Using the LI-870 CO_2/H_2O Analyzer





Using the LI-870 CO₂/H₂O Analyzer

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Printing History

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Publication number: 984-17878

Created on: Friday, February 3, 2023.

Notes on Safety

This LI-COR product has been designed to be safe when operated in the manner described in this manual. The safety of this product cannot be assured if the product is used in any other way than is specified in this manual. The product is intended to be used by qualified personnel. Read this entire manual before using the product.

Equipment ma	arkings:
\triangle	The product is marked with this symbol when it is necessary for you to refer to the manual or accompanying documents in order to protect against injury or damage to the product.
Â	The product is marked with this symbol when a hazardous voltage may be present.
	The product is marked with this symbol if a Chassis Ground connection is required.
	The product is marked with this symbol to indicate that a direct current (DC) power supply is required.
WARNING	Warnings must be followed carefully to avoid bodily injury.
CAUTION	Cautions must be observed to avoid damage to your equipment.
Manual marki	ngs:
Warning	Warnings must be followed carefully to avoid bodily injury.
Caution	Cautions must be observed to avoid damage to your equipment.
Note	Notes contain important information and useful tips on the operation of your equipment.

CE Marking:

This product is a CE-marked product. For conformity information, contact LI-COR Support at envsupport@licor.com. Outside of the U.S., contact your local sales office or distributor.

California Proposition 65 Warning

WARNING: This product contains chemicals known to the State of California to cause cancer and birth defects or other reproductive harm.

Federal Communications Commission Radio Interference Statement

WARNING: This equipment generates, uses, and can radiate radio frequency energy and if not installed in accordance with the instruction manual, may cause interference to radio communications. It has been tested and found to comply with the limits for a Class A computing device pursuant to Subpart J of Part 15 of FCC rules, which are designed to provide a reasonable protection against such interference when operated in a commercial environment. Operation of this equipment in a residential area is likely to cause interference in which case the user, at his own expense, will be required to take whatever measures may be required to correct the interference.

Waste Electronic and Electrical Equipment (WEEE) Notice

This symbol indicates that the product is to be collected separately from unsorted municipal waste. The following applies to users in European countries: This product is designated for separate collection at an appropriate collection point. Do not dispose of as household waste. For more information, contact your local distributor or the local authorities in charge of waste management.



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Standard Terms and Conditions

Section 1. Overview of the LI-870

The LI-870 is a CO_2/H_2O Gas Analyzer that is designed for use with the Smart Chamber and LI-8250 Multiplexer in soil gas flux systems. This document provides basic operating instructions for the LI-870. Refer to the Smart Chamber and LI-8250 manuals for additional information.

What's what

If you have just taken delivery of your LI-870, check your packing list to ensure the following items have been included.

LI-870 CO₂/H₂O Analyzer

Part number: 870-01

The LI-870 is a portable gas analyzer designed for use with the Smart Chamber or LI-8250 Multiplexer for soil CO_2 flux measurements.



The LI-870 measures CO_2 in air at concentrations from 0 to 20,000 ppm using nondispersive infrared gas analysis technology. This technology is well-established in other LI-COR products, including the widely-published LI-8100A Automated Soil CO_2 Flux System, LI-830 and LI-850 CO_2 and CO_2/H_2O Gas Analyzers, and LI-COR eddy covariance analyzers. Water vapor measurements are used in corrections to report CO_2 concentrations with high accuracy. Power to the LI-870 is supplied from the Smart Chamber or LI-8250 Multiplexer. The LI-870, in turn, provides CO_2 data to the Smart Chamber or LI-8250 Multiplexer for storage and processing.

LI-870 cable and tube assembly

Part number: 9982-010

A 1.2 meter cable and tubing assembly is included with the LI-870 to connect the LI-870 with the Smart Chamber or LI-8250 Multiplexer. This assembly includes:

- Sealed USB-A to USB-B cable (part number 392-17654).
- Sealed 2.5 × 5 mm IP68 power cable (part number 9982-008).
- Two lengths 1.2 meter 1/4" Bev-A-Line® tubing (part number 222-01824) with quick-connect fittings (part numbers 300-07124 (male) and 300-07125 (female)).

The assembly components are zip tied in plastic conduit.

Shoulder strap

The shoulder strap is to carry the LI-870.

Split ring assembly

Part number: 9882-019

Part number: 604-18146

The LI-870 ships with a split ring and standoff assembled for attaching the shoulder strap. The rings are attached near the clasps of the case. Each assembly consists of a machined standoff (part number 9882-019), screw (part number 122-07715), split ring (part number 610-10353), and two washers (part number 167-00154).



Spares kit

Part number: 9982-020 A spares kit is shipped with the LI-870 and contains the following.

Description	Quantity	Part Number
1/4" Bev-A-Line® IV Plastic Tubing (12 meters)	1	8150-250 ^a
1/4" Quick-connect Straight Union	2	300-03123
Quick Connect Plug 0.165 with Hose Barb (Male)	1	300-07124
Quick Connect Plug 0.165 with Hose Barb (Female)	1	300-07125
Optical Bench Cleaning Kit	1	9980-066
USB-A to USB-B, Unsealed, 2 meter	1	392-06652

Software

The LI-870 can be calibrated using the LI-830/LI-850 user interface software, which is available from the LI-COR support site at licor.com/830-850-support. Select software, and find the installer appropriate for your operating system. This software is available for both Windows® and macOS® operating systems and is used to calibrate your LI-870 and view live data.

^aAdditional tubing can be repurchased as a 15 meter roll.

Section 2. Using the LI-870

The basic operation of the LI-870 involves connecting the USB data cable, connecting the tubing, and connecting the power cable between the LI-870 and Smart Chamber or LI-8250 Multiplexer, as described here.

Connecting the cable assembly

Connecting the LI-870 to the Smart Chamber or LI-8250 Multiplexer is simple, only requiring a few steps.



First, attach each end of the cable assembly to the LI-870. The USB-B end of the USB-A to USB-B cable is attached to the LI-870, while the USB-A end is attached to the Smart Chamber or LI-8250.

