Effects of temperature and pressure on CO_2 infrared absorption with special emphasis on problems resulting from operation at high flow rates.

D. K. McDermitt, R. D. Eckles, G.L. Biggs, and J .M. Welles.
LI-COR, Inc., Lincoln, NE 68504 USA

Introduction

LI-COR infrared gas analyzers are widely used in applications that require high air flow rates, often with air that comes into the analyzer at a temperature different from the analyzer optical cell temperature. This can cause errors when the optical cell temperature is used as an estimator of air temperature in CO_2 calculations. High flow rates also generate pressures within the optical bench that can degrade measurement accuracy.

A. Temperature effects

The purposes of this section are: (1) to examine how quickly air temperature equilibrates with optical cell temperature; (2) to show the magnitudes of CO_2 measurement errors that result from assuming air temperature equals cell temperature; and (3) to provide a way to estimate the appropriate average cell air temperature using the inlet air temperature, optical cell temperature, and flow rate.

Materials & Methods

A LI-COR gas analyzer optical cell was placed into a constant temperature recirculating oven. Inlet and outlet air stream temperatures, and internal temperatures of the inlet end and outlet end of the optical cell were measured with thermocouples placed as shown in *Diagram 1.*

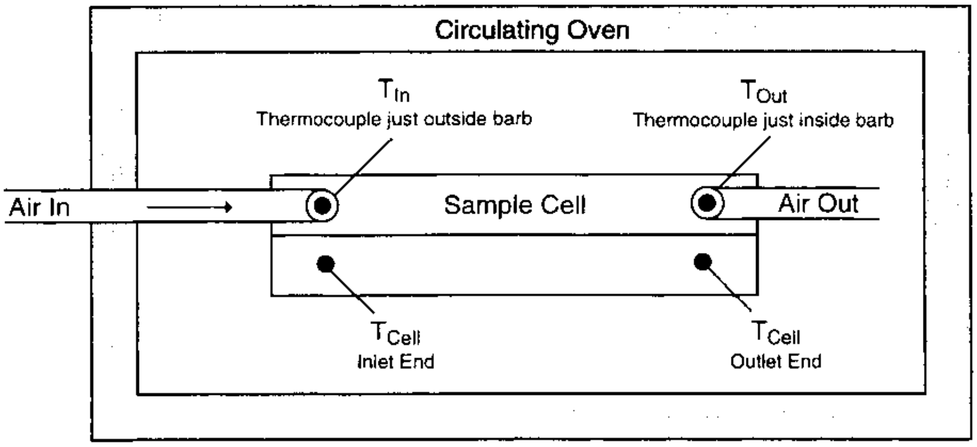


Diagram 1.
All volumetric flow rates were measured with a Tylan mass flow controller (Model FC-261) calibrated in standard liters per minute (SLPM), which is proportional to mass flow.

Results

Figure 1 shows inlet and outlet air temperatures and optical cell interior temperatures when the oven was set at 50 °C and the incoming room air was 24.5 °C. It can be seen that:

(a) The inlet air temperature drops sharply with increasing flow rate because it must flow through about 10 cm of warm tubing before reaching the air inlet thermocouple. The warm short tubing has a large effect on air temperature at low flow rates, but a only a small effect at flow rates above 2 SLPM.

(b) High flow rates affect the optical cell temperature by a small amount, and there is almost no gradient from inlet to outlet, so optical cell temperature can be considered constant for any given flow rate and inlet air temperature. Therefore, the temperature measured in the middle of the optical cell will provide a good estimate of overall cell temperature.

(c) Outlet air temperature is equilibrated with optical cell temperature only below 2 SLPM. Above 2 SLPM, the outlet air temperature is increasingly depressed below the cell temperature as the flow rate increases.

An appropriate average air temperature is needed within the optical cell so that accurate CO_2 calculations can be performed. This requires a model to compute the air temperature profile within the optical cell. *Equation 1* (*Box 1*) gives the temperature profile with distance, and *equation 2* calculates the average air temperature for different flow rates, inlet air temperatures, and optical cell temperatures.

Figure 1.

