Detection of hydrogen peroxide based on long-path absorption spectroscopy using a CW EC-QCL

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ABSTRACT

A sensor system based on a CW EC-QCL (mode-hop-free range 1225-1285 cm^{-1}) coupled with long-path absorption spectroscopy was developed for the monitoring of gas-phase hydrogen peroxide (H_2O_2) using an interference-free absorption line located at 1234.055 cm^{-1}. Wavelength modulation spectroscopy (WMS) with second harmonic detection was implemented for data processing. Optimum levels of pressure and modulation amplitude of the sensor system led to a minimum detection limit (MDL) of 25 ppb using an integration time of 280 sec. The selected absorption line for H_2O_2, which exhibits no interference from H_2O, makes this sensor system suitable for sensitive and selective monitoring of H_2O_2 levels in decontamination and sterilization processes based on Vapor Phase Hydrogen Peroxide (VPHP) units, in which a mixture of H_2O and H_2O_2 is generated. Furthermore, continuous real-time monitoring of H_2O_2 concentrations in industrial facilities employing this species can be achieved with this sensing system in order to evaluate average permissible exposure levels (PELs) and potential exceedances of guidelines established by the US Occupational Safety and Health Administration for H_2O_2.

1. INTRODUCTION

Hydrogen peroxide (H_2O_2) is a highly reactive species of relevance in different industrial processes including the production of pulp and paper and the synthesis of multiple chemical products. H_2O_2 also participates in different atmospheric processes and plays a crucial role in the degradation of distinct environmental pollutants through advanced oxidation processes.[1, 2] The strong oxidation potential of H_2O_2 and its decomposition to water and oxygen have led to the extensive use of gas-phase H_2O_2 for decontamination of health care and pharmaceutical facilities, as well as for sterilization of medical equipment and packing materials in the food industry.[3-5] Gas-phase H_2O_2 used for sterilization is usually generated using Vapor Phase Hydrogen Peroxide (VPHP) units, which produce gas-phase H_2O_2 concentrations between 200 and 1200 ppm based on aqueous H_2O_2 solutions (~35% w/w).[6, 7] These concentration levels are maintained for a short period of time (usually ~10 min) in a location undergoing decontamination. Once generation of H_2O_2 is suspended, the levels of this species need to be monitored to assure that exposure limits do not exceed permissible exposure levels (PELs), which according to US Occupational Safety and Health Administration agency guidelines correspond to an average level of 1 ppm (8 h interval).[8] Hydrogen peroxide concentrations in industrial facilities using this species in their process trains are generally monitored using detector tubes based on colorimetric techniques, which have minimum detection levels of ~ 100 ppb with

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uncertainties varying between 8 and 25%.[8] In addition to the non-continuous nature of this technique, which prevents the evaluation of PELs, gas species such as chlorine and nitrogen dioxide interfere significantly with this detection method.

Real time, continuous and sensitive H_2O_2 detection can be achieved using mid IR laser-based sensor systems. Previous research has explored distinct H_2O_2 absorption lines located in the mid-IR using different system configurations and detection techniques. McManus et al.[9] reported a system for detection of sub-ppb levels of H_2O_2, using a CW DFB QCL and long-path length absorption spectroscopy targeting an absorption line at 1267 cm^{-1}. A minimum detection limit of 1 ppb for 100 sec integration time was achieved by employing a multi-pass absorption cell (MPAC) with an effective optical length of 260 m.[9] Recently, a quartz-enhanced photoacoustic spectroscopy-based sensor system for H_2O_2 detection was reported, targeting an absorption line located at 1295.55 cm^{-1} and employing a CW-DFB QCL with emission at ~ 7.73 µm. Sensitivity of this sensor configuration was determined to be 12 ppb for a 100 sec integration time.[10] Long-path absorption spectroscopy employing this CW-DFB QCL (emission at ~7.73 µm) was also reported in a recent publication. This system, based on a multi-pass absorption cell with optical length of 76 m targeted an H_2O_2 absorption line at 1296.02 cm^{-1}, and achieved a MDL of 1.5 for a 200 sec integration time.[11] Although these systems allow H_2O_2 detection at ppb levels, the presence of significant interference by H_2O lines on the selected H_2O_2 absorption lines is a common feature in these configurations. The impact of these H_2O lines on sensor operation was not studied by McManus et al. and Rei et al. [9, 10]. However, Cao et al. [11] demonstrated that interference by H_2O was problematic when the sensor system was used for the monitoring of atmospheric H_2O_2 concentrations. The presence of interfering H_2O lines led to the report of particularly high H_2O_2 atmospheric concentrations of >100 ppb. Comparison with a commercial H_2O_2 detection instrument (AL 2021, Aero-Laser, Germany) indicated that atmospheric H_2O_2 levels were significantly overestimated by the QCL-based system, further demonstrating a significant impact of interfering H_2O lines.[11]

