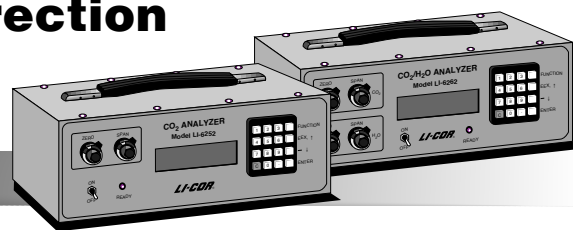


Implementing Zero and Span Adjustments, and the Band Broadening Correction On Measured Data



Application Note 123

Sometimes it is necessary to correct LI-COR Gas Analyzer measurements after they have been made. These corrections might include making a zero or span adjustment, or implementing the band broadening correction, if you forgot to have the instrument do it for you. Normally, these adjustments involve using the raw mV signal, temperature, and pressure at the time of the original measurement, and recomputing using the analyzer's calibration equation. But what if you didn't record the original raw mV readings? This application note describes a method of doing span and band broadening corrections without any knowledge of the original conditions or signal, or even knowledge of the IRGA's calibration coefficients. Zero corrections are discussed on page 5.

Span Adjustment

Span adjustments can be made using Equation (1)

$$C = C' + (C_s - C'_s) \frac{C' Y_c(C')}{C'_s Y_c(C'_s)} \quad (1)$$

where C is the corrected CO_2 concentration, C' is the original measurement, C_s is the true span concentration, and C'_s is the measured span concentration (all CO_2 concentrations in $\mu\text{mol mol}^{-1}$). The function $Y_c(C)$ is

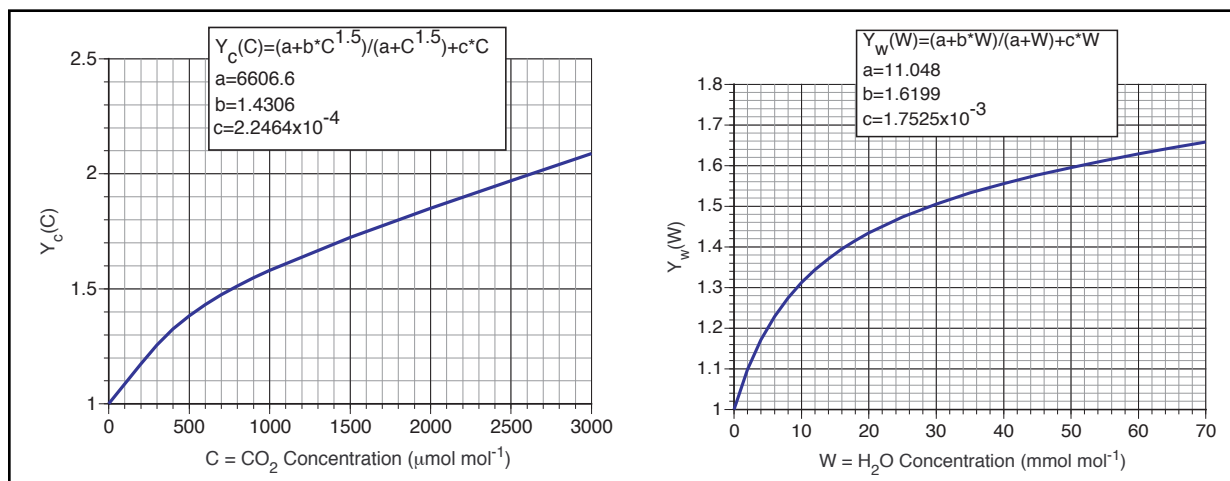


Figure 1. Standardized functions used in Equations (1) through (3).

shown in Figure 1. Equation (2) can be used for correcting water vapor measurements.

$$W = W' + (W_s - W'_s) \frac{W' Y_w(W')}{W'_s Y_w(W'_s)} \quad (2)$$

where W is the corrected water vapor concentration, W' is the original measurement, W_s is the true span concentration, and W'_s is the measured span concentration (All H_2O concentrations are in mmol mol^{-1}). The function $Y_w(W)$ is shown in Figure 1.

Band Broadening Correction

The band broadening correction can be made using Equation (3).

$$C = (1 + 0.5w)C'(1 - 0.5wY_c(C')) \quad (3)$$

where C is the corrected CO_2 concentration ($\mu\text{mol mol}^{-1}$), w is the water vapor mole fraction (mol mol^{-1}), and C' is the original measurement in which no band broadening correction was applied.