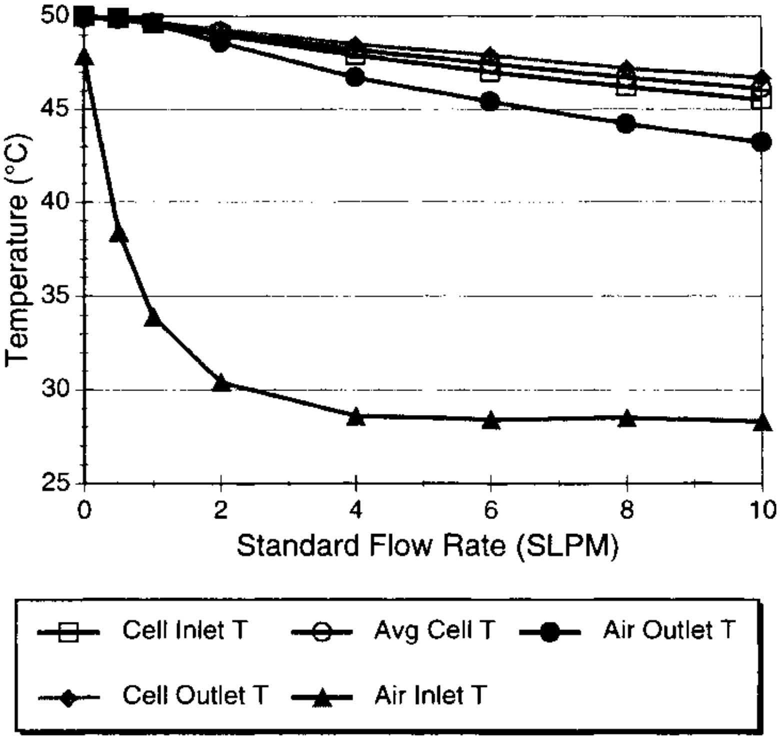


Figure 2 shows an experiment with oven temperature equal to 35 °C. Using a least squares procedure, *equation 1* was fit to the outlet air temperature using the inlet air temperatures and optical cell temperatures shown. The fit is reasonably good; bL has a value of 15.8 SLPM, and since L = 15.2 cm, b has a value of 1.04.

Figure 2.

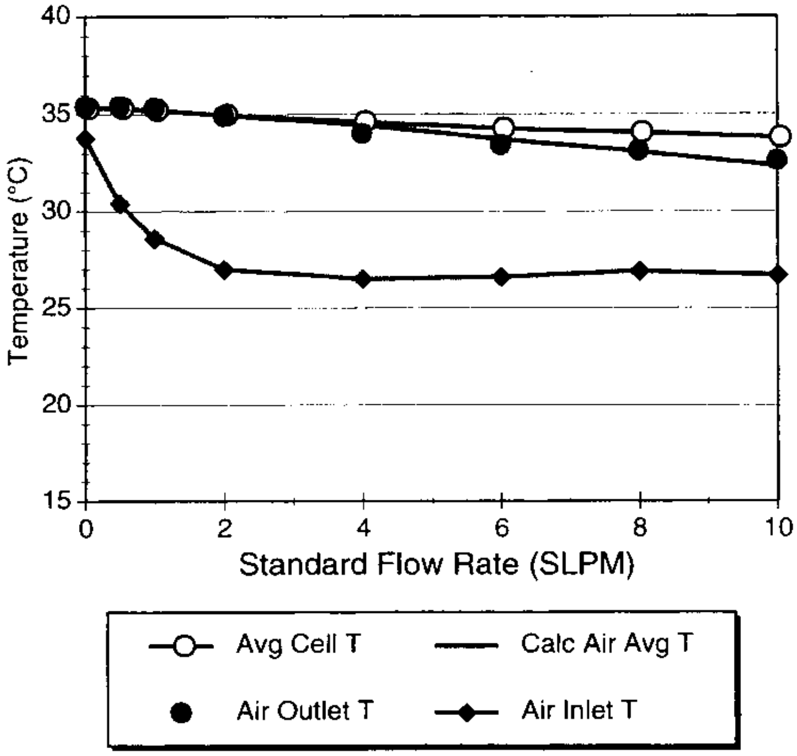


Figure 3 shows the model tested against the 50 °C data using the model parameters found from the data in figure 2. Lack of fit is more apparent here, but the model is applied over an extremely wide temperature range: hopefully, wider than one would ever encounter under normal operating conditions. Simple arithmetic averages of cell and inlet air temperatures are shown for comparison. Note that the modeled average air temperatures from equation 2 agree with the arithmetic average only at 10 SLPM, where m = 0.50.

Figure 3.

