Development of Trace Methane and Trace Carbon Dioxide Analyzers - Performance Evaluation Studies, GCWerks Integration, and Results of Field Deployment

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Introduction

Global CO_2 and CH_4 monitoring requires instruments that meet the stringent requirements for accuracy, precision and stability. In order to serve multiple application needs, a design that also meets low power consumption, field portability, and limited maintenance is critical. Utilizing Optical-Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS), in a multi-purpose design, two new field portable analyzers were developed to address these requirements:

- LI-7810 $CH_4/CO_2/H_2O$
- LI-7815 CO_2/H_2O

We report on recent laboratory testing of both instruments with a view to verifying suitable performance for long-term atmospheric measurements of methane and carbon dioxide.

Analyzer Specifications

LI-7810 $CH_4/CO_2/H_2O$

Response Time (T_{10}-T_{90}): CH_4 ≤ 2 seconds, 0 to 2 ppm

CH_4 Measurements:
Range: 0.1 to 50 ppm
Precision (1σ): 0.25 ppb with 5 second averaging
Maximum drift: <1 ppb per 24-hour period

CO_2 Measurements:
Range: 1 to 10,000 ppm
Precision (1σ): 1.5 ppm with 5 second averaging

H_2O Measurements
Range: 100 to 60,000 ppm
Precision (1σ): 20 ppm with 5 second averaging

LI-7815 CO_2/H_2O

Response Time (T_{10}-T_{90}): CO_2 ≤ 2 seconds, 0 to 400 ppm

CO_2 Measurements:
Range: 1 to 10,000 ppm
Precision (1σ): 0.04 ppm with 5 second averaging
Maximum Drift: <0.2 ppm per 24-hour period

H_2O Measurements
Range: 100 to 60,000 ppm
Precision (1σ): 20 ppm with 5 second averaging

Experimental Objectives and Set-up

Atmospheric monitoring stations are often located at remote locations, requiring continuous operation of gas analyzers and other hardware with infrequent site visits for routine maintenance, including the replacement of exhausted calibration gas standards. A set of experiments were defined and implemented to assess the suitability of the LI-7810 and LI-7815 Trace Gas Analyzers for long-term measurements of atmospheric methane and carbon dioxide respectively. Key objectives were to assess the following:

- Measurement drift and precision to determine required frequency of instrument calibration.
- Sensitivity (measured / assigned) of the instrument for the high standard relative to the low standard and its stability over time. Results will determine if a high bracketing standard is required.

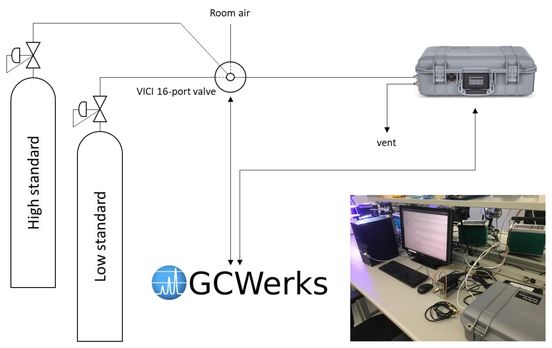

Figure 1. Experimental set-up. High and low gas standards (CH_4 in air, and CO_2 in air) were connected to the LI-7810 and LI-7815 respectively via a VICI Valco 16-port dead-ended selector valve. The valve and gas analyzer were integrated using GCWerks, allowing for gas standard selection, and instrument data acquisition, visualization, and processing.

Results – LI-7810 (CH_4)

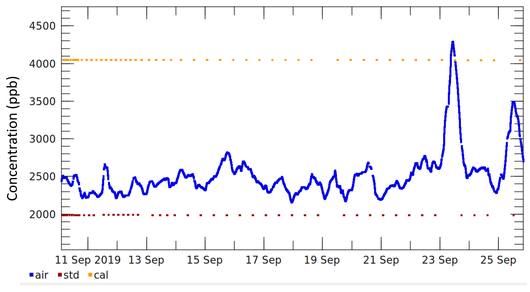

Figure 2. All data. CH_4 1-minute means acquired with GCWerks, showing ambient air and low and high standards (approximately 2000 and 4000 ppb).

