High-Precision Continuous and Real-Time Measurements of Atmospheric Oxygen Using Cavity Ring-Down Spectroscopy

PICARRO

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Abstract

Oxygen is a major and vital component of the Earth atmosphere representing about 21% of its composition. It is consumed or produced through biochemical processes such as combustion, respiration, and photosynthesis. The observed variations of oxygen in the atmosphere are very small, in the order of the few ppm's. This presents the main technical challenge for measurement since a very high level of precision on a large background is required. Only few methods including mass spectrometry, fuel cell, and paramagnetic cell are capable of achieving it.
Here we present new developments of a high-precision gas analyzer that utilizes the technique of Cavity Ring-Down Spectroscopy to measure oxygen concentration. Its compact and ruggedness design combined with high precision and long-term stability allows the user to deploy the instrument in the field for continuous monitoring of atmospheric oxygen level. Measurements have a 1-σ 5-minute averaging precision of 1-2 ppm for O2 over a wide dynamic range of 0-50%. We will present comparative test results of this instrument against the incumbent technologies such as the mass spectrometer and the paramagnetic cell. In addition, we will demonstrate its long-term stability from a field deployment at the Beromünster tall tower in Switzerland

Instrumentation

Picarro Oxygen analyzer, G2207-*i*, features:
- Cavity Ring Down Spectroscopy (CRDS) Technology
- Measure simultaneously [O_2] and [H_2O]
- 1 PPM level of precision for [O_2]
- High stability, low calibration frequency

Figure 1. Picarro G2207-*i* Analyzer

The analyzer contains two lasers that measure Oxygen at the absorption line: 7878.806 cm^{-1} and H_2O absorption line: 7817 cm^{-1}

As illustrated in Figure 2, CRDS measures the exponential decay (ring-down) of the optical power circulating in a high-finesse resonant cavity. The absorption coefficient of the cavity is calculated based on the measured decay time cosntant. The cavity is kept at constant pressure and temperature: P = 255 torr and T = 45° C.

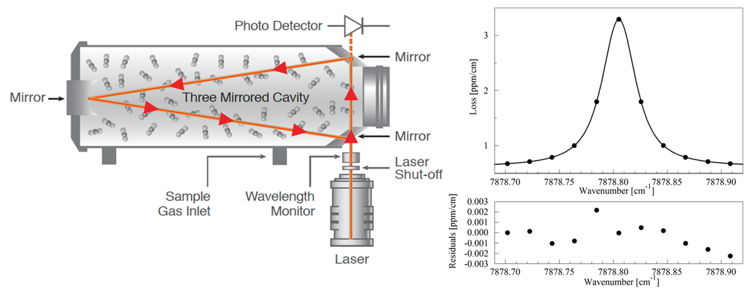

Figure 2. Schematic CRDS cavity and absorption spectrum.

The Allan variance of repeated concentration measurements was used to characterize precision. The analyzer was attached to a cylinder of synthetic air and made repeated measurements over the course of three days. Figure 4 shows the Allan standard deviation (square root of Allan variance) as a function of averaging time, τ. The precision of the concentration measurement reaches 1 ppm, equivalent to 5 per meg in the O_2/N_2 ratio, after 200s of averaging. The Allan standard deviation continues to fall, following the $\tau^{-1/2}$ line that corresponds to ideal averaging of white noise, until it reaches minimum of 0.4 ppm at about 1 hour averaging, and remains below 1 ppm for several hours. Also notable is the excellent long-term stability of the measurement.

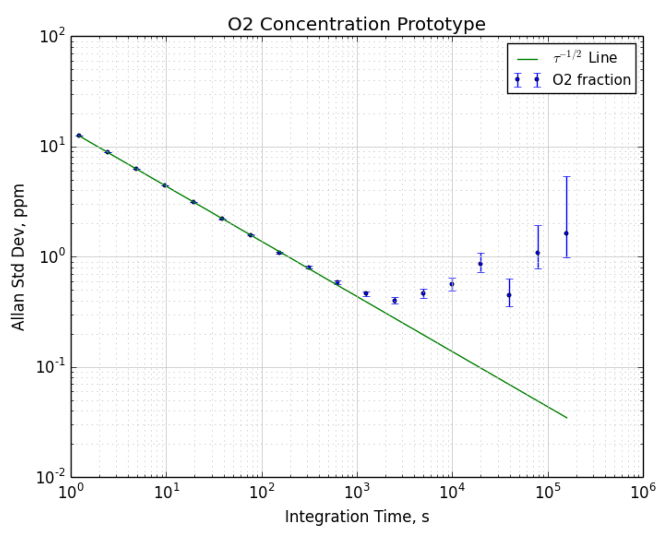

Figure 4. Allan standard deviation vs. time for the molecular oxygen concentration measurement.