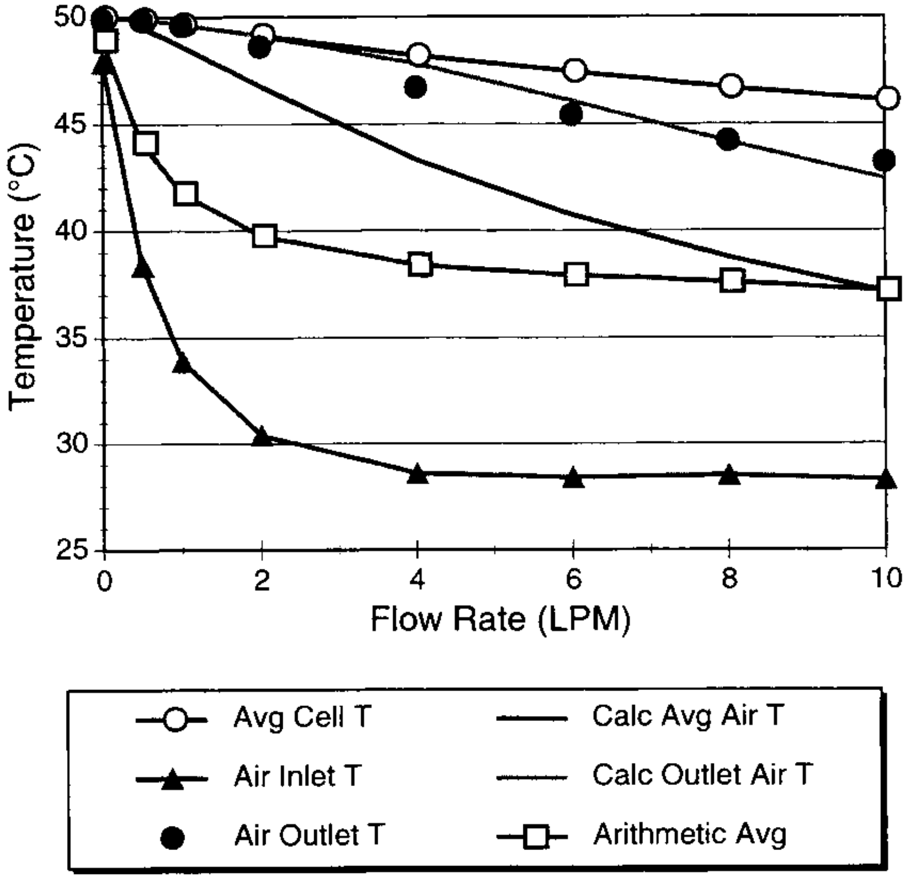


Figure 4 shows calculated cell temperature profiles and average air temperatures for typical experimental conditions in which air enters the cell at 27 °C while the optical cell is at 30 °C. At 10 SLPM, the average air temperature can be taken as a simple numerical average between the inlet air temperature and optical cell temperature (m = 0.50 in *equation 2*), but that clearly is not the case at the lower flow rates. Experimental validation of these profiles is desirable

