

PICARRO

G2121-*i* Analyzer for Isotopic CO₂ User Manual



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Picarro Analyzer User Manual

Thank you for purchasing a Picarro product. Your Picarro system is a quality product that has been designed and manufactured to provide reliable performance.

This User Manual (UM) is an important part of your purchase as it will help familiarize you with the system and explain the numerous features that have been designed into it. Please read this manual thoroughly before using your Picarro system.

Please contact Picarro or your authorized Picarro distributor should you have questions regarding specific applications or if you require additional information.

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1. INTRODUCTION TO TECHNOLOGY

Picarro analyzers use time-based, optical absorption spectroscopy of the target gases to determine concentration. They are based on wavelength-scanned cavity ring-down spectroscopy (WS-CRDS), a technology in which light re-circulates many times through the sample, creating a very long effective path length for the light to interact with the sample, thus, enabling excellent detection sensitivity in a compact and rugged instrument.

The Picarro analyzer is comprised of two modules:

- The **Analyzer** contains the spectrometer, sample chamber, and a computer with a hard drive to store and analyze data. The single analyzer module controls the operation of the system and converts spectroscopic measurements into gas concentration data.
- The **External Vacuum Pump** draws the sample gas through the instrument.

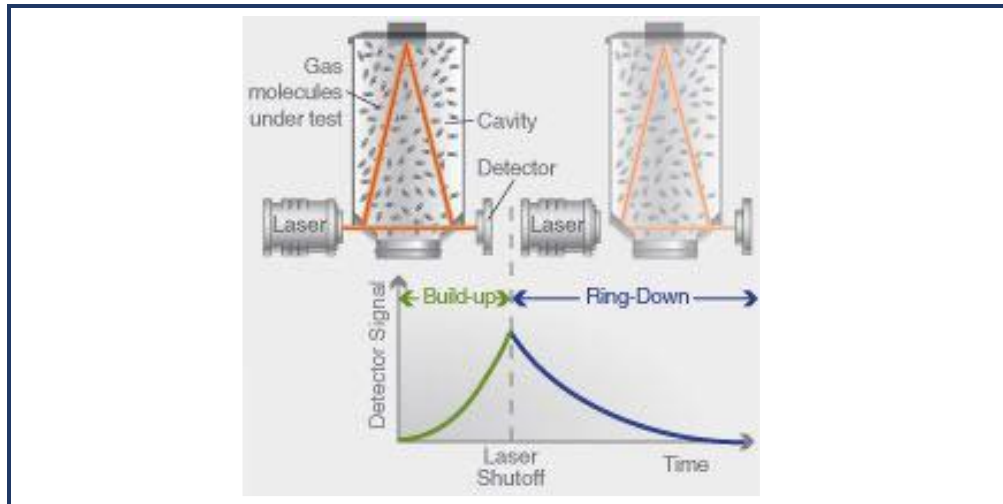
1.1 Cavity Ring-Down Spectroscopy (CRDS)

Nearly every small gas-phase molecule (e.g., CO₂, H₂O, H₂S, NH₃) and isotopologue (e.g., H₂¹⁸O, ¹³CO₂, ¹⁵N¹⁴N¹⁶O) uniquely absorb specific wavelengths of near-infrared light. The strength of the light absorption is related to the concentration of a molecule in a sample and the distance that light travels through the sample, called the path length.

Conventional infrared spectrometers are typically only sensitive enough to detect trace gases at levels in the part-per-million. Cavity Ring-Down Spectroscopy (CRDS), on the other hand, is one thousand to one million more times sensitive.

In Picarro analyzers, light from a single-frequency laser enters a cavity where three mirrors reflect the laser light as seen in Figure 1. The light enters through the mirror closest to the laser, bounces off the angled mirror in the lower right corner of the cavity, travels to the hemispherical mirror at the top of the cavity, bounces toward the mirror in the lower left corner of the cavity, and then returns to the first mirror. This motion becomes a continuous traveling light wave, which is represented by the dark orange path in **Figure 1**.

Figure 1:
Schematic of
the Picarro
CRDS analyzer
cavity



When the laser is on, the cavity quickly fills with laser light. A small amount of the laser light is transmitted through the mirror closest to the photodetector, which turns the incident light into a signal that is directly proportional to the light intensity in the cavity.

When the photodetector signal reaches a threshold level (in a few tens of microseconds), the laser is turned off. The light contained within the cavity continues to bounce between the mirrors (about 40,000 times). Since the mirrors have slightly less than 100% reflectivity (99.999%), the light inside the cavity steadily leaks out of the cavity. The intensity of the light reaching the detector decreases, falling exponentially until it reaches zero. This decay, or "ring-down," is measured in real time by the photodetector.

1.2 Relating Ring-Down Time to Absorption Intensity

The time it takes to ring-down is inversely related to the total optical loss in the cavity, including the strength of molecular absorption at a given wavelength of light. For an empty cavity, the time it takes for the intensity to decrease by a given percent is determined solely by the reflectivity of the mirrors. A cavity containing gas that absorbs light will have a shorter ring-down time than an empty cavity. As the light circulates in a cavity with a gas sample, the molecular absorption by the gas results in a decrease of the light intensity.

Determining absorption intensity at a specific wavelength requires comparing the ring-down time of an empty cavity to the ring-down time of a cavity that contains gas. Picarro instruments gather measurements from an “empty” cavity by switching the light to wavelengths that are not absorbed by the target molecules. The analyzer subsequently measures ring-down times at wavelengths that are absorbed by the target gas. The analyzer automatically and continuously compares these two types of ring-down times, and the software uses those comparisons to calculate absorption intensities.

Figure 2:
Light intensity
as a function of
time in a CRDS
system

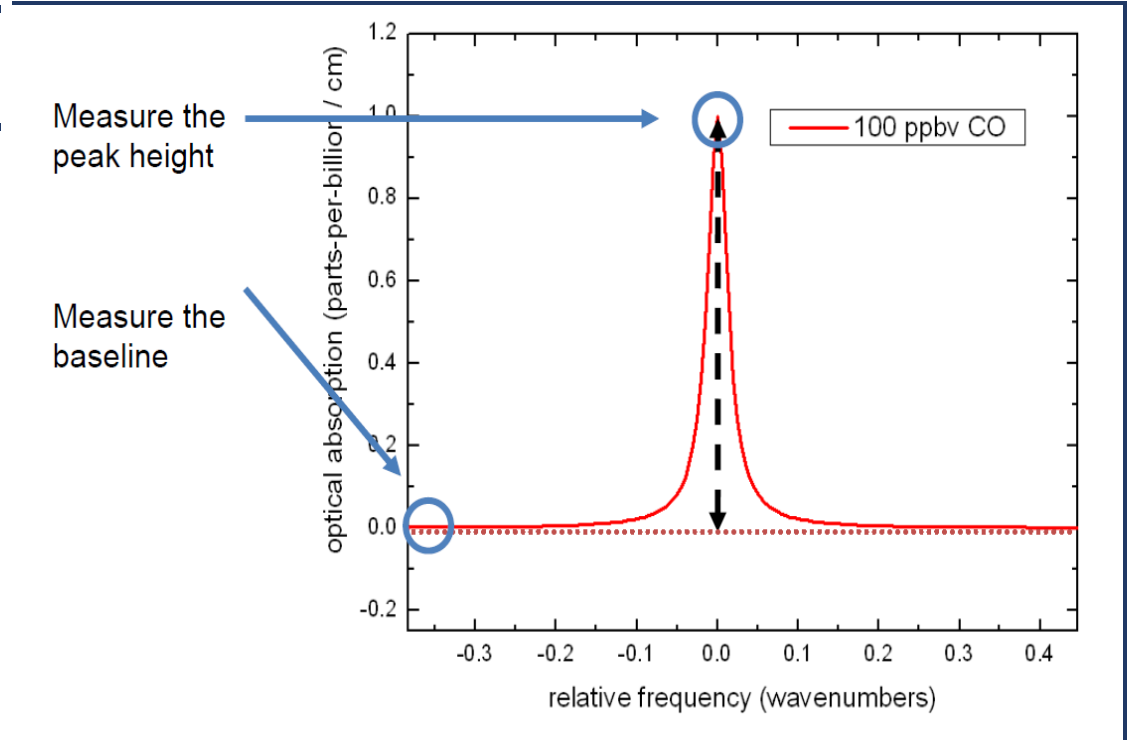


1.3 Converting Absorption Intensity to Concentration

Plotting the absorbance at each measured wavelength generates an optical spectrum. This spectrum contains absorbance peaks that are unique to each molecule in the sample. The height of a particular absorption peak is proportional to the concentration of a molecule that generated the signal.

The height of the peak is calculated by subtracting the maximal absorbance from the baseline absorbance. **Figure 3** shows a plot of ideal optical spectra with a clean, uniform baseline on either side of the absorption peak.

Figure 3:
Absorption
Spectral Curve



Optical spectra often contain several absorption lines, nested closely together. A particular absorption peak may be visible between lines, but the absorption may not return to the baseline before it rises in response to another molecule. Picarro analyzers calculate the baseline underneath a poorly resolved peak by modeling the absorption peaks from other surrounding molecules and subtracting contributions from neighboring peaks to the absorption intensity.

1.4 Spectral Precision and High Sensitivity Measurements

Picarro analyzers contain two features that provide high spectral precision:

- Proprietary **wavelength monitor (WLM)** that measures the absolute laser wavelength to a precision that is a few orders of magnitude narrower than the spectral linewidth: Picarro's patented WLM measures absolute laser wavelength to a precision more than 1,000 times narrower than the observed Doppler-broadened linewidth for small gas-phase molecules. The instruments lock the laser to the WLM, and then the monitor tunes to wavelengths known to be maximally and minimally absorbed by the target molecule. The result is closely clustered absorption intensities at and around the wavelength of peak absorption.







- Precise temperature and pressure control in the sample cavity:
Accurate absorption measurements at precisely known wavelengths account for little unless the temperature and pressure of the CRDS measurement cavity are known. The observed line intensity and shape depend on the temperature and pressure inside the sample cavity. To completely minimize instrument measurement drift, temperature and pressure must be actively stabilized to constant values.

For precise temperature control, the sample cavity is surrounded by layers of thermally insulating material to provide a high degree of passive thermal stability. The cavity is further actively stabilized by means of a solid-state heating system locked to the output of a thermal sensor. This enables the temperature of the cavity to be within 20 mK of the set temperature.

For precise pressure control, the cavity pressure is monitored using a high-linearity pressure transducer. The system computer uses this pressure data in a feedback loop to control proportional valves that adjust the inlet and outlet gas flow of the cavity.

2. CONVENTIONS

The following icons are used throughout this manual to emphasize important information in the text. These icons indicate dangers to either the operator or to the analyzer, and other important information.

	<p>Consult the user's manual for important information (When you see this symbol placed at hazard points on equipment, consult the user manual).</p>
	<p>NOTE is important information that you should be aware of before proceeding.</p>
 <p>WARNING</p>	<p>WARNING indicates an imminent danger to the user.</p>
 <p>WARNING</p>	<p>LASER WARNING alerts you of a laser danger.</p>
 <p>CAUTION</p>	<p>CAUTION alerts you of a potential danger to equipment or to the user.</p>
 <p>REMINDER</p>	<p>REMINDER is a helpful hint to procedures listed in the text.</p>

3. ACRONYMS

This manual includes various acronyms. For definitions, see below:

Acronym	Definition
CRDS	Cavity Ring-Down Spectroscopy
GUI	Graphical User Interface
cm	centimeters
mm	millimeters
" (as in 1/4")	Inches
N ₂ O	Nitrous Oxide
CH ₄	Methane
H ₂ O	Water
NH ₃	Ammonia
CO ₂	Carbon Dioxide
HB	Hotbox
WB	Warm box
ppm	Parts Per Million
ppb	Parts Per Billion
‰	per mil
°C	degrees Celsius

4. SAFETY

4.1 General Safety

CDRH Certification

This Picarro Analyzer complies with 21 CFR Chapter 1, sub-chapter J, and is classified as a Class 1 laser system when all panels and covers are on.

CE Certification

This Picarro Analyzer complies with the European standards and the instrument is affixed with a CE label. This CE label is located on the rear of the instrument.



Using this analyzer in a manner not specified by Picarro may result in damage to the analyzer and render it unsafe to operate.



