Near-Infrared QEPAS Sensor for Trace Ethylene Monitoring at Atmospheric Pressure

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Abstract: A sensor based on quartz enhanced photoacoustic spectroscopy was evaluated for the detection of trace levels of ethylene at atmospheric pressure using a fiber coupled DFB diode laser probing an absorption peak at 6177.15 cm^{-1}.

OCIS codes: (300.6430) Spectroscopy, optoacoustic and thermo-optic; (280.3420) Laser sensors

1. Introduction

Ethylene (C_2H_4) is a plant hormone that plays an essential role in nature by regulating the growth, development, ripening and decaying of fruits and vegetables. This gaseous species is emitted during the ripening process and furthermore acts as a catalyst to initiate or fasten ripening and decaying, so that the presence of even small amounts of ethylene gas during the shipping and storage of fruits (from ppm down to ppb level depending on the fruit variety) causes a premature degradation of most fresh produces. The control of the trace C_2H_4 concentration during fruit transportation is thus essential to improve the quality of the shipped fruits and to deliver the best possible products to consumers. The typical required C_2H_4 detection sensitivity is ~1 ppm for the transport of bananas.

We investigated the potential of quartz enhanced photoacoustic spectroscopy (QEPAS) in conjunction with cost-effective, commercially available laser diodes in the near-infrared (NIR) spectral region to develop a prototype C_2H_4 sensor with the objective to address this particular application. The advantage of the QEPAS technique is its simple and compact architecture combined with an enhanced immunity to environmental acoustic noise. The technique has already demonstrated ppm to sub-ppm sensitivity for many molecules in the NIR [1], but different operating conditions have been considered in the present work in order to address the specific requirements for fruit transportation. In particular, operation at atmospheric pressure was examined, while optimum sensitivity in QEPAS is generally achieved at reduced pressure [2].

2. Sensor description

A traditional QEPAS configuration was used as previously described [2, 3]. The optical radiation of a λ~1.62 μm DFB diode laser was fiber-coupled to an absorption detection module (ADM) consisting of a quartz tuning fork (TF) and an organ pipe micro-resonator. The absorption of the wavelength-modulated laser radiation (at half the resonant frequency of the TF, *f*~16.4 kHz) by the C_2H_4 molecules generates acoustic waves at the different harmonics of the modulation frequency through the photoacoustic effect. The second-harmonic (2*f*) component is strongly amplified by the TF (*Q*-factor is ~ 8000 at ambient pressure) and converted to electrical signal. A further ~15-fold signal enhancement results from the micro-resonator that acts as an acoustic cavity designed to have its first longitudinal resonance at 32.7 kHz. The 2*f* component of the TF generated electrical signal is used to quantify the ethylene concentration.

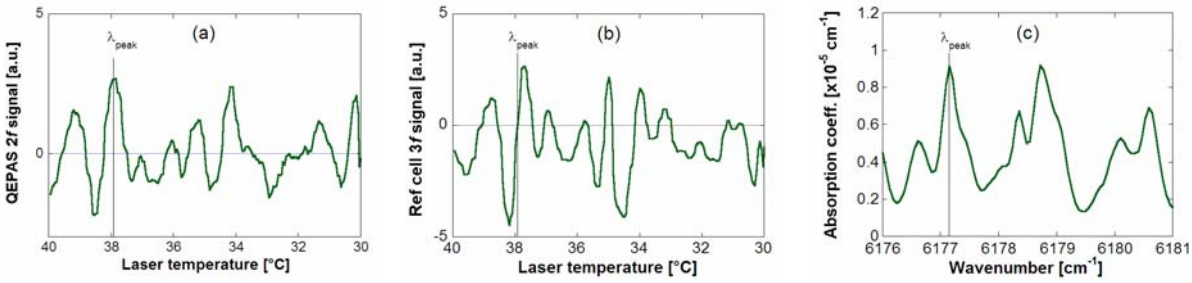

Fig. 1. (a) 2*f* wavelength modulation QEPAS spectrum measured for 100ppm C_2H_4; (b) 3*f* signal from the reference cell; (c) comparative C_2H_4 FTIR spectrum (scaled to 100 ppm) from the PNNL database [4]. The selected C_2H_4 absorption peak is indicated by λ_{peak} in each plot.

A small fraction (~3%) of the laser radiation was also directed to a C_2H_4-filled reference cell and a photodiode (PD). The 3*f* component of the PD signal was used as an error signal in a stabilization loop to keep the laser locked to the selected optical absorption peak of ethylene at 6177.15 cm^{-1}, which provides the highest QEPAS signal in the laser tuning range as shown in Figure 1. Signals from the TF and PD were measured and processed by a dedicated control electronics unit which also controlled the laser current and temperature.

