Smart Material Serves Other Smart Materials: Comparison of Measurement of CO₂ Concentration by Optical and Optoacoustic Methods

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Abstract. In this study, we compare the sensitivity of the Wavelength Modulation Spectroscopy (WMS) to the Quartz enhanced photoacoustic spectroscopy (QEPAS) method on a sample of CO₂ gas at various concentrations. We show the advantages of the QEPAS method, the essential part of which is a crystalline segment made of smart material.

1. Introduction

One of the urgent problems of present civilization is content of carbon dioxide in the air. Within this context, the importance of smart materials, which can serve as the basis for various devices to reduce emissions of this gas, such as scrubbers or catalysts, is increasingly important [1–5]. No less important role is played by various types of detection methods of carbon dioxide. Besides classical optical methods [6–8], photoacoustic spectroscopy, has some advantages over the optical methods.

In this study, we focus on comparing the optical method WMS [9] with QEPAS method where the function of sensor is performed by acoustic detector – Quartz Tuning Fork (QTF). Modified commercial device (KB Spektrolap TM) was used as optoacoustic spectrometer, which key part (fork of Mrs. Vice-dean) is also made from smart material and is used thanks to its specific material properties.

Both employed spectroscopy methods are based on wave modulation technique. Main advantages of the WMS are high sensitivity, fast reaction, simple construction and maintenance, noninvasive measurement and low operating cost [10]. It is possible to measure trace amounts of gases up to ppm in Near Infrared Range (NIR) with weak “overtones” and combination spectral bands. Often several different substances can be selectively measured using a single laser diode. Laser diodes typically have narrow emission lines allowing the measurement of narrow separated rotational-vibrational bands of absorbing substances.

The Quartz Enhanced Photoacoustic Absorption Spectroscopy (QEPAS) [11] method is based on the sensing of acoustic waves in a confined space using WMS principles. Acoustic waves are generated by
rotational-vibrational relaxation of molecules due to modulated infrared laser radiation. The acoustic signal in a cell can be easily measured using the Quartz Tuning Fork (QTF) with a high quality factor $Q$ [11–13]. These QTFs are commonly used in electrical engineering as crystal oscillators and are made of silicon crystal cut, making them smart. The signal generated by QTF is amplified using a high input resistance transimpedance preamplifier. This method is described in Kosterev [14, 15] or Zheng [16], where they use parallel crystal oscillations.

The laser is focused using optical elements between the QTF tips and modulated at $f/2$ where $f$ is the QTF resonant frequency. This arrangement creates acoustic waves with a corresponding frequency in the cell, which influence the oscillation of the crystal.

**Figure 1.** Experimental Setup, case 1 is the wiring for the QEPAS method, case 2 is the wiring for the optical WMS method.

### 2. Experimental

#### 2.1. QEPAS method

The experimental set-up enabled measurement by both QEPAS and WMS methods on the same sample (Figure 1). A QTF with a resonant frequency $f = 12454.5$ Hz and a quality factor $Q > 12000$ was used as an acoustic signal detection element. A diode laser (Eblana - EP 1573-0-DM-B01-FA) with a wavelength of about 1573 nm (corresponding to the wavenumber range 6358–6362 cm$^{-1}$) was used as the infrared radiation source. CO$_2$ absorption lines occur in this region. The wavelength of the infrared radiation emitted by the laser diode is dependent on the electrical current flowing through the laser diode and its temperature (kept at 28 °C). By changing both of these parameters, the wavelength of the emitted radiation can be varied continuously over a narrow wavelength range. The current and temperature stabilization of the diode was ensured by the control unit (Throlabs ITC 4001). The laser wavelength was externally modulated using a two-channel generator (LeCroy Wavestation 2012) with a slow asymmetric triangular signal at 20 mHz and a fast sinusoidal signal (6227.25 Hz) corresponding to $f/2$ with an amplitude of 100 mV. The laser beam was directed through a fiber optic to a QEPAS cell (Thorlabs ADM01). An InGaAs photodetector (Thorlabs PDA10T-EC) was placed behind the QEPAS cell to measure the intensity of radiation passing through the system. The
photodetector was connected to an oscilloscope. The signal measured by the QEPAS detector was then demodulated using a phase-sensitive lock-in amplifier (Standford Research AS830DSP). The lock-in amplifier was set to demodulate the second harmonic component of the signal corresponding to a frequency $f$ (sensitivity 200 mV, time constant 300 ms). The amplified sine signal from the function generators, as described above, was used as a reference signal for demodulation. The output of the Lock-in amplifier is the $X$ and $Y$ components of the demodulated signal $R$.

