

Effects of Temperature, Pressure and Water Vapor on Gas Phase Infrared Absorption by CO₂

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Introduction

Infrared analysis of CO₂ in air is one of the most widely used techniques in physiological ecology studies. The purposes of this paper are (1) to show the experimental derivation of the calibration function used in LI-COR CO₂ analyzers; and (2) to interpret the calibration function in terms of a theoretical development that will provide significant practical insights.

Theory

Absorption in the infrared involves vibrational and rotational energy transitions. The 4.26 μm CO₂ absorption band is due to infrared energy absorption by a particular bond stretching mode that is coupled to rotational energy transitions that produce a large number of individual absorption lines.

Individual absorption line widths are sensitive to intermolecular collisions and become broader with increasing pressure. Therefore, total absorption across a band per mole of absorber increases with pressure.

A. Non-overlapping line approximation

Full description of an absorption band is complex, but approximate expressions can be used over limited ranges of absorber mole fraction, pressure and pathlength. It can be shown that the “non-overlapping line approximation” applies at ambient pressure and CO₂ mole fraction over the short pathlengths found in LI-COR infrared gas analyzers (Wolfe and Zissis, 1978). This leads to a “scaling law” that allows absorption measured under one set of conditions to be scaled to other conditions (Jamieson, et al., 1963),

$$A / P = f(u / P) \quad (1)$$

where A = total band absorption, P = total pressure (kPa), u = absorber amount (mol m^{-2}) = ρL ; ρ is mol density (mol m^{-3}), and L is pathlength (m); f is a general unspecified function.

From the ideal gas law, the absorber mole density $\rho = p / RT = XP / RT$, where p is absorber partial pressure and X is absorber mole fraction (mol absorber / mol air). Therefore,

$$u / P = XL / RT \quad (2)$$

Substituting equation (2) into (1) and incorporating the constants L and R into a new function g gives,

$$A / P = g(X / T) \quad (3)$$

In principle, equation (3) can be solved for mole fraction, giving

$$X = g^{-1}(A / P) T \quad (4)$$

LI-COR gas analyzers produce an output voltage that is proportional to absorbance,

$$V = K A \quad (5)$$

The proportionality constant K is given on the calibration sheet of each LI-COR analyzer (mV). Substituting (5) into (4),

$$C = F(V P_0 / P) T / T_0 \quad (6)$$

where C is the CO₂ mole fraction in μmol / mol, and the constants 10^6 , K , P_0 and T_0 are included in the general function F ; $P_0 = 101.3$ kPa, and T_0 is the calibration temperature in degrees Kelvin. Equation (6) is the LI-COR calibration function, where $F(Z) = a_1 Z + a_2 Z^2 + a_3 Z^3$, and $Z = V P_0 / P$.

B. Equivalent Pressure

All gases are not equally effective in causing pressure broadening of absorption lines. The equivalent pressure P_e is defined as

$$P_e = p_{N_2} + \sum a_i p_i + b p_{CO_2} \quad (7)$$

where p_{N_2} is the partial pressure of nitrogen, and p_i gives the partial pressures of other diluent non-absorbing gases. The partial pressure of each non-absorbing gas is multiplied by a weighting factor a_i called the *foreign gas broadening coefficient*. The coefficients a_i reflect the ability of each diluent gas to cause pressure broadening relative to $a_{N_2} = 1$; b is the *self-broadening coefficient* for the absorbing gas, and it gives the relative effect of its own partial pressure on absorption (Burch et al., 1962).

Broadening coefficients for the effect of various gases on CO₂ absorption at 4.26 μm are given in Table 1. For example, the equivalent pressure of a binary mixture that is 80% (v/v) nitrogen and 20% oxygen at a total pressure of 100 kPa is $P_e = 80(1) + 20(.81) = 96.2$ kPa.

Table 1. Typical foreign gas and self-broadening coefficients for the CO₂ 4.26 μm absorption band (Burch et. al. 1962).

