LI-6251
CO_2 Analyzer

INSTRUCTION MANUAL

LI-COR®

LI-6251 CO_2 Analyzer

Operating and Service Manual

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NOTICE

Printing History

New editions of this manual will incorporate all material since the previous editions. Update packages may be used between editions which contain replacement and additional pages to be merged into the manual by the user.

The manual printing date indicates its current edition. The printing date changes when a new edition is printed. (Minor corrections and updates which are incorporated at reprint do not cause the date to change).

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LI-6251 History

Date	Serial Number	Modification
February, 1990	IRG1-166 & above	Calibration to 3000 ppm.
April, 1990	IRG1-172 & above	4 1/2 digit panel meters, 2-position function switches, new detector housings installed.
July, 1991	IRG1-202 & above	New instrument back panels and terminal strips, charging power supplies installed.

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Section I
Unpacking and Initial Inspection

1.1 What's What

This procedure should be followed if you have just taken delivery on your LI-6251. Check the packing list to verify that you have received everything that was ordered and that you have also received the following items:

Calibration Sheet - This data sheet contains a copy of the calibration information which was measured at the factory. Keep this sheet in a safe place for future reference.

Spare Parts Kit - This bag contains replacement parts for your LI-6251. As you become familiar with the analyzer you will learn which items to keep close at hand and which items can be stored away.

External Scrubber and Desiccant Tube - This tube is used during normal operation. Several spare gaskets and adhesive disks have been included for future use.

There are several optional accessories available for use with the LI-6251, including:

> **6000B Rechargeable Battery** (provides 3.2 hours of battery life).
>
> **6200B Rechargeable Battery** (provides 6.4 hours of battery life).
>
> **LI-6020 Battery Charger** (92-138/184-276 VAC, 47 to 63 Hz).
>
> **LI-670 Flow Control Unit** - the LI-670 is a valuable accessory for the LI-6251, which can be used for a variety of calibration and gas exchange measurement functions. The simplest use of the LI-670 is for a constant source of air flow to the LI-6251. Independent pumps and rotameters allow variable flow rates through the LI-6251 sample and reference cells. Soda lime and desiccant tubes provide a zero gas

source for calibration of the LI-6251; a span gas can be swapped between cells to adjust for any zero offset present during calibration. The LI-670 can also be used as a power source for the LI-6251; a built-in low battery detection circuit monitors battery life of the system. Mounting brackets are included for attaching the LI-670 and LI-6251, making the system completely portable.

1.2 Checking the Batteries (If purchased)

Batteries are tested and fully charged when they leave the factory, but they may discharge during shipping. It is a good idea to test each battery to see if it is charged. If the batteries are below 12V, they should be charged before use. Refer to Section 8.1 for charging instructions.

NOTE: Never store batteries in a discharged state. Recharge stored batteries every 3 months.

Section II
Pre-Operation

2.1 Power On

1. If a LI-COR rechargeable battery is being used, connect it to the 10.5-16VDC battery connector on the rear panel. A fully charged 6000B Rechargeable Battery will provide power for approximately 3.2 hours at 25 °C, or 2.4 hours at 40 °C. The 6200B Rechargeable Battery has twice the capacity of the 6000B. Instructions for recharging these batteries are given in Section 8.1.

   One set of battery leads with a 3-pin plug is included in the spare parts kit for connection to a user-supplied battery (10.5 - 16VDC, 1.5 amp maximum) or other DC power supply.

   If AC line voltage is being used, make sure the AC VOLTAGE selector on the back panel is set correctly (choose the 115 setting for 100-130VAC, or the 220 setting for 200-260VAC), and plug the line cord into the receptacle on the back panel.

2. Turn the power switch on the front panel ON. The fan will run, and after a few seconds, the chopper motor will come up to speed. The READY light on the front panel will come on after 1-3 minutes. (The higher the ambient temperature, the longer it takes). Any one of the following conditions will cause the READY light to fail:

   - Ambient temperature greater than about 55 °C.
   - Level of CO_2 is too high in the reference cell (greater than about 3000 ppm).
   - CO_2 or water vapor in the detector, caused by the internal soda lime/desiccant bottle being exhausted.

Low Battery

IMPORTANT: The LI-6251 has no built-in circuitry for monitoring battery voltage. When battery voltage drops below approximately 10.5 volts, the analyzer will shut down, and data transmission will stop. It is therefore suggested that battery voltage be monitored regularly to avoid system shutdown.

You may wish to monitor battery voltage with an external voltmeter, or use a timer with an alarm to alert the user to possible system shutdown. If you intend to operate the LI-6251 with battery power for more than 3 hours with the 6000B (6 hours with the 6200B), it is recommended that a user-supplied battery with a larger storage capacity be connected using the battery leads included with the LI-6251, or that several batteries be used in parallel for longer operation.

Alternatively, the LI-670 Flow Control Unit's built-in low battery detection circuit can be used to monitor battery life of the system.

2.2 Set-up

Prepare a soda lime tube, as described in Section 8.4, and attach to the **SCRUBBER** holder on the back panel.

Differential Mode Operation

- Attach the bottom hose from the scrubber tube assembly to the **FROM CHOPPER** fitting, and the other hose to the **TO CHOPPER** fitting (Figure 2-1).

Figure 2-1. Hose connections for operation in differential mode.

Absolute Mode Operation

- Attach the bottom hose from the soda lime tube to the **FROM CHOPPER** fitting.

- Attach the top hose to the **REFERENCE IN** fitting.

- Attach a jumper hose between the **REFERENCE OUT** and **TO CHOPPER** fittings.

Figure 2-2. Hose connections for operation in absolute mode.

2.3 CO_2 Voltage Outputs

The CO_2 voltage output can be measured by connecting a metering device to the terminal strip on the back of the analyzer. The output for CO_2 is approximately 0 to 15 volts full scale (typically 4V at 1000 ppm and 7V at 3000 ppm) and is measured through one of three terminals which provide a choice of response times (1, 4, or 15 seconds).

To measure the non-linearized voltage output of the analyzer (1 second response time) with a data logger or chart recorder, connect the positive input of the data logger to the first terminal from the top labeled **CO_2 1S,** and the negative lead to the terminal labeled **GND**. If the cable from the data logger is shielded, the shield can be connected to the **CHASSIS GND** terminal. To measure analyzer temperature or the voltage output with a different response time, connect the appropriately labeled terminal to the positive input of another channel on the data logger.

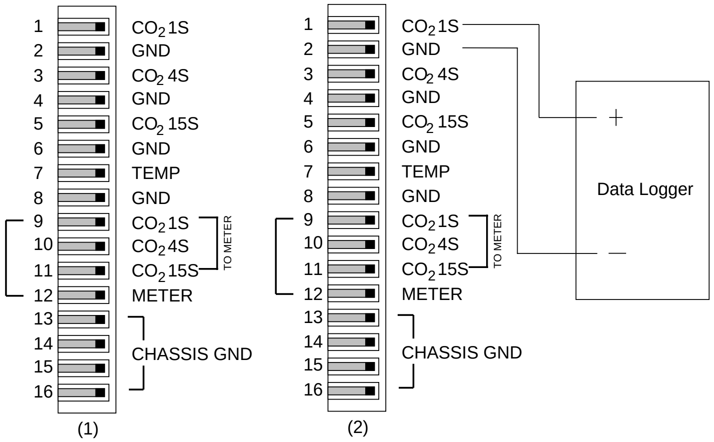


Figure 2-3. 1) Connection of the panel meter jumper. 2) Connection of the panel meter and a data logger.

2.4 Temperature Voltage Output

The voltage output of the analyzer temperature thermistor is a 0 to 5 volt linear signal, where 0 volts = 0 °C and 5 volts = 50 °C. To measure the temperature output voltage, connect the positive input of the data logger or meter to the **TEMP** terminal on the terminal strip, and the negative input to the **GND** terminal.

2.5 The Panel Meter

The front panel meter can display either the millivolt output of the CO_2 analyzer or the temperature of the analyzer in °C. The output that is displayed is selected by the meter function switch located next to the ready light on the front panel.

The CO_2 signal is not internally connected to the meter. To use the meter, connect a jumper (provided) between the CO_2 output terminal with the desired time response and the terminal labeled **METER** (Figure 2-3). The analyzer temperature is connected directly to the meter and requires no external jumpers.

Section III
Computing CO_2 Concentration

3.1 Definition of Terms

The LI-6251 is not capable of computing CO_2 concentrations. It only provides two mV signals (one for CO_2, and one for temperature) from which the CO_2 concentration may be calculated using constants provided on the calibration sheet accompanying your instrument. The equations needed to compute CO_2 concentration are provided in this section, along with discussions and examples to make them clear. Derivations and theoretical discussions are given in Sections V and VI. All of the equations are summarized in Section 3.2.

A DOS (version 2.11 or higher) program called `COMPCO2.EXE` (part #6200-28) is provided with each LI-6251. The program can be used to perform individual calculations, or as a benchmark for comparison with hand or computer calculations. A source code listing for a sample program that has a somewhat simpler input/output format is given in Appendix C.

These symbols will be used in the discussion that follows:

$\mathbf{C_r}$	reference CO_2 mole fraction (µmol/mol).
$\mathbf{C_s}$	sample CO_2 mole fraction (µmol/mol).
$\mathbf{V_t}$	temperature signal (mV).
$\mathbf{V_c}$	measured CO_2 voltage in absolute or differential mode (mV).
$\mathbf{V_r}$	computed voltage that would result if C_r were measured in the sample cell against 0 µmol/mol in the reference cell (mV).
$\mathbf{V_s}$	computed voltage used in the calibration polynomial in differential mode (mV).
T	IRGA temperature (°C or °K, depending upon context).
$\mathbf{T_o}$	IRGA calibration temperature (°C or °K, depending upon context).
K	differential mode calibration factor (mV).
P	local barometric pressure (kPa).
$\mathbf{P_o}$	standard barometric pressure (101.3 kPa).
G	gain increase correction factor for differential mode ($G \leq 1$, dimensionless).
s	approximate differential voltage multiplier (ppm/mV).

F(x) calibration polynomial (µmol/mol).

$$F(x) = a_1 x + a_2 x^2 + a_3 x^3 \tag{3-1}$$

where x is a function of voltage and pressure, and a_1, a_2 and a_3 are calibration coefficients given on the calibration sheet. The general form of the calibration function is

$$C = F\left(V \frac{P_o}{P} \right) \left(\frac{T}{T_o} \right) \tag{3-2}$$

where x in equation (3-1) is equal to V P_o/P in equation (3-2).

If pressure is not measured, and you are not at high altitude, then it is convenient to assume $P_o/P = 1$, to simplify the calculations. Changing span multiplies voltage in a way that is analogous to multiplying by the pressure ratio, so adjusting the span compensates for the effects of pressure. At high altitude there may not be enough range on the span potentiometer to compensate for the reduced pressure, and pressure will then have to be explicitly included in the calculations. Also, pressure must be measured and corrections applied during long-term, unattended measurements (See Section 4.4).

