Long-Term Atmospheric Monitoring of Background CH_4 and CO_2 at Mace Head Atmospheric Research Station, Ireland Using LI-COR LI-7810 and LI-7815 Trace Gas Analyzers

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Introduction

Global CO_2 and CH_4 monitoring requires instruments that meet 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 a six-month demonstration at the Mace Head Atmospheric Research Station, Carna, County Galway, located on the far west coast of Ireland. Here, the two instruments were operated in parallel with a $CH_4/CO_2/CO/H_2O$ analyzer, permanently installed at the facility, which reports data to both Integrated Carbon Observation System (ICOS) and World Meteorological Organization Global Atmosphere Watch (WMO GAW) networks. This summary describes the deployment of the LI-7810 and LI-7815 trace gas analyzers at the Mace Head facility, covering installation, data handling, calibration strategy, and measurement results, and presents in its conclusion that both instruments, in combination with an appropriate calibration strategy, meet instrument performance requirements for collection and submission of data to ICOS and WMO GAW networks.

Analyzer Specifications

Specification	LI-7810	LI-7815
Gases measured	$CH_4/CO_2/H_2O$	CO_2/H_2O
Primary, high-precision analyte	CH_4	CO_2
Concentration range	0-100 ppm	0-10,000 ppm
Precision (1σ, 1 second averaging)	0.6 ppb	0.1 ppm
Precision (1σ, 5 second averaging)	0.25 ppb	0.04 ppm
Drift (24 hours)	<1 ppb	<0.2 ppm
Response time (T_{10}-T_{90})	<2 seconds	<2 seconds

Instrument Stability and Precision

LI-7810 $CH_4/CO_2/H_2O$

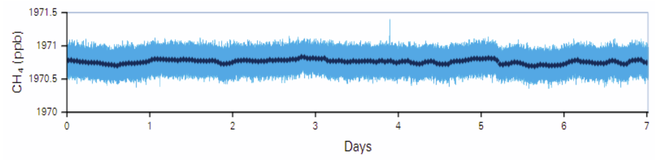

Chart 1. The instrument was operated constantly over a 7-day period with a continuous flow of reference gas. The blue line shows 1-second measurements; the dark blue line shows a 50-minute block average. The LI-7810 provides high precision CH_4 measurements. CO_2 is recommended for soil flux measurements only due to spectral features being measured.

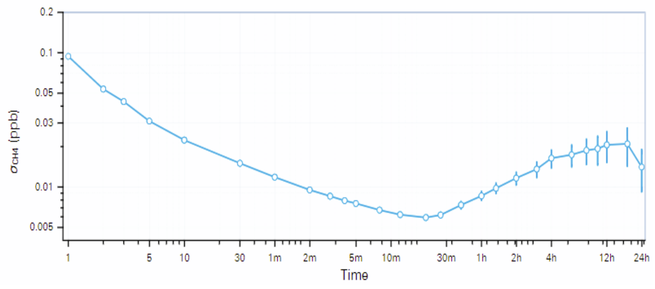

Chart 2. Allan deviation plots for the LI-7810 model. The plot shows precision starting at 1-second signal averaging, with improved precision as averaging time increases. Error bars represent 68% (±1σ) confidence intervals based on number of averaged time series available at each time.

LI-7815 CO_2/H_2O

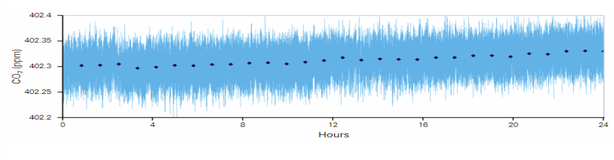

Chart 3. The instrument was operated constantly over a 24- hour period with a continuous flow of reference gas. The blue line shows 1-second measurements; the dark blue diamond-line shows a 50 minute block average. The LI-7815 provides high precision CO_2 measurements.

Chart 4. Allan deviation plot of CO_2 measurements from an LI-7815. The plot shows precision starting at 1-second signal averaging, with improved precision as averaging time increases. Error bars represent 68% (±1σ) confidence intervals based on number of averaged time series available at each time.

Mace Head Atmospheric Research Station Study

Previous independent testing by ICOS Atmosphere Thematic Centre and Scripps Institution of Oceanography represented the first steps to showing that the LI-7810 and LI-7815 are suitable for long-term background measurements of atmospheric CH_4 and CO_2, respectively. Both studies were based on relatively short-term tests, up to a maximum of approximately six weeks. The longer-term test at Mace Head shows additional confidence in terms of data stability and inter comparability, as well as reliability and convenience for continuous monitoring applications. Results from this study corroborate the conclusions from these earlier tests and show that the instruments are suitable for longer-term deployments.

