DOI 10.5162/SMSI2023/C3.1

Evaluation of photoacoustic detectors for methyl bromide sensing

H. Yassine[1], C. Weber[1,2], J. Wöllenstein[1,2], K. Schmitt[1,2]
[1] Department of Microsystems Engineering-IMTEK, Laboratory for Gas Sensors, University of Freiburg, Georges-Köhler-Allee 102, 79110 Freiburg, Germany
[2] Fraunhofer Institute for Physical Measurement Techniques IPM, Georges-Köhler-Allee 301, 79110 Freiburg, Germany
hassan.yassine@imtek.uni-freiburg.de

Summary:
We present a new approach towards measuring methyl bromide (CH_3Br) using a two-chamber photoacoustic sensor with the focus on suitable detector gas fillings. A MIR LED was selected as IR source. The absorbed spectral power in a photoacoustic detector filled with 100 vol.-% methane (CH_4) and the response of this detector to CH_3Br were simulated and compared with the response of a detector filled with 100 vol.-% CH_3Br.

Keywords: two-chamber photoacoustic gas sensor, simulation, methyl bromide, methane

Motivation

Methyl bromide (CH_3Br) is a gas used mainly in Asian countries for fumigation of containers, especially those intended for shipping [1]. This gas is highly toxic and causes harmful diseases to the human nervous system. It is therefore necessary to monitor this gas in containers to avoid fatal accidents that may occur when the container door is opened. Two-chamber photoacoustic sensors have the advantage of high sensitivity and selectivity. This is due to the fact that the detector chamber is filled with 100 vol.-% target gas and the absorption lines of this gas thus act as an IR filter. In other words, the photoacoustic detector is only sensitive to gases that absorb at the absorption lines of detector gas. In this situation, an optical filter is not necessary. A new approach to measure CH_3Br using a two-chamber photoacoustic sensor is presented. Due to the toxicity of CH_3Br we have searched for non-toxic substituent gases that have similar absorption properties in the infrared region as CH_3Br. In this way, a photoacoustic detector filled with substituent gas could be used to indirectly measure CH_3Br.

Infrared absorption of CH_3Br and CH_4

Two-chamber photoacoustic sensors generally consist of an IR source, an absorption cell and a photoacoustic detector chamber hermetically filled with the target gas or, in this case, a substituent gas. A MEMS microphone placed inside this detector cell detects the generated sound wave. In order to find a suitable substituent gas as detector filling gas, it is essential to know the absorption properties of CH_3Br.

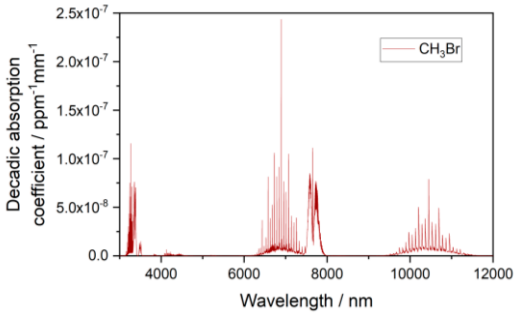

Fig. 1. Decadic absorption coefficient spectrum of CH_3Br from 3000-12000 nm from [2].

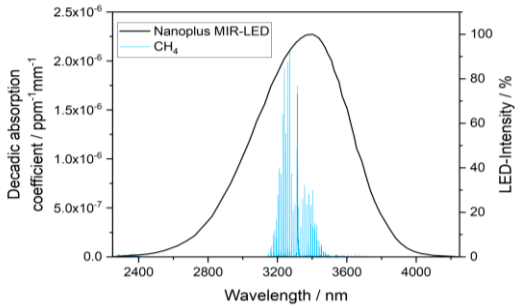

Fig. 2. Decadic absorption coefficient spectrum of CH_4 from 2250-4250 nm from [3] as well as the emission spectra of the MIR-LED from Nanoplus [4].

Fig. 1 shows the decadic absorption coefficient spectrum of CH_3Br between 3000-12000 nm from [2]. CH_3Br absorbs between 3150-3550 nm, 6300-8000 nm and between 9500-11700 nm. For various reasons, it makes most

sense to search for a substituent gas that absorbs between 3150-3550 nm. One reason is that high-power MIR LEDs are available for this wavelength region. In addition, water vapor (H_2O) does not absorb here. Methane (CH_4) could be a possible substituent gas. As can be seen in Fig. 2, CH_4 absorbs strongly at 3300 nm. The 3.4 µm MIR LED from *Nanoplus* was selected as radiation source. The emission spectrum of this LED is shown in Fig. 2.

