HIGH-PRECISION CONTINUOUS AND REAL-TIME MEASUREMENT OF OXYGEN USING CAVITY RING-DOWN SPECTROSCOPY FOR PHOTOSYNTHETIC LIGHT AND CO₂ RESPONSE CURVES

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1. ABSTRACT

Photosynthesis is a complex process that consumes carbon dioxide and water to produce oxygen and glucose. Studies to investigate leaf-level photosynthetic activity have been conducted using systems that control certain parameters such as light intensity or partial pressure of CO₂. For instance, the LI-COR LI-6800 Portable Photosynthesis System enables the user to control and measure light, temperature, CO₂ and water vapor concentrations. Measurement of O_2 fluxes concurrent with CO_2 exchange and other parameters is a technical challenge since a very high level of precision on a large O_2 background is required. Only few analytical methods including mass spectrometry, fuel cell, ultraviolet and paramagnetic cells can achieve the required high-precision O_2 analysis.

Here we present new developments of a high-precision gas analyzer that utilizes the technique of Cavity Ring-Down Spectroscopy to measure oxygen concentrations. Its compact and rugged design combined with high-precision and long-term stability allow 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 dynamic range of 0-25%. We present collaborative work with LI-COR where we coupled the Picarro G2207-i O₂ analyzer with the LI-6800 Portable Photosynthesis System to enable O₂ analysis for laboratory studies of photosynthesis. To validate the setup, we conducted light and CO_2 response experiments.



3. METHOD

Flow configurations

2. INSTRUMENTATIONS

CRDS Technology and Picarro G2207-i Analyzer

Cavity Ring-Down Spectroscopy (CRDS) Technology utilizes the unique infrared absorption spectrum of gas-phase molecules to quantify the concentration of Mirror → (and sometimes isotopes of) H_2O , CO_2 , CH_4 , N_2O , $CH_2O, NH_3.$

CRDS Features:

- Small 3-mirrored cavity ~ 35 cc
- Long effective path-length (> 10 km)
- Time-based measurement
- Laser is switched on and off, and scanned across wavelengths

The Picarro G2207-*i* analyzer uses the CRDS technology to measure continuously $\delta^{18}O$ in O_2 and O_2 concentrations.

G2207-*i* Performance Specifications:





4. RESULTS

Light-response and CO₂ Response curves



[O₂] Mode

Precision, dry [O ₂] at ambient concentration $(1-\sigma, 5 \text{ sec}/5 \text{ min}, \text{ at } 21\% \text{ O}_2)$	<20 ppm/<2 ppm
Max Drift at STP O ₂ (over 24 hrs, peak-to-peak, 1 hr interval average, at 21% O ₂)	<6 ppm
[O ₂] Operating Range	5-25%
Precision [H ₂ O] (1-σ, 5 sec)	5 ppm + 0.1% of reading

LI-6800 Portable Photosynthesis System

The LI-COR LI-6800 Portable Photosynthesis System probes the carbon fixation reactions of photosynthesis by calculating fluxes for CO_2 (assimilation) from the difference in measured concentrations of CO₂ and H_2O entering and exiting a leaf cuvette.

- Flow control
- CO₂ control
- Water vapor control
- Temperature control



- CO₂ analysis (IRGA)
- H₂O analysis (IRGA)
- Fluorometer

REFERENCES

[1] Von Caemmerer. Biochemical Models of Leaf Photosynthesis. CSIRO publishing, 2000.

Incident Light Intensity (umol m⁻² s⁻¹)

Inter-cellular CO₂ concentration, C₁ (umol CO₂ mol air⁻¹)

Electron transport rate (ETR) for Zea mays



5. CONCLUSION

- High-precision continuous and real-time measurement of O₂ with the Picarro G2207-i (<2ppm 1- σ uncertainty with 300 seconds averaging)
- Straightforward coupling of the G2207-i O₂ analyzer and the LI-COR LI-6800 Portable Photosynthesis System for combined O_2 and CO_2 measurements for leaf-level physiological research
- Light response curves for the C_3 plant *Phaseolus vulagris* (bean) and CO_2 response curve for the C₄ plant Zea mays (corn) are in line with expectations (expected stoichiometry for $CO_2:O_2$ is about 1, see [1, 2])
- Electron transport rates (ETR) for Zea mays from fluorescence measurements and derived from CO_2 and O_2 gross fluxes agree well.







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