The potential impact of H_2O on H_2O_2 absorption lines explored in previous research indicated the necessity of selecting interference-free absorption lines that allow accurate and selective H_2O_2detection. In this paper we report the development of a sensor system based on a CW EC-QCL with a mode-hop-free range of 1225-1285 cm^{-1} and targeting a selected interference-free H_2O_2 absorption line located at 1234.055 cm^{-1}. This absorption line allows the specific detection of H_2O_2 in the gas phase without restrictions of acceptable relative humidity levels, which make the sensor system suitable for selective monitoring of H_2O_2 concentration levels in industrial facilities and H_2O_2-based decontamination and sterilization sites.

2. EXPERIMENTAL METHODS

A H_2O_2 absorption line located at 1234.055 cm^{-1} was selected for the detection of this species (Figure 1). Although this line exhibits reduced absorption levels compared with other spectral lines explored by our group previously[10, 11], the absence of interference by other gas species makes this line suitable for specific and selective H_2O_2 detection. A CW EC-QCL (Model 21080-MHF, Daylight Solutions, San Diego, CA) with a tuning range between 1175 and 1300 cm^{-1} (mode-hop-free range 1225-1285 cm^{-1}) coupled into a MPAC with an optical path length of 76 m (AMAC-76, Aerodyne Inc., Billerica, MA) was developed for monitoring of gas-phase hydrogen peroxide. Scanning over a narrow wavelength range was accomplished by controlling the EC-QCL internal diffraction grating with a unipolar voltage from an external PZT controller (MDT691, Thorlabs, Newton, NJ). A function generator (AFG 3102, Tektronix, Portland, OR) provided a low frequency sinusoidal waveform (0.5 Hz), which was connected to the PZT controller. A sinusoidal signal of higher frequency (20 KHz), provided by a lock-in amplifier (SR 830, Stanford Research Systems, Sunnyvale, CA) was used to add modulation to the injection current of the EC-QCL. Figure 2 depicts the general layout of the sensor system. The EC-QCL beam is directed into a beam splitter located immediately after the QCL laser, the main beam is then focused using two plano-convex lenses (f=5 cm and f=4 cm) separated by a 400 µm pinhole (Thorlabs, Newton, NJ). The laser beam subsequently is focused into the center of the MPAC using two mirrors. The laser beam radius at this location was determined using an IR-camera (PV320, Electrophysics Corp., Fairfield, NJ, USA). The beam exiting the MPAC is collected via a plano-convex lens (f=4 cm) and directed to an IR detector (PVIM-3TE-8, Vigo Systems, Poland). One of the reflected beams is passed through a reference cell containing pure CH_4. The CH4 absorption line at 1233.96 cm^{-1} is measured by an IR

detector (PVM 10.6, Vigo Systems, Poland) and used for line-locking. The selected operating pressure in the MPAC is maintained by a vacuum pump (DS 102, Varian, Santa Clara, CA) using a pressure controller with a range of 0-100 Torr (640, MKS Instruments, Inc., Andover, MA). In order to minimize adsorption of H_2O_2 on the MPAC walls, the temperature was kept at ~40 °C by covering the MPAC surface with a flexible heating tape (Briskheat Corporation, Columbus, OH) controlled by a temperature PID controller (CNi3222, Omega Engineering, Inc, Stamford, CT). Alignment of the mid-IR laser beam and examination of the beam pattern on the MPAC mirrors was accomplished by using a visible red laser (Coherent, Inc). Wavelength modulation spectroscopy (WMS) with second harmonic detection was incorporated using a lock-in amplifier (SR 830, Stanford research Systems, Sunnyvale, CA), and data acquisition was performed using a DAQ card (6062E, National Instruments, Austin, TX).

