

Development of IR²-Hi5 multipass MIR isotope analyzer for plant photosynthesis and respiration study

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Abstract: A fast, low-sample-volume mid-infrared carbon isotope ratio analyzer was developed and characterized. It's employed to demonstrate real-time monitoring the CO₂ concentration and carbon isotope fractionation in plant photosynthesis and respiration processes.

OCIS codes: (300.6340) Spectroscopy, infrared; (120.6200) Spectrometers and spectroscopic instrumentation.

1. Introduction

The carbon isotope analysis is one of powerful methods to perform the environmental research [1]. It's desired to have an isotope analyzer that can do high-precision in-situ real-time measurement at a low gas sample consumption and fast sampling rate. The benchmark Isotope Ratio Mass spectrometer (IRMS) provides an excellent precision at low sample consumption. However, the critical work environmental requirement make IRMS unsuitable for field deployment. Optical absorption spectroscopy based isotope ratio analyzers can be field deployed due to the inherent stability of optical absorption spectroscopy. The typical working principle is that a laser beam propagates in a cell through which the gas sample flows at the same time, and the absorption spectrum is obtained by detecting the output laser beam. Because the laser beam travels in free space inside the cell, the cell has a large volume (>10s ml) and thus requires high gas volume sample and also inherently limits the sampling rate. The large cell volume limits its application in the situation where only a small amount of gas sample (e.g. <10 ml) is available. Arrow Grand Technologies solved this problem by coupling a MIR laser beam into a hollow waveguide (HWG) through which the CO₂ gas flows [2]. A single path commercial HWG isotope analyzer has been developed. Thanks to the low gas flow rate, it has been successfully integrated with a gas chromatography to do well-site carbon isotope analysis in the oil industry [3]. In order to measure the carbon isotope ratio at atmospheric CO₂ concentration level (~400 ppm) for the environmental research, we lengthened the optical path by updating 1 pass HWG to 5 passes and built an IR²-Hi5 multipass isotope analyzer.

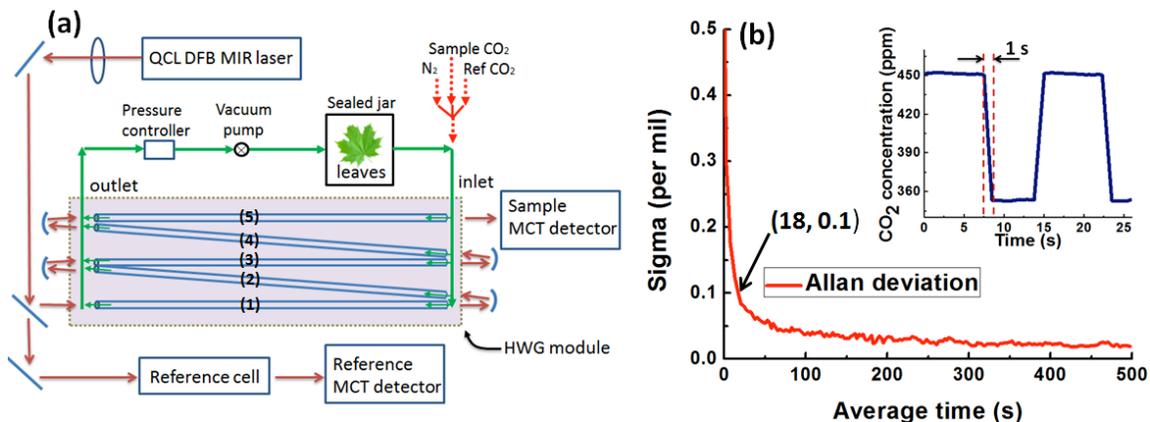


Figure 1. (a) Schematic diagram of IR²-Hi5 multipass isotope analyzers and experimental set up. (b) Allan deviation of the isotope analyzer. Inset: rise/fall time plot of CO₂ concentration in the calibration experiment.

Here, we report the analyzer's performance (HWG coupling efficiency, sampling rate, sample flow rate, Allan deviation) and demonstrate its application in photosynthesis ecology study.

