DOI 10.5162/SMSI2023/C3.3

Photoacoustic Sensor for isotopologic analysis of highly concentrated methane

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Summary:
Photoacoustic spectroscopy (PAS) is typically used for the detection of trace gases. However, there are a number of applications where highly concentrated mixtures need to be analyzed. In some cases especially the isotopologic composition of certain hydrocarbons needs to be determined. We present PAS-based isotopologic analyses of two digit percentage-level methane concentrations in nitrogen and its AI-based evaluation. The investigation allows conclusions to be drawn about the extent to which PAS is suitable for an isotopologic analysis of undiluted natural gas-like mixtures.

Keywords: photoacoustic spectroscopy, $^{12}CH_4$, $^{13}CH_4$, interband cascade laser, natural gas

Introduction

The impact of methane emissions on the climate change is up to 34 times higher in comparison to CO_2, due to its global warming potential [1]. Based on that fact, it is of outmost importance to detect methane, its concentrations and emission sources. Methane exhibits a source dependent individual isotopologic “signature” which depends on the $^{13}CH_4$ and $^{12}CH_4$ shares as quantified by the following equation:

$$\delta^{13}C = \left(\frac{R_{sample}}{R_{std}} - 1\right) \cdot 1000‰, \quad (1)$$

where R_{sample} is the $^{13}CH_4/^{12}CH_4$ ratio of the sample and $R_{std} = 0.0112372$. The $\delta^{13}C$ value of anthropogenic methane sources tend to be slightly higher in comparison to biogenic sources which helps to identify them and, thus, reduce their contribution to climate change [2]. Furthermore, the short-chained hydrocarbon composition of natural gas is decisive for its numerous industrial applications. The energy content of the natural gas is strongly dependent on the hydrocarbon shares and must be compensated in production processes by parameter adjusting [3]. In addition, the $\delta^{13}C$ value can be used to evaluate and optimize the natural gas conveyor technique [4].

A well-known and precise method for the analysis of gas mixtures is gas chromatography in combination with isotope-ratio mass spectrometry (IRMS) [5]. PAS is a very established method for detection of methane isotopologues in the single-digit per mill range, down to the parts per million (ppm) range [6].

In the following, we present to the best of our knowledge the first time PAS-based measurement of $^{13}CH_4$ and $^{12}CH_4$ isotopologue mixtures in the percentage range. Finally, the measurement results are then evaluated using cross-validation in conjunction with Partial Least Squares Regression (PLSR).

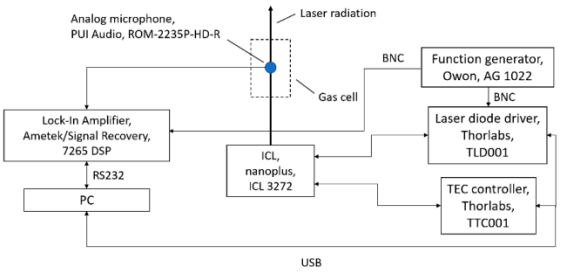

Fig. 1. Experimental setup.

Methods and Material

The measurement setup is schematically shown in Figure 1. The interband cascade laser ICL 3272 used in this investigation was manufactured by nanoplus GmbH (Gerbrunn, Germany) and exhibits a center wavelength of 3323 nm with a spectral linewidth below 20 MHz. The used measurement cell is designed according to the established H geometry featuring a longitudinal resonance around 3 kHz. The resulting measurement signal is detected by the analog microphone ROM-2235P-HD-R from PUI Audio (Fairborn, OH/United States). The Ametek / Signal Recovery lock-in amplifier DSP LIA (Berwyn, IL/United States) performs the 1*f* amplitude detection of the microphone signal. The measurement setup including the PLSR algorithm is

controlled using a MATLAB script on a PC. The gas mixtures in the gas cell are generated using the 6 Channel Gas mixer from QCAL (Munich, Germany), which is controlled by a PC.

The measurement were done for three different $^{12}CH_4$ concentration: 25%, 50% and 70% combined with three different $^{13}CH_4$ shares, as displayed in the Tab. 1. The residual gas to 100% was always N_2.

Tab. 1: $^{12}CH_4$ and $^{13}CH_4$ concentrations of the nine investigated mixtures (rest: N_2).