Note: Only use the supplied USB-A to USB-B cable from the LI-870 to cable assembly (part number 9982-010).

Next, attach the cable assembly to the Smart Chamber or LI-8250. Connect the steel quick connect fittings for the air tubing, and thread the power cable on to the power-in and power-out connectors on each panel. Tighten snugly to ensure a water-



tight seal. Follow the detailed instructions in the Smart Chamber or LI-8250 instruction manual for additional details.

USB-A Power Out Air Out Air In



Warning: The power output is 10-17 VDC --- with a center positive pin $\bigcirc -\odot -\odot$. The output has a 2 amp maximum and is designed to only power the LI-870 CO₂/H₂O Analyzer Accessory. Only use the power cable supplied with the LI-870 cable assembly (P/N 9982-010), and do not attempt to power any other devices with the Smart Chamber or LI-8250. Drawing a current in excess of 2 amps will trip the self-resetting breaker. If you trip the self-resetting breaker, you will need to wait for a few minutes before attempting to re-power the LI-870.

Powering the analyzer and making measurements

After connecting the power cable, you should power on your Smart Chamber or LI-8250 and launch the user interface software. Power to the LI-870 is supplied directly from the Smart Chamber or LI-8250.

Identifying the LI-870 serial number

In the **Settings** page of the Smart Chamber or LI-8250 interface, you will need to connect to your LI-870 using the serial number. The label is on the bottom of the case.



Warm up time

The LI-870 will boot up as soon as power is supplied from the chamber. The optical bench should be allowed to warm up prior to taking measurements. The LI-870

optical bench is temperature- and pressure-controlled, so a sudden influx of ambient air into an optical bench that has not been allowed to warm up and stabilize will likely produce noisy data. For this reason, it is critical that your analyzer is allowed to warm up prior to taking measurements. In most cases, 10 to 15 minutes of warm up time will allow the optical bench to stabilize, but warmup time depends largely on ambient temperature.

In the Smart Chamber and LI-8250 interface, you can see when your LI-870 optical bench has stabilized when the dot in the upper-left portion of any screen by the time stamp is green. If the bench is not stabilized, this dot will be red.

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You can also visualize the optical bench temperature and pressure from the Home Page of the Smart Chamber or LI-8250 interface to assess whether they have stabilized. After connecting to the Smart Chamber or LI-8250, from the Home Page, select Click to Set. In the Select a variable... window that opens, open the LI-870 list, and you can select Cell Temperature and Cell Pressure.

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	Stat	us	Repetition			
Start	Measu Id	Select a variable	•	8	Click To Set	Click To Set
	Chan Op	Smart Chamber	~	·		
	L	Soil Probe	~	, c		
		LI-870	^	、	Click the emp	ty box to
		CO2	µmol mol *1	l		
		CO ₂ (Wet)	µmol mol -1			
	F	H ₂ O	mmol mol *1	_	Click To Set	Click To Set
		Cell Temperature	*C			
		Cell Pressure	kPa			
		Flow Rate	Ipm		Click To Set	Click To Set



These variables will now be in the grid on the **Home Page**. Click them again to graph the values live.

The axes auto-scale, so pay close attention to the axis labels to assess stability. In the example graph above, the bench temperature, for example, is stabilized within roughly \pm 0.1 °C from the median value/middle of the graph. Once the values have stabilized like this, you can begin taking measurements following the instructions in the Smart Chamber or LI-8250 manual.

Storing the LI-870

The post-purge function of the Smart Chamber is designed to allow for ambient air to flush CO_2 - and water vapor-rich air from the cable assembly tubing and analyzer after each measurement. When you are performing your last measurement(s) of the season, or when you return to the lab or desk after taking your last measurements, you should perform a measurement or two with the Smart Chamber to allow dry ambient air to flow through your chamber. This will help to remove humidity before storage.

Note: For more information on post-purge, consult the Smart Chamber manual or find resources online at licor.com/env/support.

The LI-870 should be stored in non-condensing conditions. If the instrument is stored in high humidity or moderate humidity for a long time while powered off, some optical components may temporarily become saturated with humidity. If this occurs, the instrument may need to run for several days before readings return to normal. If possible, store the instrument in an air conditioned environment.

Section 3. Troubleshooting

In this section, we describe how to identify some potential problems with the LI-870 and how to resolve them. If you can't find a solution here, if you need further assistance performing maintenance, or if you have other questions, contact your local distributor or LI-COR technical support for more help.

Smart Chamber or LI-8250 software not recognizing LI-870

Power is supplied from the Smart Chamber or LI-8250, and assuming your connection is completed correctly, the gas analyzer is always powered on when the Smart Chamber or LI-8250 is powered on. The Smart Chamber or LI-8250 will automatically recognize your device with no further steps needed. Simply expand the LI-870 drop-down in the Connections menu of the Measurement Settings page of the Smart Chamber or LI-8250 software, select your instrument serial number, and press Update.

If you open the drop-down menu and your instrument does not appear,

- Is your power cable fully connected to both devices? Make sure the cable is fully inserted and the threaded nut is snugly fastened.
- Is your USB cable fully connected to both devices? Ensure that the connectors on both sealed cables are clipped to the prongs on each device.

If your cables are fully connected but you still cannot identify your device, you can open your device to see if power is being supplied. Next to the connection panel inside the case, a red LED light will be blinking if power is being supplied. **Note:** Do not open the LI-870 enclosure in the field. This can cause the temperature and pressure of the optics to become destabilized. More importantly, this can allow dust and debris into your analyzer. If possible, you should confirm whether your analyzer is working properly and troubleshoot any issues before taking it out to the field.

If your Smart Chamber or LI-8250 is on and your cables are properly connected, the light should be blinking. If it is not blinking, something could be wrong with your power cable, the chamber power-out connector, analyzer power-in connector, or other electronics inside the case. Check for dust and debris in the connectors and for damage to the cable itself. For power-related issues, it is recommended that you call LI-COR technical support for further instructions.

If the light is blinking but you still cannot identify your device through the Smart Chamber or LI-8250 software, check your USB cable for damage. Is there dust or debris in the cable heads or the connectors? Try refreshing the interface software, clearing your browser cache, and rebooting your Smart Chamber or LI-8250. If you still cannot connect, contact LI-COR technical support.