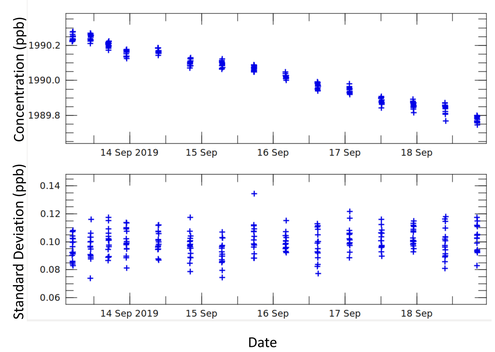

Figure 3. Drift. Top panel shows 1-minute mean of measured CH_4 low standard. Bottom panel shows standard deviation of 1-minute means.

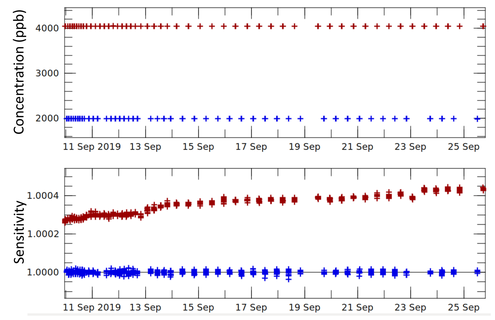

Figure 4. Relative sensitivity. Top panel shows low and high standards (approximately 2000 and 4000 ppb). Bottom panel shows drift corrected sensitivity (sensitivity = measured / assigned). The drift correction is based on linear interpolation to the low standard.

Results – LI-7815 (CO_2)

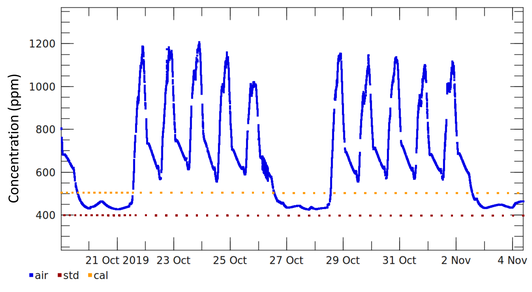

Figure 5. All data. CO_2 1-minute means acquired with GCWerks, showing ambient air and low and high standards (approximately 400 and 500 ppm).

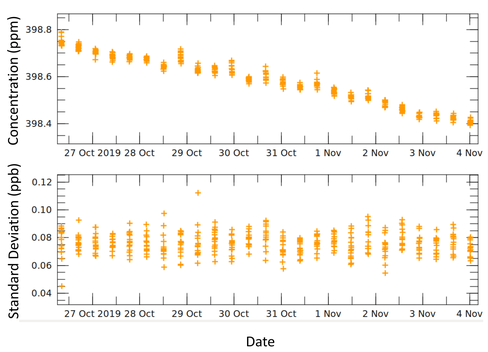

Figure 6. Drift. Top panel shows 1-minute mean of measured CO_2 low standard. Bottom panel shows standard deviation of 1-minute means.

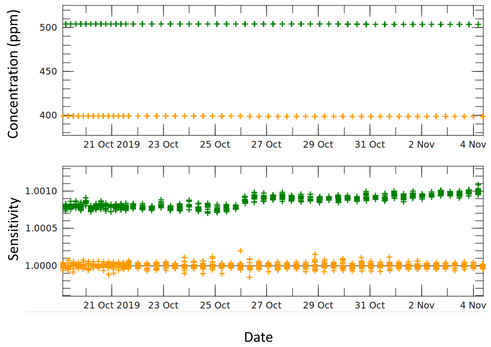

Figure 7. Relative sensitivity. Top panel shows low and high standards (approximately 400 and 500 ppm). Bottom panel shows drift corrected sensitivity (sensitivity = measured / assigned). The drift correction is based on linear interpolation to the low standard.

Conclusions

Note that results presented here are associated with single examples of standard production units. The performance of these specific units should not be taken as representative of all production units, for which our published specifications apply.

- LI-7810 - CH_4 drift <0.1 ppb/day, LI-7815 CO_2 drift <0.1 ppm/day.
- Daily calibration is sufficient.
- High/low standard ratio drift <0.02 % over two-weeks
- A single near ambient concentration standard is sufficient. High bracketing standard not required.
- These experiments confirm the suitability of the LI-7810 and LI-7815 instruments for long-term measurements of atmospheric methane and carbon dioxide respectively.

Acknowledgements

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