3.2 Equation Summary

a. Analyzer temperature (°C)

$T = 0.012207\ V_t$ (serial numbers IRG1-171 and below). (3-3)
$T = 0.01\ V_t$ (serial numbers IRG1-172 and above).

b. CO_2 mole fraction, *absolute mode* (µmol mol^{-1})

$$C = F\left(V_c \frac{P_o}{P} \right) \left(\frac{T}{T_o} \right) \tag{3-4}$$

where T and T_o are absolute temperature in °K.

c. CO_2 mole fraction, *differential mode.* Method 1. C_r known and constant.

$$C_s = F\left[\left(V_c G + V_r\right)\frac{P_o}{P}\right]\left(\frac{T}{T_o}\right) \tag{3-5}$$

$$V_r = F^{-1}\left[C_r\left(\frac{T_o}{T}\right)\right]\left(\frac{P}{P_o}\right) \tag{3-6}$$

V_r can be obtained from equation (3-2) using a lookup table, by Newton iteration given C_r, T and P (Section 3.4, Example 4), or by direct measurement (see Section f, below).

$$G = \left(1 - \frac{V_r}{K}\right) \tag{3-7}$$

$$\Delta C = C_s - C_r \tag{3-8}$$

Use Method 1 when V_r is updated each time ΔC is calculated. It is very sensitive to small differences in T or P values used in equations (3-5) and (3-6).

d. CO_2 mole fraction, *differential mode*. Method 2. CO_2 differential computed directly from the voltage differential. C_r known and constant.

$$\Delta C = \left(A_1 X + A_2 X^2 + A_3 X^3\right)\left(\frac{T}{T_o}\right) \tag{3-9}$$

where

$$\begin{aligned} A_1 &= a_1 + 2a_2(V_r P_o/P) + 3a_3(V_r P_o/P)^2 \\ A_2 &= a_2 + 3a_3(V_r P_o/P) \\ A3 &= a_3 \end{aligned} \tag{3-10}$$

and

$$X = \left(V_c G \frac{P_o}{P}\right) \tag{3-11}$$

V_r and G are obtained from equations (3-6) and (3-7). Use Method 2 when V_r is updated less often than ΔC is calculated. Computations are more elaborate than Method 1, but Method 2 is much less sensitive to small differences in T or P values used in equations (3-6) and (3-9) to (3-11). See Table 3-3.

e. CO_2 mole fraction, *differential mode.* Method 3. Approximate. C_r known and constant.

$$s = A_1\left(\frac{T}{T_o}\right)\left(\frac{P_o}{P}\right)G \tag{3-12}$$

$$\Delta C \cong s\, V_c \tag{3-13}$$

A_1 and G can be obtained from a table on the calibration sheet, or from equations (3-10) and (3-7). Enter the table with $C_r\, T_o/T$ to find $V_r\, P_o/P$ and A_1 ("SLOPE"), and enter with V_r to find G. Error with this method is less than 2% when $|V_c| < 100$ mV.

f. Direct measurement of V_r when the sample cell is scrubbed; $C_s = 0$, C_r unknown.

$$V_r = \frac{-V_c}{1 - \frac{V_c}{K}} \tag{3-14}$$

C_r is computed from equation (3-2) with $V = V_r$.

3.3 Computing Temperature

Temperature is a linear function of the temperature thermistor output voltage, V_t. Instruments with serial numbers of IRG1-171 and below have a 3 1/2 digit display, and temperature output voltages of 0-4096 mV over 0-50 °C. So,

$$T(°C) = 0.012207\, V_t\, \{mV\}$$

For example, a signal of 1500 mV corresponds to 18.31 °C. Instruments with serial numbers IRG1-172 and above have 4 1/2 digit displays, and temperature output voltages of 0-5000 mV over 0-50 °C. So,

$$T(°C) = 0.01\, V_t\, \{mV\}$$

A signal of 1500 mV would correspond to 15 °C.

3.4 Computing CO_2 Mole Fraction: Absolute Mode

Absolute mode means that the sample cell CO_2 concentration C_s is measured against zero in the reference cell ($C_r = 0$). The CO_2 mole fraction is computed by combining equations (3-1) and (3-4).

$$C_s = F\left(V_c \frac{P_o}{P}\right)\left(\frac{T+273}{T_o+273}\right),$$

or,

$$C_s = \left[a_1\left(V_c \frac{P_o}{P}\right) + a_2\left(V_c \frac{P_o}{P}\right)^2 + a_3\left(V_c \frac{P_o}{P}\right)^3\right]\left(\frac{T+273}{T_o+273}\right) \qquad (3\text{-}15)$$

Example 1. Assume your analyzer has calibration constants K = 19130, $T_o = 40.2$, $a_1 = 0.142$, $a_2 = 2.258E\text{-}5$ (E-5 is equivalent to x 10^{-5}), $a_3 = 1.787E\text{-}9$, and it gives the following signals when $C_r = 0$ and P = 99.5 kPa: $V_c = 2150$ mV and $V_t = 2500$ mV. Find the sample cell CO_2 mole fraction.

Solution. (Assume here and in subsequent examples that the instrument serial number is below IRG1-171). Analyzer temperature is computed from equation (3-3) as, T = 0.012207 x 2500.0 mV = 30.5 °C, and $V_c\ P_o/P$ = 2150.0 (101.3/99.5) = 2188.9 mV. So, from equation (3-15),

$$C_s = \left[0.142(2188.9) + 2.258E\text{-}5\ (2188.9)^2 + 1.787E\text{-}9\ (2188.9)^3\right]\left(\frac{303.5}{313.2}\right)$$

C_s = 424.2 µmol/mol

3.5 Computing CO_2 Mole Fraction: Differential Mode.

Method 1. C_r is known and constant.

Differential mode means that the sample cell CO_2 concentration C_s is measured against a known and non-zero reference cell CO_2 concentration C_r. The measured voltage V_c is related to the CO_2 concentration difference ΔC, but the analyzer is designed in such a way that detector gain increases as CO_2 is added to the reference cell. The reasons for this gain increase are explained in Section V, but one of its consequences is that the measured output voltage must be corrected for the gain change, because the calibration polynomial was generated with $C_r = 0$, and no gain increase.

To compute sample cell CO_2 mole fraction, measure the voltage V_c arising from the CO_2 mole fraction difference between sample and reference cells, multiply by G to correct for the gain increase, add the voltage V_r that would develop if C_r were in the sample cell measured against 0 in the reference cell, and then insert the result into the calibration polynomial. This idea can be illustrated by considering that $C_s = \Delta C + C_r = (C_s - C_r) + C_r$. Similarly, $V_s = V_cG + V_r = \Delta V + V_r = (V_s - V_r) + V_r$, where ΔV is the value V_c would have if there were no gain increase, and V_r is computed from the known value of C_r. V_s is then put into the calibration function to compute C_s.

$$C_s = F\left[\left(V_cG + V_r\right)\frac{P_o}{P}\right]\left(\frac{T + 273}{T_o + 273}\right) \qquad \text{equation (3-5)}$$

The CO_2 difference is

$$\Delta C = C_s - C_r \qquad \text{equation (3-8)}$$

V_r can be obtained in three ways: (1) by direct measurement while scrubbing the sample cell (see Section 3.6), (2) from a lookup table given on the calibration sheet, or (3) by solving $C_r = F(V_r\ P_o/P)\ T/T_o$ for V_r, given C_r. The calibration polynomial is 3rd order making the solution awkward, but it can be accomplished by iteration using Newton's method. An algorithm for doing that is given later in this section.

The gain correction G is computed from V_r according to

$$G = \left(1 - \frac{V_r}{K}\right) \qquad \text{equation (3-7)}$$

where K is obtained from the calibration sheet. Note that G is always less than 1 when $V_r > 0$.

Calibration table. A lookup table designed to simplify calculations is provided on every LI-6251 calibration sheet. A portion of a calibration sheet is shown in Table 1. The table gives CO_2 mole fraction (ppm), voltage (mV), gain correction G, and the slope of the calibration function at the given voltage (ppm/mV). The column marked "ppm" gives C = F(V), and computes CO_2 mole fraction from voltage using equation (3-1) with x = V.

Any temperature or pressure corrections must be applied to C or V before entering the table. The form of those corrections is given by equation (3-2), and is repeated in slightly different form in equation (3-16)

$$C\frac{T_o}{T} = F\left(V\frac{P_o}{P}\right). \tag{3-16}$$

The table can be used in either direction,

$$V\frac{P_o}{P} = F^{-1}\left(C\frac{T_o}{T}\right), \tag{3-17}$$

and it can be used in either absolute or differential mode. Table entries are exact when appropriate temperature and pressure corrections are applied. The slope can be used to simplify linear interpolation calculations for values falling between table entries. Slightly better accuracy will result if you interpolate from lower known values to higher unknown values of C or V.

Equation (3-17) is the inverse of equation (3-16). Given a function $y = f(x)$, the notation $f^{-1}(y) = x$ specifies the solution of the function $y = f(x)$ for the independent variable x, given the dependent variable y. We will use this convenient notation frequently.

Table 3-1. LI-6251 CO_2 Analyzer Calibration Data (1600-3020 mV)

Low Range (0-1000 ppm)
$a_1 = 0.1420$
$a_2 = 2.258E-05$
$a_3 = 1.787E-09$

In the table below, V is the CO_2 signal in mV, PPM = F(v), SLOPE = $a_1 + 2a_2V + 3a_3V^2$, and G = (1-v/K).

V	PPM	SLOPE	G	V	PPM	SLOPE	G
1600	292.3	0.228	0.916	2320	473.3	0.276	0.879
1620	296.9	0.229	0.915	2340	478.8	0.277	0.878
1640	301.5	0.230	0.914	2360	484.4	0.278	0.877
1660	306.1	0.232	0.913	2380	490.0	0.280	0.876
1680	310.8	0.233	0.912	2400	495.6	0.281	0.875
1700	315.4	0.234	0.911	2420	501.2	0.283	0.873
1720	320.1	0.236	0.910	2440	506.9	0.284	0.872
1740	324.9	0.237	0.909	2460	512.6	0.286	0.871
1760	329.6	0.238	0.908	2480	518.3	0.287	0.870
1780	334.4	0.239	0.907	2500	524.0	0.288	0.869
1800	339.2	0.241	0.906	2520	529.8	0.290	0.868
1820	344.0	0.242	0.905	2540	535.6	0.291	0.867
1840	348.9	0.243	0.904	2560	541.5	0.293	0.866
1860	353.7	0.245	0.903	2580	547.4	0.294	0.865
1880	358.6	0.246	0.902	2600	553.2	0.296	0.864
1900	363.6	0.247	0.901	2620	559.2	0.297	0.863
1920	368.5	0.248	0.900	2640	565.1	0.299	0.862
1940	373.5	0.250	0.899	2660	571.1	0.300	0.861
1960	378.5	0.251	0.898	2680	577.1	0.302	0.860
1980	383.6	0.252	0.896	2700	583.2	0.303	0.859
2000	388.6	0.254	0.895	2720	589.3	0.304	0.858
2020	393.7	0.255	0.894	2740	595.4	0.306	0.857
2040	398.8	0.256	0.893	2760	601.5	0.307	0.856
2060	404.0	0.258	0.892	2780	607.7	0.309	0.855
2080	409.1	0.259	0.891	2800	613.9	0.310	0.854
2100	414.3	0.260	0.890	2820	620.1	0.312	0.853
2120	419.6	0.262	0.889	2840	626.3	0.313	0.852
2140	424.8	0.263	0.888	2860	632.6	0.315	0.850
2160	430.1	0.265	0.887	2880	638.9	0.317	0.849
2180	435.4	0.266	0.886	2900	645.3	0.318	0.848
2200	440.7	0.267	0.885	2920	651.7	0.320	0.847
2220	446.1	0.269	0.884	2940	658.1	0.321	0.846
2240	451.5	0.270	0.883	2960	664.5	0.323	0.845
2260	456.9	0.271	0.882	2980	671.0	0.324	0.844
2280	462.3	0.273	0.881	3000	677.5	0.326	0.843
2300	467.8	0.274	0.880	3020	684.0	0.327	0.842

Note that in the calibration table (Table 3-1) "V" may mean V_s, V_r, $V_s\ P_o/P$, $V_r\ P_o/P$, etc.; and "C" may mean C_r, C_s, $C_r\ T_o/T$, or $C_s\ T_o/T$. The tables know nothing of temperature or pressure corrections, or distinctions between sample and reference. The precise meaning of tabulated values depends upon the context in which they are applied.

Example 2. Assume that C_r = 381ppm, P = 99.5 kPa, V_c = -300 mV and V_t = 1988 mV. Find V_r from the example calibration sheet given in Table 1, and compute C_s for the analyzer given in Example 1.

