	2ppmv/~10 ⁻⁶	72 73 74
	[7]	4.3	760	0.08	(Custom	10 ppmv/-	75 76
	[8]	1.6	100	0.42	CRDS	3 ppmv/~10 ⁻⁴	78
_	present work	2.73	270	1	WMS (HWG cell)	1.7 ppmv/~10 ⁻⁶	79 80 <u>81</u>
19							82 83 84 85

X. CONCLUSIONS

A mid-infrared TDLAS gas sensor based on HWG gas cell for real-time eCO₂ detection is reported. An HWG with a length of 1 m was used as a gas chamber. Compared to SNR, laser-to-HWG and HWG-to-detector coupling alignment of light and HWG plays more important role to the stability of the sensor system. Due to the smaller volume (0.78 cm³) of HWG, the response time of 2.7 s and 2.2 s in the rising and falling process was achieved. In addition, a detection limit of 1.7 ppmv corresponding detection sensitivity of 1.3×10^{-8} cm⁻¹Hz^{-1/2} was reached at the optimal integration time of 26 s. It is shown that WMS can greatly improve the detection sensitivity and have a high measurement precision for CO₂ detection. HWG has a fast concentration response time and space saving features, and it is easy to develop into a compact portable instrument, which has practical significance for clinical respiratory detection. Furthermore, TDLAS has better selectivity to target the gas absorption line and has the potential for other exhaled gases detection.

31

32

33

34

35

36

37

38

39

40

41

 $\begin{array}{r} 42 \\ 43 \\ 44 \\ 45 \\ 46 \\ 47 \\ 48 \\ 49 \\ 50 \\ 51 \end{array}$

REFERENCES

- J. Wojtas, Z. Bielecki, T. Stacewicz, J. Mikołajczyk, and M. [1] Nowakowski, "Ultrasensitive laser spectroscopy for breath analysis," Opto-Electron. Rev., vol. 20, no. 1, pp. 26-39, Mar. 2012.
- [2] C. Wang, and P. Sahay. "Breath analysis using laser spectroscopic techniques: breath biomarkers, spectral fingerprints, and detection limits," Sensors, vol. 9, no. 10, pp. 8230-8262, Oct. 2009.
- B. Braden et al., "13C-breath tests: current state of the art and future [3] directions," Digest Liver Dis., vol. 39, no. 9, pp. 795-805, Sep. 2007.
- R. W. Solarz, "Applications of Laser Absorption spectroscopy," in [4] Laser spectroscopy and its applications, 10th ed., vol. 11, New York: Routledge, 2017, pp. 261-335.
- [5] J. A. Vogt et al, "Optimised NDIR Technology for ¹³CO₂ Breath Tests of ie Drug/Drug-Interactions or Gastric Emptying for Intensive Care Patients: New Diagnostic Opportunities," in WC, Munich, Germany, Sep. 2009, pp. 851-854.
- K. Namjou, C. B. Roller, T. E. Reich, J. D. Jeffers, G. L. McMillen, P. J. [6] McCann, and M. A. Camp, "Determination of exhaled nitric oxide distributions in a diverse sample population using tunable diode laser absorption spectroscopy," Appl. Phys. B., vol. 85, no. 2-3, pp. 427-435, Nov. 2006.
- T. A. Vincent, B. Urasinska-Wojcik and J. W. Gardner, "Development [7] of a low-cost NDIR system for ppm detection of carbon dioxide in
- exhaled breath analysis," *Proc. Eng.*, vol. 120, pp. 388-391, Sep. 2015. E. R. Crosson *et al*, "Stable isotope ratios using cavity ring-down [8] spectroscopy: determination of ¹³C/¹²C for carbon dioxide in human breath," Anal. Chem., vol. 74, no. 9, pp. 2003-2007, Mar. 2002.
- M. R. McCurdy, Y. A. Bakhirkin, G. Wysocki, and F. K. Tittel, [9] "Performance of an exhaled nitric oxide and carbon dioxide sensor using quantum cascade laser-based integrated cavity output spectroscopy," J. Biomed. Opt., vol. 12, no. 3, pp. 034034, May. 2007.
- [10] K. L. Moskalenko, A. I. Nadezhdinskii, and I. A. Adamovskaya, "Human breath trace gas content study by tunable diode laser spectroscopy technique," Infrared Phys. Technol., vol. 37, no. 1, pp. 181-192, Dec. 1996.
- [11] A. Hartmann, R. Strzoda, R. Schrobenhauser, and R. Weigel, "CO2 sensor for mainstream capnography based on TDLAS," Appl. Phys. B., vol. 116, no. 4, pp. 1023-1026, Sep. 2014.
- [12] K. Krzempek et al, "Continuous wave, distributed feedback diode laser based sensor for trace-gas detection of ethane," Appl. Phys. B., vol.106, no. 2, pp. 251-255, Feb. 2012.
- [13] J. A. Harrington, "A review of IR transmitting, hollow waveguides," Fiber Integrated Opt., vol. 19, no. 3, pp. 211-227, Oct. 2000.
- [14] J. Chen, A. Hangauer, R. Strzoda, M. Fleischer, and M. C. Amann, "Low-level and ultralow-volume hollow waveguide based carbon monoxide sensor," Opt. Lett., vol. 35, no. 21, pp. 3577-3579, Aug. 2010