In our case, the phase shift of the Lock-in amplifier has been set so that all output is concentrated on the $X$ component of the signal. This output was connected to the first oscilloscope channel (LeCroy wavesurfer 42XS) through which the data was recorded. The output from the optical detector was connected to the second channel.

2.2. WMS method

For the optical WMS measurement, a photodetector located behind the photoacoustic cell was used to measure the change in intensity of the laser beam after passing through the cell. The output of the detector was connected to the Lock-in input of the amplifier, which was set with the same parameters as the QEPAS method. Also, the laser modulation frequency and modulation depth were set with the same parameters as the previous method. The output of the lock-in amplifier was connected to the first channel of the oscilloscope and the output from the photodetector was connected to the second channel.

2.3. Gas sample preparation

The defined concentration of CO$_2$ in N$_2$ was prepared using a flowmeter system (Bronkhorst F201-CV series). The selected concentration was first mixed into an expansion vessel and then filled into a cell. After filling with gas, the cell was closed.

3. Results and discussion

Figure 2 shows measured CO$_2$ spectra by WMS and QEPAS at two defined concentrations. From the measured data we can conclude that the QEPAS method achieves much higher sensitivity under the same conditions (absorption path).

![Figure 2](image_url)

**Figure 2.** Measured CO$_2$ absorption spectra by QEPAS compared to WMS at two different concentrations. Case a) 100% CO$_2$, case b) 50% CO$_2$.

The most significant difference between the two methods is seen in case b) at a CO$_2$ concentration of 50%. While QEPAS still reliably detects this amount, the WMS optical method is at its threshold. Note that QEPAS can also detect units of percent of CO$_2$ concentration. Case a) clearly shows how optical components bring undesirable interference into spectroscopic information. In contrast, QEPAS does not show artifacts of this kind.
The measured data were analyzed using relevant mathematical models of spectral lines. The middle absorption line at 6369.5 cm$^{-1}$ was chosen for the modeling. The analysis shows that under given experimental conditions the measured data differ by $\pm$ 2% from the model case by the QEPAS method (Figure 3). From this we can conclude that the QEPAS method has a very good signal to noise ratio. Note that the measured data were processed using the algorithm described in the articles [17, 18].

![Figure 3. Spectral profile of R (16) absorption line of carbon dioxide and results of line-shape.](image)

4. Conclusion
The experiment was focused on testing the possibility of using a crystalline QTF oscillator for gas detection using the QEPAS method compared to the optical WMS method. Under comparable conditions, e.g. the same absorption pathway, QEPAS has proven to be a much more sensitive and flexible CO$_2$ detection tool.

5. References
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Acknowledgment
The authors are grateful for the financial support from the Czech Science Foundation, Project No. 17-05167S, from the project No. VI20192022127 funded by the Ministry of the Interior of the Czech Republic and this work is a part of a research series funded by ERDF/ ESF “Centre of Advanced Applied Sciences” (No. CZ.02.1.01/0.0/0.0/16019/ 0000778). VSB-Technical University of Ostrava (Faculty of Safety Engineering) is also acknowledged for support via project No. SP2018/179 and project No. SP2019/158