Evaluation at University of Bern

The G2207-*i* was tested at the University of Bern in the fall on 2016. The objective of the evaluation was to compare its performance against those from a paramagnetic cell analyzer and a Mass Spectrometer.

Illustrated in Figure 4, the experimental setup consists of:
1) An intake on the roof of the lab building sampling outdoor air.
2) A drying system to remove water from outdoor air sample.
3) A conditioning unit that controls and maintains constant the sample pressure and temperature (mainly for the Paramagnetic system)
4) Part of the sample feed feeds to the Paramagnetic cell analyzer and the other part goes into the Picarro analyzer.

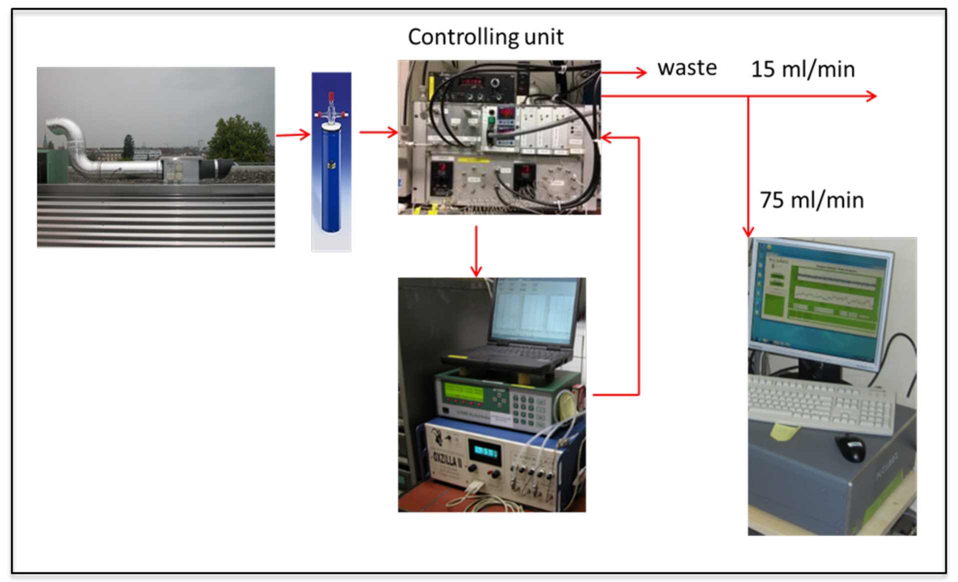

Figure 4. Test Setup at the University of Bern

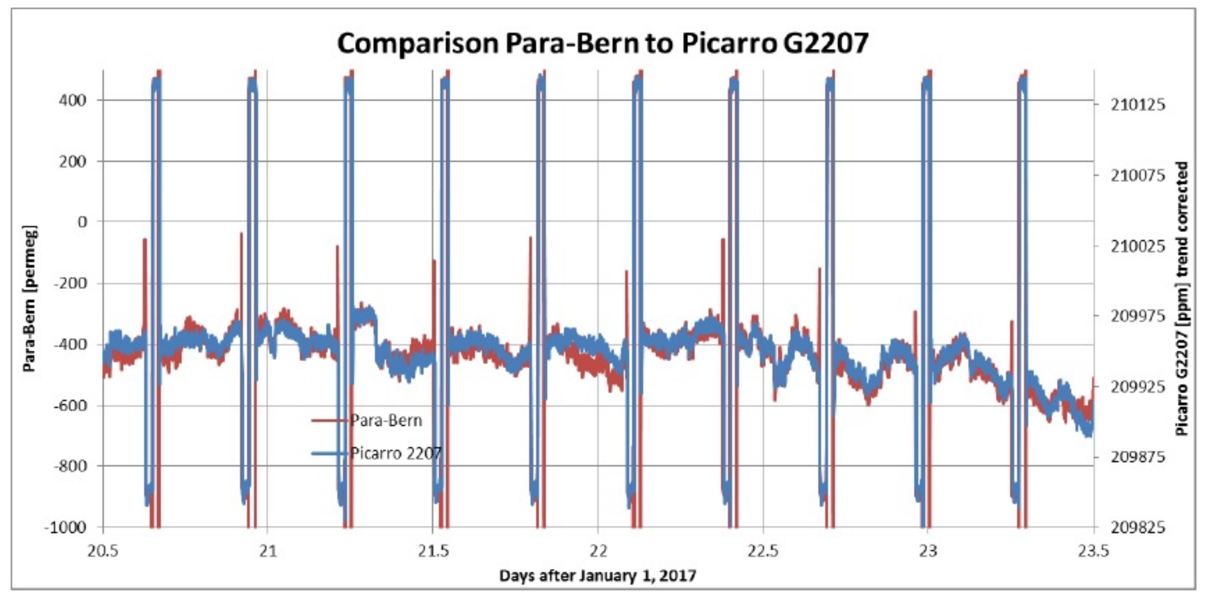

Figure 5. Calibrated dried outside air measurements from Picarro and Paramagnetic cell analyzer.