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Derivations

Band Broadening Correction

The general form of the CO₂ calibration equation that accounts for band broadening is

$$C = (1+x)f_c\left(\frac{VP_o}{(1+x)P}\right)\frac{T}{T_o} \quad (4)$$

where C is CO₂ concentration ($\mu\text{mol mol}^{-1}$), V is the signal (mV) from the gas analyzer, P is pressure (kPa), P_o is standard pressure (101.3 kPa), T_o is the calibration temperature (K), T is the measurement temperature (K), and the function $f_c()$ is the calibration polynomial. The quantity x is related to mole fraction of water vapor w (mol mol^{-1}) and band broadening factor a (1.5 for water vapor) by

$$x = (a-1)w \quad (5)$$

Since x is always small (typically < 0.02), Equation (4) can be written as

$$C \cong (1+x)f_c(u(1-x))\frac{T}{T_o} \quad (6)$$

where $u = V\frac{P_o}{P}$. Again, since x is small,

$$f_c(u(1-x)) \cong f_c(u) - ux\frac{\partial f_c}{\partial u} \quad (7)$$

Note that a measurement without water corrections is $C' \equiv f_c(u)\frac{T}{T_o}$. Using this relation, and substituting (7) into (6), yields

$$\begin{aligned} C &= (1+x)\left(f_c(u) - ux\frac{\partial f_c}{\partial u}\right)\frac{T}{T_o} \\ &= (1+x)f_c(u)\frac{T}{T_o}\left(1 - x\frac{u}{f_c(u)}\frac{\partial f_c}{\partial u}\right) \quad (8) \\ &= (1+x)C'\left(1 - x\frac{u}{f_c(u)}\frac{\partial f_c}{\partial u}\right) \end{aligned}$$

At this point we note that $\frac{u}{f_c(u)}\frac{\partial f_c}{\partial u}$ has a remarkably small variation from one instrument to the next, when plotted as a function of concentration $f_c(u)$ (Figure 2).

Substituting $Y_c(f_c(u)) \equiv \frac{u}{f_c(u)}\frac{\partial f_c}{\partial u}$ and $a = 1.5$ into (8) yields

$$C = (1+0.5w)C'\left(1 - 0.5wY_c\left(C'\frac{T_o}{T}\right)\right) \quad (9)$$

Since the $Y_c()$ relation is so flat, the temperature term can safely be ignored, leaving Equation (3).

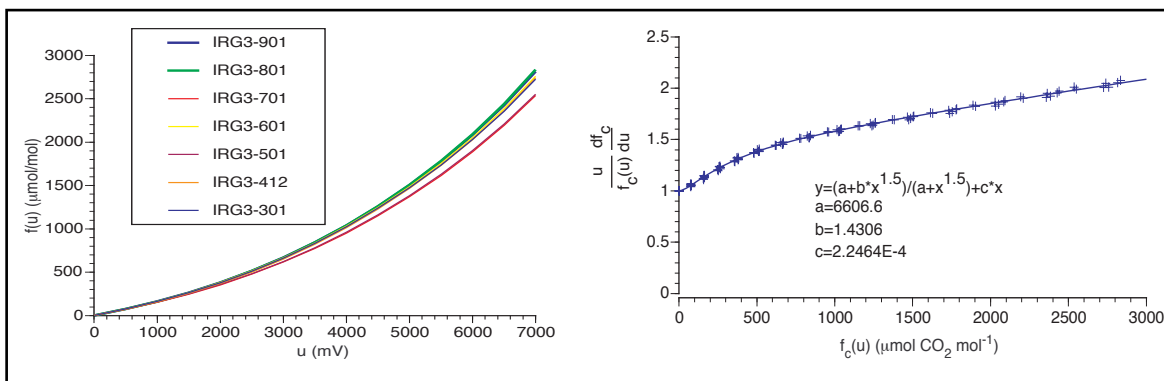


Figure 2. Seven LI-6262 calibration polynomials (left) were used to generate data relating normalized slope ($u/f_c du/df$) to CO₂ concentration (right).