Figure 4. Modeled Cell Air Temperature Profile

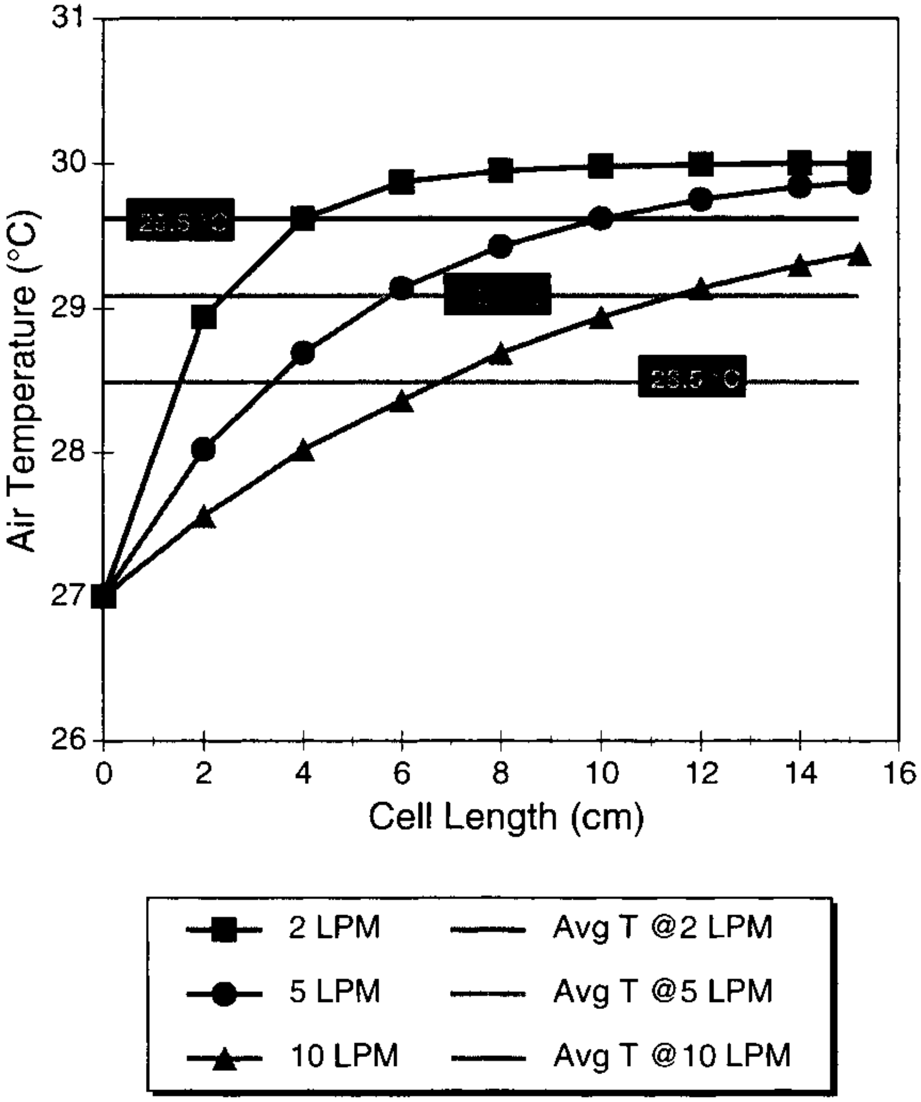
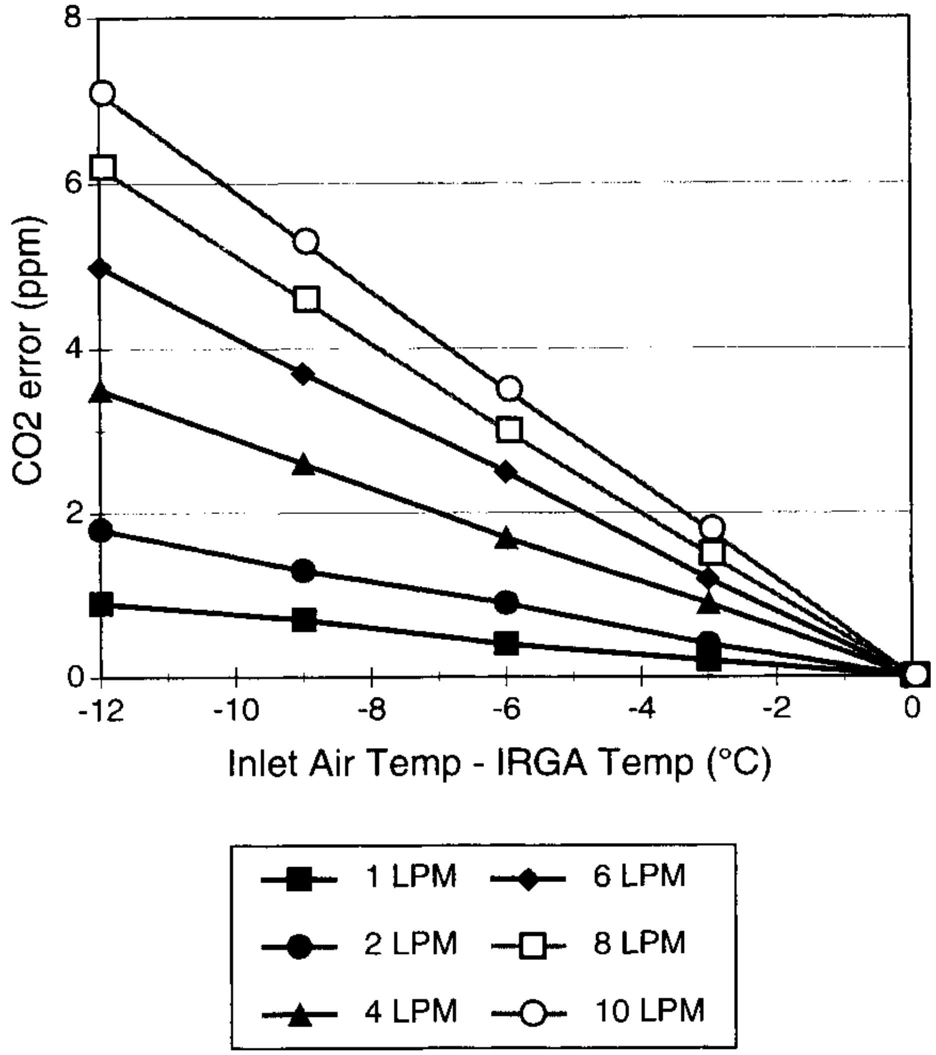


Figure 5 shows CO_2 measurement errors that would result if cell temperature is used in place of average air temperature for different flow rates and a true CO_2 mole fraction of 350 ppm. The figure assumes that <T> from *equation 2* is a good estimator of the the true average air temperature T_{true}. The CO_2 error (δC) is calculated as $\delta C = C_{true}\{(273+T_c)/(273+T_{true}) - 1\}$, which can be derived from a consideration of LI-COR gas analyzer calibration equations.

Figure 5.



Conclusions Regarding Temperature

1. Significant CO_2 measurement errors can result if large differences exist between incoming air temperature and the analyzer optical cell temperature, especially at high flow rates.

2. An appropriate average air temperature can be computed as $\langle T \rangle = T_c + m\,(T_{in} - T_c)$, where m is a function of flow rate according to equation 2. In the special case where flow rate is 10 SLPM, m = 0.5, so $\langle T \rangle_{flow=10\ SLPM} = (T_{in} + T_c)/2$.

3. If the inlet air temperature is substantially different from the optical cell temperature, then it may be necessary to measure the air temperature just before it enters the optical cell, especially with high flow rates (cf figure 5).

4. The best strategy is to bring the air temperature to the optical cell temperature before the air enters the cell, then large temperature corrections will not be necessary. This can be done by passing the air through an appropriate length of tubing held at the analyzer temperature.