This analyzer is for indoor use only and has an ingress protection rating of IPx-0. Analyzer is NOT protected against exposure to water including dripping, spraying, splashing or immersion.



Do not operate in an explosive atmosphere! Do not operate in the presence of flammable gases or fumes.



The analyzer contains no user serviceable components except the particulate filter. Do not attempt repairs; instead, report all problems to Picarro Customer Service or your local distributor. Please contact Picarro if you have any questions regarding the safe operation of this equipment.



The inlet gas connector on the back panel of the Analyzer, and its immediate vicinity, runs hot during operation of the analyzer. Take care when connecting gas lines or working at the rear of the instrument to wear protective gloves or avoid contact with these surfaces.



WARNING

This analyzer weighs 46 lbs. (20.9 kg). Use the technique described below when lifting the analyzer.

- a. Before lifting, inspect the unit for slippery substances or sharp edges.
 - b. Lift with two people, one on each side of the analyzer.
 - c. Crouch down and stay close to the unit. Always keep your back as straight as possible.
 - d. Position your feet for sturdy balance. Lift with your legs, not your back.
 - e. Do not twist the back while carrying the unit. Rotate direction with hip joints.
 - f. Lower the unit by bending at the knees.
-

4.2 Laser Safety



WARNING

This equipment is classified as a Class 1 laser product with an embedded 3B laser in accordance with EN 60825-1:2014. Do not to open the enclosure where this label is placed; there are no user serviceable parts inside.

The following Laser Safety Label is affixed to the outer cover of the analyzer.



WARNING

The laser is a Class3B when exposed. Only operate or service this device in accordance with the instructions in this guide, and only open the device in an approved laser safe service area using appropriate laser-safety glasses.

The following **Laser Safety Label** is affixed to the inside of the analyzer:

Figure 4:
Laser Safety
Label



Use of controls or adjustments or performance of procedures other than those specified herein may result in hazardous radiation exposure.

5. UNPACKING THE ANALYZER

5.1 Inspect the Shipping Boxes

Picarro products are inspected and tested before leaving the factory. Their packing containers have been designed to keep the equipment safe from damage during transit.

Inspect the condition of the boxes upon arrival. The larger box includes the analyzer and most of the accessories. Even if the outer box shows damage, the inner box holding the analyzer is cushioned enough that it will protect the instrument under most circumstances.

If the equipment does appear to be damaged, photograph the damages and contact Picarro (email pictures if possible) as soon as possible.

5.2 Unpack the Shipping Boxes

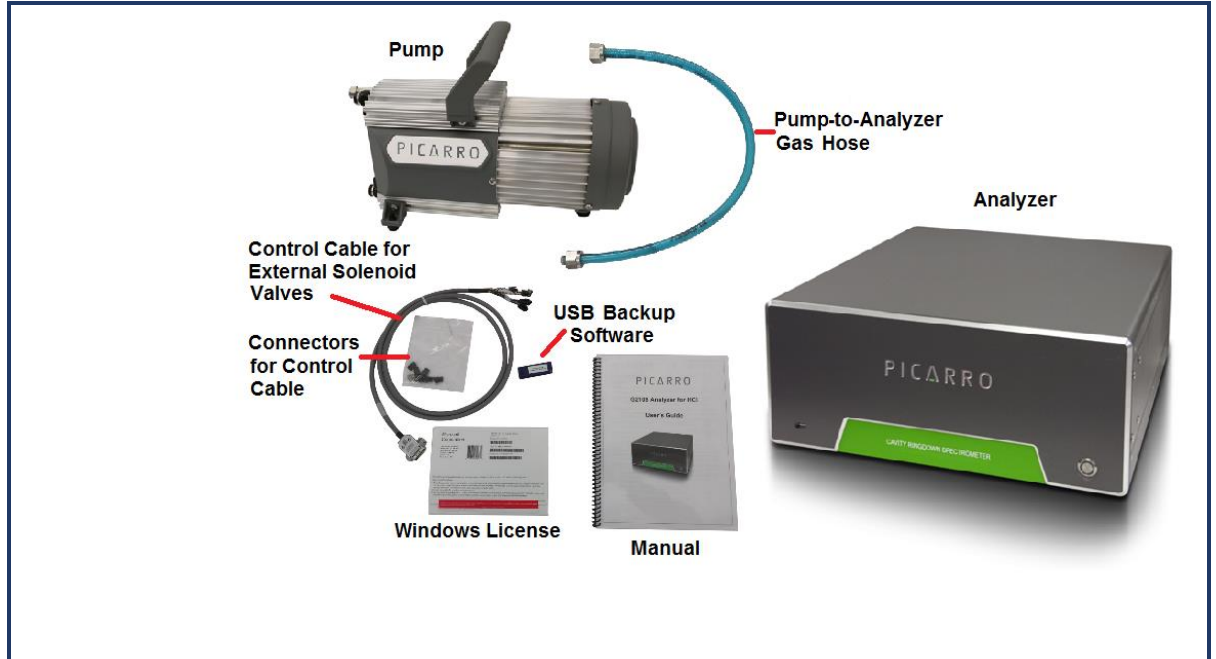
This section describes the contents of the shipping boxes:

- Inspect each item to ensure it is not damaged.
- If items are missing, contact Picarro.
- Keep the shipping packages to reuse when transporting the analyzer.
- Contact Picarro for options on transporting systems to remote labs.



This analyzer weighs 46 lbs. (20.9 kg). Use the technique outlined in the General Safety section on page 16 when lifting or moving the analyzer.

Figure 4:
Box Contents



Box One: Analyzer and Accessories

Item (qty)	Description
Analyzer (1)	Includes all the data acquisition, control, and communications hardware and firmware to perform all gas handling, spectral collection and analysis.
A/C Power Cables (1)	A power cable with connectors appropriate to your country is provided. The analyzer automatically adjusts to local voltage.
Keyboard (1)	USB keyboard
Mouse (1)	USB mouse
Control Cable (1)	For External Solenoid Valves
Nut (1) and Ferrules (2)	For connecting input line to analyzer INPUT
Document Packet (1)	Includes this manual, certificate of compliance, and Windows License.
USB Flash Drive	Contains backup software.

Box Two: Vacuum Pump and Accessories

Item (qty)	Description
Pump (1)	Provides vacuum required for sample gas sequencing into and out of the analyzer.
A/C Power Cable (1)	A power cable with connectors appropriate to your country is provided.
Vacuum Hose (1)	Hose to connect the pump to the analyzer.
Pump Manual (1)	Detailed instructions for pump.
BOX 3 (G2508 only)	Vacuum lines and fittings for G2508 recirculation pump (refer to Recirculation Pump Manual 40050)

6. ANALYZER OVERVIEW

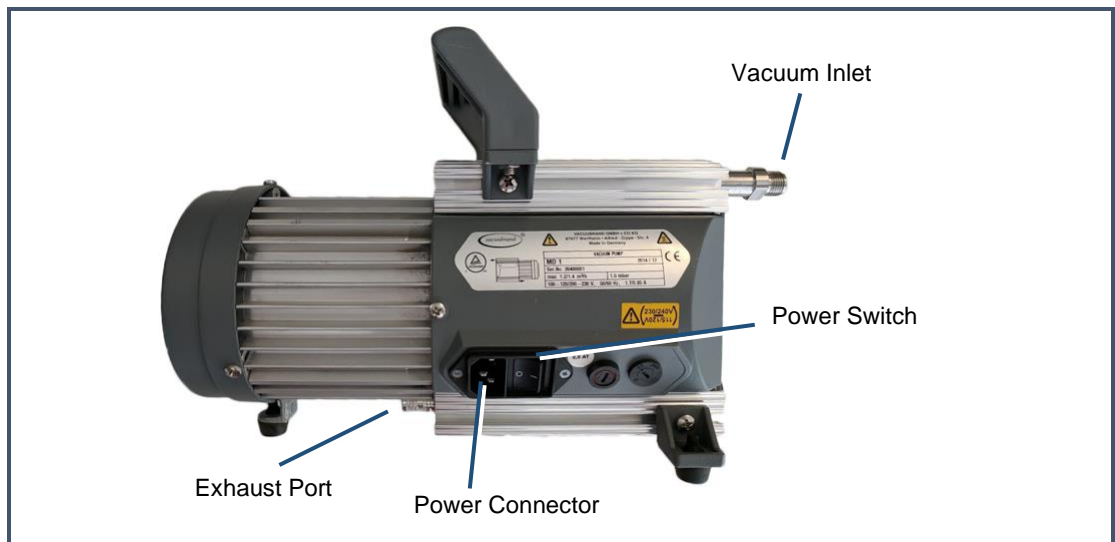
6.1 Intended Use

The G2121-I Analyzer measures concentrations of Isotopic CO₂ precisely using Picarro's patented Cavity Ring-Down Spectroscopy (CRDS) technology. The analyzer can be deployed in a lab or in the field, allowing in-situ analysis for both trace and ambient amounts of Isotopic CO₂ monitoring applications.

6.2 External Vacuum Pump

The external vacuum pump is used to maintain cavity pressure inside the analyzer. The pump should be connected and running whenever the analyzer is in use.

Figure 5:
External
vacuum pump



6.3 Analyzer Specifications

Weight (Total)	60.4 lbs. (27.4 kg), Including external pump
Analyzer	46 lbs. (20.9 kg)
Pump	14.4 lbs. (6.5 kg)
Analyzer Dimensions	Length: 17.55" (43.2 cm) Width: 17" (44.6 cm) Height: 7" (17.8 cm)
Temperature Range	Storage: -10 °C to 50 °C; Operation: 10 °C to 35 °C
Sample Flowrate	<0.1 slm at 760 torr (101 kPa)
Ambient Humidity Range	<85% R.H. non-condensing
Maximum Altitude	10,000 ft. (operation)
Clearance	Front: 6" (15.3 cm); Rear: 6" (15.3 cm)
Power Requirements	100 to 240 VAC; 47 to 63 Hz (auto-sensing)
Startup Power	<375 W at start-up (Analyzer and Pump)
Steady-state Power	120 W (Analyzer), 150 W (Pump) Steady-state operation
Mains Supply Voltage	±10% of the nominal voltage
Fluctuation	
Minimum Rated Circuit Amperage	10 A @115 VAC 5 A @230 VAC
Liquid Ingress Protection	None

7. INSTALLATION

This section describes the setup and installation of the Picarro Analyzer. Please read and understand this section thoroughly before proceeding with the installation.



WARNING

Using this analyzer in a manner not specified by Picarro may result in damage to the analyzer and render it unsafe to operate.



WARNING

Do not attach electrical power to or start the analyzer until *after* attaching and turning on the External Vacuum Pump. Do not disconnect the vacuum line while the analyzer is running. Failure to do so could result in damage to the optics.



WARNING

Picarro sells USB enabled devices, such as GPS, which is approved for use. Please do not connect USB hubs or unapproved USB devices, other than flash drives to the computer because they can interfere with the operation of the analyzer.



WARNING

If rack mounted, the Analyzer cannot support itself using a front rack mount kit alone. The instrument *must* be supported by a shelf or additional rails attached to the rack.



CAUTION

If the analyzer has been stored at less than 10 °C, allow the components to equalize to room temperature before starting the installation process.



CAUTION

Analyzer is for indoor use only and has an ingress protection rating of IPx-0. Analyzer is NOT protected against exposure to water including dripping, spraying, splashing or immersion.



CAUTION

When the analyzer is being integrated to an external system, the safety of that system is the responsibility of the assembler of that system.



CAUTION

During installation and operation, do not position the analyzer so that it is difficult to operate the disconnecting device.



NOTE

Take care to ensure that warm air is exhausted from an enclosure in which the analyzer is mounted.



CAUTION

It is imperative that the analyzer have adequate ventilation and/or cooling to maintain the ambient temperature below 35 °C when operating. Failure to provide adequate airflow, especially clearance at the front and rear panels, to ensure proper airflow and/or cooling to the analyzer will result in overheating of the analyzer causing a shutdown and potential damage. There should be 4" (10cm) of clearance in the front and back of the analyzer.

Thermal Specifications	Min	Max	Description
Ambient Operating Temperature	10 °C	35 °C	Worst-case environmental limits (unless otherwise specified)

7.1 Analyzer and Vacuum Setup

1. Remove the Analyzer and the External Vacuum Pump from their respective shipping containers.



WARNING

This analyzer weighs 46 lbs. (20.9 kg). Use the technique outlined in the General Safety section on page 16 when lifting or moving the analyzer.