$^{12}CH_4$	$^{13}CH_4$
25%	0.28%, 0.75% and 1.25%
50%	0.56%, 1.75% and 2.25%
75%	0.78%, 2.25% and 3.00%

Results

Figure 2 shows exemplarily the recorded photoacoustic spectra, i.e. the PA signal as function of the average laser current for 50% $^{12}CH_4$ share. All measurements were taken at a sample temperature of 26°C and a pressure of 1016 hPa.

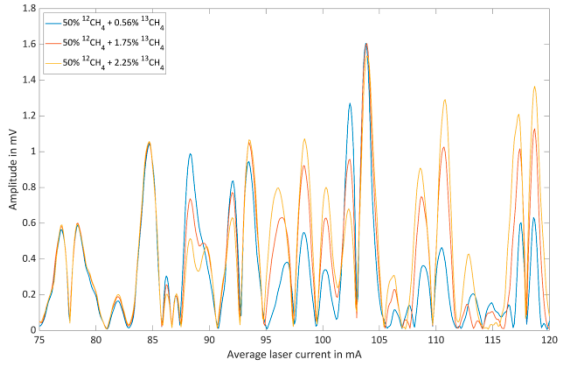

Fig. 2. Photoacoustic signal as function of the average laser current for 50% $^{12}CH_4$ with three different $^{13}CH_4$ shares in nitrogen.

Due to the complexity of the collected spectra a quantitative multivariate approach is implemented to validate the methane isotopologue mixtures and to test the suitability of the method. Figure 3 shows the true and the predicted methane isotopologue concentrations, after leave-one-out cross-validation based on PLSR was applied to all nine investigated mixtures. The mixture numbers in Fig. 3 corresponds to the order given in Tab. 1.

The absolute root-mean-square-errors for the predicted $^{12}CH_4$ and $^{13}CH_4$ concentrations were calculated to 3.08% and 0.29%, respectively.

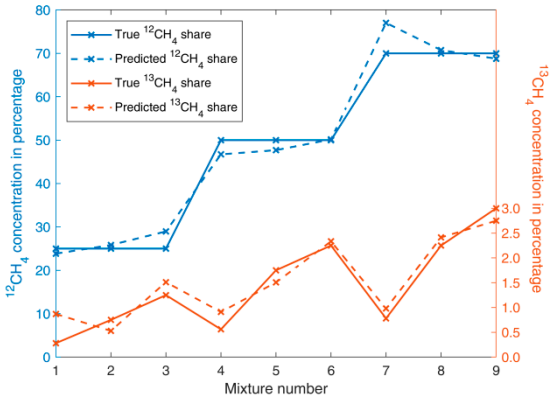

Fig. 3. Evaluation of the investigated methane isotopologue mixtures by leave-one-out cross-validation based on PLSR.

Conclusion

In conclusion, the evaluation in Fig. 3 in conjunction with the calculated errors prove to a satisfactory extent that PAS is a suitable method for the isotopologic analysis of highly concentrated methane. Adding more measurements to the training data set of the PLSR algorithm would improve the accuracy of the predictions. The presented results make it appear possible to analyze undiluted natural gas samples.

References

[1] M. Z. Jacobson, *100% clean, renewable energy and storage for everything*. Cambridge: Cambridge University Press, 2021.

[2] M. Schroll, F. Keppler, M. Greule, C. Eckhardt, H. Zorn, and K. Lenhart, “The stable carbon isotope signature of methane produced by saprotrophic fungi,” *Biogeosciences*, vol. 17, no. 14, pp. 3891–3901, 2020, doi: 10.5194/bg-17-3891-2020.

[3] J. Leicher, A. Giese, K. Görner, M. Werschy, H. Krause, and H. Dörr, “Natural gas quality fluctuations – surveys and statistics on the situation in Germany,” *Energy Procedia*, vol. 120, pp. 165–172, 2017, doi: 10.1016/j.egypro.2017.07.161.

[4] T. Zhang and B. M. Krooss, “Experimental investigation on the carbon isotope fractionation of methane during gas migration by diffusion through sedimentary rocks at elevated temperature and pressure,” *Geochimica et Cosmochimica Acta*, vol. 65, no. 16, pp. 2723–2742, 2001, doi: 10.1016/S0016-7037(01)00601-9.

[5] A. L. Sessions, “Isotope-ratio detection for gas chromatography,” *Journal of separation science*, vol. 29, no. 12, pp. 1946–1961, 2006, doi: 10.1002/jssc.200600002.

[6] A. Loh and M. Wolff, “Photoacoustic Detection of Short-Chained Hydrocarbon Isotopologues,” in *7th International Symposium on Sensor Science*, p. 23.