Solution. The temperature is 1988(0.012207) = 24.3 °C; T_o/T = (273+40.2)/(273+24.3) = 1.0535; C_rT_o/T = 381 (1.0535) = 401.4 ppm. From Table 1 and equation (3-17), 401.4 ppm corresponds to V_{Table} = 2050 mV = $V_r\ P_o/P$; P_o/P = 101.3/99.5 = 1.0181, so V_r = 2050 /1.0181 = 2013.6 mV. The gain correction is G = 1 - 2013.6/19130 = .8947, and V_s = -300 (.8947) + 2013.6 = 1745.2 mV. Therefore,

$$\begin{aligned} C_s &= F[1745.2\ (1.0181)]\ (.9492) \\ &= [0.142(1776.8) + 2.258\text{E-}5(1776.8)^2 + 1.787\text{E-}9(1776.8)^3]\ (.9492) \\ &\mathbf{= 316.7\ ppm} \end{aligned}$$

Algorithm for Newton iteration. The theory of Newton iteration is discussed in most introductory calculus or numerical analysis textbooks and will not be elaborated here. But we would like to present the algorithm in a way that can be easily applied to the present problem. Given C_r, solve $C_r = F(V_r\ P_o/P)\ T/T_o$ for V_r. The problem is simplified if a new variable x is defined such that $x = V_r\ P_o/P$. So

$$C_r \frac{T_o}{T} = F(x) \qquad (3\text{-}18)$$

The strategy is to find a recursion formula that uses an initial guess at the solution to compute a second better guess, and so on, until the successive guesses converge on the solution. Newton's formula works very well and converges in 5 or fewer iterations,

$$x_2 = x_1 - \frac{F(x_1) - C_r \frac{T_o}{T}}{\frac{dF(x_1)}{dx}}, \qquad (3\text{-}19)$$

where $F(x_1)$ is defined by equation (3-1) and $dF(x_1)/dx = a_1 + 2a_2x_1 + 3a_3x_1^2$. The solution is found when the difference between the last two guesses is less than some predetermined tolerance, $|x_i - x_{i-1}| < \text{tol}$ (e.g. 0.1mV), and

$$V_r = x_i \frac{P}{P_o} \tag{3-20}$$

Example 3. Find C_s from Example 2 using Newton's method with x_1 =2500 mV, and tol = 0.1 mV.

Solution. $C_r\, T_o/T$ = 381 (40.2+273)/(24.3+273) = 401.4 ppm. Equation (3-19) becomes

$$x_2 = x_1 - \frac{a_1x_1 + a_2x_1^{\,2} + a_3x_1^{\,3} - 401.4}{a_1 + 2a_2x_1 + 3a_3x_1^{\,2}}$$

The iteration procedure is illustrated in the following table:

Iterations (i)	x_i	x_{i+1}	$\|x_i - x_{i+1}\|$
1	2500.00	2074.66	425.34
2	2074.66	2050.04	24.62
3	2050.04	2049.96	0.08
4	2049.96	2049.96	0.00

V_r = $x_4\, P_o/P$
V_r = 2049.96 (99.5/101.3) = 2013.53

C_s = $F(V_c\, G + V_r)\, P_o/P]\, T/T_o$
= F[(-300(.8947) + 2013.53) 1.0181] .9492
= [0.142 (1776.7) + 2.258E-5$(1776.7)^2$ + 1.787E-9$(1776.7)^3$] 0.9492
Cs = 316.65 µmol/mol

which, except for roundoff errors, is the same answer as Example 2. The answers are identical if more digits are carried along in the calculations.

Method 2. ΔC computed directly from voltage differential. C_r is known and constant.

Method 1 works well when V_r is continually recomputed from C_r using the current temperature and pressure. However, large errors result if V_r is computed from C_r at one temperature and pressure, while ΔC is computed at a different temperature or pressure. This might arise, for example, if V_r is computed and then used as a constant over some time period during which variable temperatures or pressures are used to compute ΔC from equations (3-5) and (3-8). The errors occur both as zero offsets when $V_c = 0$, and span errors when $V_c \neq 0$ (Table 3-2).

Table 3-2. Sensitivity of Method 1 and Method 2 to differences in temperature and pressure used in the calculation of V_r and ΔC. Tabulated values give the apparent CO_2 differentials that would result if the analyzer reads V_c=0, or V_c= -100mV, at the indicated temperatures and pressures, when V_r is computed using T=30 °C, P=100 kPa, and C_r=350 ppm. In the controls, V_r and ΔC are both computed at the indicated temperature and pressure.

		Method 1		Method 2		Control	
T	P	V_c=0	V_c=-100	V_c=0	V_c=-100	V_c=0	V_c=-100
°C	kPa	ΔC, µmol mol^{-1}					
25	100	-5.8	-27.0	0	-21.2	0	-21.3
30	100	0	-21.6	0	-21.6	0	-21.6
35	100	5.8	-16.1	0	-21.9	0	-21.8
30	99	4.6	-17.3	0	-21.9	0	-21.8
30	101	-4.5	-25.7	0	-21.2	0	-21.3

Temperature and pressure sensivity can be greatly reduced if ΔC is computed directly from the measured voltage differential V_c, instead of by difference, as in Method 1 (Table 3-2). The initial calculations are a little more complex, but they are worth the effort if V_r is not continually updated. ΔC is computed according to equations (3-9) to (3-11), and V_r is computed in the same way as described in Method 1.

$$\Delta C = \left(A_1X + A_2X^2 + A_3X^3\right)\left(\frac{T}{T_o}\right) \qquad \text{(equation 3-9)}$$

where

$$A_1 = a_1 + 2a_2(V_rP_o/P) + 3a_3(V_rP_o/P)^2$$
$$A_2 = a_2 + 3a_3(V_rP_o/P) \qquad \text{(equations 3-10)}$$
$$A3 = a_3$$

and

$$X = \left(V_c G \frac{P_o}{P}\right) \qquad \text{(equation 3-11)}$$

Examination of equations (3-9) to (3-11) shows that $\Delta C = 0$ when $V_c = 0$ regardless of the values of T or P, so zero errors are eliminated. Furthermore, T or P errors would rarely be more than a percent or so, and in Method 2 those errors appear more or less as span scalars that lead to comparable-sized span errors. By contrast, errors arising from Method 1 are on the order of 1 ppm per °C, when $C_r = 350$ ppm. This can cause relative errors in ΔC that are many times larger than those that occur with the same temperature or pressure uncertainties using Method 2 (Table 3-2).

Example 4. Assume T = 30 °C, P = 95 kPa, $C_r = 700$ ppm, and $V_c = -200$ mV. Find ΔC.

Solution. From the iteration procedure, $V_r = 2943.97$. So, G = 1 - 2943.97 / 19130 = 0.8461, $V_r\ P_o/P = 3139.2$ mV and X = -200 (.8461) (101.3) / 95 = -180.44 mV. Using these values in equations (3-10), $A_1 = 0.3366$, $A_2 = 3.9409\text{E-}5$, and $A_3 = 1.787\text{E-}9$. From these coefficients and equation (3-9), ΔC = -57.53 ppm.

If we now assume T changes to 31 °C, and recompute ΔC without recomputing V_r, we find that Method 1 gives ΔC = -55.41 ppm, and Method 2 gives ΔC = -57.72 ppm. When V_r is recomputed with T = 31 °C, both methods give ΔC = -57.64 ppm. Method 2 gives much more accurate answers when temperature or pressure varies but V_r is not recomputed for each new ΔC value.

Method 3. Approximate; ΔC must be small. C_r is known. Many times it is desirable to be able to estimate the CO_2 differential from the displayed panel voltage or a recorder trace. An approximate voltage multiplier s can be derived from the first derivative of the calibration function evaluated at $V = V_r$. The first term of equation (3-9), along with the definitions of A_1 and X from equations (3-10) and (3-11) provide the required result.

$$s = A_1 \left(\frac{T}{T_o} \right) \left(\frac{P_o}{P} \right) G \qquad \text{(equation 3-12)}$$

$$\Delta C \cong s\, V_c \qquad \text{(equation 3-13)}$$

A_1 and G are given in Table 3-1 and on the calibration sheet accompanying each LI-6251. A_1 is given by the column labeled "SLOPE", and s is the desired voltage multiplier. Error is less than 2% when $|V_c|$ is 100 mV or less for any reference CO_2 mole fraction below 2000 µmol/mol, and is shown graphically in Figure 1 for a range of CO_2 differentials and C_r values.

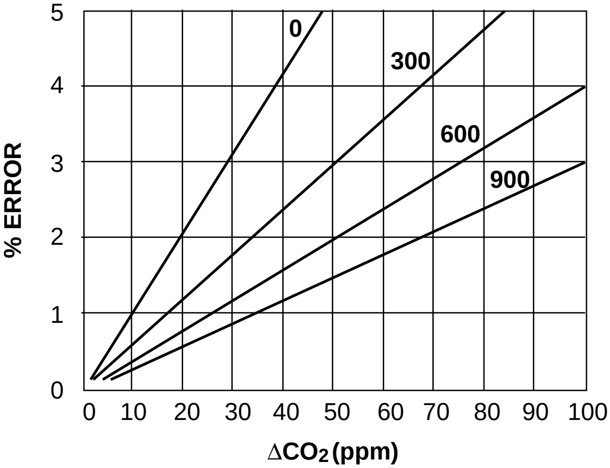


Figure 3-1. Percent error when assuming a linear response of the analyzer while in differential mode, shown for 4 reference gas concentrations: 0, 300, 600, and 900 ppm.

Table 3-3 shows that Method 3 is well suited to changes in C_r, T and P, within the accuracy limits of the calculation. There is probably no need to recompute s unless environmental variables change by more than |ΔC| > 10 ppm, |ΔT| > 5 C, and |ΔP| > 1 kPa.

Table 3-3. Comparison of ΔC approximated using equations (3-12) and (3-13) with exact values. Approximate ΔC computed with C_r = 350 ppm, P = 100 kPa, and T = 30 °C. Exact ΔC values were computed for the conditions indicated in the table. All calculations assume V_c = -100 mV.

T (°C)	P (kPa)	C_r (ppm)	s (ppm mV^{-1})	Approx. ΔC (ppm)	Exact ΔC (ppm)	Error (%)
25	100	350	—	—	-21.3	2.3
30	100	350	0.218	-21.8	-21.6	0.9
35	100	350	—	—	-21.8	0.0
40	100	350	—	—	-21.9	-0.5
30	99	350	—	—	-21.8	0.0
30	101	350	—	—	-21.3	2.3
30	100	340	—	—	-21.4	1.9
30	100	360	—	—	-21.7	0.5

Example 5. Suppose you are working at an elevation of 1600m and want to measure photosynthesis using 369 ppm as a reference gas. Use Table 1 and equations (3-12) and (3-13) to compute the resulting CO_2 differential when P = 85 kPa, T = 24.4 °C, and V_c = -80 mV.

Solution. A change in pressure multiplies voltage in the same way as a change in electronic span, so pressure variations can be compensated with span changes (see Section 4.2). However, the span potentiometer has a limited range and cannot accomodate very large pressure variations, as would occur at high elevations. Therefore, pressure must be explicitly included in the calculations. At low elevations we could let $P_o/P = 1$.

1. Compute $C_r\, T_o/T$ = 369 (273 + 40.2)/(273 + 24.4) = 388.6 ppm.

2. Look up 388.6 ppm and find $V_{Table} = V_r\, P_o/P$ = 2000 mV, and slope = 0.254.

3. The gain correction G depends upon V_r, not $V_r\, P_o/P$ (equation 3-7); therefore, compute V_r = 2000 (85/101.3) = 2000 (.8391) = 1678 mV.

4. Look up 1678 mV and find G = 0.912.

5. From equation (3-12), compute s = (.254) (0.9496) (1.1918) (0.912) = .262 ppm/mV.

Perform the experiment and observe that V_c *= -80 mV.*

6. Compute ΔC = .262 (-80) = -21.0 ppm. s = 0.262 can be used in subsequent estimations of ΔC as long as C_r, T or P do not change dramatically. The exact value of ΔC is -20.7 ppm.

Summary

Assume pressure is explicitly included in the calculations. If not, $P_o/P = 1$. Estimate ΔC as follows:

1. Compute $C = C_r\ T_o/T$.
2. Look up $V_{Table} = V_r\ P_o/P$, and slope, at C.
3. Compute $V_r = V_{Table}\ P/P_o$.
4. Look up G at V_r.
5. Compute s = Slope $(T/T_o)\ (P_o/P)$ G.
6. Compute $\Delta C = s\ V_c$.

You may wonder why G varies with V_r, while C_r and s depend upon $V_r\ P_o/P$. The reason is that C_r and S both relate a voltage to CO_2 absorptance and concentration, which vary with pressure; however, once the conditions leading to a given V_r are established, the gain change that follows is strictly electronic, having nothing to do with pressure.

3.6 C_r is unknown. Measuring C_r against $C_s = 0$.

Sometimes a CO_2 differential must be measured when the reference CO_2 mole fraction is not precisely known. For example, one might be measuring photosynthesis in the field with ambient air as the reference gas, the exact CO_2 mole fraction of which is not known. One could scrub the reference cell and measure the incoming CO_2 concentration in absolute mode. However, there will be a small zero shift when the reference gas is reduced from around 350 ppm to 0 ppm, so a zero adjustment must be made each time the reference cell is scrubbed. The same is true when ambient air is returned to the reference cell.