2. Place the Analyzer on a bench top or flat surface. Place the External Vacuum Pump near-by or on the floor. Don't push the analyzer into position yet, there are cables to be installed on the back panel.

3. Unpack the analyzer accessories. The Certificate of Compliance and USB drive should be stored in a safe place and may be required if you contact Picarro with questions about your analyzer.
4. Remove the caps from the analyzer's INLET and VACUUM connection ports. Save the caps; you should reinstall them when the analyzer is stored, moved or shipped.
5. Remove the cap from vacuum pump's inlet. Save the cap for later use. Reinstall the caps when the pump is stored, moved or shipped.
6. Connect one end of the vacuum hose to the pump: hand tighten the nut and then use an 11/16" wrench (not included) to make an additional turn of one flat (about 60 degrees).
7. Connect the analyzer to a power source using the supplied AC power cable.



CAUTION

Use the AC power cables supplied with the analyzer or a similarly rated cable. Check with Picarro technical support if you have questions about power cable replacement. An inadequately rated power cable can result in equipment damage.

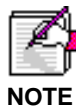
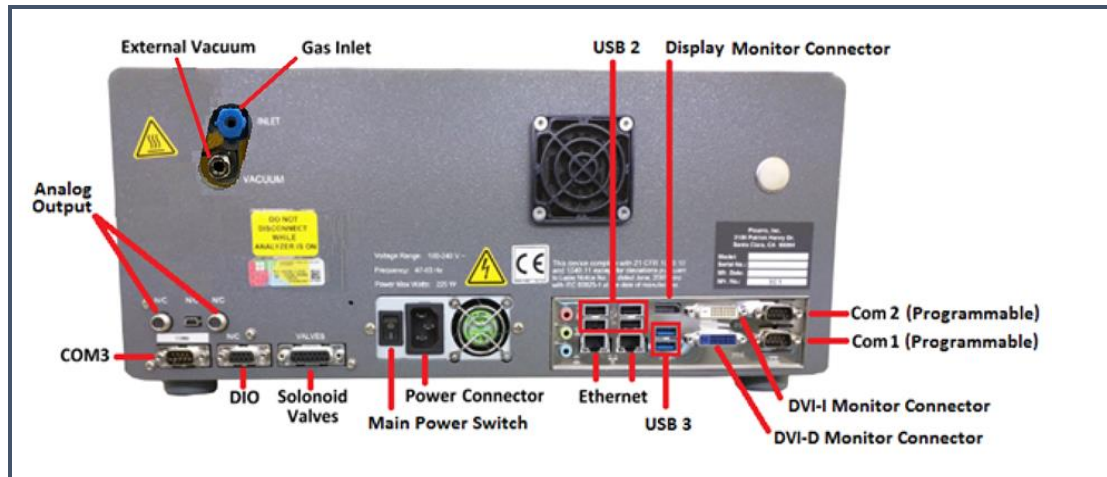


CAUTION

Cords shall be RATED for the maximum current for the equipment and the cable used shall meet the requirements of IEC 60227 or IEC 60245. Cords certified or approved by a recognized testing authority are regarded as meeting this requirement. The connector type used should be: IEC320 C13.

8. If desired, attach a tube to the External Vacuum Pump exhaust port and direct to a safe place for venting the mixture of sample gases.
9. Select the appropriate voltage, 110V or 220V, for the External Vacuum Pump using the Power Switch located on the pump.
10. Connect the External Vacuum Pump to a power source using the other AC power cable.

Figure 6:
Analyzer Back Panel



NOTE

The software to operate the instrument will start automatically after the operating system has loaded. The user interface will appear a few seconds after the instrument software starts. See Startup in Section 8.1.

7.2 Connecting to the Analyzer Inlet

Connect to the inlet of the analyzer using ¼" OD PTFE or PFA tubing using the supplied plastic ¼" PFA inlet nut and ferrules.



WARNING

When using compressed gases, follow all appropriate safety conventions, including use of eye protection, physical restraint of cylinders, etc.

Making a new connection:

When using new tubing, follow these steps.

1. Place the two ferrules inside the nut as shown.

Figure 7:
Orientation of
ferrules and nut



2. Loosely connect the nut to the **INLET** on the back panel of the analyzer about a full turn, being careful not to let the ferrules fall out.
3. Insert the tubing into the back of the nut, feeding it in as far as possible without deforming the tubing.
4. Hand tighten the nut.
5. Using a 5/8" wrench (not included), tighten the nut approximately seven flats (420 degrees).

Replacing a connection

When reattaching tubing that already has a nut connected:

1. Inspect ferrules. If you see any damage, replace the ferrules and follow the directions above for making a new connection.
2. If there is no damage, hand tighten the connector to the analyzer's **INLET**.
3. Using a 5/8" wrench (not included), tighten the nut approximately one flat (60 degrees).

7.3 Setting Up a Monitor, Keyboard, and Mouse

A video monitor (not included), keyboard, and mouse are required for monitoring device operations, viewing, or changing settings (including setting user permissions), or validating device performance.



NOTE

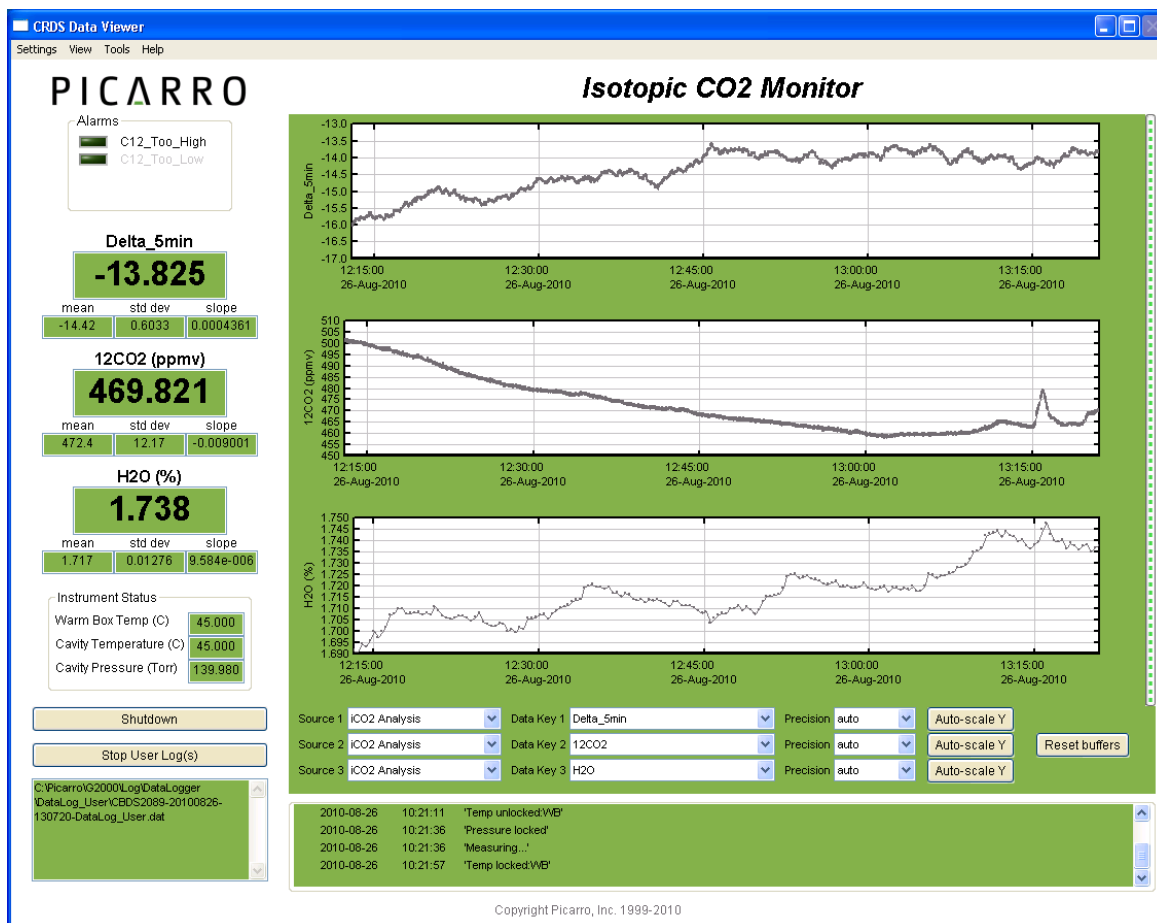
This device will operate under its default settings without any direct control of the internal software.

1. Connect a keyboard to one of the available USB ports.
2. Connect a mouse to one of the available USB ports.
3. Connect a monitor to one of the DVI monitor ports. The analyzer will detect the connection and adjust the resolution to match the monitor.
4. Connect the monitor to a power source.
5. Turn on power to the monitor.

8. BASIC OPERATION AND INITIAL ANALYZER CALIBRATION

8.1 Startup

When the main power is turned on, the analyzer will automatically start, including the Graphical User Interface (GUI). The GUI will look like the image below. A full explanation of the GUI functions can be found in the section called **List of GUI Functions**.



Layout of the Picarro analyzer GUI, G2000 series.

The analyzer will not begin producing data until all the measurement parameters have reached their operational set points. A message will be displayed in the Status Log window (in the bottom panel of the interface shown above) when each set point is reached. A full explanation of each status log message can be found in the section called **Status Log Messages**.

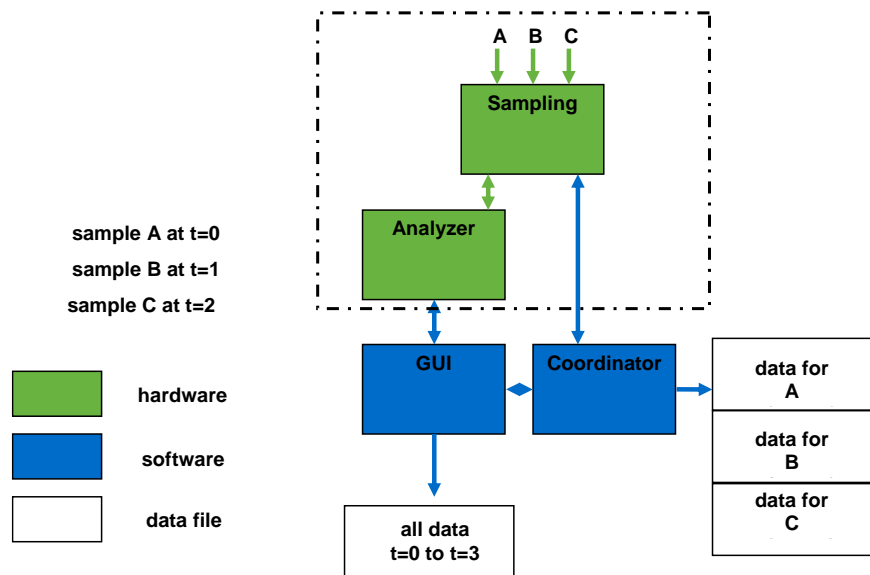
The various icons and folders in the desktop allow you to start the instrument, switch between different measurement modes (See **Switching Between Measurement Modes** and **G2101 Mode Switcher** sections), see graphical representation of your data, and more. For more information about these icons, please refer to **Desktop Icons and Folders** in this manual.

Data will be saved automatically once the analyzer starts to produce data. The data in the GUI is the continuous real-time read out from the analyzer. A user relevant subset of this data is stored in C:\Userdata\DataLog_User\YYYY\MM\DD, where Y=year, M=month, D=day. Further details can be found in the **Data** section of the manual.

You can change the various settings of data saving through a .ini file (See **Data** for more information). The Setup Tool also allows you to change data file saving details, in addition to allowing you configure which data element files are written to data files, digital data output (via serial port or TCP/IP), remote data delivery (via email. Also see **Remote Data Access** section for more information), GUI properties and more. The section called **Setup Tool** contains more details about these functions.

To shut down your analyzer and/or the software correctly, please refer to Section 8.4.

In order to measure discrete samples (such as individual gas bags) or samples from multiple locations (when switching valves draw in ambient air from different heights -- see **External Valve Sequencer** for more information), a separate software window (coordinator) is used to control the sample source and match the corresponding real-time read out with the sample source. Depending on system configuration, coordinator programs may not be included.



Overview generalized schematic of Picarro analyzer system hardware, software, and data file generation.