Model Derivation

Assume that a plug of well-mixed turbulent air with temperature T (°C) and volume *V* (liters) moves down the cell of length L (cm) with flow rate F (SLPM). As it moves, the change in heat content, dQ/dt is given by $V\rho C_p dT/dt$. If heat flux occurs primarily across the cell surface to air interface, then dQ/dt also equals the heat flux density J times plug surface area *S*, dQ/dt = J*S*. Since we assumed the air is turbulent and well-mixed, then we can write, $J = -K\,(T - T_c)$, where K is a transfer coefficient, and T_c is the constant cell surface temperature. Therefore, $dT/dt + aT = aT_c$, where $a = KS/V\rho C_p$, and $T(0) = T_{in}$, the air inlet temperature. Integrating, $T(t) = T_c + (T_{in} - T_c)\exp(-at)$. The time t that elapses as the plug passes through the cell is given by, $t = V/F = Al/F$, where A is the cell cross sectional area (cm^2), and l is distance along the cell (0 to L). So,

$$T(l) = T_c + (T_{in} - T_c)\, e^{-bl/F} \qquad (1)$$

where b = aA is treated as an empirical coefficient. The appropriate average air temperature computed over the length of the cell is given by $\langle T \rangle = \int T(l)\,dl / \int dl$, which is

$$\langle T \rangle = T_c + m\,\Delta T \qquad (2)$$

where $m = (F/bL)(1 - \exp(-bL/F))$, and $\Delta T = (T_{in} - T_c)$. The average temperature depends upon the temperature difference between air and optical cell, and the slope is a function of flow rate.

Box 1

B. Pressure effects

The purposes of this section are (1) to measure pressures that develop in an LI-6262 optical cell at different flow rates; (2) estimate expected CO_2 measurement errors that result from uncertainties in pressure; and (3) discuss ways to use a pressure transducer to improve CO_2 measurement accuracy.

Materials & Methods

The effect of flow rate on optical cell pressure was evaluated with a specially modified optical cell in which a hose barb and pressure transducer was inserted into the optical cell as shown in *Diagram 2*. This allowed direct measurements of optical cell pressure. Various fittings were attached to the optical cell gas outlet port as shown. Air flow was provided by a tank of CO_2 in air (408 ppm), and flow rate was controlled by a Tylan mass flow controller (Model FC-261).

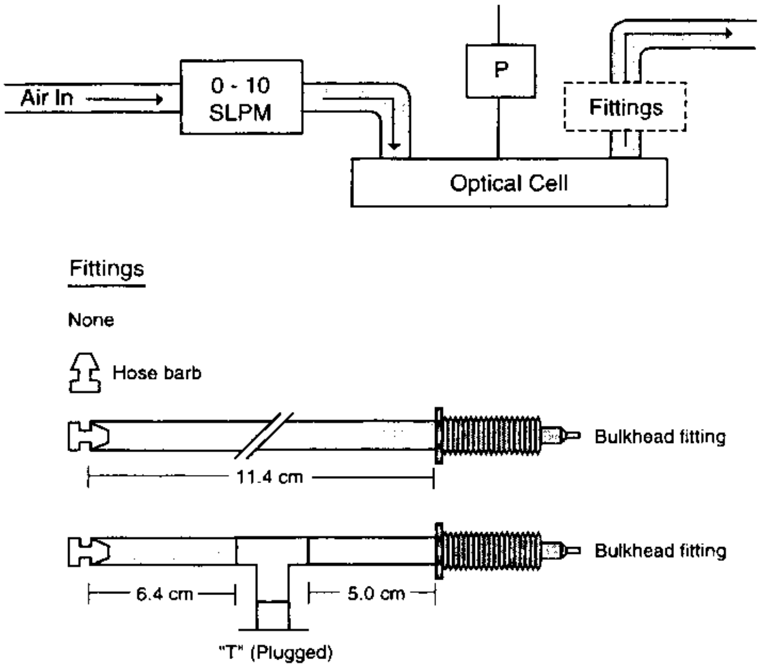


Diagram 2

It is not advisable to attach a pressure sampling port directly to the optical cell under normal circumstances, because the sampling tube dead volume will contain CO_2 and water vapor that will slowly exchange with the optical cell and compromise measurement accuracy. Therefore, a sampling port was placed in a "T" in the outlet tubing as shown in *Diagram 3.* Pressure differences between the optical cell and sampling port at various flow rates were measured with a differential pressure sensor (part no. 610-03), as shown in *Diagram 4.*

