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Development of a miniaturized differential photoacoustic gas sensor

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Abstract

Photoacoustic spectroscopy is one of the most sensitive techniques used to monitor chemical emission or to detect gas traces. However the sensors bulkiness, cost and complexity prevent their use in applications where mass deployment is required. In this paper, the development and characterization of centimeter sized photoacoustic sensors is presented. With a 2.2 mW optical power interband cascade laser at 3.36 μm wavelength, a limit of detection of 320 ppbv is obtained for methane.

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1. Introduction

Photoacoustic (PA) spectroscopy is used to detect gas traces with a high sensitivity, below the part per billion by volume (ppbv) level [1]. This spectroscopy technique has other advantages such as being a zero background measurement technique and its simplicity and robustness of implementation. The principle of PA spectroscopy relies on the excitation of a molecule of interest with a light source emitting at the wavelength of an absorption line of the molecule. The light source is modulated at the acoustic frequency of a resonant cell containing the gas mixture. During the molecules relaxation, kinetic energy exchange creates local temperature waves, and thus acoustic waves, in the resonant cell.

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Miniaturization obviously aims at system compactness and, simultaneously, at improved performances because the PA sensor response is inversely proportional to the cell volume [1]. However, at the sub-millimeter scale of the chambers and capillaries diameters, the thermal and viscous boundary layers constitute a non-negligible part of the cell volume. Thus, a complete viscothermal model taking into account the dissipation effects must be used to design miniaturized PA sensors [2]. In this paper the miniaturized PA cells developed at CEA-LETI are presented and their detection performances are assessed.

2. Experimental setup

In this work a continuous-wave distributed feedback interband cascade laser (DFB-ICL) operating around $\lambda = 3.36 \mu\text{m}$ is used (Nanoplus, Germany). This laser is driven in current and in temperature by a LDC-3724C laser controller and thermoelectric cooler (Newport, USA). At the temperature of 23°C, the DFB-ICL has a tuning range of 2978-2980 cm^{-1} and the mean power is 2.2 mW. A SCB-68A electronic board (National Instruments, USA) is used to generate the sinusoidal signal, injected in the laser controller to modulate the laser wavelength. The laser wavelength is set close to the 2979 cm^{-1} methane absorption line and the sinusoidal modulation allows the wavelength to travel across the absorption line.

Two miniaturized differential Helmholtz resonators [3] were developed to detect gas traces. The first cell (#1) is made by stacking several laser-cut 3.5 cm x 3.5 cm stainless steel sheets. Its volume is 34 mm^3 . The two opposite walls of the illuminated chamber are constituted by SiO_2 windows. Top port SPU0409HD5H MEMS microphones (Knowles, USA) are glued on the sensor and a 3D-printed plastic part ensures the interface with the gas supply system constituted by Tygon S3™ tubing (Saint-Gobain, France). The second cell (#2) is made of stainless steel by direct metal laser sintering (DMLS). Its dimensions are 2 cm x 3.5 cm and the cell volume is 25.5 mm^3 . The cell windows are in BaF_2 (Edmund Optics Inc., USA). By the means of the DMLS technique, chambers, capillaries, microphones, windows locations and tubing connectors are built in a same block. Fig. 1 shows photographs of the two PA cells on their base. Batteries provide microphones alimentation. A SR830 lock-in amplifier (Stanford Research, USA) retrieves the signal measured at the excited and non-excited chambers, as well as the differential measurement, which correspond to the PA signal amplitude. The PA signal is transferred by the electronic board to a personal computer. A diagram of the experimental setup is presented in Fig. 2.

The experiments are carried out in two steps. The first one consists in finding the resonance frequency of the cell by measuring the cell frequency response with a single mixture of nitrogen with a high concentration of methane (2000 ppmv). The second step allows determining the limit of detection by drawing a calibration graph with signal mean values recorded, at the cell resonance frequency, for different concentrations of the methane in nitrogen.

