Correcting for Changes in O_2 Concentration in the LI-6400 Photosynthesis System

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ABSTRACT

In this study, we characterized the effects of oxygen concentration on the LI-6400 IRGA and flow meter. In the worst case (removing all oxygen), the effect on the LI-6400 is to **a)** increase the apparent CO_2 by about 2 parts per million at ambient CO_2, **b)** increase the true flow through the system (due to decreased viscosity of the air) by 2.7%, and **c)** cause a small error (less than +0.4%) in the LI-6400 flow meter reading. In order to correct the apparent CO_2 concentration for O_2 concentration, the effective pressure of the air mixture must be calculated from the product of the partial pressure of each constituent gas and its corresponding band broadening coefficient. We found the apparent band broadening coefficient for oxygen to be 0.9 for the LI-6400. We present the equations necessary to make corrections online or after the fact.

INTRODUCTION

For certain gas exchange studies, it is important to carry out experiments under non-photorespiratory conditions by lowering the oxygen concentration from 21% to 1 or 2%. Changing the oxygen concentration affects the pressure broadening of CO_2 infrared absorption lines and thus has an influence on infrared gas analyzers (IRGAs).

To correct the apparent CO_2 concentration for the change in background O_2 concentration, the effective pressure of the air mixture must be calculated. The form of the LI-6400 calibration equation (LI-COR, 1998) for CO_2 is:

$$C = B(o,w)\frac{T}{273.15} f\left(\frac{vP}{101.3B(o,w)}\right) \tag{1}$$

Where *C* is CO_2, f() is the calibration polynomial, *v* is raw signal (mV), *T* is temperature (K), *P* is pressure (kPa), *o* is oxygen mole fraction, *w* is water mole fraction, and *B(o, w)* is the band broadening factor, which is a function of water vapor concentration *w* (mol H_2O/mol air):

$$C(o,w) = 1 + (a_o - 1)o + (a_w - 1)w \tag{2}$$

The LI-6400 uses an empirically based water vapor band-broadening coefficient a_w of 1.5. The present objective is to determine the value of a_o. From Burch, et. al. (1962), we predict it to be approximately 0.8.

MATERIALS AND METHODS

An LI-6400 Portable Photosynthesis System with a 6400-01 CO_2 Injector was used in this study, along with four certified (±1%) tanks of varying oxygen concentration in nitrogen: 21%, 10%, 2%, and 0 (pure nitrogen). Figure 1 illustrates the plumbing: Tank airflow was controlled by each tank's regulator and an additional needle valve to reduce the flow to about 2 lpm. The flow from the tank was fit into a T, with one end venting to the room, and the other end connected to the air inlet of the LI-6400. To ensure sufficient tank over-pressure, the vented airflow was monitored with a rotameter. The LI-6400 chemical columns of soda lime and Drierite were used to completely scrub the tank air of any CO_2 and water vapor. To generate a stable, fixed, CO_2 concentration, the internal CO_2 mixer was used, operated at fixed control voltage set points. Before and after each CO_2 measurement, the flow was connected to a precision flow meter (Brooks (www.emersonprocess.com/brooks) Vol-U-Meter® Model 1057, modified with optical encoder switches to automatically measure piston rise times) to determine the true flow through the system, and also the effect of oxygen on the LI-6400's flow meter. The LI-6400 software was modified to compute CO_2 concentration using 4 different band broadening coefficients (a_w 0.8, 0.85, 0.9, and 1, which is equivalent to no correction).

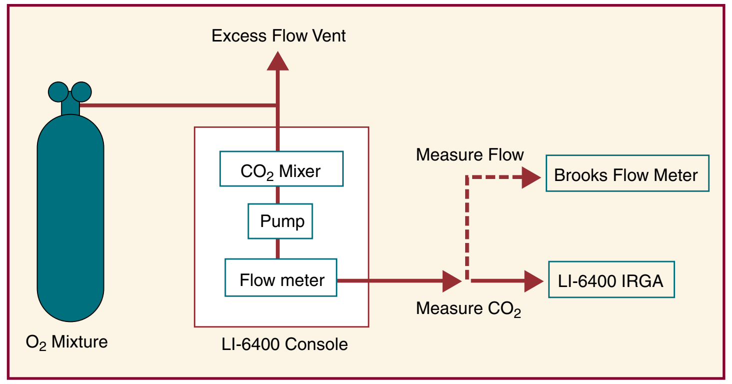

Figure 1. Flow schematic for the measurements.

RESULTS AND DISCUSSION

As the O_2 concentration is lowered, the viscosity of the air decreases and the flow rate of air through the CO_2 injector system increases. Figure 2 shows the relation between flow rate through the system as a function of oxygen concentration, normalized to the ambient (21%) case. This mixing factor is applied to the raw measured CO_2 values to compensate for these flow changes.

$$C_f = C_m(1.0286 - 0.0014\chi_o) \tag{3}$$

where C_f is flow corrected CO_2 , C_m is raw measured CO_2, and χ_o is oxygen concentration (%). The error in the LI-6400 flow meter was found to be less than +0.4% under oxygen-free conditions. Variation in C_f with oxygen is assumed due to band broadening effects. Figure 3 illustrates the flow correction, and also a band broadening correction with a value of a_w = 0.9. Figure 4 illustrates the effect of the band broadening correction with a range of values for a_o. The optimum value of a_o was chosen by plotting the slopes of the error plots in Figure 4 as a function of a_o, and finding the average intercept (Figure 5). The average intercept value is 0.9 (Table 1). This band broadening formulation (Equation 1) has been implemented in the LI-6400 in OPEN version 5.2.