Absorbed spectral power in the detector and the detector response to CH_3Br

Simulations have been performed to estimate whether or not CH_4 is a suitable substituent gas for CH_3Br. These simulations determine the sensitivity of a detector filled with 100 vol.-% CH_4 gas to different CH_3Br concentrations in the absorption cell at a known optical path length. The simulations were done similarly as in [5]. Fig.3 shows the absorbed spectral power in a detector chamber filled with 100 vol.-% CH_4 at two different gas concentrations in the absorption cell. The optical path length was set to 1.6 m. The results show that the absorbed spectral power in the detector has decreased much more in the wavelength range 3350-3400 nm than in the wavelength range 3200-3300 nm when the CH_3Br concentration was increased from 0 vol.-% to 1 vol.-% CH_3Br in the absorption cell. This is partly because CH_3Br has more overlapping absorption lines with CH_4 in this wavelength range than in the wavelength range 3200-3300 nm and partly because the absorption lines in this wavelength range are stronger here.

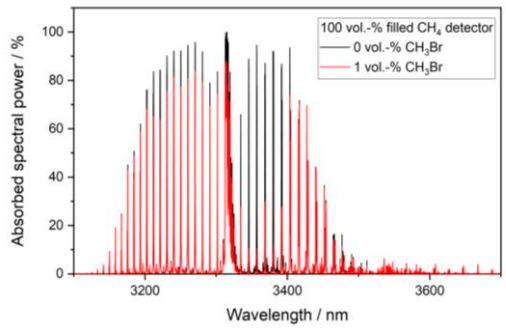

Fig. 3. Absorbed spectral power in a detector filled with 100 vol.-% CH_4 at two different CH_3Br concentrations in the absorption cell (0 vol.-% CH_3Br in black and 1 vol.-% CH_3Br in red). The optical path length was 1.6 m.

Furthermore, simulations concerning the sensitivity of a detector filled with 100 vol.-% CH_4 detector as well as a detector filled with 100 vol.-% CH_3Br to 0-1000 ppm CH_3Br (in 20 ppm steps) at an optical path length of 1.6 m were done. The variation of the signal of both detectors is linear with respect to the variation of the CH_3Br concentration in the absorption cell. The signal of the detector filled with pure CH_3Br drops to ~87.5 %, while the signal of the detector filled with pure CH_4 only to ~94.8 % when there are 1000 ppm CH_3Br in the absorption cell. This result seems reasonable because the highest sensitivity can be achieved with the target gas as detector gas. The results show that there is a possibility to use substituent gases as CH_4 as detector filling gas in order to indirectly measure CH_3Br.

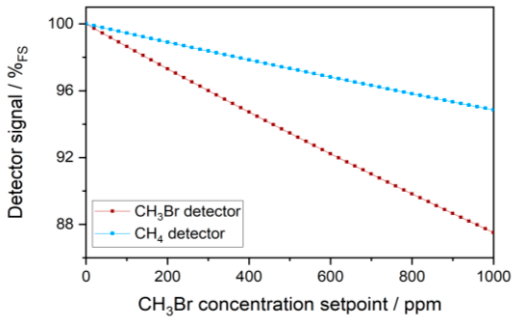

Fig. 1. Simulated variation of the signal of a detector filled with 100 vol.-% CH_3Br and one filled with 100 vol.-% CH_4 with respect to CH_3Br concentration setpoint between 0-1000 ppm.

Conclusion

The sensitivity of a CH_4 and a CH_3Br photoacoustic detector to CH_3Br was simulated. The results have shown that it is possible to replace CH_3Br with CH_4 as the detector filling to measure CH_3Br using the two-chamber photoacoustic principle. However, the signal change of the detector filled with CH_4 is ~ 41% lower than that of the detector filled with CH_3Br (assuming 1000 ppm CH_3Br in the absorption cell). These results look promising and CH_3Br can be measured using a two-chamber photoacoustic sensor without using a detector filled with CH_3Br.

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