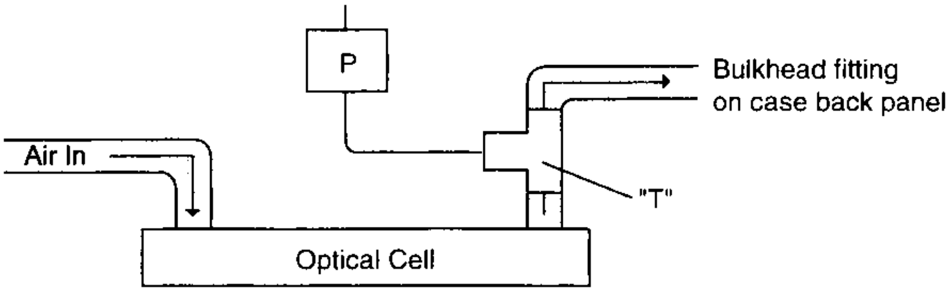


Diagram 3

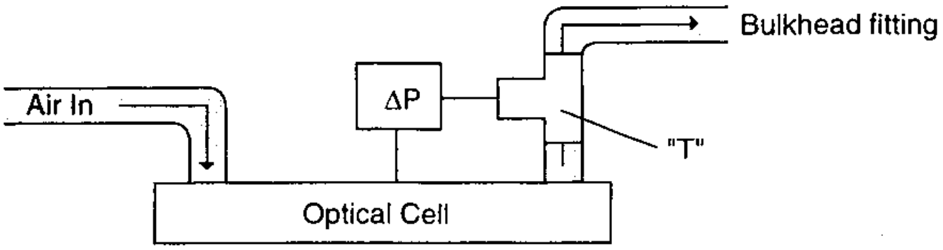


Diagram 4

Results

Figure 6 shows optical cell pressures that developed with different fittings attached to the outlet port over flow rates from zero to 10 SLPM. An open port with no fitting produces about 0.2 kPa at 10 SLPM, and the hose barb plus tubing needed to route exit air to the backpanel produces an optical cell over-pressure of more than 1.5 kPa at 10 SLPM. A "T" fitting produced the least pressure perturbation, compared to a "Y" fitting, or custom manifold with 90° ports (data not shown).

Figure 6.

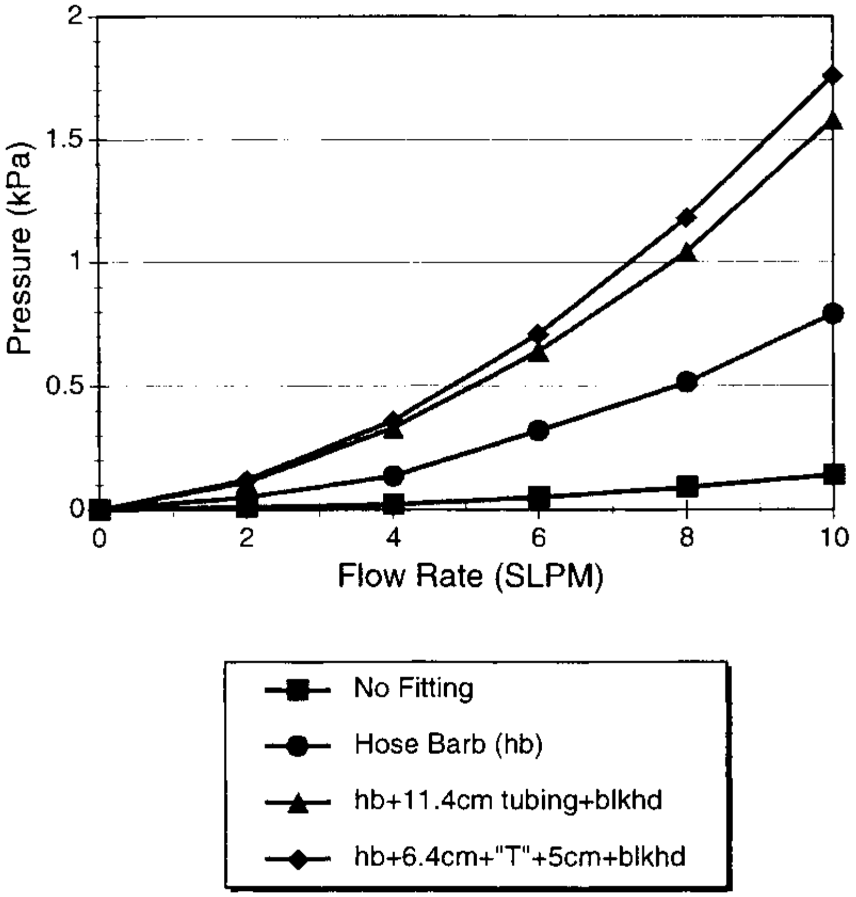


Figure 7 shows the consequences of pressure errors for a typical gas analyzer. A pressure error of 1 kPa to 2 kPa will produce CO_2 measurement errors of 10 ppm to 20 ppm, depending upon the actual CO_2 concentration. Similar errors would be expected for water vapor.