In the figure above, samples A, B, and C are introduced into the analyzer sequentially by a sampling module, if present. The sampling module could be a set of customer-supplied valves, a valve manifold, a discrete sampling module, or other device. The timing of sample introduction is controlled by the coordinator or valve sequencer software. The analyzer measures continuously and reports the data to the GUI, which saves a single file where all data is reported as a function of time. The coordinator gets data from the GUI and creates a single file, and the data is reported as a function of sample.

8.2 Desktop Icons & Folders

On the Windows™ desktop, there will be the following icons & folders:

1. **Start Instrument:** When clicked, the analyzer will start measuring in the configuration that it was in when the software/analyzer was shut down.
2. **Coordinator Launcher:** Depending on the system's configuration, the coordinator program may not be included. Clicking on this icon will lead you to a window that will allow you to control the introduction of discrete samples (such as individual gas bags) or measure from multiple locations.
3. **Picarro Mode Switcher:** When clicked, you will be led to a window that will allow you to switch between various measurement modes.



4. **Picarro Controller:** When clicked, you will be led to a useful diagnostic panel allowing the user to see the analyzer’s internal temperatures, pressure, and spectroscopy in real time. This program has user-accessible functions, but it cannot change anything related to analyzer functionality. It is intended for diagnostics purposes only.

5. **Picarro Utilities Folder:**

- **Data file Viewer:** When clicked, you will be led to a window that will allow you to convert between *.dat & H5 data files and to make various graphical representations of your data.
- **Data Recal:** When clicked, you will be led to a window that will allow you to recalibrate your data based on known, certified data.
- **Setup Tools:** When clicked, you will be led to a window that will allow you to edit various settings for your analyzer (See the **Setup Tools** section of this manual for information about these settings).

6. **Diagnostic Folder**

- **Stop Instrument:** When clicked, you will be led to a window that will allow you to turn off the analyzer in an emergency event. Upon clicking on this icon, the following window will pop up. Please see **Shutdown Procedure** section of this manual to shut down the analyzer in normal circumstances.





CAUTION

CAUTION: EXCEEDING GAS INLET PRESSURE OR TEMPERATURE SPECIFICATIONS COULD RESULT IN DAMAGE TO THE INSTRUMENT. In the case of higher input pressure or flow, configuring a sampling bypass manifold system is recommended. Use a 'tee' at the gas inlet and either return the remainder to the main gas stream or exhaust appropriately.



CAUTION

CAUTION: Do not disconnect the AC power to the analyzer, vacuum line, or the AC power to the External Vacuum Pump while analyzer is operating. Damage may be caused by current surges if power is applied while attaching or removing cables.



CAUTION

CAUTION: Analyzers that include the external valve control option are provided with a cable consisting of five electrical connections intended for controlling solenoid valves (typically 12VDC <1A max). It is important to **electrically isolate the solenoid valves from the analyzer's ground** to avoid electrical interference, which could compromise the analyzer's accuracy.

8.3 Initial Analyzer Calibration

Picarro strongly recommends that you calibrate your CRDS analyzer upon receiving it from the factory. For CO₂ measurements, two quantities should be calibrated:

- the concentration of ¹²CO₂
- δ¹³C-CO₂, the isotopic abundance of ¹³C compared to ¹²C in a sample relative to a standard

This section will describe the calibration process for δ¹³C-CO₂. The same steps can be followed to calibrate the concentration of ¹²CO₂.



NOTE

The CRDS analyzer may be part of a multi-component system that involves a front-end interface, such as the Combustion Module-CRDS (CM-CRDS), AutoMate-CRDS (AM-CRDS), Aurora-CRDS and Small Sample Introduction Module-CRDS (SSIM-CRDS). These front-end interfaces help introduce samples into the analyzer. This means they should also be used to introduce calibration standards, so that the standard or reference samples are treated in the same way as the samples.

Stable isotopic composition is expressed in terms of a delta value, δ , in permil (‰). This value reflects the part-per-thousand difference in a sample's isotope concentration relative to a standard. For ^{13}C , this value is calculated using this equation:

$$\delta^{13}\text{C} = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1 \right) * 1000$$

For an instrument to deliver meaningful delta values for samples, it must first be calibrated with standards of known delta values. Calibrating Picarro analyzers generates a linear transformation specified by a slope and offset, which are stored in the file C:\Picarro\G2000\InstrConfig\Calibration\InstrCal\UserCal.ini. When the analyzer is delivered, the user calibration slope and offset are set to 1 and 0, respectively. Performing the calibration procedure explained below generates a new slope and offset, which replace the factory settings. Then, delta values reported in the analyzer's data logs will include this additional, user-specified transformation.

To simplify the process of user calibration, Picarro supplies a Data Recal Software Utility. This utility enables users to save copies of the user calibration slope and offset, with a time stamp, so that the entire calibration history of the analyzer is available for later analysis. More details are provided in the **Data Recal Software Utility** section in this manual.

To perform a calibration, the user simply introduces the first calibration standard into the analyzer for an interval long enough for the analyzer to yield a stable measurement of that sample. Examples of standards include a permeation tube or calibrated gas bottle.

For each calibration standard, the user records the stated delta of the calibration sample and the value the analyzer reads for that sample. These values can then be plotted using the Data Recal Software Utility to determine the linear relationship between the known calibration values and the analyzer's reported values. For more details about how the analyzer calculates $\delta^{13}\text{C}$ from spectroscopic data, please refer to **Appendix A**.

It is important to plot the analyzer's reported values on the horizontal axis and the standards' certified values on the vertical axis. The slope and intercept of the best-fit line through these points are the two values that are used to calibrate the analyzer.

Since Picarro gas analyzers are extremely linear, it is only necessary to use three calibration standards to calibrate each gas or isotopic species. Two points define the calibration line and a third intermediate point is used for verification. The exact value of each calibration standard is not of particular importance, as long as the collection of standards represents the range of values over which the analyzer will typically be operated. Although it is not necessary to use more than three standards, additional standards can be used to further constrain the linear calibration coefficients.

8.4 Shutdown Procedure

To shut down the analyzer using the GUI:

1. Click on the “**Shutdown**” button located on the left side of the Data Viewer window.
2. A window will pop-up (see below) prompting the user to confirm the shutdown. Once confirmed, the analyzer software and hardware will turn off.
3. Manually turn off the pump(s) and dry gas (only if your system requires it).



CAUTION

A flow of clean, relatively dry gas should always be directed to the instrument for several minutes prior to shutting down. Trapping a high-moisture content gas sample in the cavity can cause condensation damage to the mirrors as the instrument cools from its operating temperature.



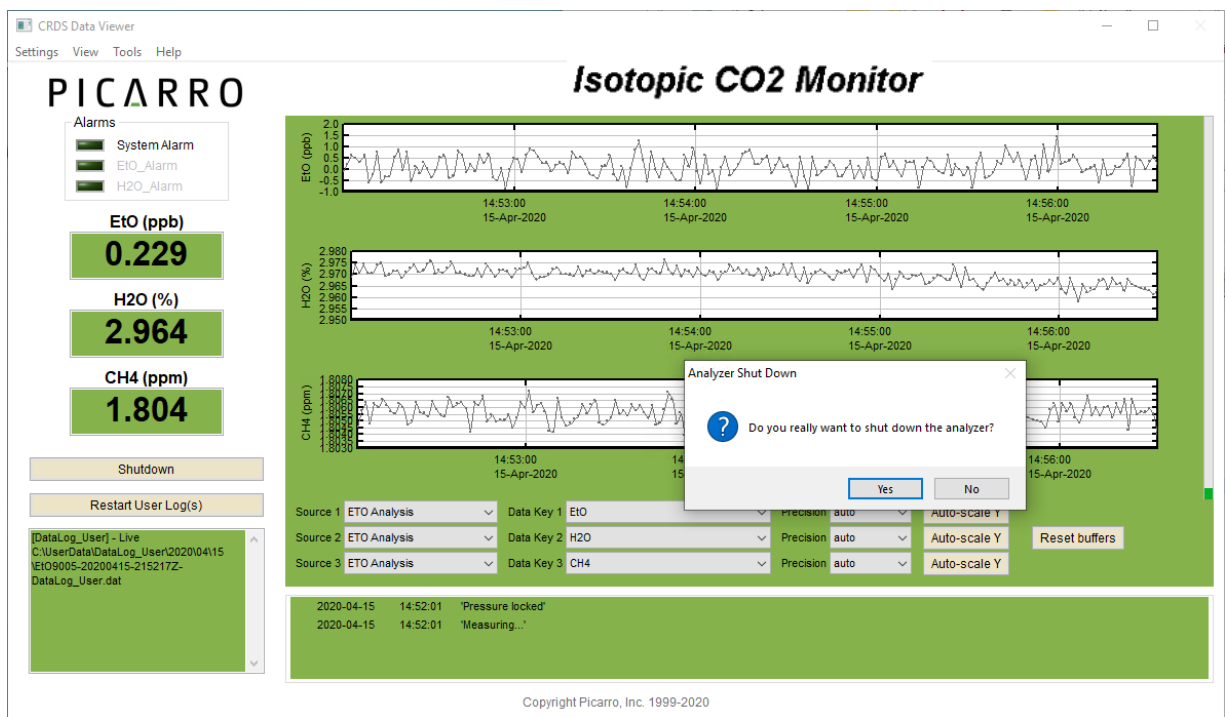
CAUTION

Do not turn off the pump or disconnect the vacuum line while the instrument is operating.



CAUTION

FOR G2xxx ANALYZERS: If you have trouble turning off the analyzer software, do not kill the process(es) in the task manager; rather, double-click on the “Stop Instrument” icon in the Diagnostics folder on your desktop.



Shutdown confirmation pop-up dialog

8.5 In Case of an Electrical Power Outage

If power to the analyzer is cut-off for any reason, the analyzer will cease operation. However, when the power is reapplied, the analyzer will restart automatically. The Picarro software tools will also properly close out previous files and open new files for data collection so that previously collected data, instrument diagnostics, and other parameters recorded up to the time of power outage are retained.

If short power outages will be a routine operating environment, Picarro recommends use of a power conditioning and/or uninterrupted power supply that will work to prevent the more damaging operating system and software corruption problems that can occur with repeated crashes.

9. STATUS LOG MESSAGES

9.1 Normal Start Up Messages

Temperature Locked: WB (HB)

The system waits for the warm box (“WB” – the temperature-controlled electronics and wavelength monitor chamber) to reach operating temperature. Similarly, the temperature of the hot box (“HB” – the temperature-controlled chamber containing the analyzer’s optical cavity and gas handling system) is stabilized. This is typically the longest step in the startup sequence. The duration of this step can range from 5 to 60 minutes, depending on the ambient temperature and how much time has elapsed since the last startup.

Entering Measurement

Spectral scanning has started. Concentration measurements will be available in approximately 30 seconds. The instrument will continue to scan and report concentration measurements until the instrument is shutdown using the procedure below.

Pressure Stabilizing/Locked

The valve control system begins to allow flow through the analyzer and stabilizes the pressure inside the cavity.

Measuring

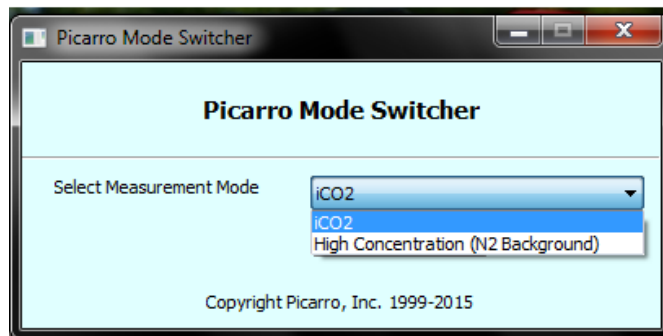
This is the normal mode of operation after startup has completed.