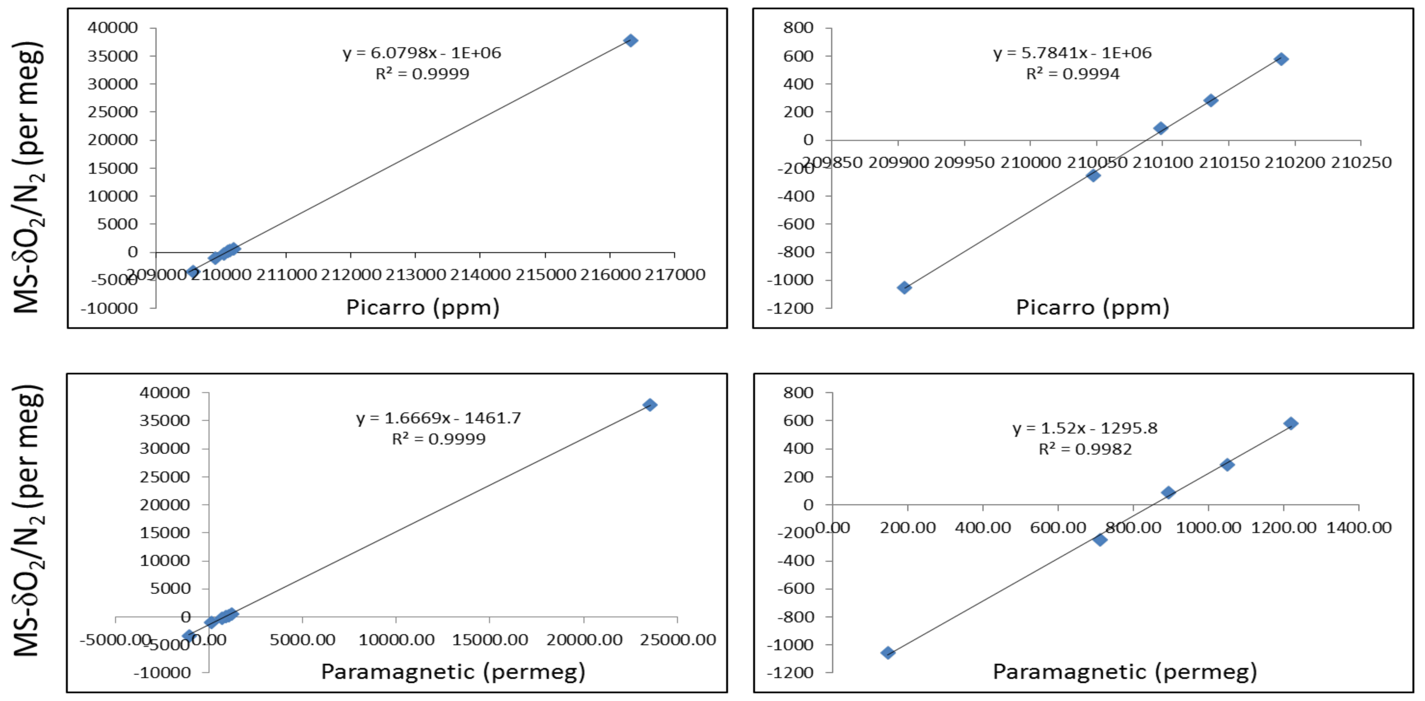

Figure 6. Measurement Correlation: MS vs Picarro and MS vs Paramagnetic

Figure 5 shows continuous measurements of outside air for 3 days with a calibration every 6 hours using two gas standards. Paramagnetic analysis are reported in permeg units (O_2/N_2) while Picarro measurements are in ppm [O_2]. During the test period, the outside O_2 concentration varies from 209875 to 209975 ppm. The results demonstrate very good correlation between the two instruments.
In Figure 6, results of 6 gas standard measurements on Picarro, Paramagnetic and MS are reported in plots that compare MS vs Picarro and MS vs Paramagnetic. The two plots on the right-hand side are re-scaled graphs that focus on the measurements at the lower [O_2] range. Overall, there is a good correlation of the Picarro and Paramagnetic cell with MS where the R^2 is 0.9999. At lower range, the Picarro have a slightly better correlation with MS than the Paramagnetic cell (0.9994 vs 0.9982).

Beromünster Tower Experiment

Also in the fall of 2016, the G2207-*i* was deployed at Beromünster tall tower in Switzerland. The site has a permanent Picarro G2401 to measure CH_4, CO_2, and CO. The tower has five sampling points at different heights ranging from 12 m to 212 m.

The objective was to evaluate the height dependence of changes in CO_2 and O_2 concentrations.