	Gas	Broadening Coefficient
Foreign gases	N ₂	1.00
	O ₂	0.81
	H ₂	1.17
	A	0.78
	He	0.59
	H ₂ O	?
Self-broadening	CO ₂	1.30

C. Calibration in terms of P_e

Equivalent pressure can be written in terms of mole fractions and total pressure. For air with dry gas mole fractions X_i, and water vapor mole fraction w,

$$P_e = P [1 + (a_w - 1) w + \sum (a_i - 1) X_i] \quad (8)$$

(LI-COR, 1990). X_{CO₂} is small (3.5 x 10⁻⁴) and is neglected. LI-COR analyzers are calibrated with CO₂ in dry air, not nitrogen. If dry air is taken as reference instead of nitrogen, then equation (8) becomes,

$$P_e = P [1 + (\alpha_w - 1) w] \quad (9)$$

$$P_e = P \chi(w) \quad (10)$$

where $\chi(w) = [1 + (\alpha_w - 1) w]$ (LI-COR, 1990). The foreign gas broadening coefficient for water vapor is denoted α_w in equation (9) to indicate that it uses dry air as reference, instead of nitrogen.

A calibration equation similar to (6) that includes the pressure broadening effects of variable water vapor can be obtained by substituting P_e for P in equations (1) and (2), and carrying through the subsequent steps to give

$$C = \chi(w) F [V P_o / (P \chi(w))] T / T_o \quad (11)$$

Finding an appropriate value of α_w for use in equation (11) forms the basis of the pressure broadening correction for water vapor in LI-COR gas analyzers.

Materials and Methods

CO₂ calibration curves

A LI-COR LI-6250 infrared CO₂ analyzer was placed into a large airtight PVC cylinder. Analyzer voltage output as a function of CO₂ mole fraction was recorded over a wide range of cylinder pressures and temperatures. Air temperature was controlled with a fan and radiator connected to an external temperature-controlled water bath. Pressure was controlled by a vacuum pump and pressure regulator. The analyzer sample cell opened to the internal atmosphere and CO₂ was supplied at about 0.5 LPM from tanks with known CO₂ mole fractions.

Water correction

A LI-COR LI-6262 infrared CO₂/H₂O analyzer was used to measure infrared absorption by CO₂ and H₂O simultaneously. CO₂-free air was humidified with a bubbler and dewpoint controller and then 10% CO₂ in dry air was added using a Tylan Mass Flow Controller providing a gas with known CO₂ mole fraction and dewpoint. The airstream was passed to the LI-6262 via a needle valve flow restriction. The analyzer sample cell was connected to a ballast tank, the pressure of which was controlled by a vacuum pump and pressure controller. CO₂ and water vapor mole fractions were then measured by infrared absorption. The actual CO₂ mole fractions were known independently after dilution corrections were applied, and a foreign gas broadening coefficient for water vapor that reconciled the infrared measurements with the known values was calculated using a least squares procedure.

Results and Discussion

A. CO₂ absorption spectrum

Figure 1 shows a low resolution absorption curve for CO₂ along with a typical filter transmission spectrum. The entire CO₂ spectrum is included in the transmission window, as it must be for theoretical band models to apply.

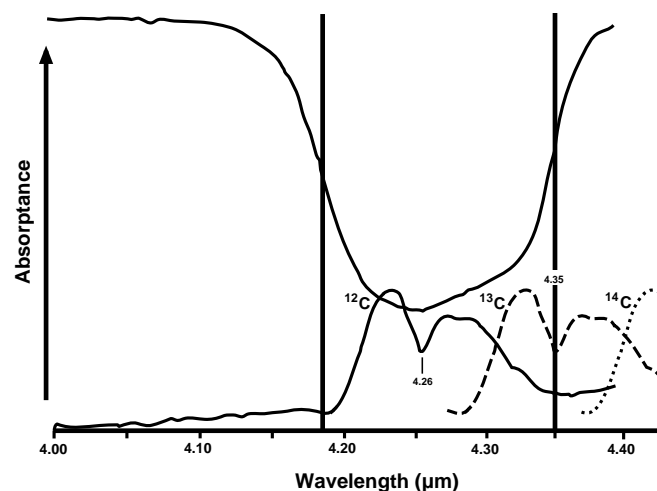


Figure 1. Absorption spectrum for CO₂ and transmission spectrum for a typical interference filter measured through a LI-COR CO₂ analyzer optical path. ¹³C and ¹⁴C spectra are computed from the measured spectrum using a simple harmonic oscillator

¹³CO₂ and ¹⁴CO₂ spectra were computed for comparison. About 1/3 of the ¹³CO₂ spectrum is included in the window, and virtually none of the ¹⁴CO₂ is included. This means that the analyzer will lose about 2/3 of its sensitivity when measuring ¹³CO₂, and it will have almost no sensitivity to ¹⁴CO₂.