Figure 7. CO_2 Error Resulting From a P Error

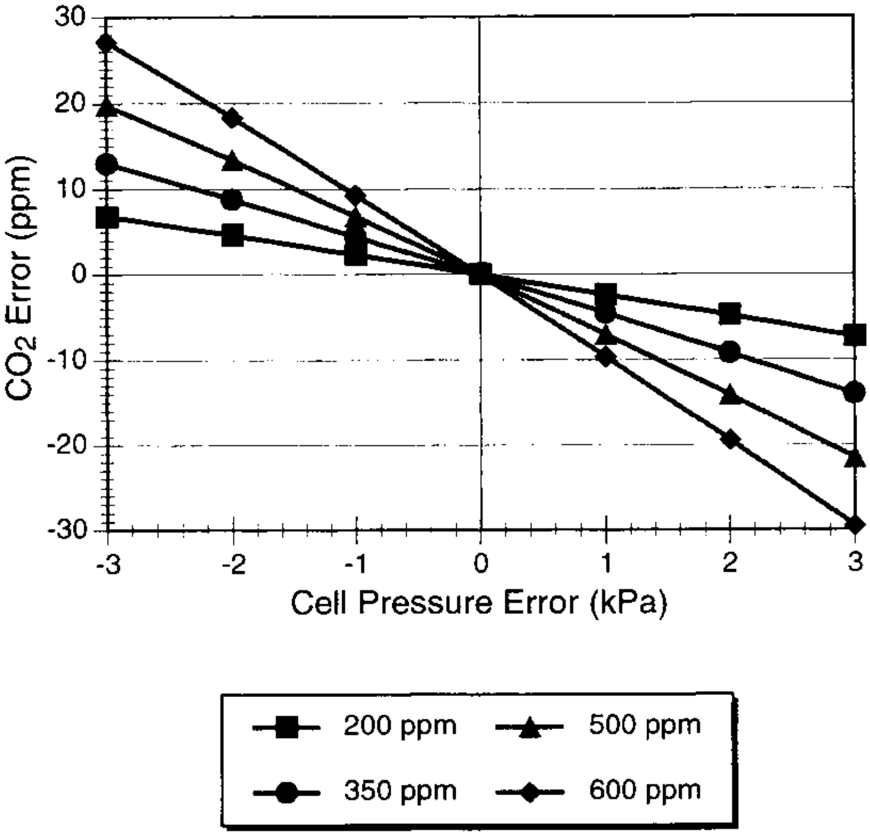


Figure 8 shows the CO_2 mole fraction displayed by an LI-6262 supplied with air at various flow rates from a tank of compressed gas, with and without pressure correction. Errors of 12 ppm were observed at 10 SLPM when a constant pressure was entered into the instrument. The errors were reduced when the signal from a pressure transducer connected as shown in *Diagram 3* was used to automatically compensate for pressure variation, but they were by no means eliminated.

Figure 8.