Span Adjustment

Suppose a known concentration C_s is measured to be

C'_s . The pressure corrected signal $V_s \frac{P_o}{P}$ is u_s , and the amount the signal needs to be changed to make the IRGA read correctly is Δu_s . That is, $C' = f_c(u'_s)$ and $C = f_c(u'_s + \Delta u_s)$. If Δu_s is not zero, then some other concentration C will be measured incorrectly as C' , with u' being the pressure corrected signal, and $\Delta u'$ being the amount it needs to be corrected. That is, $C' = f_c(u')$, and $C = f_c(u' + \Delta u')$. For a true span error, Equation (10) would predict the relation between the raw signals and the corrections needed.

$$\frac{\Delta u_s}{u_s} = \frac{\Delta u'}{u'} \quad (10)$$

Can we compute C knowing only C' , C_s , and C'_s ? We start with the following relations:

$$C_s \cong C'_s + \Delta u_s \frac{\partial f_c}{\partial u} \bigg|_{u_s} \quad (11)$$

$$C \cong C' + \Delta u' \frac{\partial f_c}{\partial u} \bigg|_{u'} \quad (12)$$

Solving (10) for $\Delta u'$, and substituting into (12) yields

$$C \cong C' + \Delta u_s \frac{u'}{u_s} \frac{\partial f_c}{\partial u} \bigg|_{u'} \quad (13)$$

Solving (11) for Δu_s , and substituting into (13) yields

$$C = C' + (C_s - C'_s) \frac{u' \frac{\partial f_c}{\partial u} \big|_{u'}}{u_s \frac{\partial f_c}{\partial u} \big|_{u_s}} \quad (14)$$

Substituting the normalized slope relation (Figure 2) yields

$$C = C' + (C_s - C'_s) \frac{C' Y_c(C')}{C'_s Y_c(C'_s)} \quad (15)$$

The form of Equation (15) can be applied to water vapor mole fraction as well (Equation (16)).

$$W = W' + (W_s - W'_s) \frac{W' Y_w(W')}{W'_s Y_w(W'_s)} \quad (16)$$

Figure 3 shows the normalized slope relation for water, which exhibits more scatter than that for CO₂.

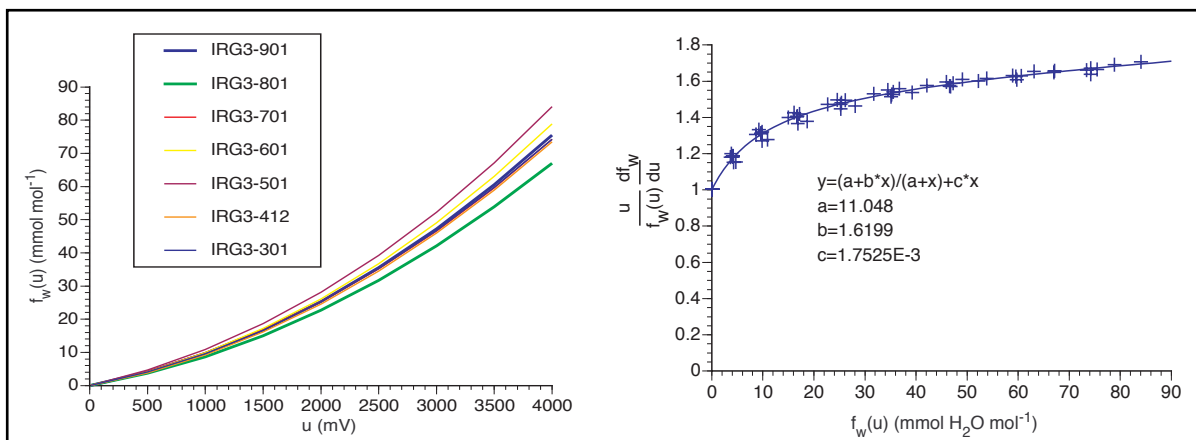


Figure 3. Seven water calibration polynomials (left), and their corresponding normalized slope relations (right).

Examples

The following examples use a randomly chosen analyzer (IRG3-726), whose calibration coefficients for CO₂ are $T_o=35.5$, $A=0.14389$, $B=1.08464E-5$, $C=7.2296E-9$, $D=-9.5548E-13$, and $E=6.7586E-17$.

The Span Correction

When measuring a 500 $\mu\text{mol mol}^{-1}$ tank at 25C and 98.0 kPa, the signal should be 2688.5 mV. (We know this by iterating the calibration equation.) If the instrument had a span error of 0.97 (that is, it reads 3% low), the signal would be $0.97 \times 2688.5 = 2607.8$ mV, which corresponds to 479.61 $\mu\text{mol mol}^{-1}$. A concentration of 350 $\mu\text{mol mol}^{-1}$ corresponds to a signal of 2050.7 mV, but with the same span error, it would be 1989.2 mV instead, which is 336.8 $\mu\text{mol mol}^{-1}$.