Different concentrations of gas-phase H_2O_2 were generated by flowing air over aqueous solutions of H_2O_2 of distinct strengths located in a closed container. Gas-phase concentrations of H_2O_2 were determined by fitting the direct absorption signal at each concentration to the standard HITRAN database.

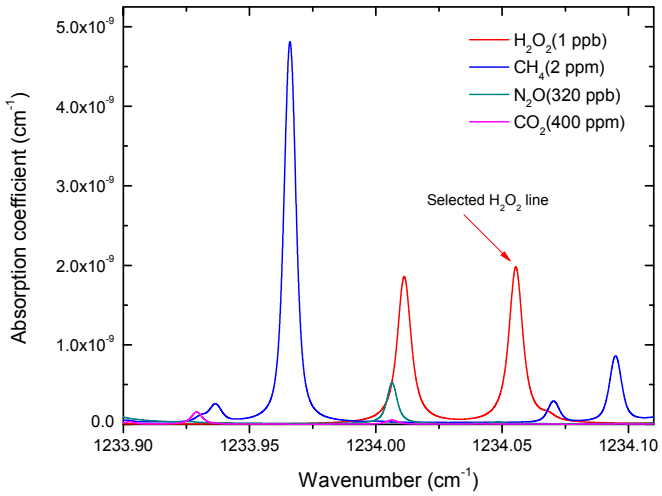

Figure 1. H_2O_2 absorption based on HITRAN examining potential interference by other gas species (CH_4, N_2O and CO_2) at a pressure of 20 Torr

3. RESULTS

Direct absorption and the WMS-2f signal for H_2O_2 produced from an aqueous solution 7% w/w is shown in Figure 3. The effect of pressure and modulation amplitude on the 2f signal was examined. Tests at different pressure levels and modulation voltages were conducted and optimum operation parameters for an improved signal to noise ratio (SNR) were determined. The modulation voltages used in these tests were limited to a maximum of 2 V, according to the EC-QCL operation manual. The results of these tests are presented in Figure 4, which indicates that operation at reduced pressure and maximum allowed modulation voltage leads to the highest 2f signal. However, a maximum 2f value is not observed at any pressure level, indicating that the EC-QCL voltage prevents obtaining the optimum modulation voltage for maximum SNR.