- [15] B. Xiong, Z. Du, L. Liu, Z. Zhang, J. Li, and Q. Cai, "Hollow-waveguide-based carbon dioxide sensor for capnography," Chin. Opt. Lett., vol. 13, no. 11, pp. 111201, Sep. 2015.
- [16] S. S. Kim, N. Menegazzo, C. Young, J. Chan, C. Carter, and B. Mizaikoff, "Mid-infrared trace gas analysis with single-pass Fourier transform infrared hollow waveguide gas sensors," Appl. Spectrosc., vol. 63, no. 3, pp. 331-337, Apr. 2009.
- [17] P. Patimisco et al, "Low-Loss Coupling of Quantum Cascade Lasers into Hollow-Core Waveguides with Single-Mode Output in the 3.7-7.6 75
- μm Spectral Range," *Sensors*, vol. 16, no. 4, pp. 533, Apr. 2016. 75 M. S. Vitiello *et al*, "High efficiency coupling of Terahertz micro-ring 76 [18] quantum cascade lasers to the low-loss optical modes of hollow metallic 77 waveguides," Opt. Express., vol. 19, no. 2, pp. 1122-1130, Jan. 2011.
- [19] J. Reid, and D. Labrie, "Second-harmonic detection with tunable diode lasers-comparison of experiment and theory," Appl. Phys. B., vol. 26, no. 3, pp. 203-210, Nov. 1981.
- [20] H. Li, G. B. Rieker, X. Liu, J. B. Jeffries, and R. K. Hanson, "Extension of wavelength-modulation spectroscopy to large modulation depth for diode laser absorption measurements in high-pressure gases," Appl. Optics., vol. 45, no. 5, pp. 1052-1061, 2006.
- [21] I. E. Gordon, et al, "The HITRAN2016 molecular spectroscopic database," J. Quant Spectrosc. Ra., vol. 203, pp. 3-69. Dec. 2017. 85
- J. Li, G. Luo, Z. Du, and Y. Ma, "Hollow waveguide enhanced 86 [22] dimethyl sulfide sensor based on a 3.3 µm interband cascade laser,' 87 Sensor. Actuat. B-Chem., vol. 255, pp. 3550-3557. Feb. 2018.
- [23] J. Li, H. Deng, J. Sun, B. Yu, and H. Fischer, "Simultaneous 88 atmospheric CO, N2O and H2O detection using a single quantum 89 cascade laser sensor based on dual-spectroscopy techniques," Sensor. 90 Actuat. B-Chem., vol. 231, pp. 723-732. Aug. 2016.
- [24] R. Ghorbani, and F. M. Schmidt, "ICL-based TDLAS sensor for 91 real-time breath gas analysis of carbon monoxide isotopes," Opt. Express., vol. 25, no. 11, pp. 12743-12752, May. 2017.
- [25] D. Halmer, S. Thelen, P. Hering, and M. Mürtz, "Online monitoring of ethane traces in exhaled breath with a difference frequency generation spectrometer," Appl. Phys. B., vol. 85,no. 2-3, pp. 437-443. Nov. 2006.
- $\begin{array}{c} 18\\ 19\\ 20\\ 22\\ 23\\ 24\\ 25\\ 26\\ 27\\ 28\\ 29\\ 30\\ 32\\ 33\\ 35\\ 36\\ 37\\ 39\\ \end{array}$ [26] P. O. Werle, R. Mücke, and F. Slemr, "The limits of signal averaging in atmospheric trace-gas monitoring by tunable diode-laser absorption spectroscopy (TDLAS)," Appl. Phys. B., vol. 57, no. 2, pp. 131-139, Aug. 1993.
- 40 V. Weldon, J. O'Gorman, P. Phelan, J. Hegarty, and T. Tanbun-Ek. 99 [27] 41 "H₂S and CO₂ gas sensing using DFB laser diodes emitting at 1.570042 µm," Sensor. Actuat. B-Chem., vol. 29, no. 1-3, pp. 101-107, Oct. 1995101
- 43 [28] R. Ghorbani, F. M. Schmidt, "Real-time breath gas analysis of CO and ()2