B. CO₂ analyzer calibration

Analyzer voltage output as a function of mole fraction is shown in Figure 2a for all the temperatures and pressures tested. A large spread is seen, as expected. Figure 2b isolates the 20 °C data showing the pressure effect.

Figure 2a.

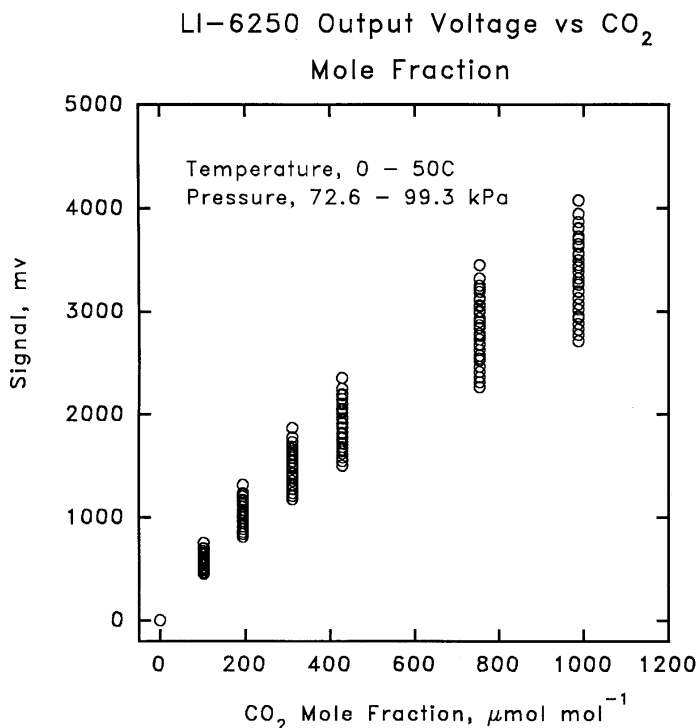
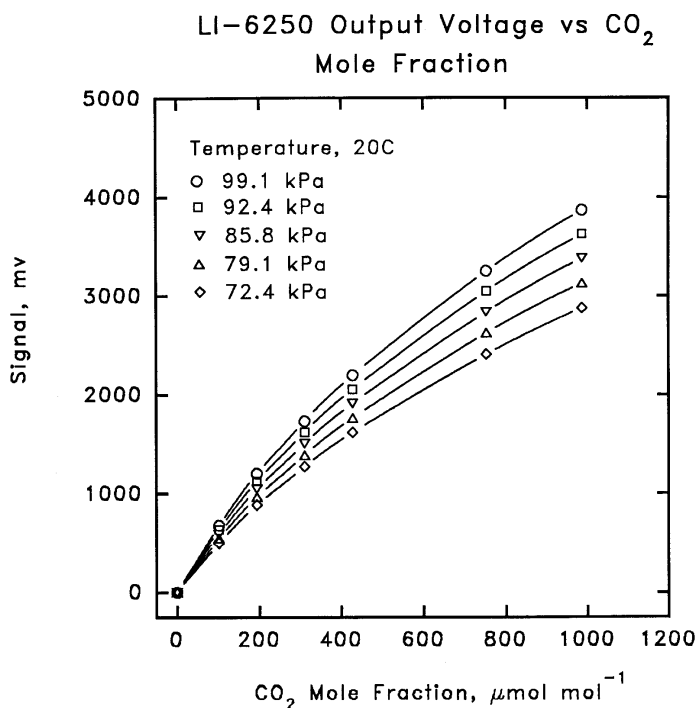
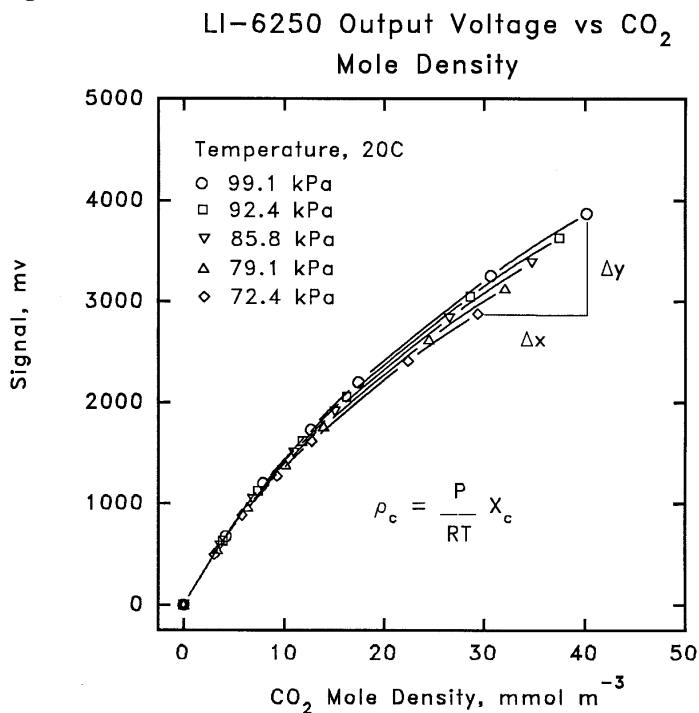