Unable to Zero or Span the Instrument

Is there dirt in the optics? If the optical cell becomes contaminated, the instrument will drift in either the zero or span. See *Cleaning the optical bench* on page 4-1 for details on cleaning your optical bench.

Instrument Reports -50 ppm CO₂ or Measurements Jump Around

If the instrument measures -50 ppm or the measurements are going between negative and positive values, or just simply not making any sense, the optical source may have failed or be in the midst of failure. Contact technical support for additional troubleshooting help.

Section 4. Maintenance

Cleaning the optical bench

The LI-870 optical bench can be removed and cleaned with just a few steps if necessary. Generally speaking, you shouldn't undertake this procedure unless you've ruled out other potential problems. While the process itself is not difficult, you will have to set the instrument zero and span after reassembling the optical bench.

An optical bench cleaning kit (part number 9980-066) is included with your LI-870 spares kit. You will also need a small Phillips screwdriver. Follow these steps to remove and clean your optical bench and replace the O-rings. Note that the images included in this section were taken from a prototype LI-870. The wiring and plumbing in your instrument may appear slightly different.



Warning: Be sure that you are properly grounded to avoid electrostatic discharge that can damage the electronics. Use an anti-static wrist strap, electrostatic discharge grounding mat, or occasionally touch bare metal that has a clear path to ground, such as an unpainted computer case.

- 1 Unplug your instrument from the Smart Chamber or LI-8250. If you've been operating the instrument recently, you should allow the optical bench to cool down to room temperature.
- 2 Open the analyzer and remove the plate covering the optical bench.



The bench cover is held in place by four screws. Remove these screws, remove the plate and foam, and set aside. The insulated optical bench will now be visible.

3 Gently lift the optical bench out of the insulating foam and remove the cable connectors from the source and detector circuit boards.



4 Gently grasp the plugs and pull them free.



5 Remove the screws that secure the source and detector (4 each), then separate the source and detector housings (with circuit boards attached) from the optical path.



- 6 Clean the optical bench, source, and detector.
- 7 Retrieve an optical path swab from the accessories kit.

____ Optio

Optical Path Swab

Source/Detector Swab

Dip one end into a 50:50 ethanol:water mixture (mild dish washing soap and water will work too) and carefully swab both ends of the optical path. Then, dip a Source/Detector swab into the solution and then swab around the source and detector to remove any residue.



Warning: Do not use abrasive cleansers. Abrasive cleaners can irreparably damage the gold plating on the optical path, source, or detector.

8 Inspect the hose barbs and tubing.

If the tubes are dirty or damaged, cut a new length of tubing from the extra tubing included in your spares kit, and replace them. Carefully remove them from the hose barbs. If the tubes are in good condition and clean, you may be able to reuse them. If the hose barbs are dirty, remove them and clean them with rubbing alcohol or soapy water. Use caution and do not scratch the hose barbs because scratches may cause leaks.

9 Inspect the O-Rings.



Four O-rings are included in the Optical Bench Cleaning Kit (part number 9980-066), and additional O-rings can be purchased from LI-COR. Replace them if they are smashed flat or damaged in any way.

10 Let the optical components dry and reassemble the optical bench.

Attach the source and detector. The orientation of the optical path cylinder is unimportant — either end can be inserted into the source and detector housing. Tighten each of the screws snugly.

- 11 Place the optical bench back into the foam, re-insert the cable connectors to the source and detector, and screw the cover plate back to complete the re-assembly.
- 12 Perform a zero and span calibration (see User calibration on page 4-6 for instructions).

Connecting to LI-870 for calibration

Though the primary interface for the LI-870 is through the Smart Chamber or LI-8250 software, you may also connect your LI-870 to the LI-COR LI-830/850 software to view data and for user calibration.

After downloading and installing the software from the LI-COR support site (licor.com/env/support), launch the software. It should display No Analyzer Connected.

Note: You must connect the power cable from a powered-on Smart Chamber or LI-8250 to power to analyzer when using the software.

Connect your analyzer to your computer using the USB-B to USB-A cable included with your purchase. You may see a notification that says **Setting up device**, or something similar. After the automatic device setup is complete, go back to the software, and click **Connect**. In the box that opens, expand the **Connect to** drop-down menu, and you will see your device.

Important: The LI-830/850 software will recognize your LI-870 as an LI-850. This is normal. Go ahead and click **Update**, and you will connect to your LI-870.



After connecting, the software presents you with live data and graphs.

Here you can see important diagnostic information like **Cell Temperature** and **Cell Pressure**. You can also turn the pump on by clicking the power button next to **Pump**: in the bottom-right of the software.



The software offers a variety of other features you may choose to explore. A more thorough explanation of the software is available at the LI-COR support site. However, for LI-870 soil applications, you will likely only the use the software for instrument calibration.

User calibration

If the instrument is not measuring as expected, or if you have disassembled the optical bench for any reason, you should check the zero and span settings and set them if necessary. The zero and span are an offset and slope. The zero value ensures that the instrument shows zero when the gas has a zero concentration. A change in the zero will affect every measurement. The span setting ensures a correct measurement at a known non-zero concentration. A change in the span affects higher concentration measurements more than lower ones. The recommended order of operation for user calibration is

- 1 Set the H₂O zero.
- 2 Set the CO₂ zero.
- 3 Set the H₂O span.
- 4 Set the CO₂ span.

For user calibration, additional tubing (part number 222-01824) and quick connects (part numbers 300-07124 (male) and 300-07125 (female)) are included with your spares kit.

Setting the H₂O zero and spans

The water vapor span can be set with a dew point generator such as the LI-610. The procedure is the same as setting the CO_2 zero and spans, only this uses known concentrations of water vapor rather than CO_2 .

Caution: Setting the zero and span incorrectly for either CO_2 or H_2O will adversely impact the performance of your instrument. If you do not have the proper equipment to span the analyzer, it is best to leave it alone.