3. Sensor performance

The sensor response to varying C_2H_4 concentration (in N_2) is displayed in Figure 2a. A noise equivalent signal of ~4 ppm C_2H_4 was obtained with ~16 mW average optical power launched into the ADM and a bandwidth of 0.785 Hz. A sub-ppm detection limit may be achieved using a longer data acquisition times of ~500 sec as shown by the Allan plot in Figure 2b. Such a long integration time is fully compatible with the requirement of the application, since fast monitoring of C_2H_4 is not required for fruit transport. With an averaging of ~100 sec, a C_2H_4 step from 0 to 2 ppm becomes clearly distinguishable as shown in Fig 2c.

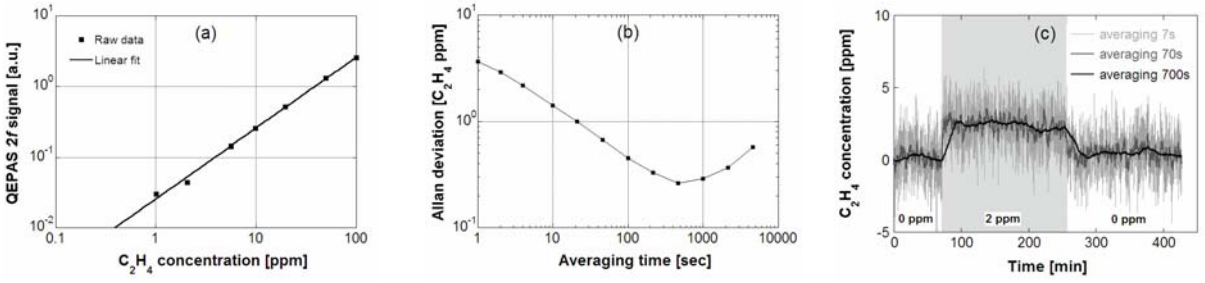

Fig. 2. (a) Sensor response to varying C_2H_4 concentration; (b) Allan plot for a 13-hour measurement of the sensor zero level; (c) 0-2 ppm C_2H_4 step observed with longer averaging times.

The temperature behavior of the sensor has been investigated in a 40°C temperature range by inserting the ADM in a computer-controlled climatic chamber and applying a slow temperature ramp (typ 0.1°C/min). Figure 3a displays the temperature variation of the QEPAS signal corresponding to 100 ppm C_2H_4. The observed variation mainly results from the temperature dependence of the C_2H_4 absorption and *Q*-factor (see below). No sensitivity decrease resulting from a temperature-dependent mismatch between the TF and the micro-resonator resonances is noted. The temperature dependence of the TF frequency and *Q*-factor observed in this measurement is shown in Figure 3b. The frequency vs temperature curve is quadratic with a coefficient $\Delta F/\Delta T^2 = -0.04 \cdot 10^{-6}$ Hz/°C^2 which is similar as in vacuum. However, the parabola maximum is shifted from $T_0 = 25$°C design position in vacuum to $T_0 = 35$°C at atmospheric pressure. The measured overall frequency variation over the 40°C temperature range is only 2 Hz, whereas the *Q*-factor scales linearly with temperature with a measured coefficient $(\Delta Q/Q)/\Delta T = -0.4\%/°C$.

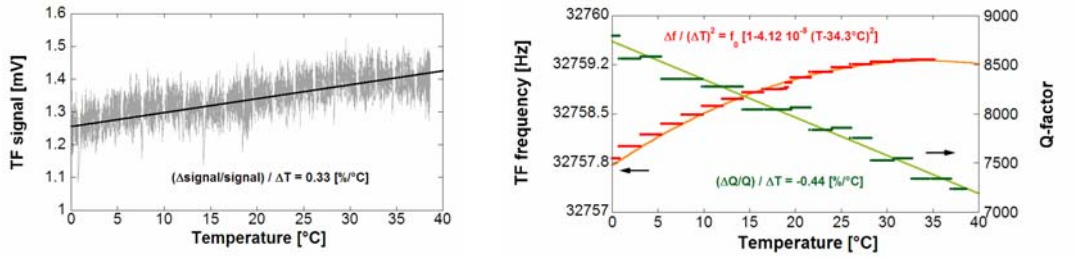

Fig. 3. Temperature dependence of the QEPAS signal (0.7 s data acquisition time) for 100ppm C_2H_4 (a) and of the TF *Q*-factor and resonance frequency (b).

4. References

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