Figure 2b.



Intuitively, one expects absorption to be proportional to the number of absorber molecules in the light path, not to mole fraction (Ball, 1987). But when the data from Figure 1b are replotted in Figure 3 as a function of mole density, it is clear that a single functional relationship still does not exist. The desired functional form is obtained when both voltage and mole density are divided by pressure (Figure 4a). Figure 4b shows all of the data plotted as V/P versus ρ_c/P .

Figure 3.



The results shown in Figures 4a and 4b are consistent with the non-overlapping line approximation as described by equation (1). The x axis reduces to mole fraction divided by temperature (equation (2)), and the dependence on gas density becomes implicit. The actual calibration function, equation (6), is computed by fitting a 3rd order polynomial to $C T_0 / T$ vs $V P_0 / P$.

The pressure and temperature corrections in the calibration function (equation (6)) can be expected to be accurate over the range of conditions for which the non-overlapping line approximation is valid. Criteria given in Wolfe and Zissis (1978) suggest that the non-overlapping line approximation will be valid up to about 1100 ppm. Note that the pressure corrections in Figures 4a and 4b are most accurate at CO₂ mole fractions up to about 500 ppm, and are still good, but slightly less accurate at the high concentrations. This may be due to fundamental limitations on the form of the calibration function as the non-overlapping line approximation approaches its limit of validity.

An empirical calibration function can be extended to 3000 ppm or more, but the pressure correction will probably work best at 1000 ppm, or lower. This means that span adjustments may be necessary if large pressure changes occur at high CO₂ mole fractions. The pressure corrections have not been tested above 1000 ppm.

Figure 4a.

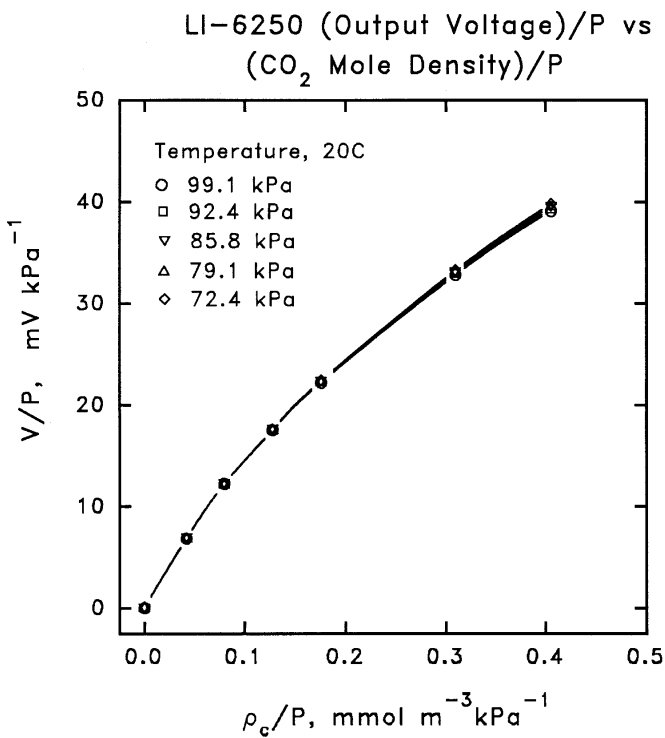
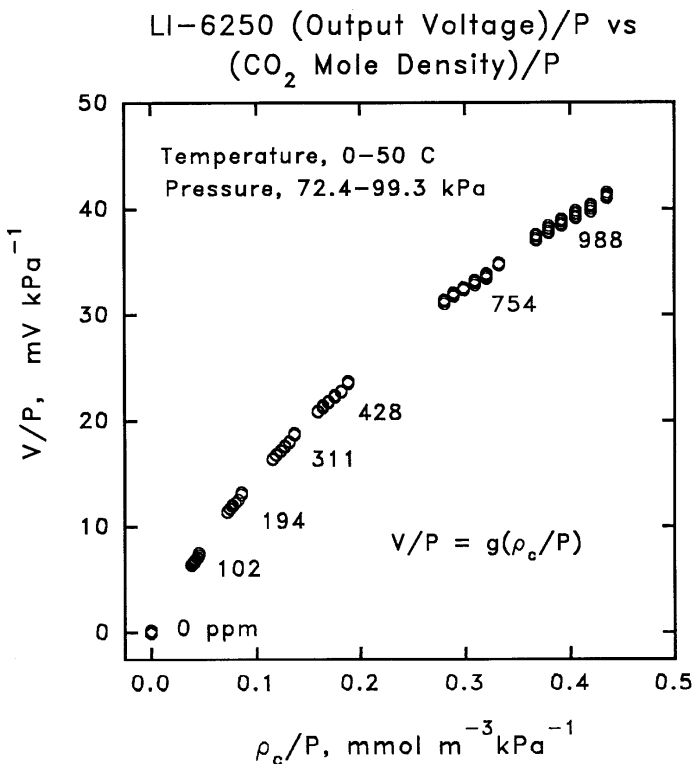