Measurements are taken within the context of the ICOS framework and the associated gas analyser performance specification as shown in Table 1.

Component	Guaranteed Specification Range	Precision[1] *Std. dev. (1-σ); 1' / 60' average raw data*	Repeatability[2] *Std. dev. (1-σ); 10' average raw data*
CO_2	350 - 500 ppm	< 50 ppb / 25 ppb	< 50 ppb
CH_4	1700 - 2900 ppb	< 1 ppb / 0.5 ppb	< 0.5 ppb

Test conditions: dry air; room temperature: 20 °C ± 2°C; room pressure: atmospheric pressure with a natural variation.

[1] Measuring a gas cylinder (filled with dry natural air) over 25 hours; first hour rejected (stabilization time).
[2] Measuring alternately a gas cylinder (filled with dry natural air) during 30 minutes and ambient air (not dried, except for O_2 measurement) during 270 minutes over 72 hours. Statistics based on the last 10 minute average data of each 30 minute cylinder gas injection (first 20 minutes rejected as stabilization time).

Table 1: *Gas analyzer performance required by ICOS (as of June 2020)*

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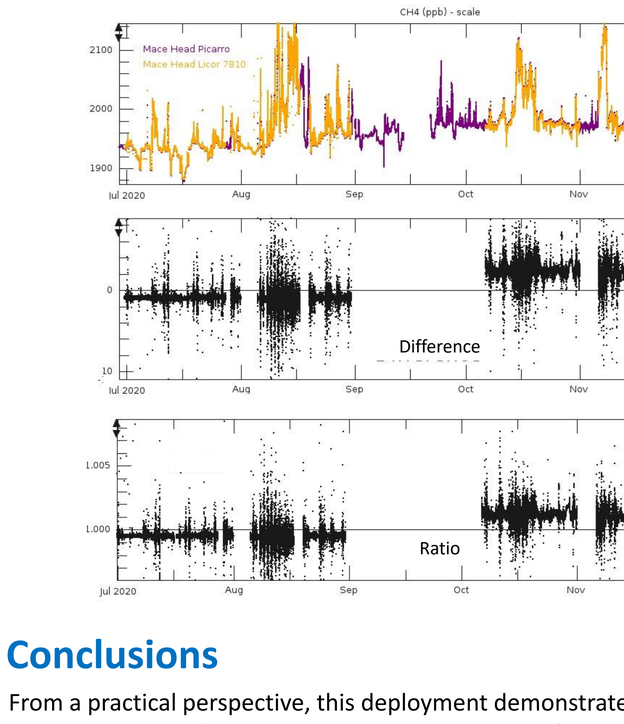
Experimental Set-up



The experimental objectives are defined as follows:

- Compare and contrast instrumental precision for repeated tank analysis.
- Understand the magnitude of any instrumental drift.
- Contrast performance of instruments under different water removal regimes.
- Understand the effect the above have on ambient monitoring.

Calibration strategy (following ICOS protocol):

- Two short-term target tanks (daily).
- One long-term target tank (monthly).
- Four calibration cylinders (monthly).

Tank	CH_4 (ppb)	CO_2 (ppm)
Short-term Target 1	1947.95	410.44
Short-term Target 2	1910.35	410.77
Long-term Target	2198.66	420.25
Calibration 1	2298.13	451.08
Calibration 2	2009.89	411.58
Calibration 3	1956.82	390.93
Calibration 4	1802.78	371.16

Results

Ambient CH_4 Comparison between LICOR LI-7810 and PICARRO G2401
(A)Mixing Ratios
(B)Difference
(C)Ratio

Conclusions

From a practical perspective, this deployment demonstrated how the LI-7810 and LI-7815 instruments can be installed into existing sampling and measurement network infrastructure, with minimal impact to gas sampling or data handling hardware, and GCWerks compatibility for both data collection and gas sample selection.

In this application, the LI-7810 $CH_4/CO_2/H_2O$ and LI-7815 CO_2/H_2O Trace Gas Analyzers show their compatibility with WMO GAW and ICOS instrument specifications and their ability to be used with varying calibration standards and protocols.

'Concerning measurement data, both instruments demonstrated that over the campaign, that with suitable calibration standards, protocols and a standard water removal regime, WMO GAW network inter-laboratory measurement compatibility goals can be achieved for ambient air sampling.'