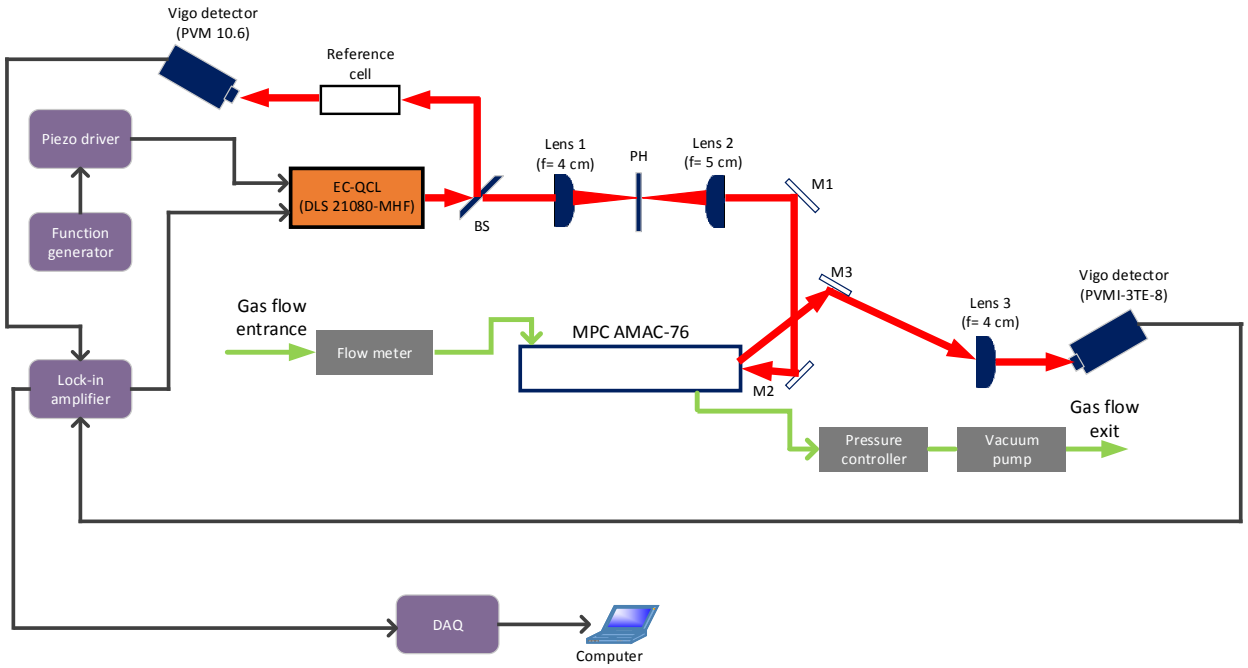

Figure 2. Architecture of H_2O_2 sensor system. BS: beam splitter, PH: 400 µm pinhole, and mirrors: M1, M2, M3..

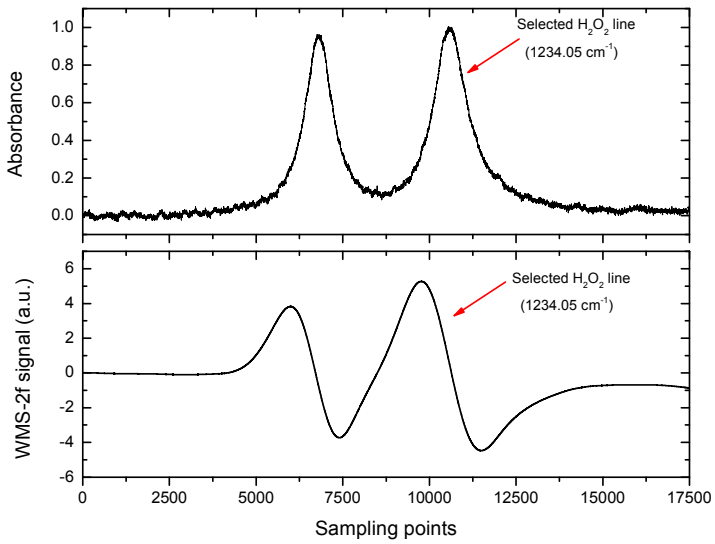

Figure 3. Sensor system response to H_2O_2 generated from an aqueous solution 5% w/w.

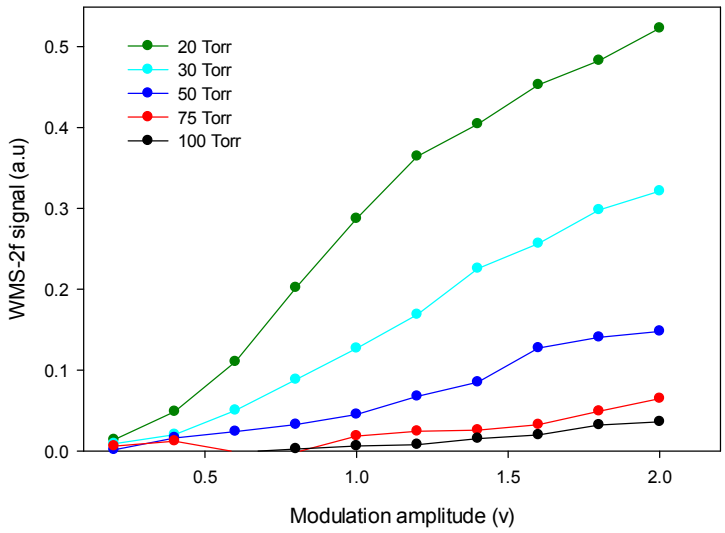

Figure 4. 2f signal at different pressure and modulation amplitude levels.