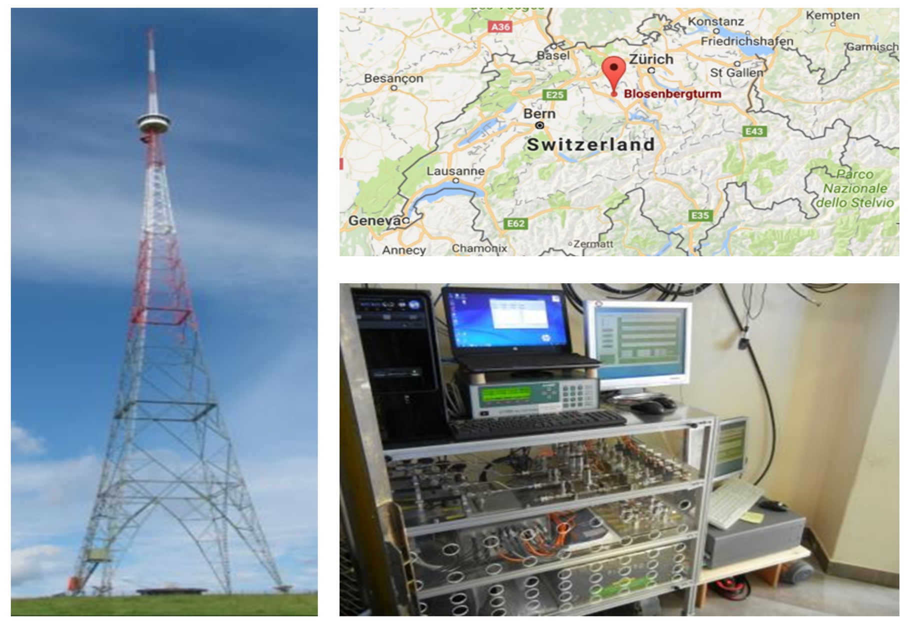

Figure 7. Beromünster Tall Tower

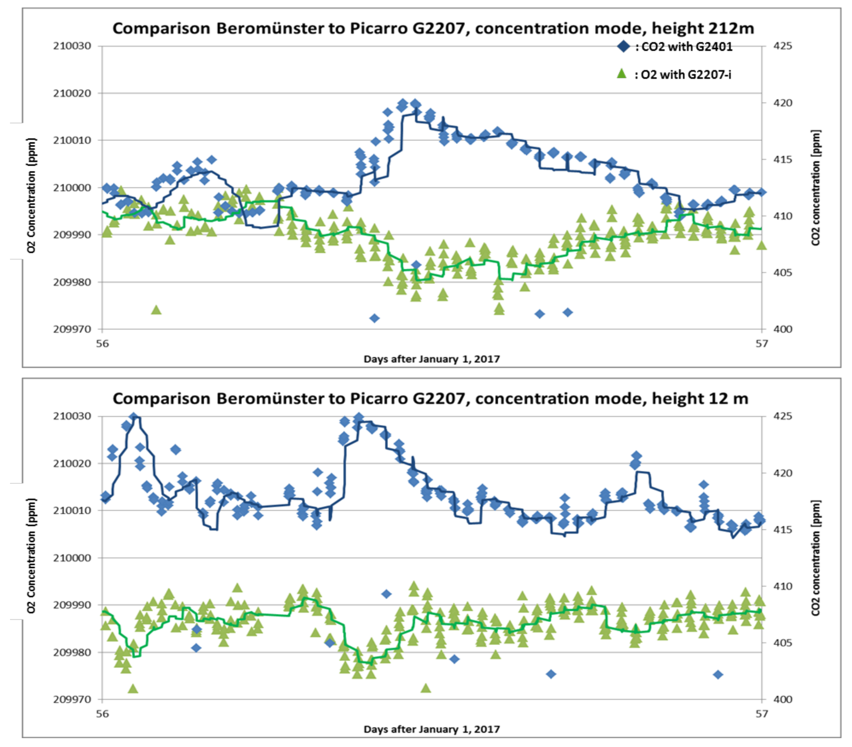

Figure 7. CO_2 and O_2 measurements at 12 and 212 m.

- The blue and green points respectively represent the CO_2 and O_2 measurements. The lines correspond to 5-min running average. The results shows the anti-correlation between [CO_2] and [O_2].
- At high altitude, [CO_2] is lower while [O_2] is higher than at low altitude.
- At low attitude, both concentrations shows shorter variations and sharper peaks.

- [CO_2] is plotted against [O_2] at 12 and 212m and a linear fit is applied.
- At high altitude, the correlation factor (slope) is ~-1.58. This value corresponds to those found in fossil fuel process where CO_2 is produced from combustion.