Setting the CO₂ zero

Always perform the zero first. To set the zero, you'll need either a tank of dry air that is free of CO_2 or a CO_2 scrubbing chemical such as wet soda lime and a desiccant such as Drierite.

1 Plumb the zero-gas tank or scrubber to the air inlet.

Be sure to use an air filter to prevent contaminants from entering the optical path.

- If using tank air, the pressure of the tank is sufficient to flow the gas through the analyzer. Allow at least 0.75 liters per minute to flow through the cell (no more than 1.0 lpm).
- If using a scrubbing chemical, use a pump to draw air through the analyzer.
- **2** Install a 10 to 20 cm length of tubing to the air outlet.

This vent prevents ambient air from diffusing upstream into the optical cell.



3 When the CO₂ concentration has stabilized, click the Zero CO₂ button.



Setting the primary CO₂ span

When choosing a span gas, we recommend a gas concentration that is close to - but still slightly above - the upper limit of what you expect to measure. For example, if you are measuring near-ambient levels, choose a span gas that is near 400 ppm CO_2 (as opposed to 18,000 ppm). Similarly, if you are measuring concentrations near 15,000 ppm CO_2 , a span gas with 100 ppm would not be ideal.

4 After zeroing, flow a gas with a known CO₂ concentration through the analyzer at a rate of 0.5 liters per minute.



- 5 Enter the CO₂ concentration of the span gas into the software.
- 6 When the CO₂ reading has stabilized, click Span CO₂.



Setting the secondary CO₂ span

You can set a second span (using a gas that has a CO_2 concentration that is higher or lower than the primary span gas) to improve the precision of the analyzer. The pro-

cess is exactly the same as setting the primary span, only you'll enter a different concentration and click Span2 CO₂.

Recovering from a bad zero or span

If your attempt to zero or span does not go as planned, you can restore the factory default zero and span settings. The information you need is provided on the calibration sheet (included with the instrument or available for download from www.licor.com/env/support/). Under **Settings > Calibrations > Advanced**, enter the factory zero and span values for your instrument.

Appendix A. **Specifications**

General

Case dimensions: 28.4 cm L × 27.9 cm W × 12.4 cm H (11.2 in × 11 in × 4.9 in) Weight: 2.31 kg (5.1 lbs.) Measurement rate: 1 per second (1 Hz) Operating temperature range: -20 to 45 °C, without solar loading Relative humidity range: 0 to 95% RH, non-condensing Measurement principle: Non-dispersive infrared (NDIR) Operating pressure range: 50 to 110 kPa Flow rate (nominal): 0.75 liters min⁻¹ Power Requirements: Input voltage: 10-17 VDC, 2 A max After warmup (without pump): 0.33 A @ 12 VDC (4.0 W) average After warmup (with pump): 0.42 A @ 12 VDC (5.0 W) average Power source: 8200-01S Smart Chamber or LI-8250 Multiplexer

CO₂ Measurements Measurement range: 0 to 20,000 ppm Accuracy: Within 1.5% of reading

H₂O Measurements

Measurement range: 0 to 60 mmol mol⁻¹ **Accuracy:** Within 1.5% of reading

Appendix B. Equations summary

The LI-870 computes CO₂ concentrations using an equation of the form

$$c = f(\alpha'')(T + 273.15)$$
 B-1

where *c* is concentration, f() is the calibration function, α'' is the absorptance, $g(\alpha, P)$ is the pressure correction, $S(\alpha)$ is the span, and *T* is the temperature (°C) of the gas in the cell, typically 51.5 °C. Absorptance is computed from

$$\boldsymbol{\alpha}^{\prime\prime} = \boldsymbol{\alpha}^{\prime} \boldsymbol{g} \left(\boldsymbol{\alpha}^{\prime}, \boldsymbol{P} \right)$$
B-2

 α' is a span corrected absorptance, and $g(\alpha', P)$ is the pressure correction.

$$\alpha' = \alpha S(\alpha)$$
 B-3

 $S(\alpha)$ is the span function, and raw absorptance α is computed from

$$\alpha = \left(1 - \frac{V}{V_o}Z\right)$$
B-4

where V and V_o are the raw detector sample and reference readings, and Z is the zeroing parameter.

Span is a linear function of absorptance.

$$S(\alpha) = S_o + S_1 \alpha$$
 B-5

H₂O Equations

Absorptance α_{ω} for water vapor is computed from

$$egin{aligned} lpha_w &= \left(1 - rac{V_w}{V_{wo}} Z_w
ight) \ lpha'_w &= lpha_w S_w\left(lpha_w
ight) \ lpha''_w &= lpha' g_w\left(lpha'_w, P
ight) \end{aligned}$$

where V_w and V_{wo} are the sample and reference raw detector readings, and Z_w is the zero parameter. The pressure correction for water vapor is an empirical function $g_w()$ of absorptance and pressure *P*:

$$g_w(\alpha'_w, P) = \frac{P_o}{P\left(1+0.8\alpha'_w\left(\frac{P_o}{P}-1\right)\right)}$$
B-7

The value of P_o is 99 kPa. When the pressure correction is not enabled, $g_w()$ is simply 1.0. Water vapor concentration W (mmol mol⁻¹) is computed from

$$W = f_w(\alpha''_w)(T + 273.15)$$
B-8

where $f_w(x)$ is a third order polynomial whose coefficients are given on the calibration sheet.

$$f_w\left(x
ight) = a_{w1}x + a_{w2}x^2 + a_{w3}x^3$$
B-9

CO₂ Equations

The measurement of CO_2 is a bit more complicated than for H_2O because of the influence of water vapor. There is a slight direct cross sensitivity in the CO_2 signal to H_2O . This is measured at the factory and accounted for in the computation of absorptance (equation B-10). There is also a band broadening effect that is accounted for in the computation of concentration (equation B-14).