To draw the cell frequency response graph, a LabVIEW program sweeps the laser modulation frequency from 1200 Hz to 3200 Hz. The time interval between two frequency steps is 15 s and the acquisition is made with a lock-in time constant of 300 ms. The differential PA signal is recorded for each frequency and is divided by the optical power measured after the cell (2.2 mW), microphone sensitivity, which is constant on this range of frequency (7.94 mV/Pa) and by the absorption coefficient of the methane at 2979 cm^{-1} (0.018 cm^{-1}) calculated with the help of the HITRAN database [4]. The result corresponds to the cell response and the resonance frequency of the cell can be determined.

To draw the calibration curve, several methane-nitrogen mixtures were prepared to cover a concentration range between 0 ppmv (pure nitrogen) and 2000 ppmv. The differential PA signal is measured for each concentration with an integration time of 1 second. One hundred measurements were recorded to calculate the mean values and standard deviations. The background signal, which corresponds to the absorbance of laser radiation by the cell windows and walls, is measured. This background signal is subtracted from the mean PA signal measured at each concentration. The limit of detection is calculated as the ratio of 3 times the standard deviation (3σ) of the background signal by the slope of the linear regression fitting the signal mean values [5].

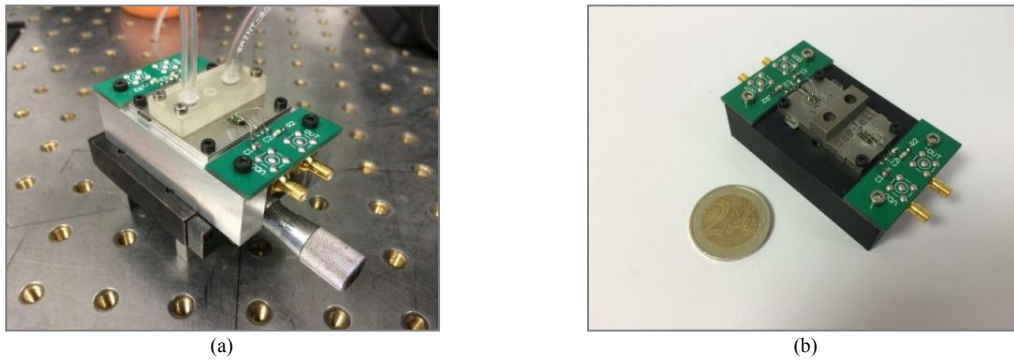


Fig. 1. Photographs of the miniaturized photoacoustic cell prototypes on their base. Cell #1 made by laser-cut (a) and cell #2 by DMLS technique (b).

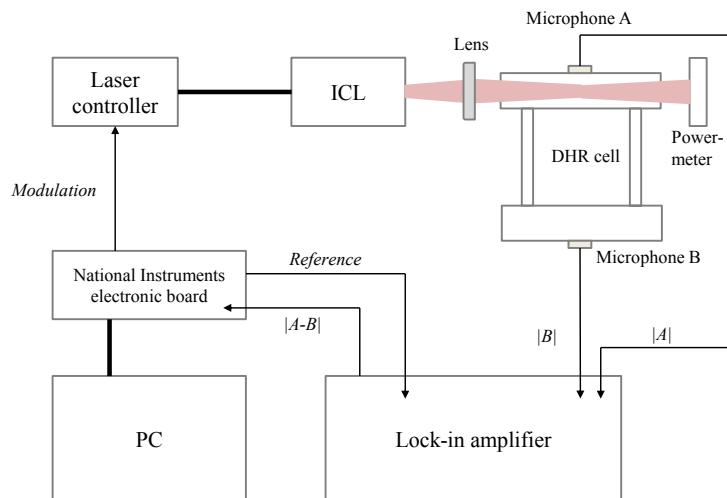


Fig. 2. Diagram of the experimental setup of a photoacoustic gas sensor.