To correct this 336.8 $\mu\text{mol mol}^{-1}$ reading without knowing the mV signals, set $C_s = 500$, $C'_s = 479.6$, $C' = 336.8$, $Y_c(479.6) = 1.37$, and $Y_c(336.8) = 1.28$ in Equation (1):

$$\begin{aligned} C &= 336.8 + (500 - 479.6) \frac{336.8 \times 1.28}{479.6 \times 1.37} \\ &= 350.18 \end{aligned} \quad (17)$$

Since the true value is 350, the error in this correction is 0.05%.

The Band Broadening Correction

The above IRGA, when measuring 350.0 $\mu\text{mol mol}^{-1}$ of CO₂ in air having 20 mmol mol^{-1} of water vapor, would read 350.91 $\mu\text{mol mol}^{-1}$ if the band broadening corrections had not been enabled. (We know this by plugging numbers into the calibration equation.) To correct the reading without knowing the mV signals, set $C' = 350.9$, $w = 0.020$, and $Y_c(350.9) = 1.29$ in Equation (3):

$$\begin{aligned} C &= (1 + 0.01)350.9(1 - 0.01 \times 1.29) \\ &= 349.85 \end{aligned} \quad (18)$$

In this example, not doing the band broadening correction caused a 0.26% (high) error. Applying Equation (3) results in a 0.04% (low) error.

For Greater Precision

You can generate the functions $Y_c(C)$ and $Y_w(C)$ for your particular gas analyzer, using any standard spreadsheet program, and following the steps below¹.

1. Make a column (A, for example) of mV values, ranging from 0 to 7000 for CO₂ (or 0 to 4000 for H₂O), in steps of 500.
2. Compute a column (B) of concentrations, using the calibration polynomial.
3. If necessary, adjust the range of Column A, so that the concentrations in Column B cover only the range of interest. You may also need to adjust the mV intervals, because you want to wind up with 5 to 10 evenly spaced data points.
4. Compute a column (C) of slopes, using the derivative of the calibration polynomial. Recall that for a polynomial

$$f(x) = ax + bx^2 + cx^3 + dx^4 + ex^5$$

the slope is

$$\frac{\partial f}{\partial x} = a + 2bx + 3cx^2 + 4dx^3 + 5ex^4$$

5. Compute a column (D) of normalized slopes

$$D = \frac{A \times C}{B}$$

6. Curve fit column D as a function of column B. Use the form of $Y_c(C)$ or $Y_w(C)$ in Figure 1, or, if you have a smaller range of concentrations than in Figure 1, you might get by with a 4th or 5th order polynomial.

Use this new equation for $Y_c()$ (or $Y_w()$, if you used the water calibration polynomial).

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1. This procedure is probably not necessary for CO₂, since that data seems very consistent from one IRGA to the next. If you are adjusting water spans after the fact, however, you may want to do this.

Zero Adjustments

Zero adjustments are not quite as accurate to do after the fact without knowledge of at least the IRGA's calibration coefficients. The form of the correction can be derived in a similar manner as the slope correction. Given some signal offset Δu that is consistent at all concentrations, we can write

$$\begin{aligned} f(u_1 + \Delta u) &= f(u_1) + \Delta u \left. \frac{\partial f}{\partial u} \right|_{x_1} \\ f(u_2 + \Delta u) &= f(u_2) + \Delta u \left. \frac{\partial f}{\partial u} \right|_{x_2} \end{aligned} \quad (19)$$

If the first equation is for the zero measurement, then $u_1 = 0$, and $f(u_1) = 0$. Combining the two equations yields

$$f(u_2) = f(u_2 + \Delta u) - f(\Delta u) \frac{\left. \frac{\partial f}{\partial u} \right|_{u_2}}{\left. \frac{\partial f}{\partial u} \right|_0} \quad (20)$$

Thus, to correct for an offset, one needs to know the reading at zero ($f(\Delta u)$), the slope of the calibration curve at 0 ($\left. \frac{\partial f}{\partial u} \right|_0$), and the slope of the calibration curve

where the measurement is to be corrected ($\left. \frac{\partial f}{\partial u} \right|_{u_2}$). If we

let R be the ratio of these slopes, we can write a CO_2 correction equation as

$$C = C' - C_z R_c \quad (21)$$

where C is the corrected reading, C' is the uncorrected reading, and C_z is zero reading. A correction equation for H_2O would be

$$W = W' - W_z R_w \quad (22)$$

where W is the corrected reading, W' is the uncorrected reading, and W_z is zero reading.

