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

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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.

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 1.0-5.0 minute averaging precision of 1.2 ppm for 2 ppm 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 Beromünter tall tower in Switzerland.

**Instrumentation**

Picarro Oxygen analyzer, G2207-i, features:
- Cavity Ring Down Spectroscopy (CRDS)
- Technology
- Measure simultaneously [O2] and [H2O] levels
- 1 ppm level of precision for [O2]
- High stability, low calibration frequency

The analyzer contains two lasers that measure Oxygen at the absorption line: 7878.806 cm⁻¹ and H2O 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 constant. The cavity is kept at constant pressure and temperature: P = 255 torr and T = 45 °C.

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. The precision of the concentration measurement reaches 1 ppm, equivalent to 5 per meg in the O2/N2 ratio, after 200s of averaging.

The Allan standard deviation continues to fall, following the 1/√t 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.

**Evaluation at University of Bern**

The G2207-i was tested at the University of Bern in the fall of 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.

**Beromünter Tower Experiment**

Also in the fall of 2016, the G2207-i was deployed at Beromünter tall tower in Switzerland. The site has a permanent Picarro G401 to measure CH4, CO2, 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 CO2 and O2 concentrations.

**Conclusions**

The G2207-i demonstrates very good measurement correlations of gas standard measurements and outdoor 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.