 CO_2 absorptance αc is computed from

$$\alpha_{c} = \left(1 - \left(\frac{V_{c}}{V_{\infty}} + X_{wc}\left(1 - \frac{V_{w}}{V_{wo}}Z_{w}\right)\right)Z_{c}\right)$$
B-10

$$lpha'_{c} = lpha_{c}S_{c}\left(lpha_{w}
ight)$$
 $lpha''_{c} = lpha'_{c}g_{c}\left(lpha'_{c},P
ight)$

where V_c and V_{co} are the raw detector signals for sample and reference, Z_c is the CO₂ zero parameter, and X_{wc} is a cross sensitivity parameter for the effect of water vapor on CO₂. Its value is reported on the calibration sheet as XS=.

The empirical pressure correction function $g_c()$ depends on CO₂ absorptance and pressure:

When
$$P = P_o, g_c() = 1$$
.
When $P < P_o$
 $g_c(\alpha_c, P) = X$
 $X = \frac{1}{A + B(\frac{1}{z - \alpha_c} - \frac{1}{z})} + 1$
 $A = \frac{1}{a(p-1)}$ B-11
 $B = \frac{1}{\frac{1}{b + q_p} + d}$
 $p = \frac{P_0}{P}$

where a = 1.10158, b = -6.1217E-3, c = -0.266278, d = 3.69895, and z is the asymptotic value of absorptance, obtained from the calibration coefficients (equation B-15).

$$z = a_{c1} + a_{c3} B_{-12}$$

When $P > P_o$

$$g_c(\alpha_c, P) = \frac{1}{X}$$
 $P = \frac{P}{P_0}$
B-13

where *X*, *A*, and *B* are computed as in equation B-11. CO_2 concentration *C* (µmol mol⁻¹) is computed from

$$C = f_c \left(\frac{\alpha''_c}{\psi(W)}\right) \psi(W) \left(T + 273.15\right)$$
B-14

where $f_c(x)$ is a function whose inverse is a double rectangular hyperbola, and whose coefficients (a1...a4) are given on the calibration sheet.

$$f_c^{-1}(C) = \frac{a_{c1}C}{a_{c2}+C} + \frac{a_{c3}C}{a_{c4}+C}$$
B-15

Solving equation B-15 for C yields the calibration function

$$f_c\left(x\right) = \frac{\left(a_2a_3 + a_1a_4\right) - \left(a_2 + a_4\right)x - \sqrt{\left(a_2 - a_4\right)^2 x^2 + Dx + \left(a_2a_3 + a_1a_4\right)^2}}{2(x - a_1 - a_3)}$$
B-16

Where

$$D = 2(a_2 - a_4)(a_1a_4 - a_2a_3)$$
 B-17

 $\psi(W)$ accounts for band broadening by water vapor.

$$\psi(W) = 1 + (h(\alpha'_c) - 1) \frac{W}{1000}$$
 B-18

The band broadening coefficient $h(\alpha'_c)$ has been determined to be 1.45 for the instrument for CO₂ concentrations near ambient. At higher concentrations, the value decreases. We capture this behavior with an empirical relationship (equation B-19).

$$h(\alpha'_c) = \frac{1}{(0.64b_w - 0.64)e^{-3\left(\frac{z}{\alpha'_c} - 1\right)} + \frac{1}{b_w}} B-19$$

Where z is from equation B-12, and b_w is the low concentration band broadening coefficient: 1.45. This is the value shown on the calibration sheet as BB = 1.45. The typical relationship between $h(\alpha'_c)$ and CO₂ concentration is shown in *Figure B-1* on the facing page. ('Typical' because the exact relationship depends on the relationship between absorptance and CO₂, which is the calibration curve.)



Figure B-1. The typical relationship between $h(\alpha'_c)$ and CO₂ concentration.

Note: We formulated equation B-19 with $0.64b_w - 0.64$ instead of the simple equivalent (0.29) because this allows band broadening corrections to be turned off by setting b_w to 1. When $b_w = 1$, $h(\alpha_c) = 1$ everywhere. Also, to avoid computational problems (underflows, overflows, and division by zero) we constrain the argument α_c when computing $h(\alpha_c)$ to be $0.1 < \alpha_c \le z$. $\alpha_c - 0.1$ is typically equivalent to about 600 ppm.

Calibration Equations

The following equations describe the implementation of zero and span calibrations.

Zeroing H₂O

When the command for zeroing water is received, the LI-870 computes the water zero from equation B-20, where \overline{V}_w and \overline{V}_{wo} are averaged for 5 seconds.

$$Z_w = \frac{\overline{V}_{wo}}{\overline{V}_w}$$
B-20

Zeroing CO₂

When the command for zeroing CO₂ is received, the instrument computes the CO₂ zero term from equation B-21, where \overline{V}_c , \overline{V}_{co} , \overline{V}_w , and \overline{V}_{wo} are averaged for 5 seconds.

$$Z_{c} = \frac{1}{\left(\frac{\overline{v}_{c}}{\overline{v}_{co}} + X_{wc} \left(1 - \frac{\overline{v}_{w}}{\overline{v}_{wo}} Z_{w}\right)\right)}$$
B-21

Spanning H₂O

When the command for setting the span for H₂O is received, along with the target concentration W_T , from the target concentration, the target absoprtance α_T is computed from

$$\alpha_{wT} = f_w^{-1} \left(\frac{W_T}{T + 273.15} \right)$$
B-22

LI-870 computes S_{w0} from equation B-23, where $\overline{\alpha}_{w}$ is averaged over five seconds.

$$S_{w0} = \frac{\beta_w}{\overline{\alpha}_w} - S_{w1}\overline{\alpha}_w$$
B-23

where

$$\beta_w = \frac{\alpha_{wT}}{g_w(\alpha_{wT}, P)}$$
B-24

The instrument retains the following values, which are used for subsequent secondary spans:

$$\alpha_{w1} = \overline{\alpha}_w$$
B-25
 $\beta_{w1} = \beta_w$

Secondary Span H₂O

When the secondary span command for H₂O is received, the instrument computes new values for both S_{w0} and S_{wl} . First, it measures a new $\overline{\alpha}w$ and computes a new β_w from equation B-24. Then, it uses these plus the retained values (α_{w1} and β_{w1} from the previous normal span) to compute

$$S_{w1} = \frac{\frac{\beta_w}{\overline{\alpha}_w} - \frac{\beta_{w1}}{\alpha_{w1}}}{\overline{\alpha}_w - \alpha_{w1}}$$
B-26

Given the new span slope S_{wl} , it updates the span offset S_{w0} by equation B-23.