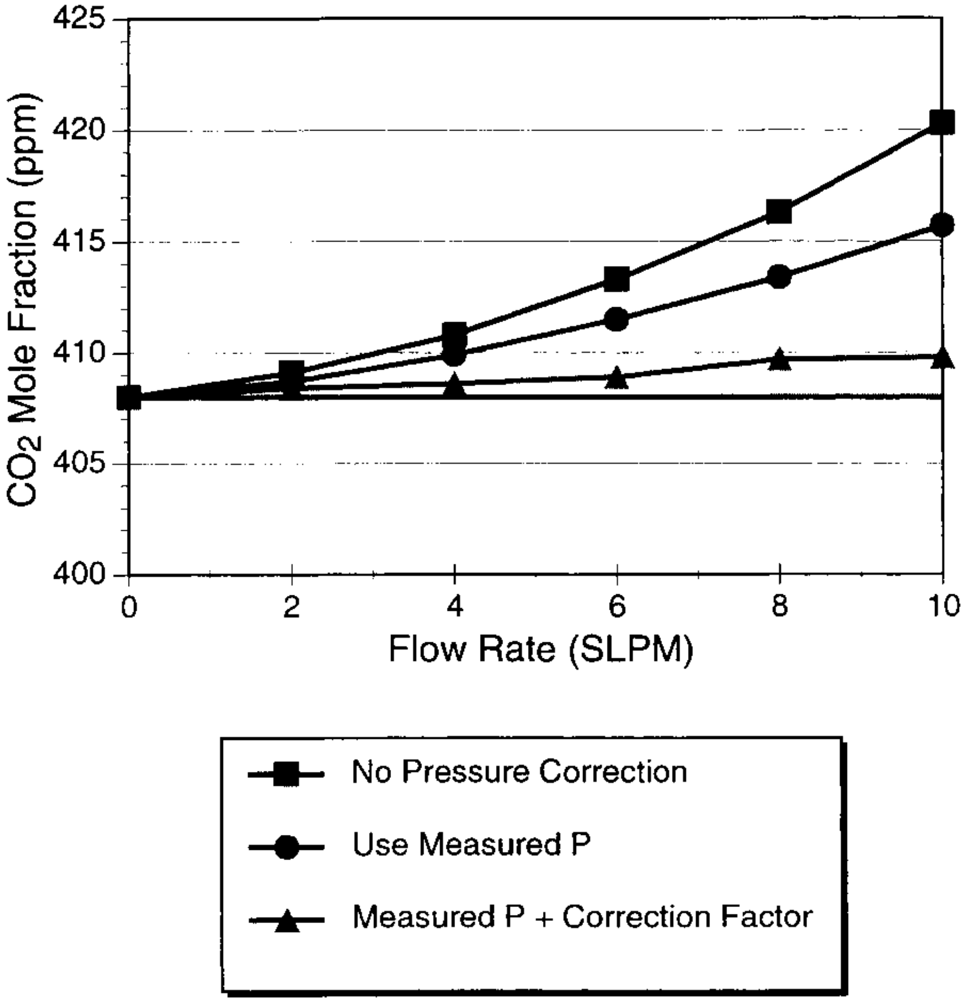
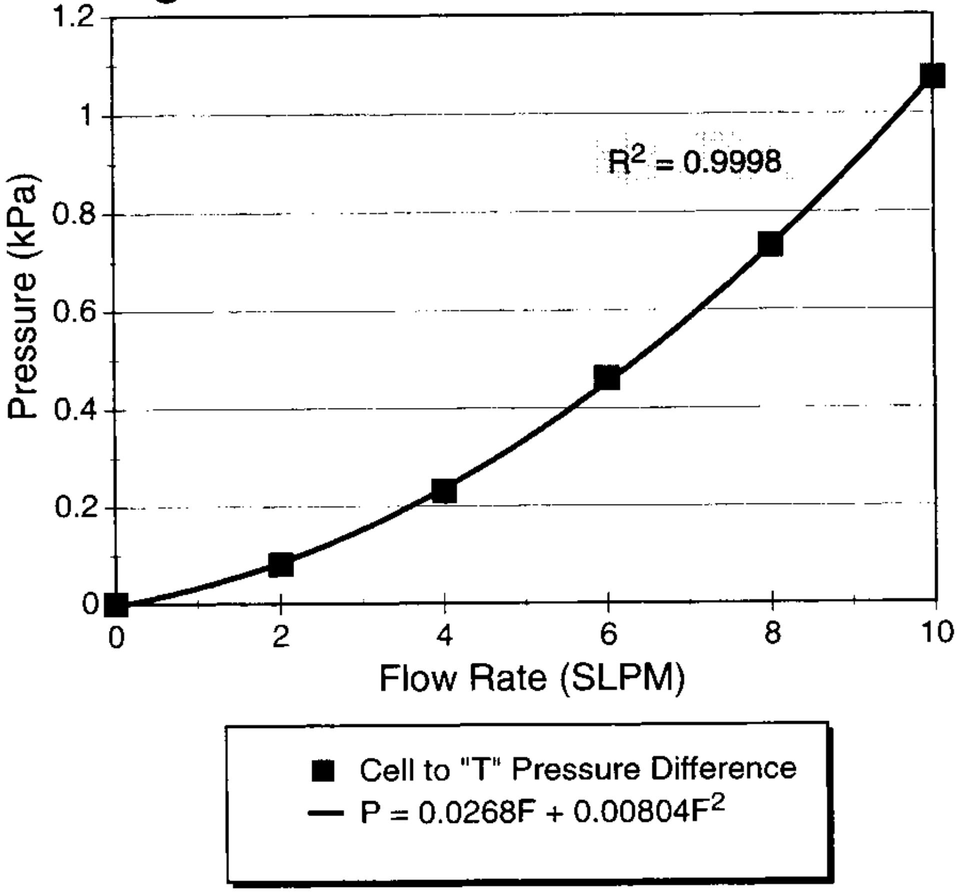


Figure 9 shows that, at high flow rates, a significant pressure difference exists between the optical cell and the pressure sampling port ("T", *Diagram 4*) in the optical cell outlet tube.

Figure 9.



Discussion & Conclusions Regarding Pressure

A pressure transducer that can be added to the LI-6252/6262 is available (part no. 6262-03). At the present time it samples pressure as shown in Diagram 3. Obviously, this or any other pressure transducer that is not connected directly to the optical cell will produce errors at high flow rates. This problem can be reduced but not eliminated by reducing the flow resistance between the optical cell outlet port and the pressure sampling port. We are evaluating a pressure sampling configuration that reduces the pressure differential across the outlet port to about 0.2 kPa at 10 SLPM, which is equivalent to a CO_2 measurement error of 1 to 2 ppm. This is near the minimum possible with the present optical cell design.

Alternatively, one can use the data of Figure 9 to estimate the pressure difference between the optical cell and pressure sampling port for whatever flow rate is being used, and then add this difference to the pressure sensor calibration function. This was done for a series of flow rates, and the results are shown in Figure 8 as "Measured P + correction factor." While this gives reasonably good results, it produces a flow rate dependent pressure calibration that is undesirable.

Regardless of the strategy used to correct for flow rate dependent pressure changes, it is always a good idea to operate a gas analyzer over as narrow a range of flow rates as possible.