Figure 5 depicts the response of the sensor system at different concentrations of H_2O_2 using the optimum levels of pressure and modulation voltage previously determined (i.e. 20 Torr and 2 V). A linear relationship between the measured WMS-2f signal and the concentration of H_2O_2 is observed as shown in Figure 5(a). The response time of the sensor at different H_2O_2 levels and the stability of the 2f signal are shown in Figure 5(b).

Pure N_2 flowing during an extended period of time was used to examine the stability of the sensor response (Figure 6(a)). An Allan-Werle deviation analysis was performed to determine the MDL of the sensor system (Figure 6(b)). According to Figure 6(b), a MDL of ~25 ppb of H_2O_2, with an optimum integration time of 280 sec can be achieved for this sensor system.

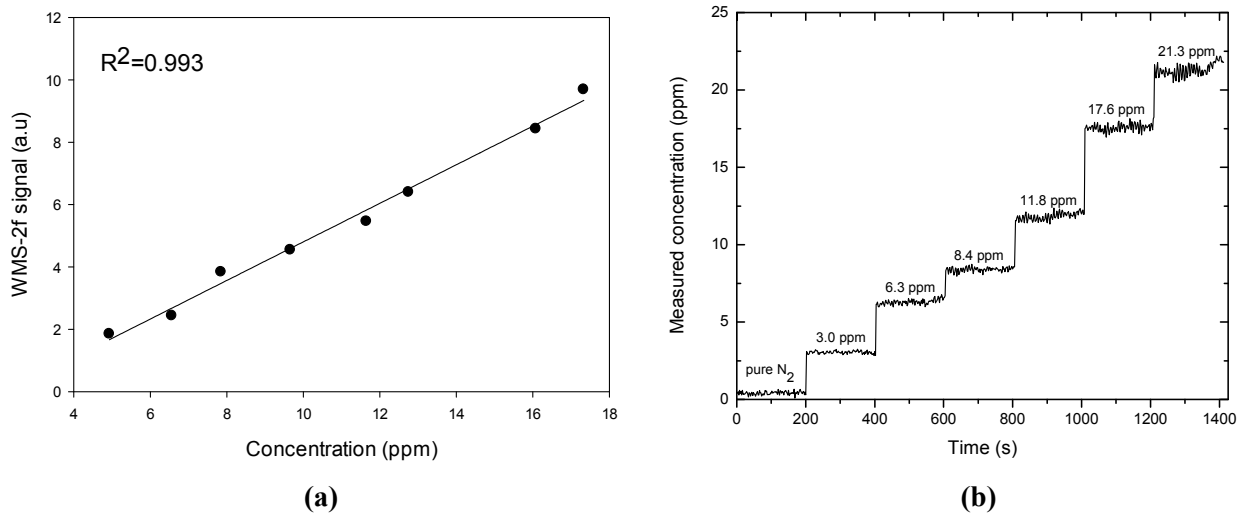

Figure 5. Calibration curve and response time at different concentration levels of the H_2O_2 sensor system.