Spanning CO₂

When the command for setting the CO₂ span is received, along with the target concentration C_T , the instrument computes S_{c0} from equation B-28, where $\overline{\alpha}_c$ and \overline{W} are averaged for 5 seconds.

$$\alpha_{cT} = f_c^{-1} \left(\frac{C_T}{(T+273.15)\psi(\bar{W})} \right)$$
B-27

$$S_{c0} = \frac{\beta_c}{\overline{\alpha}_c} - S_{c1}\overline{\alpha}_c$$
B-28

where

$$\beta_c = \frac{\alpha_{cT}\psi(\bar{W})}{g_c(\alpha_{cT}, P)}$$
B-29

Note that

$$\psi(\overline{W}) = 1 + (h(\alpha_{cT}) - 1)\frac{\overline{W}}{1000}$$
$$= \left(1 + \left(\frac{1}{(0.64b_w - 0.64)e^{-3\left(\frac{z}{\alpha_{cT}} - 1\right)} + \frac{1}{b_e}} - 1\right)\frac{\overline{W}}{1000}\right)$$
B-30

We need αcT to compute $\psi(\overline{W})$, but αcT depends on $\psi(\overline{W})$. We resolve this by using an approximation (equation B-31) instead when computing equation B-30

$$\alpha_{cT} \approx f_c^{-1} \left(\frac{C_T}{(T+273.15)} \right)$$
B-31

The instrument retains the following values, which are used for subsequent secondary spans, if necessary:

$$\alpha_{c1} = \overline{\alpha}_c$$
 B-32

$$\beta_{c1} = \beta_c$$
 B-33

Secondary Span CO₂

When the secondary span command for CO₂ is received, the instrument computes new values for both S_{c0} and S_{c1} . First, it measures a new $\overline{\alpha}_c$ and computes a new β_c from equation B-29. Then it uses these, plus the retained values (α_{c1} and β_{c1} from the previous normal span) to compute

$$S_{c1} = \frac{\frac{\beta_c}{\overline{\alpha}_c} - \frac{\beta_{c1}}{\alpha_{c1}}}{\overline{\alpha}_c - \alpha_{c1}}$$
B-34

Given the new span slope S_{cl} , it updates the span offset S_{c0} by equation B-28.

Standard Terms and Conditions

1. General. LI-COR Inc. ("LI-COR") is delivering these goods and products ("Products") subject to these Terms and Conditions of Sale ("Conditions"). Buyer will be deemed to have assented to these Conditions upon Buyer's placement of order. Notwithstanding the above, failure of LI-COR to object to provisions contained in any purchase order or other form or document from Buyer shall not be construed as a waiver of these Conditions nor an acceptance of any such provision.

2. Buyer's Use Only/No Resale. The purchase of Products only conveys to Buyer the non-transferable right for only Buyer to use the quantity of Products and components of Products purchased in compliance with the applicable intended use statement, limited use statement or limited label license, if any, in LI-COR catalogues or on the label or other documentation accompanying the Products (all such statements or licenses being incorporated herein by reference as if set forth herein in their entirety). Buyer has no right to resell the Products, or any portion of them, and any such resale is strictly prohibited unless LI-COR first accepts and approves a purchase order and acknowledges in writing that the Products may be resold by Buyer and the terms of such resales.

3. Prices/Taxes. All prices are quoted for delivery to Buyer when goods are loaded on the carrier at LI-COR premises in Lincoln, Nebraska, USA. Accordingly, unless otherwise specified by LI-COR, prices are exclusive of shipping, insurance and installation charges, all of which are Buyer's sole responsibility. All prices are exclusive of all sales, use, excise, value added, withholding and other taxes, and all customs, duties, documentation charges, and freights forwarder charges now or hereafter claimed or imposed by any governmental authority upon the sale of the Products. Any such charges will be added to the product invoice or subsequently invoiced to the Buyer. In the event LI-COR is required to pay any such tax, duty or charge, Buyer will promptly reimburse LI-COR.

4. Payment Terms. All payments shall be made in immediately available U.S. Dollars net thirty (30) days from the date of invoice for qualified accounts, without set-off, deduction or withholding of any kind, unless otherwise stated by LI-COR in writing and may be paid by check (drawn on a U.S. bank), wire transfer or major credit card. All open account invoicing must be pre-approved. Any amounts not paid when due will accrue interest at the rate of 1 1/2% per month, or the maximum amount allowed by law, if lower. In the event that any payment is more than thirty (30) days late, LI-COR shall have the right to suspend doing business with Buyer until all past due balances are made current. Buyer shall pay for all costs (including reasonable fees) incurred by LI-COR in connection with the collection of late payments. Each accepted purchase order is a separate, independent transaction, and Buyer has no right of set-off against other purchase orders or other transactions with LI-COR. Buyer hereby grants LI-COR a security interest in the Products in the amount of the unpaid balance of the purchase price until paid in full. LI-COR may file a financing statement for such security interest and Buyer shall sign any such statements or other documentation necessary to perfect LI-COR security interest.

5. Return Policy. Buyer may return non-consumable Products to LI-COR within forty-five (45) days of invoice date only with prior authorization by LI-COR, the Product(s) being returned in new and unused condition and must be resalable as new. Any returned Product(s) are subject to payment of a fifteen percent (15%) re-stocking fee on all items returned. Buyer shall be responsible to make payment to LI-COR for any and all expenses related to deinstallation of the Product(s), including but not limited to shipping, duties, and taxes. All payments subject to this provision shall be made to LI-COR within thirty (30) days of return, or de-installation, of the Product(s).

6. Delays In Performance. LI-COR shall not be liable for any delay in performance hereunder due to unforeseen circumstances or due to circumstances beyond its control including, but not limited to, acts of nature, acts of government, labor disputes, delays in transportation, delays in customs clearance and delays in delivery or inability to deliver by LI-COR's suppliers.