CO2 using an EC-QCL", Appl. Phys. B., vol. 123, pp. 144, May 2017.103

45 46

44

2 3

456789

10 11

12

13

14

15

16

17

47



B.E. Tao Zhou received degree in photoelectric information science and engineering from School of Mechanical and Photoelectric Information Physics, Huaihua University in 2017. Since 2017, he has been a Graduate Student with the School of Measuring and Optical Engineering,

55 Nanchang Hangkong University. His research interests include optical system design and gas absorption spectrum. 56

57



Tao Wu received his PH.D. degree in Optics from University of the Littoral Opal Coast and Anhui Institute of Optics and Fine Mechanics, China. In 2010, Dr. Wu joined Key Laboratory of Nondestructive Test (Ministry of Education) of Nanchang Hangkong 22

University, China. His main research interest 23 been the development of high-sensitivity laser 24 65 has spectrometer for laboratory and field studies of atmospherid 25 66 67 trace gases and aerosols. 126



Huailin Zang received the B.E. degree in photoelectric information engineering from Hefei Normal University of Electronic Information Engineering in 2016. Since 2016, he has been a Graduate Student with the School of Measuring and Optical Engineering,

Nanchang Hangkong University. His research interests include optical fiber sensing and gas absorption spectrum.



Qiang Wu received the B.S. and Ph.D. degrees from Beijing Normal University and University Beijing of Posts and Telecommunications, Beijing, China, in 1996 and 2004, respectively., From 2004 to 2006, he worked as a Senior Research Associate in City University of Hong Kong. From 2006 to

2008, he took up a research associate post in Heriot-Watt University, Edinburgh, U.K. From 2008 to 2014, he worked as a Stokes Lecturer at Photonics Research Centre, Dublin Institute of Technology, Ireland. He is currently an Associate Professor at Northumbria University, U.K. His research interests include photonics devices and fiber optic sensing.



104

105

Weidong Chen received his B.S. (1992) from Zhongshan University, M.S. (1998) and Ph.D. degree (1991) from the University of Science and Technologies of Lille in France. He is full professor of physics at the University of the Littoral Opal Coast, Dunkerque, France. His current research interests include: development

of photonic instrumentation for applied spectroscopy, optical metrology (concentration, isotope ratio) of trace gases for applications in atmospheric photochemistry and environmental science, and optical parametric laser source generation by frequency conversion and its applications to applied spectroscopy.



Chenwen Ye is a lecturer at the School of Optical Measuring and Engineering. Nanchang Hangkong University.

Xingdao He was born in Jingan, China, in 1963. He received the Ph.D. degree in optics from Beijing Normal University, Beijing, China, in 2005. He is currently a Professor with the Key Laboratory of Nondestructive Test (Ministry of Education). Nanchang Hangkong University, China. His current research

interests include light scattering spectroscopy, optical holography, and information processing.