10. SWITCHING BETWEEN MEASUREMENT MODES

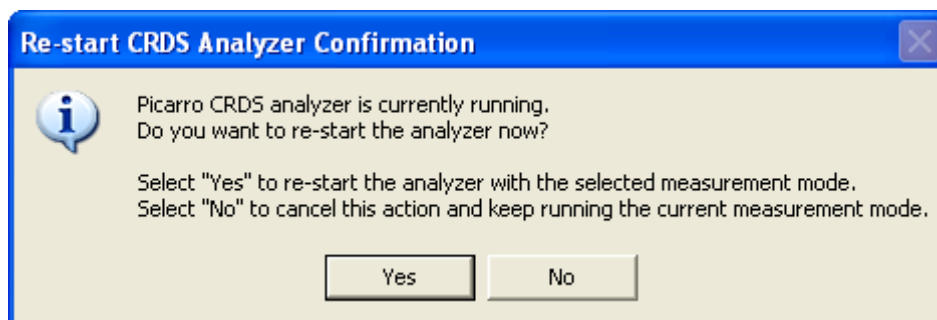
10.1 General Instructions on How to Switch Between Modes

The “Picarro Mode Switcher” allows users to operate the analyzer in various modes. Switching between measurement modes is accomplished with a few easy steps:

1. Activate the user interface by double-clicking the “Picarro Mode Switcher” icon on the analyzer’s desktop.
2. The following user interface will appear on the desktop. To switch modes, click on the drop-down box menu, select the desired measurement mode (described in the next section), and then click the launch button:

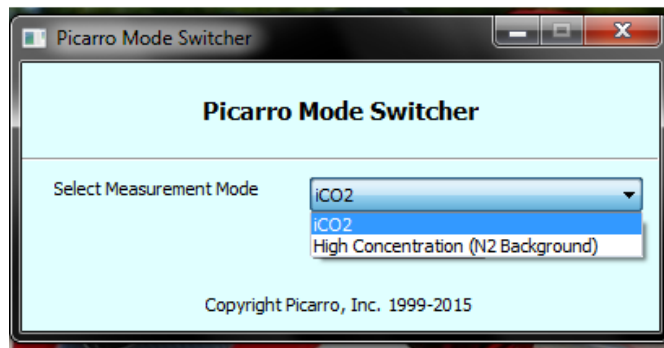


3. Confirm your selection when prompted by the confirmation dialog box:



4. The analyzer software will then re-start in the new measurement mode. There is no need to turn the vacuum pump off during this process.

10.2 G2121-*i* Mode Switcher and Measurement Modes



Mode Switcher window

The G2121-*i* analyzer has two different operational modes that the user can choose from, depending on the concentration of the sample.

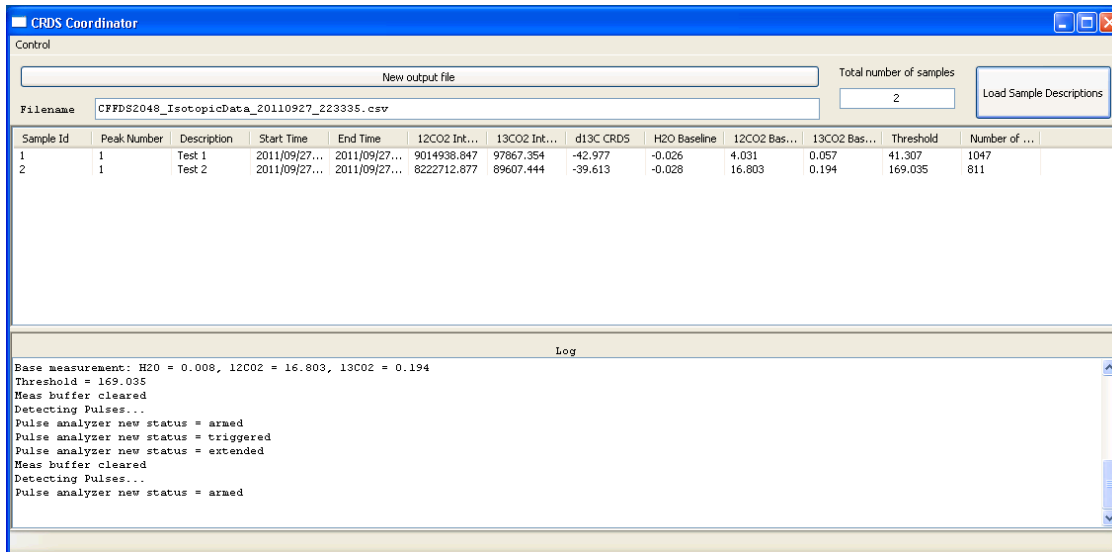
1: iCO₂

This mode measures isotopic Carbon Dioxide (iCO₂) in Air as a background gas. Choose this mode to make fast and low noise iCO₂ measurements within the 380ppm and 600ppm range. The interference of CH₄ concentration on the accuracy of the iCO₂ measurement is corrected for and guaranteed up to 500ppm of CH₄.

2: High Concentration (N₂ Background)

This mode measures isotopic Carbon Dioxide (iCO₂) in N₂ background gas, normally as part of a tandem system that includes a front-end, an interface and the CRDS analyzer. Choose this mode to make fast and low noise iCO₂ measurements within the 2000ppm to 4000ppm range. The interference of CH₄ concentration on the accuracy of the iCO₂ measurement is corrected for and guaranteed up to 500ppm of CH₄.

11. COORDINATOR TOOL



Coordinator Tool User interface

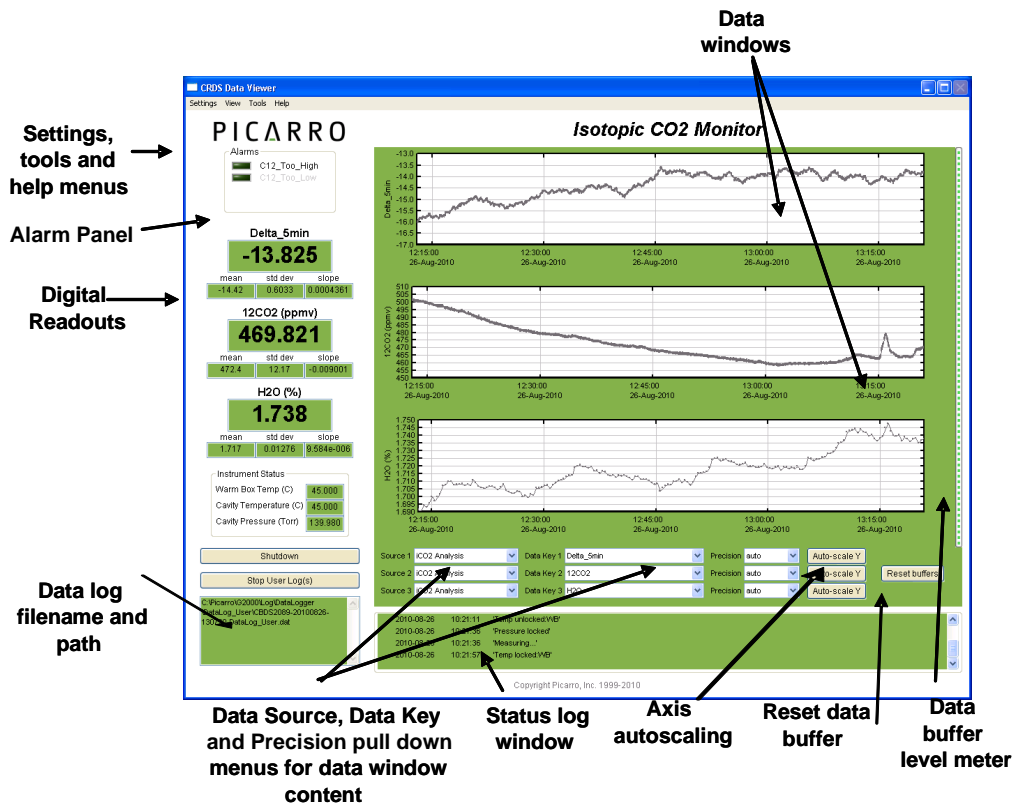
The CRDS Coordinator window shows detailed measurements made for each sample run. Below are the descriptions for each column; the columns explained in #8 and #9 (Max¹²CO₂ and Max ¹³CO₂ peak) are not shown in the above image.

1. **Sample Id:** Identification number for each trial.
2. **Peak Number:** Number of pulses for each sample analysis - Typically one for each sample.
3. **Description:** Name given for each trial.
4. **Start Time:** Date and time at the start of a sample run.
5. **End Time:** Date and time at the end of a sample run.
6. **¹²CO₂ Integration:** Concentration of ¹²CO₂ in a sample.
7. **¹³CO₂ Integration:** Concentration of ¹³CO₂ in a sample.
8. **Max ¹²CO₂:** Maximum ¹²CO₂ concentration at the apex of the CO₂ peak
9. **Max¹³CO₂ peak:** Maximum ¹³CO₂ concentration at the apex of the CO₂ peak
10. **δ¹³C CRDS:** Ratio of stable isotopes ¹³C and ¹²C in parts permil in a sample.
 - a. $\delta^{13}\text{C CRDS} = ((^{13}\text{C}/^{12}\text{C})_{\text{Sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{Standard}}) - 1) \times 1000\%$
11. **H₂O Baseline:** Water that was present before a sample run.
12. **¹²CO₂ Baseline:** ¹²CO₂ that was present before a sample run.
13. **¹³CO₂ Baseline:** ¹³CO₂ that was present before a sample run.
14. **Threshold:** Point where a trigger happens.
15. **Number of Data Points:** Number of measurements taken during one sample run to make up a curve.

12. LIST OF GUI FUNCTIONS

12.1 Additional Tools and Information

The Picarro analyzer GUI has useful features. See the figure below for more information.



Layout of the Picarro analyzer GUI, G2000 series

12.2 Settings, Tools and Help Menus:

Settings Menu

Left clicking on the Settings menu pulls down a menu that has one entry 'Change GUI Mode from Standard to Service.' This is the access point to a password protected service mode where additional operational and measurement parameters are displayed. Selecting and clicking on this entry opens the Cavity Ring-Down Spectrometer Controller. This is reserved for Picarro service operators only.

View Menu

This menu item has three entries:

1. Lock/Unlock time axis when zoomed: When locked, forces the two graphs to display the same time scale during zoom.
2. Show/hide statistics: Toggles the measurement statistics display, see **Digital Readouts** below.
3. Show/hide instrument status: Toggles the instruments status display. See **Instrument Status** below.

Tools Menu

This menu item has three entries:

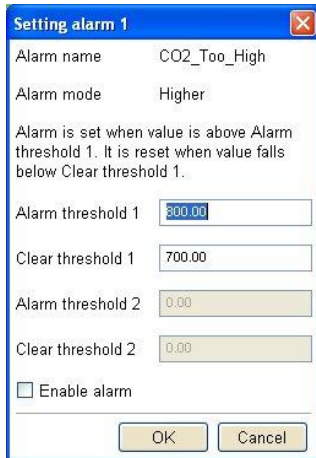
1. User Calibration: Opens the user calibration window (default password is "picarro"). The password can be reset in the QuickGui.ini file in the instrument directory: "C:\Picarro\G2000\AppConfig\Config\QuickGUI\" under the section:
2. [Authorization] UserCalPassword = Picarro Show/Hide Valve
3. Sequencer GUI: Toggles the display of the external valve sequencer window.

The calibration slope and intercept can be entered and their effects immediately seen in the data. Please refer to the section at the end of this manual concerning calibration.

Help Menu

About Displays the version number of the instrument.

Alarm Panel



The panel in the upper left-hand corner of the GUI is used to monitor the status of the internal instrument alarms. These indicators are gas concentration alarms, such as “CO₂ Too High/Low,” depending on instrument configuration. The gas concentration alarm LEDs are off (grayed) when the respective concentrations are below a certain value, and they are illuminated when the respective concentrations are above/below a certain value. To view the alarm set point, click on the LED and a dialog box will appear indicating the alarm setting and allow the user to enable it or change the setpoint.

Type the value you wish to set the alarm to and press the “OK” button, or press “Cancel” if you do not wish to change the alarm value. If you do nothing, the dialog box will disappear, and the alarm value will remain unchanged. The units are those that appear in the GUI graph.

12.3 Digital Readouts

Displays the latest value recorded for the selected Data Key for each Data Window. Changing the Data Key changes the Digital Readout as well as changes the Data Window view. If the ‘Show Statistics’ entry is enabled in the ‘View’ menu, the mean, standard deviation and slope of the data in the graph is dynamically calculated and indicated below the digital concentration readout. These numbers change to reflect statistics of whatever data is in the data window.

12.4 Start / Stop Data Log Button

The Analyzer automatically records all data collected on the instrument and saves it for later analysis. These files are called Data.dat files, which are described below in the section called **File Management**. In addition, the user can record a separate data log file. Press this button if you would like the instrument to start recording a separate data file. A dialog box will appear prompting you for a filename and location. Press this button again to stop recording the data file.