- At low attitude, the correlation factor is ~ -0.98 which indicative to biological process.

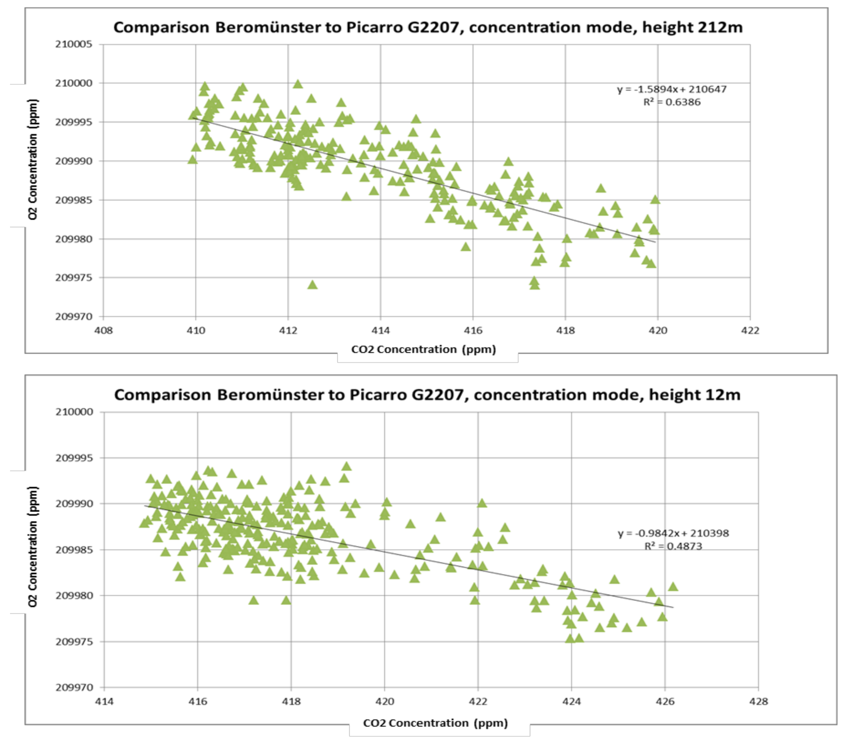

Figure 8. CO_2 and O_2 correlations at 12 and 212 m.

Conclusions

The G2207-*i* demonstrates very good measurement correlations of gas standard measurements and outside air analysis against Paramagnetic, MS with the main added benefit that the Picarro CRDS is more stable and requires less frequent calibration/check (every 6-12 hr for CRDS vs every 12 min for Paramagnetic).
The Picarro analyzer provides high precision measurement with a standard deviation of 1-2 ppm allowing scientists to observe small variations in the atmospheric oxygen concentration.