It is easier to leave the reference gas alone and scrub the sample cell; this avoids zero shifts and gain changes. One can then measure V_c and compute V_r and C_r according to equations (3-14) and (3-2).

$$V_r = \frac{-V_c}{1 - \frac{V_c}{K}} \qquad \text{equation (3-14)}$$

$$C_r = F\left(V_r \frac{P_o}{P}\right)\left(\frac{T + 273}{T_o + 273}\right) \qquad \text{equation (3-2)}$$

These values can be used as needed to compute C_s or ΔC over as long a time period as C_r and temperature are stable.

Example 6. Suppose the analyzer in Example 1 is operating in differential mode as part of a photosynthesis system, and you wish to measure C_r to check the value currently being used in calculations. The sample cell is scrubbed and the analyzer reads V_c = -2170 mV and V_t = 1988 mV. What are the values of V_r and C_r? Pressure is 99.5 kPa, as before.

Solution. V_r = -(-2170)/[1 - (-2170/19130] = 1948.9 mV. T = 1988 (0.012207) = 24.3 °C; T/T_o = .9492 and P_o/P = 1.0181. Notice that the measured voltage V_c is negative because the sample cell CO_2 concentration is less than the reference cell value, but V_r is positive as it would be if C_r were measured in the sample cell against zero in the reference cell. The absolute value of V_c is larger than V_r because the gain is elevated with C_r in the reference cell. So, C_r = F[1948.9 (1.0181)] 0.9492 = 365.1 ppm.

3.7 Moist air.

Moist air will be considered in Section 6 after a discussion of the water correction.

Section IV
User Calibration and Operation

4.1 Calibration - General Information

The factory calibration of the LI-6251 CO_2 Analyzer consists of determining the coefficients for the calibration polynomial F(V). These coefficients should be quite stable over time, but we recommend that they be checked every two years by returning the LI-6251 to LI-COR for recalibration.

The user calibration consists of adjusting the zero and span potentiometers so that the analyzer's output matches the calibration polynomial F(V). **This should be done on a daily basis, as the span varies with barometric pressure, and the zero varies with temperature.**

Figure 4-1 illustrates the effects of the zero and span adjustments.

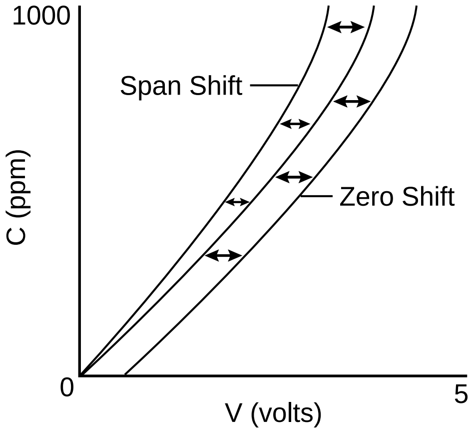


Figure 4-1. Effects of zero and span adjustments.

4.2 Calibration Procedures

It is important to remember that in differential mode the pressure on the two sides of the analyzer must be kept the same. For this reason, it is best to vent the exit ports (SAMPLE OUT and REFERENCE OUT) to the atmosphere. If you wish to flow the same gas through both sides of the analyzer, never do it by putting the sample and reference cells in series, as you will be guaranteed to have different pressures in the two cells. Instead, split the flow upstream of the analyzer, and run separate hoses to the reference and sample cells. Also, be sure the flow rates through both sides are the same.

For best repeatability, stop the flow a few seconds before making a CO_2 reading. This eliminates any pressure effects due to flow variations. This is not possible for every application, however.

There is generally a small zero shift when the reference CO_2 concentration changes. Therefore, the analyzer should be re-zeroed each time you change the reference CO_2 concentration.

We recommend that span gas concentrations be checked before you first use them, and then periodically thereafter. Calibrate the LI-6251 in absolute mode using a standard that you trust, and then use the calibrated analyzer to measure the concentration of other tanks. We find that "known" tanks are often out of specification when we receive them from suppliers, and they can change with time, especially when tank pressure drops below 500 psi (3450 kPa), or so. Your final standard might be the 6000-01 Calibration Cylinder, NIST-traceable tanks, mixed gases, etc. It is not necessary to buy expensive, high precision tanks for day-to-day working standards when this method is used.

We recommend that primary CO_2 standards be held in aluminum tanks, because they will maintain the most stable CO_2 concentrations over time. Steel tanks are fine for working standards.

Calibration gases should be mixed in air, not nitrogen. CO_2 infrared absorptance varies in different diluent gases; therefore, CO_2 in nitrogen will have a slightly different calibration function than CO_2 in air. The effects of diluent gases are discussed in more detail in Section VI.

Calibration gas concentrations should be selected so as to bracket working measurements. In absolute mode, the span should be set at a concentration higher than the highest working value; and in differential mode, the measured sample CO_2 concentrations and differentials should fall between the reference and sample cell concentrations used to set the span.

Zero and Span Calibration: Absolute and Differential Modes with one span gas.

Absolute mode. Set zero.

1. Flow dry, CO_2-free air through both the sample and reference cells.

2. Unlock and adjust the zero potentiometer until the display reads 0 mV.

Absolute mode. Set span.

3. Flow a known span gas through the sample cell.

4. Look up or compute $V_s P_o/P = F^{-1}(C_s T_o/T)$. (See Section 3.5, Method 1, or use the supplied program `COMPCO2`).

5. Unlock and adjust the span potentiometer until the display reads V_s. P_o/P may be assumed to equal 1 at lower elevations, but at high elevations V_s must be computed as, $V_s = V_{Table} P/P_o$. Include P_o/P in all subsequent calculations if the ratio does not equal 1.

The analyzer is now ready for use in absolute mode. Differential mode operation requires two additional steps.

Differential mode. Set zero.

6. Flow the span gas through both sample and reference cells.

7. Unlock and adjust the zero potentiometer until the display voltage again reads zero.

The instrument is now ready for use in differential mode. You can check the span by scrubbing the sample cell and measuring V_r using equation (3-14), Section 3.6: $V_r = -V_c / (1-V_c/K)$, where V_c is the displayed voltage. V_r should equal V_s in step 5 above. Make minor span adjustments, if necessary.

Zero and Span Calibration: Differential mode with two non-zero gases.

Set differential zero.

1. Flow dry gases with the same CO_2 mole fraction C_r through both sides of the analyzer, keeping the pressures in both sides equal.

2. Unlock the zero potentiometer and set the displayed voltage to zero.

Set differential span.

3. Flow a dry span gas with CO_2 mole fraction C_s through the sample cell while maintaining C_r in the reference cell.

4. Look up or compute $V_r P_o/P = F^{-1}(C_r T_o/T)$ and $V_s P_o/P = F^{-1}(C_s T_o/T)$. Then compute V_s, V_r, $G = 1 - V_r/K$, and $V_c = (V_s - V_r)/G$, and set the span to V_c.

Linear approximation: Differential mode with one non-zero gas.

Set differential zero as described above.

Measure differential multiplier, s.

1. Look up or calculate s as described in Section 3.5.

2. Compute $\Delta C \cong s V_c$.

Linear approximation: Differential mode with two non-zero gases.

Set differential zero as described above.

Measure differential multiplier, s.

1. Flow a dry span gas with CO_2 mole fraction C_s through the sample cell while maintaining C_r in the reference cell. Note the displayed voltage V.

2. Compute $s = (C_s - C_r)/V$, and then use $\Delta C = s V_c$ for subsequent measurements. This will have an accuracy of better than 2% for $V_c = V \pm 100$ mV.

4.3 Pressure

The LI-6251 is sensitive to both absolute atmospheric pressure and to pressure differences between the sample and reference cells. The pressure sensitivity derives from two sources. First, the CO_2 mole density (mole m^{-3}) is proportional to pressure when mole fraction is constant. Increased pressure means more absorber will be present in the light path. Second, the absorption per mole of CO_2 increases with pressure. For this reason, the pressure dependence cannot be removed simply by calibrating in terms of partial pressure or mole fraction.

Atmospheric pressure variations can be accommodated by using an electronic pressure sensor along with the LI-6251, so that pressure becomes an explicit part of the calculations (Section 3). Otherwise, the instrument must be re-spanned to take care of pressure changes. At high altitudes pressure may have to be included in the calculations if there is not enough span adjustment to compensate for the low pressure. If pressure is not being measured, set P to a reasonable value for your elevation, and set the span. P_o/P will then have to be included in subsequent calculations. A list of electronic pressure sensor suppliers in given in Section 4.4.

Pressure differences between the sample and reference side are minimized by careful plumbing and using low flow rates.

Another source of pressure error occurs when the instrument is calibrated at one flow rate (e.g. 0.5 liters/min), and used at another very different flow rate (e.g. 10 liters/min). If it is not possible to calibrate the LI-6251 at the flow rate to be used during operation, then a pressure correction factor can be computed to compensate for this:

1. Zero and span the instrument using low (calibration) flow.

2. Flow stable air through the analyzer at the high (operational) flow rate.

The concentration can be stabilized by using a large buffer volume upstream of the analyzer, if needed. Record the signal V_{high} at P_{high}.

3. Reduce the flow to the low rate, and record the signal V_{low} at P.

4. Compute the concentration C_s using V_{low}.

5. Compute the adjusted pressure P_{high}.

Now use P_{high} instead of P in the calculations. If you are not explicitly using pressure in the calculations ($P/P_o = 1$), then use $P_o/P_{high} = V_{low}/V_{high}$.

6. Check the results by computing concentration in step 2 using V_{high} and P_{high}. It should be very close to the C_s computed in step 4.

4.4 Long-term measurements

The LI-6251 has been designed to provide very high zero and span stability; nervertheless, it is best to check the zero and span periodically, preferably, at least once a day. If the LI-6251 is part of an automated data logging system, then a software zero and span should be designed into the system. Zero changes are due primarily to temperature shifts or dirt making its way into one of the analyzer optical paths. Span shifts are due to factors that affect both optical paths equally; for example, pressure changes, exhausted chemicals allowing CO_2 or water vapor to accumulate in the detector housing, dirty optics, etc.

Pressure is the most common cause of span shifts. Therefore, any automated system designed for long-term continuous operation should include an electronic barometer, so that pressure can be measured and used in calculations on a continuous basis. This should be in addition to the zero and span checking capability mentioned in the previous paragraph. Electronic barometers can be obtained from the suppliers listed below.

Water will condense on the detector if the dew point exceeds -12 °C inside the detector housing. This can cause very large zero shifts as well as span changes, so be sure to replace the detector soda lime and magnesium perchlorate as recommended in Section 8.3. After changing chemicals, *wait one day before powering up the analyzer to allow the chemicals time to work.*

Electronic barometer/pressure transducer suppliers:

MKS Instruments, Inc.
Six Shattuck Road
Andover, MA 01810
508-975-2350
1-800-227-8766

Dresser Industries-Instrument Div.
400 W. Lake St.
Suite 318
Roselle, IL 60172
708-980-9030

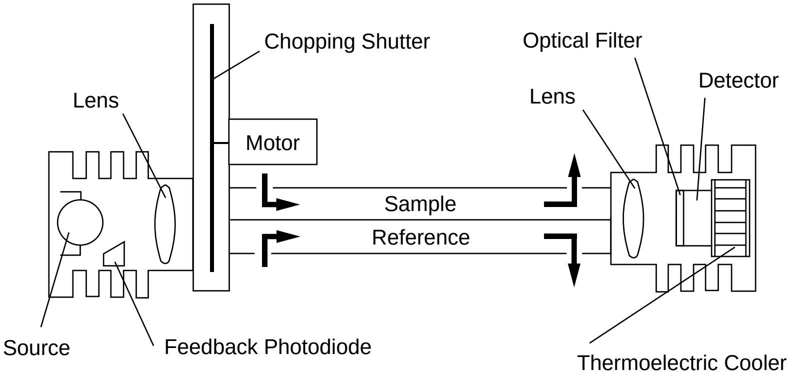
Omega
One Omega Drive
Box 4047
Stamford, CT 06907
1-800-826-6342

Druck, Inc.
4 Dunham Drive
New Fairfield, CT 06812
203-746-0400

Section V
Theory of Operation

5.1 General Description

The LI-6251 is a differential, non-dispersive, infrared (NDIR) gas analyzer. The CO_2 measurements are based on the difference in absorption of infrared (IR) radiation passing through two gas sampling cells. The **reference cell** is used for a gas of known CO_2 concentration, and the **sample** cell is used for a gas of unknown concentration. Infrared radiation is transmitted through both cell paths, and the output of the analyzer is proportional to the difference in absorption between the two.