12.5 Data Log Filename and Path

The filename and path of the active data log is displayed in this pane. The indicator is grayed-out if there is no active data log (i.e., if a new data log has not been started using the *Start /Stop New Data Log Button*). A new file will be generated at midnight, which will be saved to the same location as the original log file.

12.6 Data Window

The data window displays a graph of any stream of data vs. system time, with a format of hh:mm:ss. The user can select which data stream are displayed using combinations from the Data Source and Data Key pull down menus. The precision displayed can be adjusted using the “Precision” menu and Auto-scaling of the ‘Y’ axis is also available.

12.7 Instrument Status

If these parameters are enabled through the ‘Show Instrument Status’ entry in the ‘View’ Menu on the main toolbar digital readouts for Warm Box temperature, Cavity Temperature and Cavity Pressure are displayed to the left of the main trend graphs.

12.8 Data Source and Data Key Pull Down Menus

These two menus enable selection of the data stream that is viewed in the *data window*. Data streams available on the GUI are gas concentrations, if ‘*instrument Analysis*’ (where *instrument* represents the system installed) is selected, or if “sensors” is selected, the analyzer’s optical cavity pressure or temperature can be viewed as well as the nominal ambient temperature of the analyzer (“DAS temp”) and the temperature of the analyzer’s electronics chamber, indicated as “warm chamber temp.”

12.9 Precision Pulldown Menu

Click on this icon to select the precision displayed on the y-axis, between 0 and 4 digits of precision or “auto.” The currently selected precision is displayed during operation. This does not affect the precision of the saved data in the data log files or results files.

12.10 Status Log Window

This window displays instrument status messages, in the following form: “MM/DD/YYYY hh:mm:ss generic message text.” These messages include all messages sent to the DAS front panel display.

12.11 Reset Data Buffer Button

Press this button to clear the internal data buffer of the GUI (this clears the current data traces from the graphs). This has the effect of clearing all data in the data window. Pressing this button has no effect on any of the data log files stored by the instrument.

12.12 Data Buffer Level Meter

The meter to the right of the *Data Window* indicates how much of the internal memory of the GUI is used to retain historical data collected with the instrument. There is an internal limit of a finite number of points. Once that number of data points is collected, the buffer is full, and old data is removed from the buffer as new data is collected. This buffer affects *only* the data displayed in the *data window*, not the data stored in any files. This buffer is empty upon instrument startup, and can also be emptied by pressing the *reset data buffer button* in the lower-right-hand corner of the GUI.

12.13 Graph Zooming

To zoom the graph, simply drag the magnifying glass over the section to be zoomed and click and hold the left mouse button. While holding down the left button, move the mouse to create a box that covers the region of interest. When the box is properly drawn, release the left button and boxed area will automatically scale to fill the data window. To zoom back out, double click on the left button. To autoscale the y-axis of either graph, use the autoscale buttons below the graph. To lock or unlock the time axes of each graph during zooming, select that menu item in the ‘View’ menu.

13. DATA

13.1 Types of Data

During operation, the analyzer generates ASCII format text output file that is updated after each batch of concentration measurements are complete. During operation, the analyzer also creates directories to store the data, based on the date the data was acquired. After each data file has been closed, it is moved to an archive directory, and a new file is started in the original location. To keep the data files easy to manage and to limit the size of individual files and directories, please see “Setup Tools” in the “Utilities” folder on your desktop to modify various aspects of data storage.

There are two data directories: **UserData** & **Archived Data**. UserData directory contains the current and recent data. Archived Data directory contains the past data.

UserData

This directory contains current and recent data.

- **DataLog_User**: stores data as measurements are made.
 - Location: *C:\UserData\DataLog_User\Year\Month\Day*
 - Naming Convention:
 - Example: *CFHADS2007-20111222-000131-DataLog_User.dat*
 - CFHADS: Instrument Serial Number
 - 20111222: Year, month, and day of when file was started
 - 000131: Hour, minute, and second of when file was started (using a 24 hour clock).

Archived Data

This directory contains past data.

- **DataLog_User_Backup**: archived, older data that is stored in compressed .zip format.
 - Location:
C:\Picarro\G2000\Log\Archive\DataLog_User_Backup\Year\Month\Day
 - Naming Convention:
 - Example: *DataLog_User_Backup_20111107_005427.zip*

- 20111107: Year, month, and day of when the file was started.
 - 005427: Hour, minute, and second of when file was started (using a 24 hour clock).
- **DataLog_Private**: complete data file that includes additional parameters beyond the concentration data such as instrument temperatures and pressure, set points, and spectroscopic information. This information is generally not useful to the user, but it can be useful for diagnostic purposes. For more information, please contact Picarro.
 - Location:
C:\Picarro\G2000\Log\Archive\DataLog_Private\YearMonth\Day

13.2 File Archival and Automatic Deletion of Old Files

FILE MANAGEMENT

The analyzer can automatically compress (zip) and archive old files as mentioned above. This operation is controlled by the ini file:

C:\Picarro\G2000\AppConfig\Config\Archiver\Archiver.ini.

For each file type, there are various items along with some recommended default settings that may vary by file type:

- **Directory** = C:/UserData/DataLog_Sync
 - Optionally specifies which directory to find files to archive.
- **MaxCount** = -1
 - Specifies how many files to keep. A setting of -1 indicates that there is no maximum number of files. Generally -1 is used in conjunction with a maximum size limit, below.
- **MaxSize_MB** = 1500
 - Specifies that a maximum of 1.5 GB of data are to be kept before the system begins to delete old data.
- **Compress** = True/False
 - Specifies if archived files are to be zipped – recommended setting is true to save hard drive space. True means files are zipped, false means files are not zipped.
- **AggregationCount** = 0
 - If compression is set to TRUE, specifies how many files to be included in each zip archive.

- **StorageMode = FIFO**
 - First in first out. Specifies that old data are deleted first.
- **Quantum = 4**
 - Generally should not be changed. Specifies the files be sorted by year\month\day\hour in the archived directory structure.

In addition to the automatic file and directory management described above, the analyzer also automatically deletes various files specified in C:\Picarro\G2000\AppConfig\Config\FileEraser\FileEraser.ini. There are various settings, as described below:

- **runtime_interval_hrs = 0.5**
 - Specifies how often (in hours) to run the file eraser.
- **path = ../../Log/Archive/DataLog_Private**
 - Specifies which directory to look in for files to delete.
- **extension = dat**
 - Specifies which files having what extension are to be deleted. If empty, it deletes all files.
- **delete_time_hrs = 48**
 - Specifies how long to keep files prior to deletion.

Measuring time in Picarro data files

Since measurements performed by Picarro analyzers are asynchronous (they require a variable and unpredictable amount of time to complete), data reported by the analyzer is time stamped. Each independent measurement is given a time derived from the Windows™ computer's system clock¹. This time can be reported by one or many of the following variables.

Variable Name	Description	Units
DATE	The calendar date formatted as YYYY-MM-DD Example: August 24, 2015 is formatted as 2015-08-24	-NA-
TIME	The time of day formatted as HH:MM:SS.SS on a 24-hour clock Example: 4:18:53.12 PM is formatted as 16:18:53.12	-NA-

¹ http://en.wikipedia.org/wiki/System_time

Variable Name	Description	Units
FRAC_DAYS_SINCE_JAN1	The number of days since midnight January 1 of the current year Example: at 3:00:00 PM on January 12 the value is 11.625	days
FRAC_HRS_SINCE_JAN1	The number of hours since midnight January 1 of the current year Example: at 3:00:00 PM on January 12 the value is 279.0 (=FRAC_DAYS_SINCE_JAN1*24)	hours
JULIAN_DAYS	The number of the day of the current year Example: at 3:00:00 PM on January 12 the value is 12.625 (=FRAC_DAYS_SINCE_JAN1+1)	days
EPOCH_TIME	The number of milliseconds since midnight January 1, 1970 Example: at 3:00:00 PM on January 12 the value is 1421074800000 (= time)	ms
timestamp	The number of milliseconds since midnight January 1, 1 if the current Gregorian calendar was extended back to that time Example: at 3:00:00 PM on January 12 the value is 63556671600000	ms
time	The number of milliseconds since midnight January 1, 1970 Example: at 3:00:00 PM on January 12 the value is 1421074800000 (= EPOCH_TIME)	ms
ymd	The calendar date formatted as YYYYMMDD Example: August 24, 2015 is formatted as 20150824	-NA-

In the table above, all times are reported in GMT² (also known as Zulu time and very closely related to UTC). We express these timestamps in GMT to avoid complications during Daylight Saving Time or when instruments are moved across time zones. The accuracy of the times are, of course, only as good as the accuracy of the Windows™ clock; see section **Remote Data Access** to learn how to automatically synchronize the computer's clock to a time standard. There are many online calculators³ that convert Epoch Time to local time at any time zone, as well as many functions in commonly used data analysis programs that perform the same calculations⁴.

13.3 Column Headers

The following table provides information regarding the column headers presented in the UserData output files available on a Picarro carbon isotope analyzer.

Column Header	Definition	Units
DATE	Date of measurement	
TIME	Time of measurement (instrument time)	
FRAC_DAYS_SINCE_JAN1	Fraction of days since Jan 1 (max = 365)	
FRAC_HRS_SINCE_JAN1	Fraction of hours since Jan 1 (max = 8760)	
JULIAN_DAYS	Julian days in since Jan 1 00:00 GMT	
EPOCH_TIME	Number of seconds that have elapsed since Jan 1, 1970 GMT	
ALARM_STATUS	Binary system alarm (0 = no alarm; 1 = alarm)	
INST_STATUS	Hardware status code; should never change if the analyzer is operating properly	
CavityPressure	Cavity Pressure	Torr
CavityTemp	Cavity Temperature	°C
DasTemp	Temperature measured on the data acquisition system board	°C
EtalonTemp	Temperature measured at the wavelength monitor (WLM)	°C
WarmBoxTemp	Temperature of the stabilized enclosure containing the WLM	°C
species	Integer code designating the molecule being measured	
MPVPosition	Integer code for the valve position	
OutletValve	Integer controlling the flow through the proportional valve	
species	Integer code designating which spectrum was most recently acquired	

² http://en.wikipedia.org/wiki/Greenwich_Mean_Time

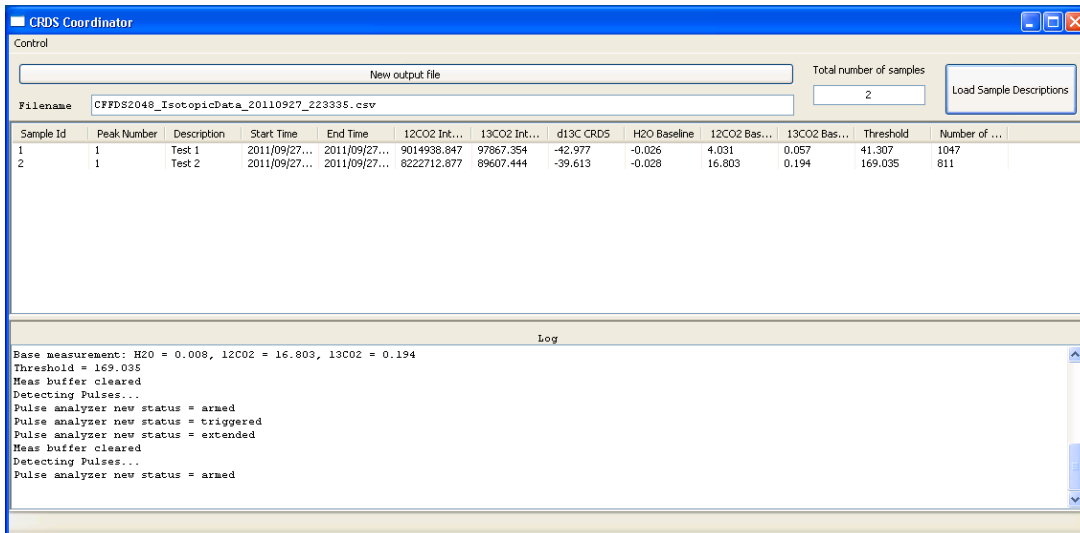
³ For example <http://www.epochconverter.com>