7. Shipment and Packing. All Product prices exclude costs of shipping and handling and insurance, in accordance with delivery terms designated by LI-COR. Unless otherwise agreed in writing, such costs will be paid by the Buyer and will appear as a separate item on LI-COR invoice. LI-COR shall ship in accordance with LI-COR standard practices. Buyer may specify different shipping instructions, subject to agreement by LI-COR. Unless otherwise agreed to in writing by LI-COR, all products shall be packaged, if appropriate, for shipment and storage in accordance with standard commercial practices. All packing shall conform to carrier requirements.

8. Partial Shipments. Any Products delivered in partial shipments may be invoiced individually. Additional shipping and handling charges may apply.

9. Title/Risk of Loss. All domestic shipments are made FOB per Uniform Commercial Code. All international shipments are made per INCOTERMS 2000 designated by LI-COR. LI-COR title to the Products and the risk of loss of or damage to the Products ordered by the Buyer will pass to Buyer at time of LI-COR delivery of Products to the carrier. The carrier shall be deemed Buyer's agent, and any claims for damages in shipment must be filed with the carrier. LI-COR is authorized to designate a carrier pursuant to LI-COR standard shipping practices unless otherwise specified in writing by Buyer.

10. Intellectual Property Rights. Title to and ownership of the documentation, and any improved, updated, modified or additional parts thereof, and all copyright, patent, trade secret, trademark and other intellectual property rights embodied in the Products, shall at all times remain the property of LI-COR or LI-COR licensors.

11. Acceptance. All sales are final and all Products shall automatically be deemed accepted upon delivery to Buyer when goods are loaded on the carrier at LI-COR premises in Lincoln, Nebraska, USA. Buyer may not return any Products to LI-COR except as provided for by LI-COR warranty or as provided herein.

12. Product Warranties. Unless otherwise specified by LI-COR:

(a) LI-COR warrants that, for a period of twelve (12) months from the date of shipment of the Products from LI-COR (the "Warranty Period"), unless otherwise specified for individual Products or extended by a Support Contract or Extended Warranty Contract, the Products sold hereunder will be free from material defects in materials and workmanship and will conform to LI-COR published specifications in effect as of the date of manufacture. LI-COR SPECIFICALLY DISCLAIMS ANY INDIRECT, SPECIAL, INCIDENTAL OR CONSEQUENTIAL DAMAGES (INCLUDING LOSS OF USE OR LOST PROFITS) WHICH MAY RESULT FROM THE USE OF PRODUCTS PURCHASED HEREUNDER, AS FURTHER SET FORTH IN SECTION 13 OF THESE CONDITIONS OF SALE. This limited warranty extends only to Buyer as original purchaser unless otherwise agreed upon in writing by LI-COR.

(b) The foregoing warranty shall not apply if the defective Product (i) has been subjected to abuse, misuse, neglect, negligence, accident, improper testing, improper installation, improper storage, improper handling or use contrary to any instructions issued by LI-COR, (ii) has been repaired or altered by persons other than LI-COR, (iii) has not been installed, operated, repaired and maintained in accordance with the documentation or operated outside of the environmental specifications for the Product; (iv) has failed due an Act of God, including but not limited to fire, flood, tornado, earthquake, hurricane or lightning or (v) has been used with any devices, accessories or products not manufactured by or approved by LI-COR. In addition, the foregoing warranty shall not apply to Products (i) LI-COR Standard Terms and Conditions of Sale – rev. 5/15/2009 marked or identified as "sample," (ii) loaned or provided to Buyer at no cost, or (iii) which are sold "as is."

c) If during the Warranty Period: (i) LI-COR is notified promptly in writing upon discovery of any defect in the Product, including a detailed description of such alleged defect, (ii) such Product is returned, transportation charges prepaid, to LI-COR designated manufacturing facility subject to the prior approval of LI-COR with a valid Return Material Authorization ("RMA") number, and (iii) LI-COR inspections and tests determine that the Product is indeed defective and the Product has not been subjected to any of the conditions set forth above, then, as Buyer's sole remedy and LI-COR sole obligation under the foregoing warranty, LI-COR will, at LI-COR option, repair or replace without charge the defective Product. In no event will the Buyer itself nor will the Buyer allow any party other than LI-COR or a third party authorized in writing by LI-COR to perform any service on the Products.

(d) During the Warranty Period, LI-COR will provide on-site warranty repair for Odyssey® Infrared Imager, Aerius Automated Infrared Imager, Pearl® Imager and/ or 4300 DNA Analyzer Products including travel costs, repair parts, and labor to maintain the hardware in proper operating condition. At LI-COR discretion, the Buyer may be required to run certain diagnostic procedures to help determine the source of the problem before on-site warranty repair is rendered. If an on-site service call is initiated, LI-COR will dispatch a service technician to the Buyer site. On-site service will be provided 8:00 a.m. to 5:00 p.m. (Buyer local time), Monday through Friday, excluding LI-COR holidays. The cost of a repair/service call for an instrument malfunction caused by third party hardware and/or software will be billed to Buyer on a time and material basis.

(e) Any Product that has either been repaired or replaced under this warranty shall have warranty coverage (parts only) for the longer of ninety (90) days or the remaining original warranty period. Replacement parts used in the repair of Products may be new or equivalent to new.

(f) EXCEPT FOR THE WARRANTIES SET FORTH IN THIS SECTION, LI-COR MAKES NO OTHER WARRANTIES, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO ANY PRODUCTS OR OTHER PRODUCTS PROVIDED IN CONNECTION WITH THESE CONDITIONS, INCLUDING WITHOUT LIMITATION ANY IMPLIED WARRANTY OF MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE, NONINFRINGEMENT, OR ARISING FROM COURSE OF PERFORMANCE, DEALING, USAGE OR TRADE.

(g) Notwithstanding anything herein to the contrary, LI-COR makes no warranty with respect to any third party products provided under these Conditions. Buyer's sole remedy with respect to such third party products shall be pursuant to the original manufacturer's or licensor's warranty, if any, to Buyer, to the extent permitted by the original manufacturer or licensor.