Figure 4b.



C. Water corrections

The calibration function used in LI-COR analyzers was first derived empirically and then confirmed theoretically, but the water correction was predicted from theory.

Figure 5a shows CO₂ measurement errors that remain after dilution corrections are applied (circles) over a range of CO₂ mole

fractions, water vapor pressures, temperatures, and total pressures. Errors increase with CO₂ mole fraction and vapor pressure, and are about 1/3 of the dilution correction when water vapor pressure broadening is not accounted for. CO₂ mole fraction is over-estimated in the presence of water vapor because $P_e > P$ leading to higher infrared absorption. Errors are reduced to about 1 ppm or less when pressure broadening corrections are applied with $\alpha_w = 1.57$ (triangles).

Figure 5a. CO₂ measurement errors in the presence of water vapor after the dilution correction was applied, and before (circles) or after (triangles) the water vapor pressure broadening correction was applied. Temperatures were 31 °C and 48 °C, pressures were distributed over the range 70.5 kPa to 97.2 kPa, and vapor pressures were 0.89 kPa to 2.46 kPa.

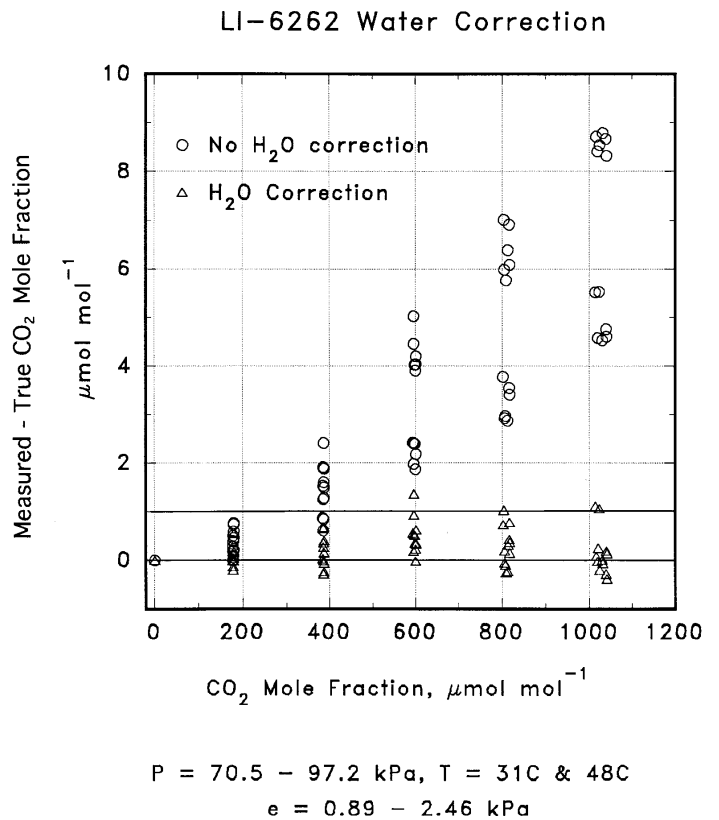
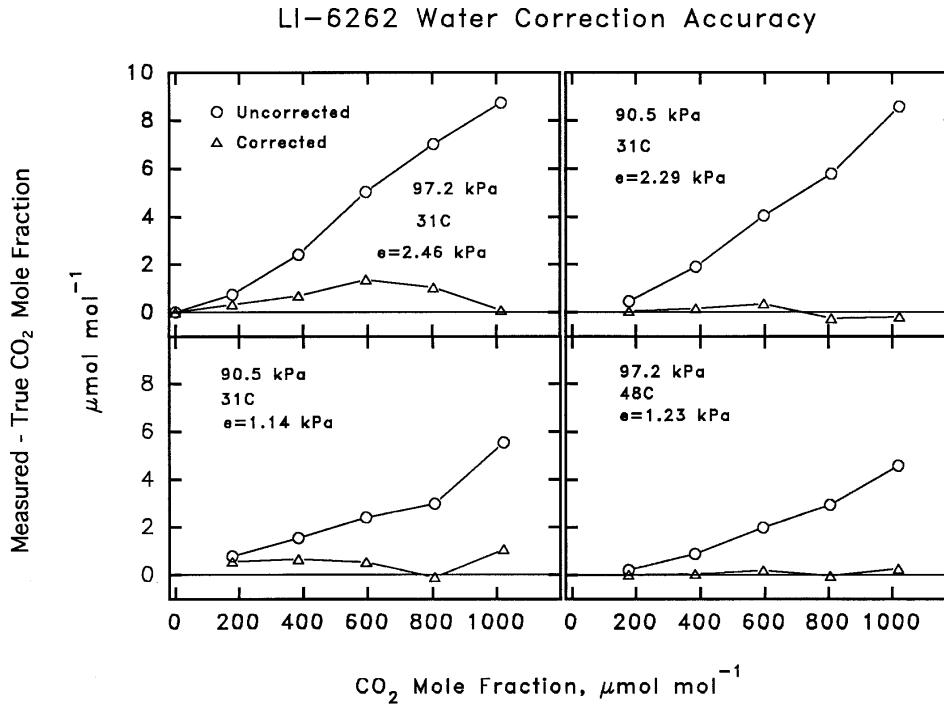


Figure 5b shows the smallest and largest errors from Figure 5a. The residual errors that remain after correcting for water vapor are correlated with the measurement errors before correction. Therefore, the residual errors probably are more a reflection of overall system accuracy than water correction accuracy, per se.

The errors shown in Figure 5a before applying the pressure broadening correction are similar to those described for the ADC Model 225 MK III analyzer by Bunce and Ward (1985). They interpreted that response as analyzer “water sensitivity.” However, it is clear from the development given here that even if an infrared CO₂ analyzer has no direct sensitivity to water vapor, it will still display a second order response to water vapor in the presence of CO₂ because of gas phase molecular interactions. This is due to physics, not to any deficiency in analyzer design.

