

A23A-0186: 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. Although atmospheric oxygen is not a greenhouse gas, it can be used as a top-down constraint on the carbon cycle¹. The variation observations of oxygen in the atmosphere are very small, in the order of the few ppm's. This presents the main technical challenge for measurement as a very high level of precision is required and only few methods including mass spectrometry, fuel cell, and paramagnetic are capable of overcoming 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 ppm for O₂ over a wide dynamic range of 0-40%.

Principle of CRDS

As illustrated in Figure 1 and 2, CRDS measures the exponential decay (ring-down) of the optical power circulating in a high-finesse resonant cavity. It was devised to enable measurement of extremely small optical loss, free from the limitations of laser technical noise. From the measured decay time constant, τ , the absorption coefficient of the cavity, in units of cm⁻¹, is computed according to

$$\alpha = 1/\tau c,$$

Where c is the speed of light.

Loss measurements at multiple frequencies generate a spectrogram of the gas in the cavity, as shown conceptually in Figure 3.

The optical absorption is proportional to concentration of the absorbing species; if the temperature and pressure of the sample is known, the mole fraction of the absorbing species can be deduced from the absorption spectrogram. The Picarro analyzers actively stabilize the temperature and pressure of the sample to enable precise concentration measurements.

The area under the absorption line (integral of absorption over frequency) is the quantity most directly related to molecular concentration; measuring the integrated absorption requires an accurate and stable frequency axis. By measuring the cavity loss on a series of modes with fixed cavity length, we obtain a molecular absorption spectrum with a precisely-known and stable frequency axis, allowing precise determination of the integrated absorption.

References:
¹R. F. Keeling and S. R. Sheriz, "Seasonal and interannual variations in atmospheric oxygen and implications for the global carbon cycle," *Nature*, **358**, 723-727 (1992).
²http://climatechange.ucar.edu/sites/default/files/styles/medium_lightbox_display/public/key_figures/climate_data_set/fo_scripps.png?itok=XsdHn16p
³http://scrippsco2.ucsd.edu/sites/default/files/pdfs/plots/daily_avg_plots/fo.pdf

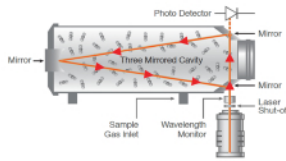


Figure 1. Schematic CRDS cavity.

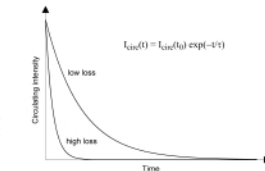


Figure 2. Schematic representation of a cavity ring-down measurement.

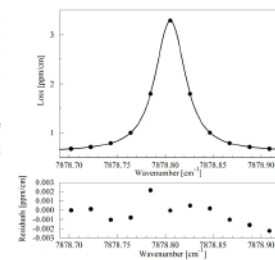


Figure 3. O₂ spectra are collected in groups of 229 ring-downs in 1 sec.

Precision Test

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 O₂/N₂ 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.

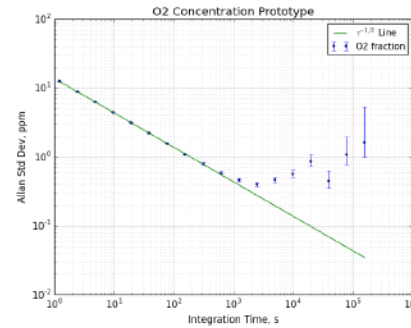


Figure 4. Allan standard deviation vs. time for the molecular oxygen concentration measurement.

Pressure and Temperature Sensitivities

Pressure and temperature in the CRDS cavity is precisely controlled to the following tolerances: +/- 0.0002 atm and +/-0.005 degC.

In addition, the spectroscopy is designed to be as insensitive as possible to variations in pressure and temperature.

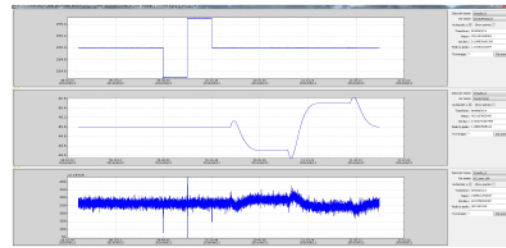


Figure 5. Sensitivity was measured by changing P and T set-points while measuring zero air

Summary, expressed as fractional change in mole fraction, f :

$$-\frac{1}{f} \frac{df}{dP} = 1.3 \times 10^{-5} \text{ Torr}^{-1}$$

$$-\frac{1}{f} \frac{df}{dT} = -2.1 \times 10^{-4} \text{ K}^{-1}$$

Water Correction

Water vapor concentration is highly variable in ambient air and can affect oxygen measurements by cross-broadening and diluting it.

Therefore, a second laser tuned to absorption line at 7817 cm⁻¹ is used to measure water. 45 ring-downs are devoted to measure water concentration to a precision better than 1 ppm.

Based on figure 6, a water correction model is determined and applied to the oxygen concentration measurement.

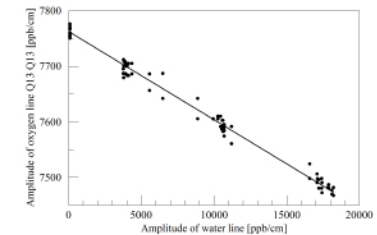


Figure 6. Oxygen amplitude vs water amplitude

Conclusion

We have demonstrated an absorption spectrometer using CRDS which achieves relative precision of 5 per meg for the absorption line strength in an integration time of 200s, which allows us to measure the oxygen mole fraction with a precision of 1 ppm in 200s. The long-term stability of the spectrometer is such that the Allan variance remains at this level for hours. Pressure and temperature sensitivities have been optimized to be negligible while water effect is corrected.

The precision that we have demonstrated here is sufficient to enable important geophysical measurements. Keeling and coworkers have shown how measurements of the O₂/N₂ ratio, together with CO₂ mole fraction, can be used to better understand the global carbon dioxide budget. In particular they show how it is possible to distinguish processes such as photosynthesis, respiration, and combustion which convert atmospheric oxygen to carbon dioxide and vice versa, from dissolution of carbon dioxide in ocean water, with subsequent conversion to carbonate and bicarbonate minerals. Figure 7 illustrates the closely linked annual cycles of atmospheric oxygen and carbon dioxide reported on the Scripps Institution of Oceanography website².

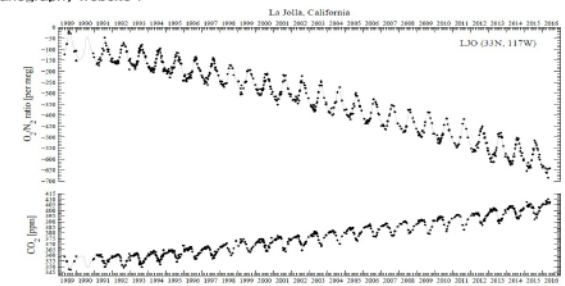


Figure 7. Measurements of $\delta(\text{O}_2/\text{N}_2)$ and CO₂ mole fraction made at La Jolla, CA, illustrating the variability of atmospheric oxygen. Reproduced from Reference 3.