3. Results and discussion

For each cell, the same methane-nitrogen mixture was used to draw the cell response. The experimental measurements, recorded with the two cells, are plotted in Fig. 3. The plate stacking technique used to fabricate cell #1 is prone to gas leakage, making the experiments impractical. Thus, improvements were carried out in cell #2 (MIR transparent windows, airtightness, slight volume diminution) to increase the cell performances. The two cells resonance frequencies are respectively 2180 Hz and 2200 Hz. At these frequencies, the cell constant is $2100 \text{ Pa}/(\text{W}\cdot\text{cm}^{-1})$ for the first cell and $3840 \text{ Pa}/(\text{W}\cdot\text{cm}^{-1})$ for the second.

Fig. 4 presents the calibration curves of the two PA cells. The background signal, the mean signal and the linear regression are symbolized in green solid line for cell #1, whereas they are in blue dashed line for cell #2. The 3σ noise of the background signal is similar for the two cells ($49.9 \mu\text{V}$ for cell #1 and $37.6 \mu\text{V}$ for cell #2). The linear regressions show that the second cell is more efficient than the first one. Thus, the methane limit of detection is around 1 ppmv for the first cell and 320 ppbv for the second one. The latter limit of detection has been confirmed using a 500 ppbv mixture, which is clearly made out from the pure nitrogen signal.

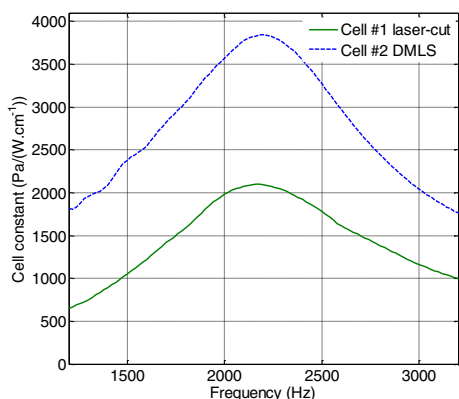


Fig. 3. Cell response of the two photoacoustic cells. Experimental measurements are represented in green solid line for cell #1 and in blue dashed line for cell #2.

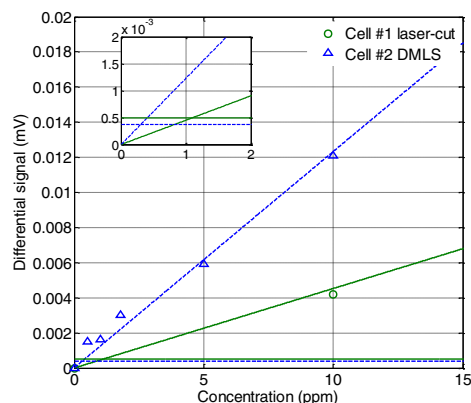


Fig. 4. Linear regression of the measurements (inclined lines) and 3σ detection noise (horizontal lines) for the two photoacoustic cells. Limits of detection are respectively 1 ppmv and 320 ppbv (insert figure).

4. Conclusion

The realization and characterization of two miniaturized PA cells, based on the differential Helmholtz resonator principle, were presented. The first cell was built by stacking several laser-cut stainless steel sheets. Commercial MEMS microphones were used to detect the differential PA signal. Using a 2.2 mW optical power DFB-ICL laser, the limit of detection is 1 ppmv of methane at 2979 cm^{-1} . The cell constant at the resonance frequency is $2100\text{ Pa}/(\text{W}\cdot\text{cm}^{-1})$. The fabrication technique, based on metal sheets stacking, is costless but gas leakage is an issue that must be managed carefully. The second cell, made with DMLS technique, has a good airtightness and is easier to build. An almost two-fold improvement of the cell constant $3840\text{ Pa}/(\text{W}\cdot\text{cm}^{-1})$ has been reached using the same laser and microphones and the detection limit is 320 ppbv of methane. The interest of miniaturized PA cell based on the DHR principle at centimeter scale has been shown in this paper and the ongoing work aims at improving the present performances.

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