The infrared **source** is vacuum sealed for long life (>10,000 hours) and high stability. A separate optical feedback circuit with a photodiode maintains the source at a constant color temperature (1000 °K). A gold reflector surrounding the IR source maximizes the radiation output from the source and decreases the power required.

The **chopping shutter** disc is spun by a phase locked loop controlled motor, whose shaft turns on high precision bearings for long life and low noise. Rotation is precisely controlled at 500 hertz. The optical path between the source and optical bench is sealed and continuously purged of CO_2 by an attached soda lime tube. This eliminates interference due to ambient CO_2.

The **sample cell** is gold-plated to enhance IR reflection and resist tarnishing over time.

A 150 nm bandpass optical **filter** is used to tune the CO_2 detector to the 4.26 micron absorption band for CO_2. It provides excellent rejection of IR radiation outside the desired band, allowing the analyzer to reject the response of other IR absorbing gases. The filter is mounted directly to the detector for thermal stability.

The **detector** is a lead selenide solid state device that is insensitive to vibration. The detector is cooled and regulated to -12 °C by thermoelectric coolers, and electronic circuits continuously monitor and maintain a constant detector sensitivity. The result of this detector circuitry is a detector system that is very stable. To keep the detector housing free of water vapor and CO_2, there is a small bottle of magnesium perchlorate and soda lime that is attached to the detector housing.

Infrared radiation from the source is focused through the gas cells and onto the detector by a lens at each end of the optical bench. Focusing the radiation maximizes the amount of radiation that reaches the detector in order to provide maximum signal sensitivity.

All of these features provide a noise level that is typically less than 0.2 ppm peak-to-peak (at 350 ppm) when using 1 second signal averaging. Signal averaging times are selectable at 1, 4, and 15 seconds and are used to achieve even lower noise levels. For example, with 15 seconds of signal averaging, the noise levels typically decrease 50%.

5.2 Calculating Gas Concentration - General

The analyzer's signal output V is proportional to the difference between the signals generated by the detector when it sees the sample cell (ν_s) and when it sees the reference cell (ν_r).

$$V = k(\nu_r - \nu_s) \tag{5-1}$$

The analyzer operates in such a way as to keep ν_r constant. If the gas concentration in the reference cell increases, the gain of the detector increases automatically to hold ν_r constant. This has important implications for operation in differential mode, as will be seen shortly. Since ν_r is held constant, we can factor it out of the proportionality constant k and use a new constant $K = k\,\nu_r$.

$$V = K\left(1 - \frac{\nu_s}{\nu_r}\right) \tag{5-2}$$

The constant K is provided on the calibration sheet. As the gas concentration in the sample cell increases, ν_s will decrease due to increased absorption of radiation. The signal output V increases in proportion to the amount of decrease of ν_s (Equation 5-2). Figure 5-1 illustrates a typical relationship between gas concentration, ν_s/ν_r, and signal output V.

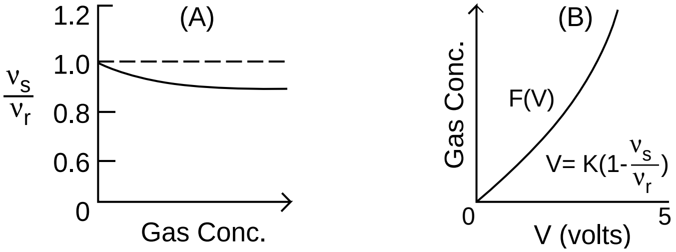


Figure 5-1. (A) The ratio of detector output while viewing the sample cell (ν_s) and the reference cell (ν_r) decreases with increasing gas concentration. (B) The signal output V is related to the ratio of ν_s to ν_r by Equation (5-2). Gas concentration in terms of V is the calibration function F(V).

The factory calibration of the analyzer consists of measuring the output V at several gas concentrations, and determining the coefficients for a third order polynomial F(V) that relates V to gas concentration, with a zero gas concentration in the reference cell.

$$F(V) = a_1V + a_2V^2 + a_3V^3 \tag{5-3}$$

Coefficients a_1, a_2, and a_3 are factory-determined for the specific gas, and are unique to each analyzer. *The calibration function F(V) is only valid for the temperature and pressure at which it was determined, and a zero gas concentration in the reference cell.* It has been found empirically that (absolute) temperature affects the gas concentration in a linear fashion, while pressure affects the signal output V in a linear fashion. Therefore, the expression relating signal output to gas concentration with a zero gas concentration in the reference cell (absolute mode) is

$$C = F\left(V\frac{P_o}{P}\right)\frac{T+273}{T_o+273} \tag{5-4}$$

Except at high altitudes, the effects of pressure can be compensated by adjusting the gain (span knob) of the analyzer.

With some other concentration in the reference cell, the gain of the detector will be higher. Recall that the analyzer seeks to maintain ν_r at a constant level. The increased gain means that the function F(V) should now be steeper, since the analyzer is now more sensitive. If we know the calibration function F(V), and the concentration C_r in the reference cell, we can predict the factor G by which the gain has changed. If ν_{sr} is what the detector's output would be with concentration C_r in the sample cell and zero concentration in the reference cell, then from Equation 5-2 we can write

$$G = \frac{\nu_{sr}}{\nu_r} = \left(1 - \frac{V_r}{K}\right) \tag{5-5}$$

where V_r is the signal output that would exist if there were zero concentration in the reference cell, and C_r in the sample cell. V_r is given by the inverse of F(V), corrected for temperature and pressure.

$$V_r = F\left[C_r\left(\frac{T+273}{T_o+273}\right)\right]\frac{P}{P_o} \tag{5-6}$$

The general expression then for gas concentration C in the sample cell given concentration C_r in the reference cell and analyzer signal output V is

$$C = F\left[(VG+V_r)\frac{P_o}{P}\right]\left[\frac{T+273}{T_o+273}\right] \tag{5-7}$$

The differential ΔC is simply $(C - C_r)$.

$$\Delta C = F\left[\left(VG+V_r\right)\frac{P_o}{P}\right]\left[\frac{T+273}{T_o+273}\right] - C_r \tag{5-8}$$

The differential ΔC can also be computed directly from the measured voltage V, instead of by difference as shown in equation 5-8. Equation 5-8 requires two sets of calculations, one to compute V_r from $C_{r,}$ and a second to compute ΔC from V and V_r. This is fine as long as the two calculations are done at the same time and use the same T and P values; however, large errors result if V_r and ΔC are computed at different times using different values of T or P. The direct method requires a little more calculation, but the resulting equation is much less sensitive to differences in T or P used in equation (5-4) to find V_r, and those used to compute ΔC.

The CO_2 mole fraction C in the sample cell, given mole fraction C_r in the reference cell is computed as

$$C = F\left[\left(VG + V_r\right)\frac{P_o}{P}\right]\frac{T}{T_o} \tag{5-9}$$

$$= \left\{a_1\left[\left(VG + V_r\right)\frac{P_o}{P}\right] + a_2\left[\left(VG + V_r\right)\frac{P_o}{P}\right]^2 + a_3\left[\left(VG + V_r\right)\frac{P_o}{P}\right]^3\right\}\frac{T}{T_o}$$

Equation (5-9) can be further expanded by distributing P_0/P through VG + V_r in each term, and raising the resulting expressions to the indicated powers. Like terms in powers of (VG P_0/P) are collected, and $C_r = F(V_r P_0/P)\, T/T_0$ is subtracted from both sides giving,

$$\Delta C = \left(A_1X + A_2X^2 + A_3X^3\right)\frac{T}{T_o} \tag{5-10}$$

where

$$\begin{aligned} A_1 &= a_1 + 2a_2(V_rP_o/P) + 3a_3(V_rP_o/P)^2 \\ A_2 &= a_2 + 3a_3(V_rP_o/P) \\ A3 &= a_3 \end{aligned} \tag{5-11}$$

and

$$X = VG\frac{P_o}{P} \tag{5-12}$$

Equations (5-10) to (5-12) can also be derived from a Taylor Series expansion of equation (5-9) about V = 0. The properties of equations (5-10) to (5-12) are described further in Section (3-5), Method 2.

5.3 Calculating CO_2 Partial Pressure and Weight Fraction

CO_2 partial pressure p_c (Pa) is computed from C and total pressure P (kPa) by

$$p_c = \frac{CP}{1000} \tag{5-13}$$

The CO_2 weight fraction C_g (µg/g) is computed as

$$C_g = \frac{44C}{M} \tag{5-14}$$

where M = molecular weight of air (g/mol), weighted for water vapor.
= 29(1 - w/1000) + 18w/1000
w = mole fraction of water vapor (mmol/mol).

Section VI
Water Corrections

6.1 General Information

The following sections will describe how water vapor affects CO_2 measurements, and how to perform the water corrections.

6.2 Pressure Broadening Due to Water Vapor

Water vapor can influence infrared detection of CO_2 in three ways: 1) direct absorption in the CO_2 waveband of interest, 2) dilution, and 3) pressure broadening. Direct infrared absorption by water vapor can be virtually eliminated by judicious choice of wavebands and filters, and methods to correct for dilution are well known (Section 6.3); however, pressure broadening is more of a problem.

Gas phase absorption of infrared radiation is due to energy-induced changes in vibrational and rotational energy states. Such energy states are altered by intermolecular collisions which increase in number as pressure increases. The kinetic theory of gases and quantum mechanics predict that absorption band widths increase with pressure, and it is observed that broad band infrared absorption increases as pressure increases at constant absorber amount.

Not all gases are equally effective in causing pressure-induced line broadening. Roughly speaking, gases that are similar are more effective than dissimilar gases.

This effect is embodied in the concept of equivalent pressure, or effective pressure, P_e (1,3). Total pressure P is equal to the sum of partial pressures of component gases, while equivalent pressure is defined as

$$P_e = a_1 p_1 + a_2 p_2 + \ldots$$

where a_i are weighting factors representing the pressure broadening effectiveness of each gas species relative to nitrogen ($a_{N_2} = 1$). For CO_2 in nitrogen, $P_e = p_{N_2} + 1.3p_{CO_2}$ (2).

Consider a simple atmosphere made up of H_2O vapor with partial pressure e, plus dry gases with pressure P_d, so that

$$P = P_d + e,$$

or, in mole fraction units,

$$1 = X_d + X_w \tag{6-1}$$

where X_d is the mole fraction of all dry gases and X_w is the water vapor mole fraction (e/P).

The equivalent pressure will be $P_e = \Sigma a_i p_i + a_w e$. In principle, P_e will vary with CO_2 partial pressure, but the CO_2 partial pressure is so small that it can be neglected. Thus, if other atmospheric components are constant, an equivalent pressure can be defined as

$$\begin{aligned} P_e &= a_d P_d + a_w e. \\ &= P(a_d X_d + a_w X_w) \end{aligned} \tag{6-2}$$

where P_d is the total pressure of dry air, and a_d is a dry air weighting factor.

LI-COR calibrates all of its analyzers using CO_2 or water vapor in air, so $a_d = 1$ is taken as the standard condition. Substituting equation 6-1 into equation 6-2 gives

$$P_e = P[1 + (a_w - 1)X_w] \tag{6-3}$$

The value of a_w is not an intrinsic constant comparable to other such values in the literature because it uses dry air as a reference instead of nitrogen. Its value has been empirically determined to be about 1.5 against dry air.

Equation 6-3 can be extended to include nitrogen as standard, and both water vapor and oxygen (or other gases) as variable components. P_e can be written in a more general form to anticipate that possibility:

$$P_e = P[1 + (a_w - 1)X_w + \Sigma(b_i - 1)X_i] \tag{6-4}$$

Equation 6-3 can be compactly rewritten as

$$P_e = P\chi(X_w), \tag{6-5}$$

where $\chi(X_w) = 1 + (a_w - 1)X_w$, and then incorporated into the CO_2 calibration function.