⁴ Many can also be found at <http://www.epochconverter.com>

Column Header	Definition	Units
solenoid_valves	Integer code for solenoid valve controller	
SpectrumID	Integer code designating which spectrum was most recently acquired	
12CO2	Concentration of $^{12}\text{CO}_2$ uncorrected for dilution & lineshape effects due to water vapor	ppm
12CO2_dry	Dry mole fraction of $^{12}\text{CO}_2$, corrected for water vapor	ppm
13CO2	Concentration of $^{13}\text{CO}_2$, corrected for methane and direct cross-talk from water only*	ppm
13CO2_dry	Dry mole fraction of $^{13}\text{CO}_2$, corrected for water vapor*	ppm
H2O	Water vapor concentration	percent
CO2	CO_2 concentration	ppm
peakheight_5	Peak optical absorption of the strongest $^{13}\text{CH}_4$ line	ppb/cm
peak30_spec	Peak absorption of the water line, corrected for offset and methane interference	ppb/cm
peak24_spec	Peak absorption of the CO_2 line, corrected for offset and methane interference	ppb/cm
Delta_2min	2 minute window average of $\delta^{13}\text{C}$ in CO_2	per mil
Delta_30s	30 second window average of $\delta^{13}\text{C}$ in CO_2	per mil
Delta_5min	5 minute window average of $\delta^{13}\text{C}$ in CO_2	per mil
Delta_Raw	raw $\delta^{13}\text{C}$ value (for each measurement)	per mil
H2O	Water vapor concentration	percent
Ratio_2min	2 minute window average of $^{13}\text{C}/^{12}\text{C}$ ratio in CO_2 *	
Ratio_30s	30 second window average of $^{13}\text{C}/^{12}\text{C}$ ratio in CO_2 *	
Ratio_5min	5 minute window average of $^{13}\text{C}/^{12}\text{C}$ ratio in CO_2 *	
Ratio_Raw	$^{13}\text{C}/^{12}\text{C}$ ratio in CO_2 (Note: this value does not equal $^{13}\text{CO}_2/^{12}\text{CO}_2$ as reported by CRDS analyzer)*	
peak_75	Absorption measured at the peak of the water line	ppb/cm
ch4_splinemax_for_correct	Absorption measured at the peak of the methane spectral feature	ppb/cm
peak87_baseave_spec	Absorption measured at the peak of the $^{12}\text{CO}_2$ line and corrected for direct water interference	ppb/cm
peak88_baseave	Absorption measured at the peak of the $^{13}\text{CO}_2$ line, NOT corrected for any interferences	ppb/cm
	* Picarro instruments have not always been consistent in their reporting of $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, and delta. We recommend ignoring all $^{13}\text{CO}_2$ reporting and regarding $^{13}\text{CO}_2$ concentration as a derived quantity, to be computed from properly calibrated $^{12}\text{CO}_2$ and $\delta^{13}\text{C}$. For more information, see Appendix A – Understanding the G2121-i Isotopic Carbon Data Log.	

13.4 Isotopic Data Files Generated by Coordinators

The CRDS coordinator window, shown below, is populated with information including the concentrations of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ in a sample, as well as the $\delta^{13}\text{C}$ for that sample. Data appears in this window as each measurement is taken, and it is stored in a .csv file. This .csv file is saved in the directory C:\Picarro\IsotopicData



Once the coordinator is closed, the data can only be viewed in the file in the IsotopicData folder. Shown below is a sample Isotopic Data file opened in spreadsheet software. $\delta^{13}\text{C}$ values for each sample are located in "Delta CRDS" column, which is highlighted in the figure below. For more information about the calculation of $\delta^{13}\text{C}$ from spectroscopic data, see **Appendix A**.

Sample Id	Peak Number	Start Time	End Time	Max 12C	Max 13C	12CO2 Int	13CO2 Int	Delta CRDS	12CO2 Bt	13CO2 Bt	Thresh	Number of d	Time interval (seconds)	St. dev.	Average	Corr
1	1	2014/05/2907.096	2014/05/2907.096	31.945	419493.771	4608.642	4608.642	-34.18	0.84	-0.005	350	260	269.047			
2	1	2014/05/3478.446	2014/05/3478.446	38.179	522659.972	5739.482	5739.482	-34.333	11.223	0.112	350	284	291.733			
3	1	2014/05/3943.082	2014/05/3943.082	43.523	605602.839	6688.245	6688.245	-27.859	14.651	0.146	350	300	309.108			
4	1	2014/05/2551.262	2014/05/2551.262	28.184	380138.431	4199.31	4199.31	-28.005	17.935	0.182	350	263	270.736			
5	1	2014/05/3917.857	2014/05/3917.857	43.229	620221.822	6848.607	6848.607	-28.117	13.107	0.129	350	308	316.931	0.13	-27.99	
6	1	2014/05/3609.67	2014/05/3609.67	39.953	541735.318	5995.435	5995.435	-25.407	20.486	0.212	350	287	294.96			
7	1	2014/05/2322.871	2014/05/2322.871	25.707	321018.982	3553.285	3553.285	-25.78	15.771	0.159	350	239	247.108			
8	1	2014/05/3039.283	2014/05/3039.283	33.643	442648.401	4898.721	4898.721	-25.675	10.407	0.1	350	268	275.957	0.19	-25.62	
9	1	2014/05/1899.838	2014/05/1899.838	20.952	263459.522	2905.015	2905.015	-30.041	13.006	0.131	350	231	238.282			
10	1	2014/05/1774.887	2014/05/1774.887	19.591	257416.862	2838.92	2838.92	-30.267	22.938	0.238	350	241	248.807			
11	1	2014/05/1897.052	2014/05/1897.052	20.931	273686.778	3018.858	3018.858	-29.928	37.325	0.396	350	245	252.209			
12	1	2014/05/2073.401	2014/05/2073.401	22.872	299826.8	3305.759	3305.759	-30.043	35.738	0.383	350	250	258.301	0.14	-30.07	
13	1	2014/05/1558.103	2014/05/1558.103	17.24	227527.561	2516.455	2516.455	-27.159	43.665	0.467	350	239	246.054			
14	1	2014/05/2239.346	2014/05/2239.346	24.784	327729.886	3624.824	3624.824	-26.641	54.441	0.586	350	260	267.408			
15	1	2014/05/2037.995	2014/05/2037.995	22.547	300983.791	3328.631	3328.631	-26.699	43.148	0.464	350	257	264.37			
16	1	2014/05/2066.116	2014/05/2066.116	22.854	303239.196	3353.306	3353.306	-26.781	42.051	0.451	350	254	262.278			
17	1	2014/05/1934.926	2014/05/1934.926	21.397	284053.925	3139.261	3139.261	-27.771	43.128	0.461	350	251	259.443	0.23	-26.82	
18	1	2014/05/1991.367	2014/05/1991.367	22.022	283948.696	3137.487	3137.487	-27.779	43.375	0.465	350	246	253.557			
19	1	2014/05/1863.798	2014/05/1863.798	20.584	280344.902	3097.179	3097.179	-28.231	34.562	0.366	350	256	263.584			
20	1	2014/05/2104.956	2014/05/2104.956	23.25	315212.127	3482.857	3482.857	-27.763	51.361	0.553	350	263	270.75	0.23	-27.89	
21	1	2014/05/2132.005	2014/05/2132.005	23.591	290596.373	3216.81	3216.81	-25.682	45.629	0.489	350	237	244.363			
22	1	2014/05/2253.812	2014/05/2253.812	24.937	310367.872	3434.733	3434.733	-25.667	16.573	0.173	350	238	245.842			
23	1	2014/05/3094.684	2014/05/3094.684	34.237	455100.187	5037.067	5037.067	-25.611	13.881	0.137	350	269	277.637			
24	1	2014/05/2137.899	2014/05/2137.899	23.626	324375.419	3582.27	3582.27	-28.353	16.572	0.168	350	263	271.098			
25	1	2014/05/1791.87	2014/05/1791.87	19.79	267325.256	2951.585	2951.585	-28.404	47.293	0.511	350	253	261.158			
26	1	2014/05/1786.758	2014/05/1786.758	19.726	267127.527	2948.766	2948.766	-28.672	44.14	0.477	350	253	261.018			
27	1	2014/05/1902.077	2014/05/1902.077	21.008	296359.043	3272.676	3272.676	-28.45	52.5	0.566	350	269	277.626	0.14	-28.47	
28	1	2014/05/2054.308	2014/05/2054.308	22.675	316399.753	3493.332	3493.332	-28.38	58.643	0.637	350	273	281.868			
29	1	2014/05/1627.487	2014/05/1627.487	17.985	242420.992	2678.367	2678.367	-28.569	63.012	0.677	350	251	259.039			
30	1	2014/05/2378.432	2014/05/2378.432	26.26	357745.223	3950.027	3950.027	-28.079	61.338	0.667	350	275	283.745			
31	1	2014/05/2192.127	2014/05/2192.127	24.215	322476.458	3560.433	3560.433	-28.203	60.682	0.66	350	262	270.691	0.21	-28.31	
32	1	2014/05/1978.571	2014/05/1978.571	21.851	298186.093	3291.538	3291.538	-28.852	45.111	0.484	350	260	268.892			
33	1	2014/05/1865.121	2014/05/1865.121	20.604	283108.26	3125.206	3125.206	-28.996	45.373	0.487	350	258	267.091			
34	1	2014/05/1821.315	2014/05/1821.315	20.143	280858.674	3100.45	3100.45	-28.964	48.963	0.525	350	261	269.625			
35	1	2014/05/1920.413	2014/05/1920.413	21.208	30074.64	3311.58	3311.58	-28.981	53.366	0.577	350	271	280.181	0.07	-28.95	
36	1	2014/05/2112.501	2014/05/2112.501	23.392	290233.317	3213.625	3213.625	-25.47	60.297	0.652	350	239	246.666			

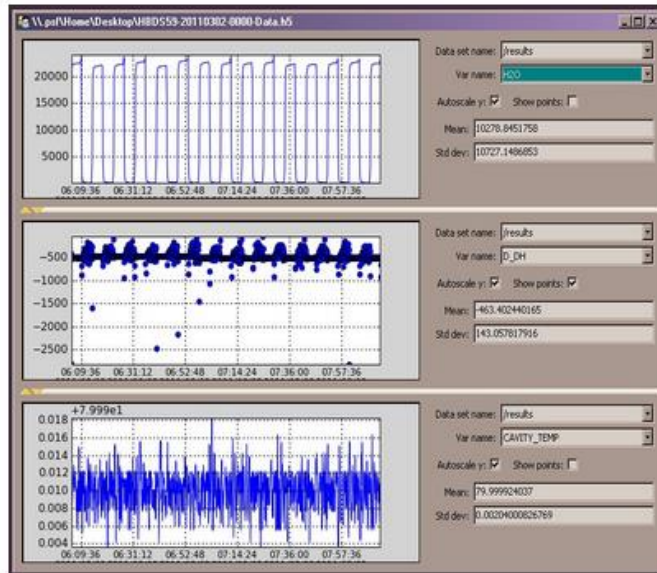
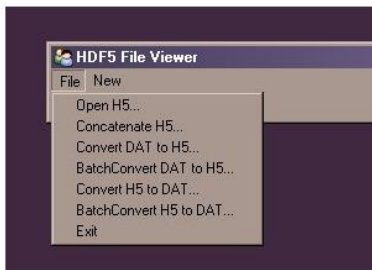
An Isotopic Data File viewed in spreadsheet software

14. DATA FILE VIEWER

Picarro 2XXX-series analyzers allow users to archive data using a highly-compressed, binary “HDF5” or “h5” format.

The screenshots below show the Data File Viewer program, which can be found in the “Picarro Utilities” Folder on the analyzer’s desktop. This programs allows you to open h5 files, convert h5 files to *.dat files (also convert *.dat to h5), and do batch conversions. Through this program, multiple h5 files can be joined and then viewed as graphs. In the graph window, you can select any of the data columns in the file, autoscale, zoom, hide/show points, and calculate statistics of data within the graph window.

If you have any questions, please contact Picarro or refer to Picarro Community for more information. <http://www.picarro.com/community/>



15. EXTERNAL VALVE SEQUENCER (OPTIONAL)

The Picarro analyzer can control two types of valves:

- Solenoid valve(s): DC voltage powered valve with normally open (NO) and normally closed (NC) positions. These can be either 2-way or 3-way valves.
- Rotary Selector valve: digitally controlled valve used to send selected flow from one of many inputs (up to 32) into the analyzer

Both types of valves can be simultaneously controlled through a common software interface called the 'External Valve Sequencer,' which is available from the Tools menu in the GUI.