Figure 4 illustrates the variation R_c across seven LI-6262's.

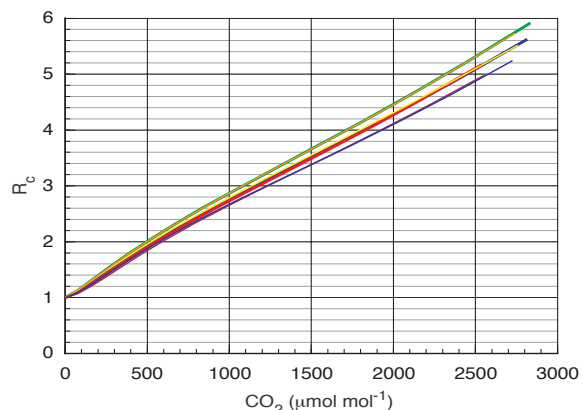


Figure 4. CO_2 zero correction factors plotted for seven different LI-6262's.

If one approximates the family of curves in Figure 4 with a straight line, R_c can be written as

$$R_c \approx 1 + 0.00164C' \quad (23)$$

R_w for water is less consistent (Figure 5).

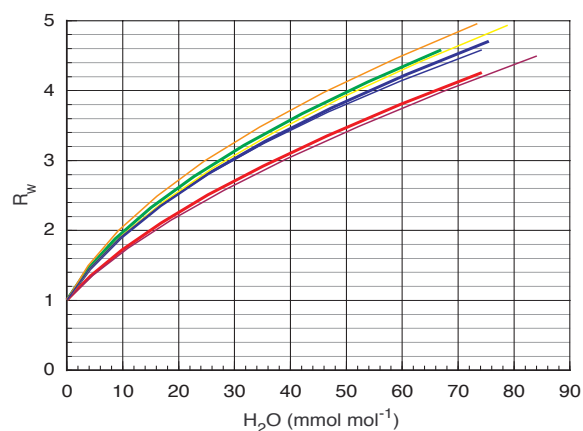


Figure 5. H_2O zero correction factors plotted for seven different LI-6262's.

If one uses a curve that sweeps through the middle of the ones plotted, the correction factor for water becomes

$$R_w \approx 1.13 + 0.0743W' - 3.67 \times 10^{-4}W'^2 \quad (24)$$

Example

Suppose IRG3-726 (calibration coefficients are listed under "Examples" on page 4) has a 100 mV offset. Its zero reading would be $14.4 \mu\text{mol mol}^{-1}$. When it is seeing $400 \mu\text{mol mol}^{-1}$ at 25°C , the reading would be 423.2

$\mu\text{mol mol}^{-1}$, however. To correct the 423.2 reading, we would use Equation (23) to compute R_c :

$$\begin{aligned} R_c &= 1 + 0.00164 \times 423.2 \\ &= 1.694 \end{aligned}$$

and then find C from Equation (21):

$$\begin{aligned} C &= 423.2 - 14.4 \times 1.694 \\ &= 398.8 \end{aligned}$$

This is an over correction of $1.2 \mu\text{mol mol}^{-1}$, or 0.3%.

A 100 mV offset in the water channel for this IRGA produces a reading of $0.661 \text{ mmol mol}^{-1}$. When measuring 30 mmol mol^{-1} gas, the IRGA would read $32.11 \text{ mmol mol}^{-1}$. To correct the 32.11 reading, we would compute

$$\begin{aligned} R_w &= 1.13 + 0.0743 \times 32.11 - 3.67 \times 10^{-4} \times 1031 \\ &= 3.14 \end{aligned}$$

and

$$\begin{aligned} W &= 32.11 - 0.661 \times 3.14 \\ &= 30.04 \end{aligned}$$

which is an under correction of $0.04 \text{ mmol mol}^{-1}$, or 0.1%.

For Greater Precision, cont'd

Improved accuracy for either Equation (23) or (24) can be achieved by following Steps 1 through 6 under "For Greater Precision" on page 4 (skip Steps 5 and 6 if you want). Then add the following steps:

7. Compute a column (E) of slope ratios

$$E = \frac{C}{a}$$

where a is your analyzer's first calibration coefficient (the A term, typically a value like 0.14 for CO_2 , or 0.006 for H_2O).

8. Plot E as a function of B, and fit a curve. A straight line is probably good enough for CO_2 , and a 2nd order polynomial is good enough for H_2O . Use this curve for R_c (Equation (23)) or R_w (Equation (24)).