The form of the CO_2 calibration function (equation 5-4) was derived empirically, but it can also be derived from a "scaling law" called the "non-overlapping line approximation" which holds when absorber concentrations are low or pathlengths are short (3). If P_e from equation 6-5 is substituted for P in that derivation, the result gives CO_2 mole fraction corrected for pressure broadening due to the presence of water vapor (McDermitt, et al., in preparation). The equations for computing CO_2 then become:

$$V_r = \chi(w_r)F^{-1}\left[\frac{C_r}{\chi(w_r)}\left(\frac{T_o + 273}{T + 273}\right)\right]\frac{P}{P_o} \tag{6-6a}$$

$$G = 1 - \frac{V_r}{K} \tag{6-6b}$$

$$C = \chi(w_s)F\left[\left(\frac{VG + V_r}{\chi(w_s)}\right)\frac{P_o}{P}\right]\left(\frac{T + 273}{T_o + 273}\right) \tag{6-6c}$$

$$\Delta C = C - C_r \tag{6-6d}$$

The water correction is based upon a theoretically justifiable procedure which requires determination of a single physically meaningful constant, and can be applied to any LI-COR 6200 series infrared gas analyzer, and perhaps others, as well.

6.3 Dilution Corrections

A dilution correction can be applied in the LI-6251, if desired. When one component gas of a multicomponent mixture is decreased at constant pressure, the partial pressures of all other components are increased accordingly. For example, if water vapor is removed at constant pressure, then the partial pressures of other components increase according to

$$P = \frac{\Sigma p_i^{wet}}{\left(1 - \frac{w}{1000}\right)} \tag{6-7}$$

where w is the water vapor mole fraction (mmol/mol) and the p_i^{wet} are partial pressures of other component gases before water vapor was removed. For individual components, Equation 6-7 becomes

$$p_i^{dry} = \frac{p_i^{wet}}{(1 - w/1000)} \tag{6-8}$$

It is often necessary to correct the CO_2 mole fraction for differences in water vapor mole fraction in sample and reference cells when CO_2 and water vapor are measured together. An apparent CO_2 mole fraction difference will develop if water vapor is added to or removed from either air stream whether a net CO_2 flux is present or not. This dilution effect can be removed by correcting the CO_2 mole fraction in the sample air stream to the water vapor mole fraction that is in the reference air stream according to

$$C_s^{wr} = C_s^{ws}\left(\frac{1 - w_{ref}/1000}{1 - w/1000}\right) \tag{6-9}$$

C_s^{ws} is the actual CO_2 mole fraction in the sample cell diluted by w, and c_s^{wr} is the equivalent sample cell CO_2 mole fraction if it were diluted by w_{ref}.

6.4 Example

Appendix C gives a computer program called CALC.C with output that provides an example calculation of the water corrections. In the sample output (p. C-6), $\chi(1.00/99.5)$ is equivalent to $\chi(w_r) = 1 + (1.5 - 1)\, e_r / P = 1.005$, and $C_r' = [C_r / \chi(w_r)]\, T_o/T = 362.61$ ppm. Equation 6.6a can then be written as

$$V_r = 1.005\ F^{-1}(362.61)\frac{P}{P_o}$$

Which, after rearrangement and inversion gives

$$F\left(\frac{V_r}{1.005}\frac{P_o}{P}\right) = 362.61\ \mu\text{mol mol}^{-1},$$

or, more simply just

$$F(V) = 362.61.$$

We solve F(V) = 362.61 for V by iteration, finding V = 1896.11 mV. So,

$$V_r = 1896.11\ \frac{P}{P_o}(1.005)$$

$$V_r = 1871.78 \text{ mV}.$$

The gain correction G = 1 - 1871.78/19130 = 0.9022, and V_s = 1730.0G + V_r = 3432.50 mV. $\chi(w_s) = 1 + 0.5\ e_s/P = 1.010$. So, from equation (6-6c)

$$C_s = 1.010\ F\left(\frac{3432.50}{1.010}\ \frac{101.3}{99.5}\right)\frac{T}{T_o}$$

$$= 798.99,$$

and

$$\Delta C = 798.99 - 345.00 = 453.99 \text{ ppm}.$$

CALC.C and other programs are provided on the LI-COR IRGA Computations Disk (part #6200-28) that is included with each LI-6251. It contains the CALC.C source code written in C, and a compiled version CALC.EXE that is ready to run under DOS on IBM PC's or true compatible computers. A similar program called COMPCO2.EXE is also included. It performs the same calculations, but has a more convenient user interface. Instructions for using the programs are given in Appendix D.

REFERENCES

1. Jamieson, J.A., R.H. McFee, G.N. Plass, R.H. Grube, and R.G. Richards, 1963. Infrared Physics and Engineering. McGraw-Hill, New York, N.Y. p. 65.

2. Lowe, P.R. 1976. An approximating polynomial for the computation of saturation vapor pressure. J. Appl. Meteor., 16:100-103.

3. Wolfe, W.L., and G.J. Zissis. 1978. The Infrared Handbook. Office of Naval Research, Department of the Navy, Washington, D.C.

Section VII
Fast Response Option

7.1 General Description

The LI-6251 can be obtained with a fast, 0.1 second response time (part #6251-01). The factory modification requires a minor hardware filter modification, which results in a 2 to 3-fold increase in analyzer noise.

To measure the voltage output (0.1 second response time) with a meter or data logger:

- Connect the positive input of the data logger to the terminal labeled **CO2 1S**.
- Connect the negative input to the terminal labeled **SIG GND**. If the cable from the data logger is shielded, the shield can be connected to the **CHASSIS GND** terminal.

The “standard” response time of the LI-COR analyzers is specified as 1 second. This means that it takes 1 second for the analyzer to respond to 95% of a one-time change in gas concentration (Figure 7-1). Similarly, the fast response analyzers will respond to a one-time change in concentration in 0.1 second.

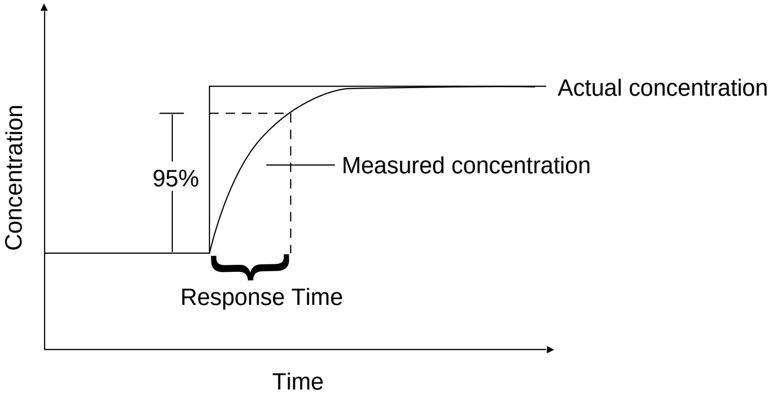


Figure 7-1. Analyzer response to a one-time change in gas concentration.

Cutoff frequency is a more useful indicator for characterizing real-world behavior in which there are fluctuating gas concentrations, rather than a one-time shift. Given a sinusoidal oscillation of concentration, the instrument's ability to measure the full oscillation amplitude diminishes as the oscillation frequency increases.

Cutoff frequency is the frequency at which the indicated amplitude is 0.707 of the real amplitude (Figure 7-2). For the fast response analyzers, the cutoff frequency is 5 Hz. The cutoff frequency is 0.5 Hz for the unmodified, 1-second response time analyzers.

NOTE: These response times refer to the electrical response of the detector circuit. The actual instrument response is also a function of the gas flow rate through the analyzer.

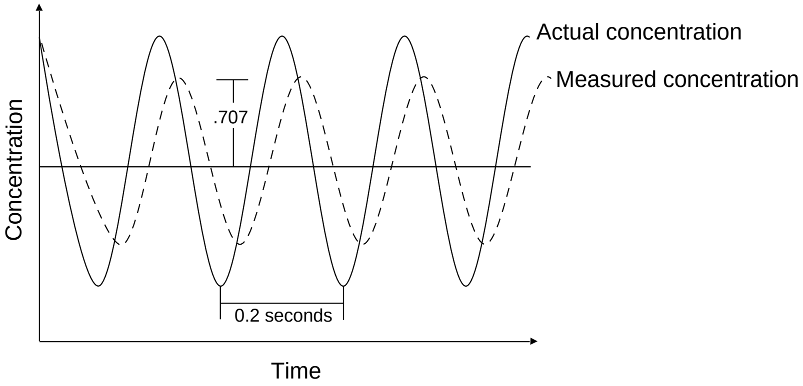


Figure 7-2. Cutoff frequency = 1/oscillation period. With the fast response option, cutoff frequency = 1/0.2 = 5 Hz.

Section VIII
Maintenance

8.1 Recharging the 6000B and 6200B Batteries

Batteries should be fully recharged as soon as possible after use. *STORING A BATTERY IN A DISCHARGED STATE CAN RUIN IT.*

Battery charging circuitry for the 6000B and 6200B batteries is built into the LI-6251, and requires only that the AC line cord be connected. If you are charging one 6000B battery, it will take 1 1/2 - 2 hours (3 - 4 hours for the 6200B) to recharge the battery to 80-90% of full capacity (with the LI-6251 power switch off). For best results, charge the batteries overnight.

Batteries may also be charged during operation of the LI-6251 with AC power. Charging times will be much longer than those given above, however.

At room temperature the 6000B will run the LI-6251 for approximately 3.2 hours and the 6200B will last about 6.4 hours.

NOTE: One set of external leads with a 3-pin plug connection is also included in the spare parts kit for installation with a user-supplied battery (10.5 - 16VDC, 1.5 amp maximum).

Storing the Batteries

STORE THE BATTERIES FULLY CHARGED, and in a cool place, if possible. For long-term storage, charge the batteries overnight every 3 months.

8.2 Opening The LI-6251

Remove the 4 screws on the bottom of the LI-6251 housing that are closest to the ends of the housing, directly opposite the 4 rubber feet. There are 2 screws near each end.

Remove all 8 screws from the top of the housing, and slide the cover off.

8.3 Internal Soda Lime/Desiccant

NOTE: Internal soda lime/desiccant must be changed annually.

There is a small plastic bottle inside the LI-6251 that contains a mixture of soda lime and anhydrous $Mg(ClO_4)_2$ (magnesium perchlorate). This bottle is located inside the nickel-plated desiccant bottle cover, which is connected perpendicularly to the detector housing, and is attached to the CO_2 analyzer's detector housing (Figure 8-1). Its purpose is to keep the detector free of CO_2 and water vapor, and to maintain the dew point below -12 °C.

If the CO_2/H_2O concentration in the detector rises, the analyzer response curves will change, and the calibration polynomial will no longer match the response curve, and the factory-supplied calibration function will be invalid. If the dew point in the detector rises above -12 °C, condensation may form, resulting in a large shift in the zero and/or span. The READY light will also fail to light. **For these reasons, the internal soda lime/desiccant must be changed annually.**

The nickel-plated bottle cover is attached with 3 hex nuts, which may be removed with the hex key included in the LI-6251 spare parts kit. Be careful not to drop the hex nuts onto the LI-6251 circuit boards, as damage may occur.

Before removing the plastic bottle, prepare a second bottle (in spare parts kit) by filling it with equal parts soda lime (on the bottom) and magnesium perchlorate (on top). Unscrew the old bottle from its top (attached to the detector), and screw the new bottle back on as quickly as possible, to prevent CO_2 and H_2O vapor from entering the detector housing. Do not remove the end cap from the detector housing. Replace the plated bottle cover and be sure to secure it tightly.

CAUTION: After installing the bottle with new chemicals, allow 12-24 hours before powering on the analyzer. Powering on too soon with water vapor in the detector may cause condensation and subsequent damage to the optical filter.

Make sure that the rubber sealing washer in the lid of the bottle is intact, and the fibrous plug is in place to hold the chemicals so they don't fall into the detector housing.

Magnesium perchlorate is the recommended desiccant since it does not interact with CO_2. **Do not use any other desiccant**. Several grades of magnesium perchlorate are available from commercial suppliers. In general, the more granular (as opposed to powdery) the grade the better. One type that works well is marketed under the name *Dehydrite*, and is available (catalog number C260-M61) from Aurthur Thomas Company, Vine St. & 3rd, Philadelphia, PA 19105. (215)574-4500.