13. Limitation of Liability. IN NO EVENT SHALL LI-COR, ITS LICENSORS OR ITS SUPPLIERS BE LIABLE TO BUYER OR ANY THIRD PARTY FOR COSTS OF PROCUREMENT OF SUBSTITUTE PRODUCTS OR SERVICES, LOST PROFITS, DATA OR BUSINESS, OR FOR ANY INDIRECT, SPECIAL, INCIDENTAL, EXEMPLARY OR CONSEQUENTIAL DAMAGES OF ANY KIND ARISING OUT OF OR IN CONNECTION WITH THE USE OF THE PRODUCTS OR THESE CONDITIONS, HOWEVER CAUSED AND ON ANY THEORY OF LIABILITY (WHETHER IN CONTRACT, TORT (INCLUDING NEGLIGENCE), STRICT LIABILITY, PRODUCTS LIABILITY OR OTHERWISE). LI-COR TOTAL AND CUMULATIVE LIABILITY ARISING OUT OF OR IN CONNECTION WITH ANY PRODUCTS PURCHASED BY BUYER HEREUNDER SHALL IN NO EVENT EXCEED THE PURCHASE PRICE PAID BY BUYER FOR SUCH PRODUCTS. THE LIMITATIONS SET FORTH IN THIS SECTION SHALL APPLY EVEN IF LI-COR OR ITS SUPPLIERS HAVE BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES, AND NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY.

14. Authorized Use of Biotechnology Products. Unless otherwise expressly indicated in LI-COR catalogues, LI-COR website or on the label or other documentation accompanying Biotechnology Products, the LI-COR Biotechnology Products are intended for RESEARCH USE ONLY and are not to be used for any other purposes including, but not limited to, unauthorized commercial purposes, in vitro diagnostic purposes, ex vivo or in vivo therapeutic purposes, investigational use, in foods, drugs, devices or cosmetics of any kind, or for consumption by or use in connection with or administration or application to humans or animals. Buyer acknowledges that the Biotechnology Products have not necessarily been tested for safety or efficacy, unless expressly stated in LI-COR catalogs or on the label or other documentation accompanying the Biotechnology Products.

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16. Severability. If any portion of these Conditions is held invalid, the parties agree that such invalidity shall not affect the validity of the remaining portions of these Conditions.

17. Export Control. Buyer acknowledges and agrees that the Products purchased under these Conditions may be subject to restrictions and controls imposed by the United States Government and the regulations thereunder. BUYER WARRANTS THAT IT WILL NOT EXPORT OR RE-EXPORT ANY PRODUCTS PURCHASED WITHOUT PRIOR WRITTEN NOTIFICATION AND APPROVAL OF LI-COR.

18. Assignment. Buyer shall not assign or transfer these Conditions or any rights or obligations under these Conditions, whether voluntary or by operation of law, without the prior written consent of LI-COR. LI-COR may assign or transfer these Conditions to any successor by way of merger, acquisition or sale of all or substantially all of the assets relating to these Conditions. LI-COR or any successor may assign all or part of the right to payments under these Conditions. Any assignment or transfer of these Conditions made in contravention of the terms hereof shall be null and void. Subject to the foregoing, these Conditions shall be binding on and inure to the benefit of the parties' respective successors and permitted assigns.

19. Entire Agreement. These Conditions of Sale take precedence over Buyer's additional or different terms and conditions, to which notice of objection is hereby given. Acceptance by Buyer is limited to LI-COR Conditions of Sale. Neither LI-COR commencement of performance nor delivery shall be deemed or construed as acceptance of Buyer's additional or different terms and conditions. These Conditions supersede all prior communications, transactions, and understandings, whether oral or written, and constitute the sole and entire agreement between the parties

pertaining to the referenced quotation or purchase order, provided that: (1) these Conditions shall not, without LI-COR prior written consent, supersede any conflicting terms of: (a) prior written agreements duly executed by LI-COR, or (b) governmental purchase orders, terms of purchase, requests for quotation or acquisition regulations relative to governmental purchasers; and (2) to the extent not in conflict with any such prior or governmental terms, these Conditions shall supplement them. No modification, addition or deletion, or waiver of any of the terms and conditions of these Conditions shall be binding on either party unless made in a non-preprinted agreement clearly understood by both parties to be a modification or waiver, and signed by a duly authorized representative of each party.

20. Entire Agreement. These Conditions of Sale take precedence over Buyer's additional or different terms and conditions, to which notice of objection is hereby given. Acceptance by Buyer is limited to LI-COR Conditions of Sale. Neither LI-COR commencement of performance nor delivery shall be deemed or construed as acceptance of Buyer's additional or different terms and conditions. These Conditions supersede all prior communications, transactions, and understandings, whether oral or written, and constitute the sole and entire agreement between the parties pertaining to the referenced quotation or purchase order, provided that: (1) these Conditions shall not, without LI-COR prior written consent, supersede any conflicting terms of: (a) prior written agreements duly executed by LI-COR, or (b) governmental purchase orders, terms of purchase, requests for quotation or acquisition regulations relative to governmental purchasers; and (2) to the extent not in conflict with any such prior or governmental terms, these Conditions shall supplement them. No modification, addition or deletion, or waiver of any of the terms and conditions of these Conditions shall be binding on either party unless made in a non-preprinted agreement clearly understood by both parties to be a modification or waiver, and signed by a duly authorized representative of each party.

21. Force Majeure. Shipping dates are approximate and may be delayed absent prompt receipt from Buyer of all necessary information. LI-COR shall not be responsible for any failure to perform or delay attributable in whole or in part to any cause beyond its reasonable control, including but not limited to Acts of God, government actions, war, civil disturbance, insurrection, sabotage, labor shortages or disputes, failure or delay in delivery by LI-COR suppliers or subcontractors, transportation difficulties, customs clearance, shortage of energy, raw materials or equipment, or Buyer's fault or negligence. In the event of any such delay the date of delivery shall, at the request of LI-COR, be deferred for a period equal to the time lost by reason of the delay.

22. Governing Law and Venue. These Conditions and performance by the parties hereunder shall be construed in accordance with the laws of the State of Nebraska, U.S.A., without regard to provisions on the conflicts of laws.

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984-17878 • 02/2023