A post-data collection correction can be formulated based on these measurements. This correction factor has the form

$$C = C_m(1 + (21 - \chi_o)F(C_m)) \tag{4}$$

where C is oxygen corrected CO_2, C_m is raw measured CO_2, and $F(C_m)$ is given by

$$F(x) = a\left(1 - e^{-bx}\right) \tag{5}$$

where a = 0.0010480, and b = 0.00087511. *F(x)* is shown in Figure 6, and was determined from the 21% oxygen measurements by differencing the flow corrected CO_2 values for a_o = 0.9 and a_o =1.0. There is an assumption of linearity with oxygen concentration.

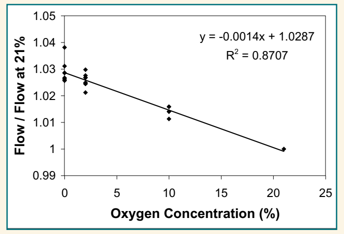

Figure 2. Effect of oxygen concentration on flow through the system.

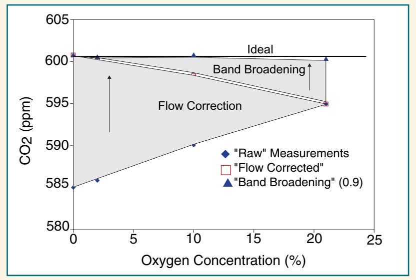

Figure 3. Illustration of the flow and band broadening corrections. Raw measurements were made at a CO_2 mixer set point of 2000 mV. At 21% oxygen, the resulting CO_2 concentration is about 595 ppm. As oxygen decreases, flow increases, and the constant rate of CO_2 injection is increasingly diluted, resulting in dropping concentrations, down to 585 ppm at 0% oxygen. The flow effect is removed by multiplying raw readings by the mixing factor (Equation 3). The flow corrected values show an apparent increase in CO_2 of about 15 ppm to 600 ppm, as oxygen decreases to 0%. Since the band broadening effect is proportional to oxygen concentration, the 0% oxygen value (600 ppm) becomes the standard; a perfect band broadening correction would transform the flow corrected values to 600 ppm at all oxygen concentrations (i.e., up to the line marked Ideal).

Table 1. Optimum band broadening coefficient values.

CO_2 µmol mol⁻¹	Intercept Value
250	0.895
415	0.909
601	0.896
1048	0.896
1610	0.906
2195	0.908
Average	0.902

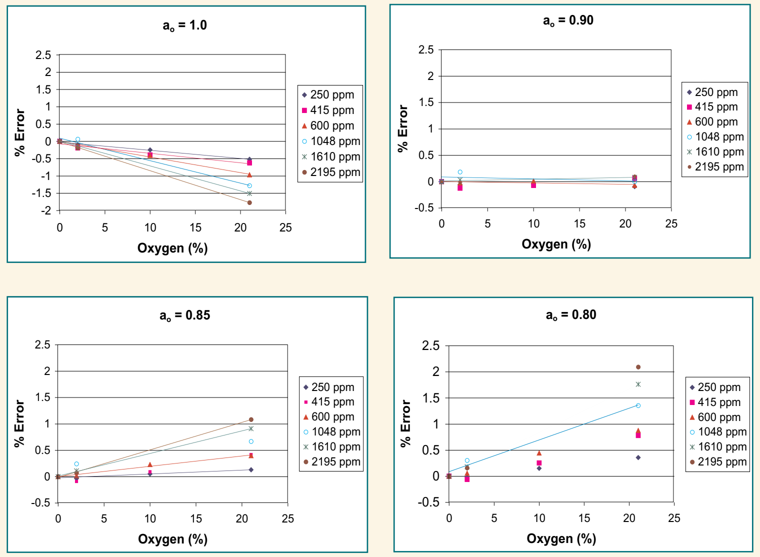

Figure 4. The effect of a range of band broadening coefficients for oxygen a_o on the apparent CO_2 concentration.

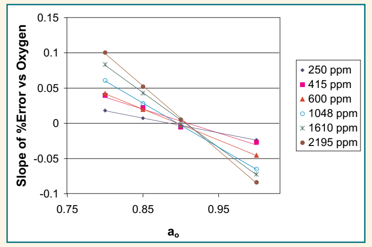

Figure 5. The optimum a_o is found by plotting the slopes of the error curves in Figure 4 as a function of a_o, and finding the X axis intercept.

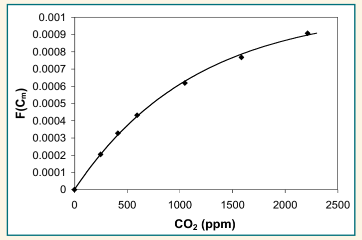

Figure 6. Plot of *$F(C_m)$*, used for post-measurement correction for oxygen concentration.

SUMMARY

The errors in the LI-6400 caused by varying oxygen concentration are negligible (0.4% for oxygen-free air). The errors caused in the LI-6400 IRGA are more significant (+2 ppm for oxygen-free air), but are compensated adequately by a band-broadening based solution that uses a band broadening coefficient of 0.9. This solution is part of OPEN 5.2 software for the LI-6400.

REFERENCES

Burch, D.E., E.B. Singleton, and D. Williams. 1962. Absorption line broadening in the infrared. *Applied Optics* 1:359-363.

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