Magnesium perchlorate cannot be regenerated after use. Check with your local environmental safety officer for the proper disposal method.

CAUTION: Magnesium perchlorate is a strong oxidizing agent. Contact with skin or mucus membranes may cause irritation. Avoid bringing it into contact with acids and organic substances such as cotton, rubber, grain dust, etc. Consult the container label.

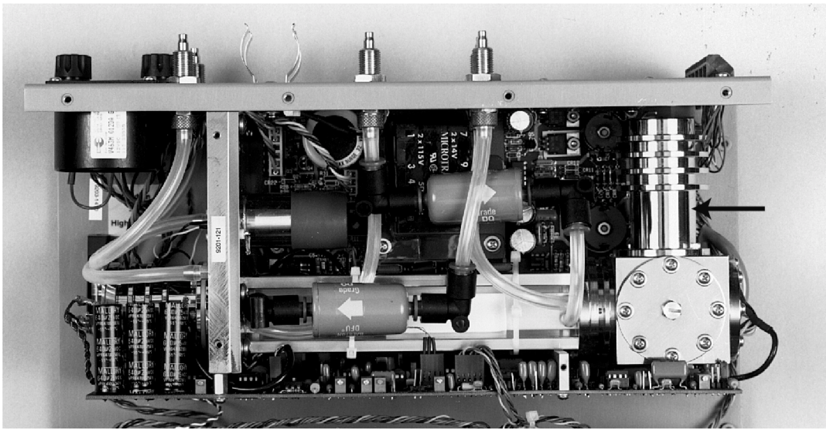


Figure 8-1. Location of internal soda lime/desiccant.

8.4 External Soda Lime

The frequency with which the external soda lime must be replaced depends greatly on the mode of operation of the analyzer and how much CO_2 it is forced to remove.

In differential mode, with the scrubber tube connected to the chopper ports, the soda lime will need to be changed every six months to one year, depending on usage. Once the scrubber tube removes the initial CO_2 from the circuit, it will only need to remove the small amounts of CO_2 resulting from tiny leaks in the system.

To refill the soda lime tube, pack completely full and place a small wad of cotton or polyester wool in one end to keep the pellets from shaking. Make sure that the filter paper discs on either end cap are not clogged (reduces flow rate) or torn. Adhesive-ringed replacement discs are included in the spare parts kit (LI-COR part # 9960-040).

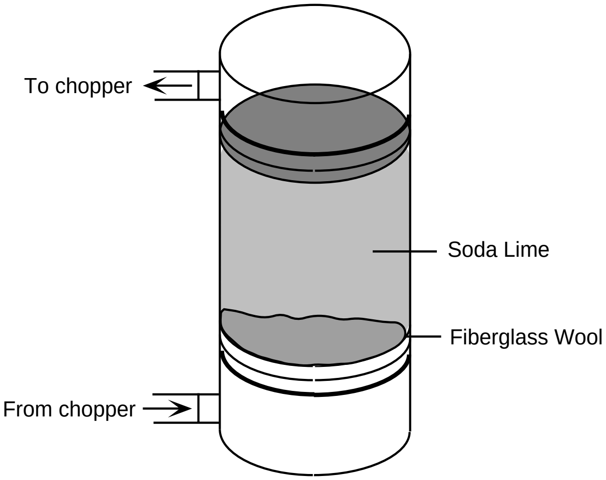


Figure 8-2. External soda lime tube assembly.

8.5 Internal Air Filters

The frequency with which the filters need to be replaced will depend upon the operating environment.

The filter on the "SAMPLE IN" inlet will generally need replacement after 1 to 6 months and the filter on the "REFERENCE IN" inlet will need replacement after 6 months to 1 year.

Before installing a new filter, blow clean dry air through it to get out any fibers or other debris that may be loose inside. If any of this material gets into the sample or reference cell, there will be a very large zero shift. Install the filters as shown in Figure 8-3.

Spare filters can be ordered from LI-COR under part number 300-01961 (1 each).

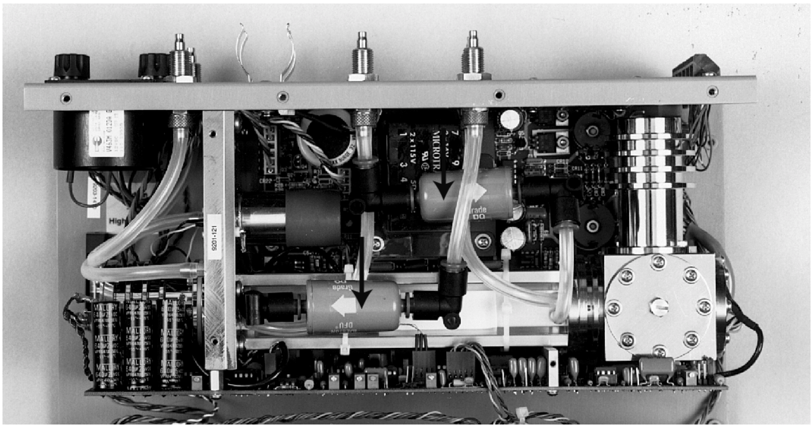


Figure 8-3. New air filters should be installed with the directional arrows in the same orientation as the photo.

8.6 Fan Filter

The external fan filter should be cleaned (rinsed out) or replaced as needed. The filter sits in a recessed cavity in the instrument case and can easily be pulled out with your fingers. Two additional external air filters are included in your spare parts kit (LI-COR part # 6560-159).

8.7 Fuses

There are two fuse holders on the back panel. The 1/2 amp slow blow fuse is for 110 VAC line voltage and the 1/4 amp slow blow fuse is for 220 VAC line voltage. The 2 amp fast blow fuse is for the external batteries. If the LI-6251 fails to turn on, check the fuse for the power source you are using (battery or AC). If the analyzer continually blows fuses it is in need of repair.

Appendix A
Specifications

Type: Differential, non-dispersive infrared (NDIR) gas analyzer. Functions in differential or absolute mode.

Differential Range: 0 - 3000 ppm absolute. Higher ranges are possible with user calibration.

Sensor: Solid state detector. No sensitivity to motion.

Chopping Frequency: 500 Hertz.

Source Life: >10,000 hours.

Response Time: 1, 4, or 15 seconds to 95% of reading (user selectable). 0.1 second optional.

Typical Signal Noise 0.2 ppm peak-to-peak typical (at 350 ppm with 1 second response time). Typically 0.1 ppm peak-to-peak when using 4 second response time at 350 ppm. Signal noise at higher CO_2 concentrations increases proportionately.

Short Term Repeatability: ± 0.2 ppm at 350 ppm.

Warm-Up Time: 5 minutes.

Zero Drift (over time):

< 1 ppm/hour at 25 °C. Typically < 2 ppm in 24 hours.

Zero Drift (with temperature):

Average: 0.12 ppm/°C.
Maximum: 0.45ppm/°C.

Span Drift: Typically < 1 ppm in 24 hours at 25 °C and 350 ppm (absolute mode, at constant pressure).

Accuracy: ± 1 ppm at 350 ppm (< 3 ppm maximum). ± 2 ppm at 1000 ppm (< 6 ppm maximum).

Gas Temperature: Measured by a thermistor, Accuracy: ± 0.5 °C, 0 to 50 °C. Resolution: 0.03 °C.

Gas Pressure: Maximum allowable pressure is 17 kPa.

Water Sensitivity: Typical sensitivity of the analyzer for dry to saturated air at 25 °C is < 2 ppm at 0 ppm concentration, < 5 ppm at 350 ppm, and < 15 ppm at 1000 ppm, dilution effects removed. Water sensitivity can be removed by using magnesium perchlorate desiccant in the flow circuit.

Calibration: 0 - 3000 ppm using NIST-traceable standard gases. Higher ranges are possible through user calibration.

Output (CO_2): ± 15 V (three outputs, one for each different response time). Readout device should have 10k Ω minimum load impedance.

Output (analyzer temperature): 5V = 50 °C. Readout device should have 10k Ω minimum load impedance.
Display: 4 1/2 digit, ± 2000 counts.
Display Resolution: ≈ 0.025 ppm in differential mode at 350 ppm, ≈ 0.5 ppm in absolute mode at 350 ppm.
Power Requirements: 100 - 130 VAC or 200-260 VAC (47-65 Hertz), or 10.5 - 16 VDC, 1.5 Amp maximum.
Power Consumption: 7 Watts.
6000B Rechargeable Battery. Provides 2 hours of battery life.
6200B Rechargeable Battery. Provides 4 hours of battery life.
LI-6020 Battery Charger. For recharging 6000B or 6200B. Requires 92 -138/184-276 VAC, 47-63 Hz, 25 watt maximum.
Recharging time (6000B) : 3 hours with 1 battery, 12 hours with 4 batteries.
Recharging time (6200B): 6 hours with 1 battery, 12 hours with 2 batteries.
Size: 33.5 L x 13 W x 24 cm D (13" x 5" x 9.5").
Sample Cell: 0.6 cm H x 1.3 cm D x 15.2 cm L (0.25" x 0.5" x 6.0").
Volume: 11.9 cm^3.
Weight: 3 kg (6.6 lb.).

Appendix B
List of Suppliers

The company names, addresses, and phone numbers are the most current we have at the time of this printing. In some cases the information may change without notice.

Soda Lime

Part #S-201-3, Mesh 6-12 (LI-COR Part #229-01828)
Fisher Scientific
711 Forbes Avenue
Pittsburgh, PA 15219
(412) 562-8300

Magnesium Perchlorate - Anhydrous

Part #M-54-500
Fisher Scientific
(Address above)

Part #C260M61 (P74935)
Thomas Scientific
Vine Street at Third
Box 779
Philadelphia, PA 19105
(215) 988-0533

Manufactured by
G. Frederick Smith Chemical Company
P.O Box 23214
Columbus, OH 43223
(614) 881-5501

Cat. #22889-004
VWR Scientific
P.O. Box 7900
San Francisco, CA 94120
(415) 467-6202