2. Experimental setup

Figure 1(a) illustrates the experimental setup for the IR²-Hi5 multipass isotope analyzer and the relevant tubing. The QCL DFB MIR laser beam is split into 2 beams. One beam propagates through a reference cell filled with reference CO₂ and gets detected by a reference MCT detector. The second beam is coupled into the 1st HWG (30 cm in length) by a lens and then redirected by mirrors to travel through the 2nd, 3rd, 4th, and 5th HWG in sequence. The gas is

pumped by a vacuum pump and flows through HWGs. The gas pressure in the HWGs is 50 Torr and controlled by a pressure controller. N₂ is used for baseline collection. For the long term drift calibration, another reference CO₂ (marked Ref CO₂ in Fig. 1(a)) is used to periodically calibrate the analyzer. In the photosynthesis and respiration experiment, 3 pieces freshly cut orange tree leaves are sealed in a 450 ml jar. The gas in the jar is pumped into the HWG for spectroscopy sampling and finally goes back to the jar at a flow rate of 10 standard cubic centimeters per minute (sccm). 3 different lighting conditions are employed.

3. Results and Discussion

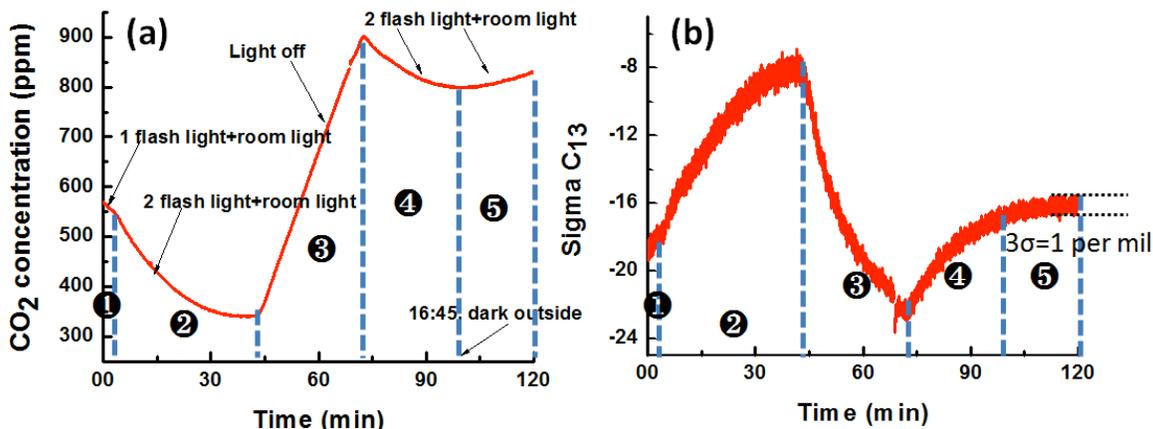


Figure 2. (a) CO₂ concentration and (b) sigma ¹³C (δ¹³C) changes in various lighting conditions.

The coupling efficiency of the laser beam into the HWG from the free space is 75% for the #1 HWG. Since HWG #1 purifies the single mode laser beam, HWGs #2, #3, #4, and #5 have a relative higher coupling efficiency (85%), which is the highest reported so far and enables further extension for the absorption pathlength. A reference CO₂ is used to calibrate the drift every 8 s. As shown in the Allan deviation in Fig. 1(b), the isotope measurement precision reaches 0.3 per mil at an average time of 1 s, and 0.1 per mil at an average of 18 s. By adding a 2nd detector after the first path (not shown here), the analyzer has a high dynamic measurement range of CO₂ concentration (300-40,000 ppm).

As described in the experimental setup section, the freshly cut 3 pieces of orange tree leaves are sealed a jar. The δ¹³C and CO₂ concentration in the jar are monitored in real time in different lighting conditions. Figure 2(a) and 2(b) show 5 stages that CO₂ concentration and carbon isotope changes differently. The measurement precision is 0.3‰/Hz^{1/2} and 100ppb/Hz^{1/2}. When the light is on, we find that the concentration of CO₂ in the jar decreases and δ¹³C increases. This is because CO₂ is consumed in the photosynthesis process and more ¹²C is absorbed due to isotope fractionation [4]. In comparison, since the respiration generates CO₂, and more δ¹³C is released to the jar from the leaves [5], CO₂ increases and δ¹³C decreases when the light is off.

In conclusion, we develop an IR²-Hi5 multipass isotope analyzer that is able to perform in-situ, real-time measurement of CO₂ concentration and carbon isotope in plants photosynthesis and respiration processes.

4. References

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