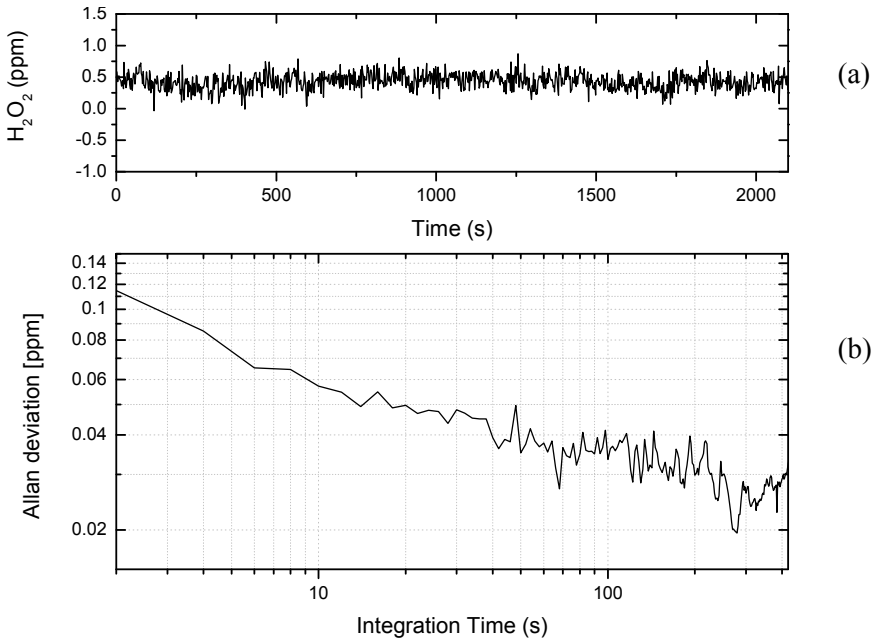

Figure 6. (a) Sensor system signal reported as H_2O_2 concentration based on pure N_2 signal and (b) Allan-Werle deviation analysis for signal in Fig. 6 (a)

4. CONCLUSIONS

An EC-QCL coupled to a commercial MPAC with an optimum optical path length of 76 m was developed for the detection of gas-phase H_2O_2. The sensor system employs an interference-free absorption line at 1234.055 cm^{-1} that alleviates interference issues reported in previous mid-IR-based sensing systems for H_2O_2 detection. Selection of this absorption line avoids the potential interference from H_2O absorption lines and makes this sensor system suitable for monitoring of H_2O_2 in decontamination/sterilization applications based on VPHP. The MDL achieved by the sensor is 25 ppb for a 280 sec integration time, which makes this sensor useful for establishing H_2O_2 PELs in industrial facilities.

REFERENCES

[1] Sakugawa, H., et al., *Atmospheric hydrogen peroxide.* Environmental Science & Technology, 1990. **24**(10): p. 1452-1462.

[2] Andreozzi, R., et al., *Advanced oxidation processes (AOP) for water purification and recovery.* Catalysis Today, 1999. **53**(1): p. 51-59.

[3] Linley, E., et al., *Use of hydrogen peroxide as a biocide: new consideration of its mechanisms of biocidal action.* Journal of Antimicrobial Chemotherapy, 2012. **67**(7): p. 1589-1596.

[4] Malik, D.J., et al., *The inactivation of Bacillus subtilis spores at low concentrations of hydrogen peroxide vapour.* Journal of Food Engineering, 2013. **114**(3): p. 391-396.
[5] Finnegan, M., et al., *Mode of action of hydrogen peroxide and other oxidizing agents: differences between liquid and gas forms.* Journal of Antimicrobial Chemotherapy, 2010.
[6] Kahnert, A., et al., *Decontamination with vaporized hydrogen peroxide is effective against Mycobacterium tuberculosis.* Letters in Applied Microbiology, 2005. **40**(6): p. 448-452.
[7] Klapes, N.A. and D. Vesley, *Vapor-phase hydrogen peroxide as a surface decontaminant and sterilant.* Applied and Environmental Microbiology, 1990. **56**(2): p. 503-506.
[8] Labor, U.S.D.o. *Occupational Safety & Health Administration*. Available from: https://www.osha.gov/dts/chemicalsampling/data/CH_246600.html.
[9] McManus, J.B., et al., *Application of quantum cascade lasers to high-precision atmospheric trace gas measurements.* Optical Engineering, 2010. **49**(11): p. 111124-111124-11.
[10] Ren, W., et al., *Hydrogen peroxide detection with quartz-enhanced photoacoustic spectroscopy using a distributed-feedback quantum cascade laser.* Applied Physics Letters, 2014. **104**(4): p. 041117.
[11] Cao, Y., et al., *Multi-pass absorption spectroscopy for H2O2 detection using a CW DFB-QCL*, in *Advanced Optical Technologies*. 2014. p. 549.