Appendix C
Sample Program

The following is a sample Borland's C program that could be used to calculate CO_2 concentration, using the water correction equations described in Section 6.

```
/*
   calc.c - Implements LI-COR IRGA equations
*/
#include <stdio.h>
#include <math.h>
double ppm(double mV, double Cr, double Tirga, double vp_r, double vp_s, double kPa);
double cal(double mv);
double temp_correction(double t);
double inverse_cal(double cppm);
double cal_slope(double mv);
double chi(double mfw);
double   K_cal = 19130,
         T_cal = 40.2,
         A_cal = .142,
         B_cal = 2.258E-5,
         C_cal = 1.787E-9,
         Aw = 1.5;
void main(void)
{
   double mV, Tirga, Cr, wr, ws, kPa, vp_r, vp_s, Cs;
   char line[80];
   while (1) {
      printf(“Enter mV, Temp, Cr, vp_r, vp_s, kPa (null entry to quit)\n”);
      gets(line);
      if (sscanf(line, “%lf %lf %lf %lf %lf %lf”,
      &mV, &Tirga, &Cr, &vp_r, &vp_s, &kPa) != 6) return;
```

```
      printf(“CO2         IRGA        Reference   Reference  Sample       Total\n”);
      printf(“Signal(mV)  Temp (C)    CO2 (ppm)   vapor(kPa) vapor(kPa)   press(kPa)\n”);
      printf(“==========  ==========  ==========  ========== ==========   ==========\n”);
      printf(“%10.2f  %10.2f  %10.2f  %10.3f  %10.3f  %10.3f\n”, mV, Tirga, Cr, vp_r, vp_s, kPa);
      Cs = ppm(mV, Cr, Tirga, vp_r, vp_s, kPa);
      printf(“Cs = %7.2f ppm, Differential = %7.2f ppm\n”, Cs, Cs - Cr);
   }
}
/* ———————————————————————————————————— */
double ppm(double mV, double Cr, double Tirga, double vp_r, double vp_s, double kPa)
{
   /* This function implements Equations 6-6 (LI-6251 or 6252 manuals) or Equations 5-19 (LI-6262 manual).
      mV - co2 signal in mV
      Cr - reference concentration (ppm)
      Tirga - Gas temp (C)
      vp_r - reference cell vapor pressure (kPa)
      vp_s - sample cell vapor pressure (kPa)
      kPa - total pressure (kPa)
*/
double Vref, gain, chi_ws, chi_wr, eff_cr, tc, eff_mv, result, inv_cal;
tc = temp_correction(Tirga);
if (Cr == 0.0) {
      /* absolute mode
      */
      chi_ws = chi(vp_s/kPa);
      eff_mv = mV/chi_ws*101.3/kPa;
      result = chi_ws * cal(eff_mv) * tc;
```

```
      printf("Sample cell water correction = chi(%6.2f/%6.2f) = %5.3f\n", vp_s, kPa, chi_ws);
      printf("Cs = %5.3f * F(%7.2f/%5.3f * 101.3 / %6.2f) * (%5.2f+273)/(To+273)\n",
           chi_ws, mV, chi_ws, kPa, Tirga);
      printf(" = %5.3f * %7.2f * %5.3f\n", chi_ws, cal(eff_mv), tc);
      printf(" = %7.2f\n", result);
      return result;
}
/* differential mode
*/
chi_wr = chi(vp_r/kPa);
printf("Reference cell water correction = chi(%6.2f/%6.2f) = %5.3f\n", vp_r, kPa, chi_wr);
eff_cr = Cr / temp_correction(Tirga) / chi_wr;
printf("Adjust Cr for temp and water:\n");
printf(" Cr' = %7.2f * (To+273)/(%5.2f+273) / %5.3f\n", Cr, Tirga, chi_wr);
printf(" = %7.2f * %5.3f / %5.3f\n", Cr, 1.0/tc, chi_wr);
printf(" = %7.2f\n", eff_cr);
printf("Iterate to find Vr such that F(Vr) = %7.2f\n", eff_cr);
inv_cal = inverse_cal(eff_cr);
Vref = chi_wr * inv_cal * kPa / 101.3;
printf("Vr = %5.3f * %7.2f * %6.2f / 101.3\n", chi_wr, inv_cal, kPa);
printf(" = %7.2f\n", Vref);
gain = (1.0 - Vref/K_cal);
printf(" G = gain factor = (1 - %7.2f / K)\n", Vref);
printf(" = %5.3f\n", gain);
printf("Compute Cs using mV = %7.2f + %7.2f * %5.3f = %7.2f\n", Vref, mV, gain, Vref + mV*gain);
return ppm(Vref + mV*gain, 0, Tirga, 0, vp_s, kPa);
}
```

```
/* ———————————————————————————————————— */
double cal(double mv)
{
   /* Equation 5-3 Basic irga cal equation
   */
   return (A_cal + (B_cal + C_cal*mv)*mv)*mv;
}
/* ———————————————————————————————————— */
double temp_correction(double t)
{
return (t + 273)/(T_cal + 273);
}
/* ———————————————————————————————————— */
double inverse_cal(double cppm)
{
   /* returns the mV that would be generated if in absolute mode with cppm in the sample cell
   */
   double mv_old = 0, mv, c;
   mv = cppm/1500 * 5000; /* crude first guess */
   while (fabs(mv - mv_old) > 0.5) {
      mv_old = mv;
      c = cal(mv_old);
      printf(“ F(%6.2f) = %6.2f\n”, mv_old, c);
      mv = mv_old - (c - cppm) / (cal_slope(mv_old));
   }
   return mv;
}
```

```
/* ____________________________________ */
double cal_slope(double mv)
{
   /* returns the slope of the cal function
   */
   return A_cal + (2*B_cal + 3*C_cal*mv)*mv;
}
/* ____________________________________ */
double chi(double mfw)
{
   /* Eqn 5-18 (LI-6262 manual) or 6-5 (LI-6251 or LI-6252 manual).
   */
   return 1 + (Aw -1) * mfw;
}
/* ____________________________________ */
```

Results

```
Enter mV, Temp, Cr, vp_r, vp_s, kPa (null entry to quit)
1730 23.5 345 1 2 99.5
CO2           IRGA           Reference     Reference      Sample        Total
Signal(mV)    Temp (C)       CO2 (ppm)     vapor(kPa)     vapor(kPa)    press(kPa)
==========    ==========     ==========    ==========     ==========    ==========
   1730.00         23.50         345.00         1.000          2.000        99.500
Reference cell water correction = chi(1.00/99.50) = 1.005
Adjust Cr for temp and water:
  Cr’      =345.00 * (To+273)/(23.50+273)/1.005
           =345.00 * 1.056/1.005
           =362.61
Iterate to find Vr such that F(Vr) = 362.61
   F(1208.70) = 207.78
   F(1966.12) = 380.06
   F(1896.75) = 362.77
   F(1896.11) = 362.61
Vr = 1.005 * 1896.11 * 99.50/101.3
   = 1871.78
G  = gain factor = (1-1871.78/K)
   = 0.902
Compute Cs using mV = 1871.78 + 1730.00 * 0.902 = 3432.50
Sample cell water correction = chi(2.00/99.50) = 1.010
Cs = 1.010 * F(3432.50/1.010 * 101.3/99.50) * (23.50+273)/(To+273)
   = 1.010 * 835.60 * 0.947
   = 798.99
Cs = 798.99 ppm, Differential = 453.99 ppm
```

Appendix D
LI-COR IRGA Computations Disk

The IRGA Computations diskette contains a collection of programs that can be used to compute CO_2 concentrations, corrected for the presence of water vapor, using raw data collected with the LI-6251.

The following programs are found on the LI-COR IRGA Computations disk included with your LI-6251:

● `CALC.EXE`	The sample 'C' program found in Appendix C.
● `CALC.C`	The source code for the `CALC.EXE` program.
● `COMPCO2.EXE`	Program using the same equations as `CALC.EXE`, but with a simpler user interface.
● `CALDATA.62`	Default calibration constants for the `COMPCO2` program.
● `OUTLIST.62`	Default output column variables for the `COMPCO2` program.

No special installation procedures are required to install the computation programs. Make a backup copy of the diskette if you plan to use the programs directly from the floppy disk, or copy the contents of the diskette onto a hard disk drive in your computer.

CALC.EXE

To run the CALC.EXE program, type CALC <Enter>.

You will be prompted with

```
Enter mV, Temp, Cr, vp_r, vp_s, kPa  (null entry to quit)
```

Enter the raw millivolt output from the LI-6251, the IRGA temperature, reference cell vapor pressure (kPa), sample cell vapor pressure (kPa), and barometric pressure (kPa), separated by a space. Press <Enter>. The program will run, and will output the sample cell and differential CO_2 concentrations (in ppm), corrected for the presence of water vapor.

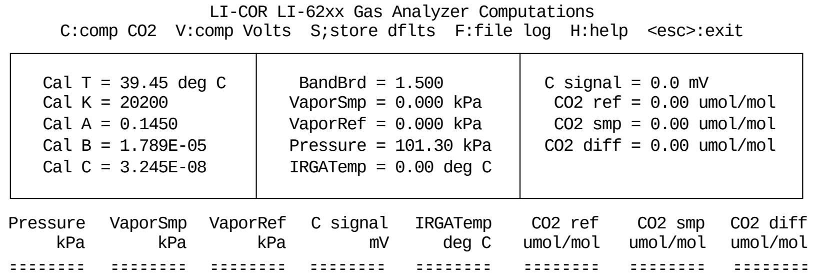
Press <Enter> again at the prompt to exit the program.

COMPCO2.EXE

The COMPCO2 program uses the same equations as the CALC program to compute CO_2 concentrations, but has a simpler user interface. In addition, the default calibration constants for the LI-6251 and the output column variables can be entered and/or edited at any time.

To run the COMPCO2.EXE program, type COMPCO2 <Enter>.

The following screen appears:



```
                     LI-COR LI-62xx Gas Analyzer Computations
     C:comp CO2  V:comp Volts  S;store dflts  F:file log  H:help  <esc>:exit

    Cal T = 39.45 deg C       BandBrd = 1.500          C signal = 0.0 mV
    Cal K = 20200            VaporSmp = 0.000 kPa       CO2 ref = 0.00 umol/mol
    Cal A = 0.1450           VaporRef = 0.000 kPa       CO2 smp = 0.00 umol/mol
    Cal B = 1.789E-05        Pressure = 101.30 kPa     CO2 diff = 0.00 umol/mol
    Cal C = 3.245E-08        IRGATemp = 0.00 deg C

Pressure  VaporSmp   VaporRef  C signal   IRGATemp    CO2 ref    CO2 smp  CO2 diff
     kPa       kPa        kPa        mV      deg C   umol/mol   umol/mol  umol/mol
========  ========   ========  ========   ========   ========   ========   ========
```

The COMPCO2 program is operated by using the arrow keys (to select fields to be edited) and the quick keys on the title bar (C, V, S, F, H, and <esc>). For example, a help file can be accessed by simply pressing 'H'.

Press 'C' to compute the CO_2 concentration based on the millivolt output of the analyzer, or 'V' to compute the CO_2 millivolt equivalent of the sample cell CO_2 concentration.

Editing the Fields

Use the arrow keys to move the cursor to the field to be edited. Type the new value, and press <Enter>.

Editing the Output Format

The values printed when 'C' or 'V' is pressed can be changed by pressing <Alt> + the number of the column to be changed. Place the cursor in the field to be output, and press <Alt> + 3, for example, to output that field in the 3rd column (VaporRef in the default configuration). **NOTE:** *Do not use the numeric keypad for this operation.*

Printing to a File

The output printed on the CRT can also be logged to a file, or to a device such as a printer. Press 'F' to start and stop logging to a file. When 'F' is first selected, you will be prompted to enter a filename. Enter the path and the filename (up to 8 characters). If no path is specified, the file will be written to the directory where the COMPCO2.EXE file is located. For example, type `C:\IRGA\TEST` to log a file named "TEST" to the IRGA directory of the C drive.

To log to a device, type the port to which you want to send the data (i.e., LPT1, COM1, COM2, etc.). **NOTE:** Data is not buffered, and will be sent to the device each time 'C' or 'V' is pressed. Some printers may require that you send a form feed to output less than a full page of data.

Saving Defaults

The calibration data and the output column headers can be saved as default values by pressing 'S'. The calibration data are saved as the file 'CALDATA.62', and the column definitions as 'OUTLIST.62'. These files can also be edited with a text editor.

Warranty

Each LI-COR, inc. instrument is warranted by LI-COR, inc. to be free from defects in material and workmanship; however, LI-COR, inc.'s sole obligation under this warranty shall be to repair or replace any part of the instrument which LI-COR, inc.'s examination discloses to have been defective in material or workmanship without charge and only under the following conditions, which are:

1. The defects are called to the attention of LI-COR, inc. in Lincoln, Nebraska, in writing within one year after the shipping date of the instrument.
2. The instrument has not been maintained, repaired or altered by anyone who was not approved by LI-COR, inc.
3. The instrument was used in the normal, proper and ordinary manner and has not been abused, altered, misused, neglected, involved in an accident or damaged by act of God or other casualty.
4. The purchaser, whether it is a DISTRIBUTOR or direct customer of LI-COR or a DISTRIBUTOR'S customer, packs and ships or delivers the instrument to LI-COR, inc. at LI-COR inc.'s factory in Lincoln, Nebraska, U.S.A. within 30 days after LI-COR, inc. has received written notice of the defect. Unless other arrangements have been made in writing, transportation to LI-COR, inc. (by air unless otherwise authorized by LI-COR, inc.) is at customer expense.
5. No-charge repair parts may be sent at LI-COR, inc.'s sole discretion to the purchaser for installation by purchaser.
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There are no warranties, express or implied, including but not limited to any implied warranty of merchantability of fitness for a particular purpose on <u>underwater cables</u> or on expendables such as <u>batteries</u>, <u>lamps</u>, <u>thermocouples</u>, and <u>calibrations</u>.

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This warranty supersedes all warranties for products purchased prior to June 1, 1984, unless this warranty is later superseded.

DISTRIBUTOR or the DISTRIBUTOR's customers may ship the instruments directly to LI-COR if they are unable to repair the instrument themselves even though the DISTRIBUTOR has been approved for making such repairs and has agreed with the customer to make such repairs as covered by this limited warranty.

Further information concerning this warranty may be obtained by writing or telephoning Warranty manager at LI-COR, inc.

Please return the User Registration Card enclosed with your shipment so that we have an accurate record of your address. Thank you.

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