Figure 5b. Data sets from Figure 5a that showed either the largest (left panels) or smallest (right panels) residual errors after the water correction was applied.



Conclusions

1. The LI-COR CO₂ analyzer calibration equation was found to be consistent with a theoretical relationship called the “non-overlapping line approximation,” which describes infrared absorption as a function of CO₂ mole fraction, pressure and temperature.
2. This theoretical model and the concept of “equivalent pressure” predicted a form for the water correction that gives good accuracy over a wide range of conditions using a single physically meaningful parameter.
3. Theory shows that all CO₂ analyzers will show some response to water vapor because infrared absorption per mole CO₂ changes with total pressure and diluent gas composition. The magnitude of the water effect is larger than those for most other gases.
4. Since absorption varies with gas composition, LI-COR gas analyzers should be calibrated with CO₂ standards mixed in air, not nitrogen. This also has implications for measuring CO₂ in the presence of different oxygen levels.
5. Infrared CO₂ analyzers should be calibrated in terms of mole fraction, not partial pressure or mole density. This is surprising.
6. Temperature and pressure corrections work well over wide ranges; however, the pressure correction will be most accurate at modest CO₂ mole fractions or lower pressures (higher elevations), because these conditions move away from the limits of model validity. Pressure corrections above 1100 ppm, or at pressures above 1 atm might be problematic.

7. Infrared absorption varies with pressure, so expect the apparent span to change daily. Most daily span adjustments are due to pressure changes. Long-term unattended measurements require continuous input from an electronic barometer.

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