15.1 Default Configuration

For all models of Picarro analyzers the rotary valve control is disabled in the factory default setting. The solenoid valve control, however, are ready to use by default for all solenoid valve connectors.

15.2 Setting up Solenoid Valves

The Valve Sequencer software can control up to six solenoid valves. Each valve should operate using 12 VDC with a current requirement of <1.5 Ampere maximum. This analyzer comes with a cable that can be connected to the solenoid valves.

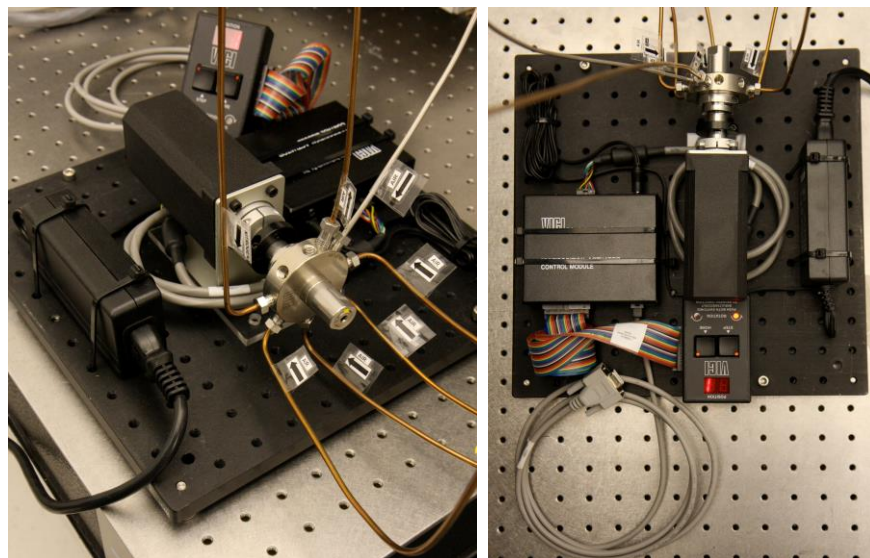
The valve connector cable should be connected to the 15-pin connector at the lower left corner of the analyzer. There are six pairs of wires with connectors labeled V1, V2, ... V6 with 2-pin female Molex connectors (Molex#43020-0200) for connection to the solenoid valves. For valves wired with matching Molex connectors, connect V1 to solenoid valve 1, V2 to solenoid valve 2, *etc.* Do not connect the solenoid valve to the analyzer ground -- use only the provided electrical connectors.

15.3 Setting Up Rotary Selector Valve

A multi-position rotary selector valve can be controlled by the Valve Sequencer software. It is controlled by standard serial commands in the Valco (VICI) protocol. Valco rotary valve models SD, SC, SF, ST, and STF are all supported. However, not all configurations will be appropriate, due to tube diameter, pressure or materials of construction. This setup will also require a Valco microelectric high torque actuator. A single combination package such as EMT2ST16MWE includes a 16 position, low-pressure ST valve in stainless steel, 1/8" tubing, 2" standoff, and microelectric high torque actuator. Please refer to http://www.vici.com/vval/st_8-1.php#16pos for further options and consult with Valco directly for more details.

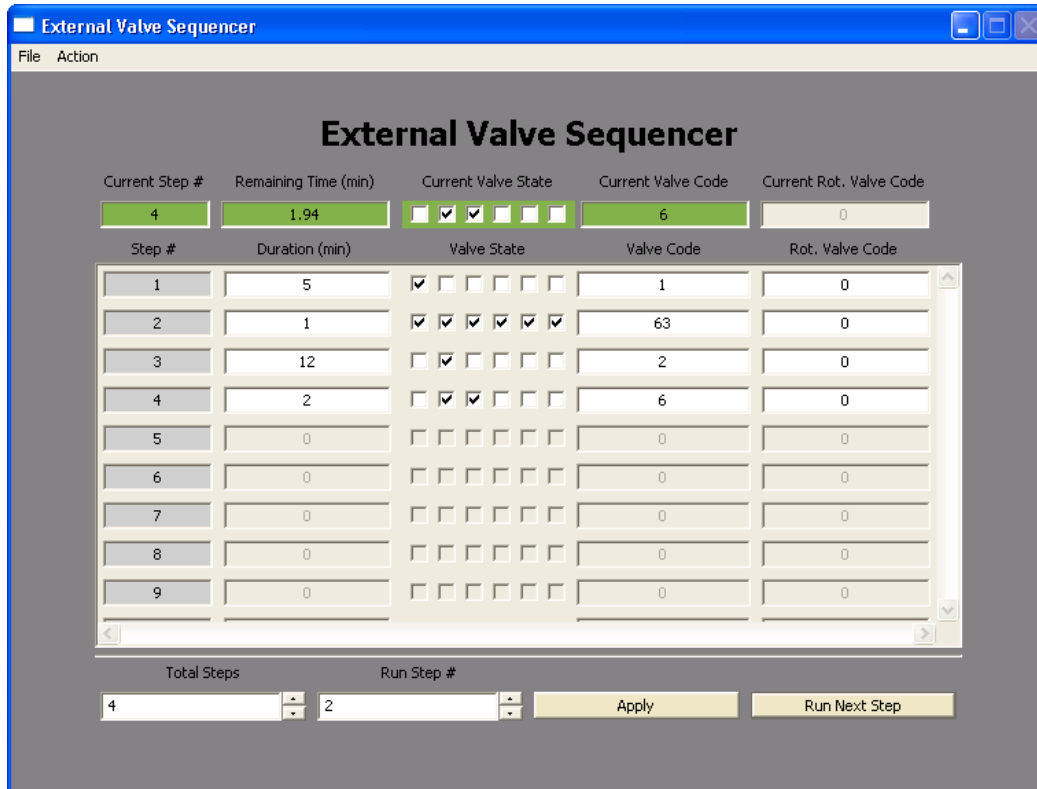
The Valco controller should be installed per manufacturer's instructions. The 9-pin female, connector cable (female) should mate with its corresponding, male port of the analyzer and labeled "MPV." Please note the 9-pin connector cable is not supplied with the instrument.

The setup will be similar to that in the pictures below:



15.4 Valve Sequencer Software

The Valve Sequencer software allows the user to set steps in which solenoid valves are turned on/off and the rotary selector valve is set to a single position. The Picarro valve sequencer window appears below:



Valve Sequencer GUI

The current step, elapsed duration, and valve states are shown in the top most row of the valve sequencer command window. The duration of each step is set in minutes; for example, 1 minute and 30 seconds corresponds to 1.5 minutes.

Please note the number of steps correlates with the total steps in the sequence, and the count of the steps starts at “0.” The first step of the sequence is designated Current Step “0,” and the second step in the sequence is designated Current Step “1.” The “Go to First Step” menu item under “Action” restarts the sequence from step 1.

Different sequences can be created and saved in the software. Use the “Sequence File #” field to select which file the sequence will be saved to (0 to 10 are the available choices). Click the up/down arrows to select the desired number.

15.5 Configuring a Valve Sequence

Each “step” sets the rotary valve to a single position and activates the indicated solenoid valve(s) for a set period of time. Multiple steps can be carried out in sequential order to switch between different gas sources, flush out a manifold, or other gas handling operation. Create the number of desired steps in the sequence by clicking the up/down arrow for “steps.”

For each step, select the box for each solenoid valve to be opened. The check mark in the “current valve state” window indicates a solenoid valve is open. Note: In this example, we assume normally closed (NC) valves are used. A check indicates current is flowing to the valve thus powering it open. The positions from left to right correspond to solenoid valves V1...V6.

The rotary selector valve position can be set in the column labeled “Rot. Valve Code.” Enter the number that corresponds to the desired valve position. A value of 1 in this field corresponds to position 2 on the Valco valve. Only one rotary position can be selected per step.

Step duration is determined by the value entered in the “duration (min)” field, where the duration of the step is in minutes. If duration values are set to <0.1 minutes, they may not be carried out correctly.

The “valve code” field is a configuration- dependent, read-only display field that shows the total state of that particular step in a numerical code. Should the most upper right grey box display a value of 512,256, or be greyed-out, either no rotary selector valve is connected to the instrument, or the valve is not functioning. For each individual measurement the analyzer makes, the valve codes and rotary valve positions corresponding to the valve state(s) at that point in time are saved alongside the concentration data.

Once the valve sequence has been programmed, it can be saved using the button “Save Valve Sequence File.” The sequence will be saved under the sequence file number selected.

15.6 Loading and Running a Saved Sequence

To load a valve sequence file, select the desired “sequence file number” and press “Load Valve Sequence File.” If the user has been running a different sequence from the one that was loaded, the user needs to press “Next Step” to initialize the newly selected sequence.

To run a sequence file, press “Enable Sequencer.” This button will turn to “Disable Sequencer” once the sequence starts. (The sequencer should be activated if it was disabled, but not necessarily to change from one sequence to another.) The sequence will repeat itself indefinitely until disabled or the software is exited. If enabled, the sequence will continue to run after the “close sequencer window” button is pressed.

If desired, the valve sequence can be forwarded to the next step of the sequence by pressing the “run next step” button. To stop the sequencer file, use the “Start/Stop Sequencer” menu item under the “Action” menu. This will leave all valves in their current state. In some situations, it is convenient to program the last step in the sequence to be a safe or default valve state. The sequencer can be advanced to the last step should the user need to put the solenoid or rotary valves into a safe/default state. The “Reset All Valves” de-activates all valves. Using the “Hide Sequencer Interface” closes the window, but if the sequencer is enabled, it will continue to run in the background. To jump to a particular step, increment the “run step 3” and click “Apply.”

Both solenoid and rotary valve codes are recorded in columns in the output data files indicating the active valve configuration respective to when data is taken. These codes can be used as event timing flags. For example, if no solenoid valves are present, the codes will be recorded regardless of whether a valve is connected or not.

16. REMOTE DATA ACCESS

16.1 The Picarro Serial Communication

The analyzer supports an RS-232 physical command interface, which can be used to control the instrument and to retrieve concentration data. Not all features of the instrument are available on the serial interface. For details on how to use the serial command interface, please see the Programming Guide (included in pdf format on the installation CD). This command set may also be used across a TCP/IP interface through an Ethernet connection. Please contact Picarro for further details.

16.2 Remote Data Access

Using the RemoteAccess.ini file, the analyzer can be configured to automatically:

1. Send data from the instrument to a list of e-mail accounts.
2. Measure the offset of the host computer system clock from a set of Internet timeservers and (optionally) to resynchronize the clock on the basis of this information.

The Internet connection need not be permanent, and may be a dial-up connection accessible via a user-supplied USB modem. The task of sending data and/or synchronizing the clock on the analyzer is performed using the C:\Picarro\G2000\HostExe\RemoteAccess.exe program. This program can be setup to run periodically using the Windows task scheduler at a user-configurable frequency. If a dial-up connection to the Internet is employed, it is used only on demand in order to minimize the connection time.

Each time that the RemoteAccess.exe program runs, it appends information to a log file, which keeps a record of the results of the time synchronization and of the files sent by e-mail. The RemoteAccess.exe program is configurable by means of an initialization file, which includes information such as the login credentials for the dial-up connection, the e-mail account and the list of timeservers.

The initialization file is:

C:\Picarro\G2000\AppConfig\Config\ RemoteAccess\RemoteAccess.ini

It should be placed in the same directory as the executable RemoteAccess.exe. The file has one required section named LOGGING and three optional sections named NTP, DIALUP and EMAIL. The logging section has a single key Logfile whose value is the path to the log file. Once this log file exceeds 64 kbytes in length, it is backed up appending a numeric extension to the file name and a new file is open. A total of ten backup log files are kept.

16.3 NTP

The NTP section controls querying the Internet time servers using the SNTP protocol (RFC4330) and the resetting of the clock on the host computer. If the section is not present, time synchronization is not carried out. The keys Server1, Server2, etc., are used to specify the URLs of the timeservers. As many of these timeservers are interrogated as possible, and the clock offset is computed on using the median of the results obtained from the available servers. If the UpdateClock key is set to true, the offset is applied to the host clock. Otherwise, the offset is recorded, but the host clock is not changed.

16.4 Email

The EMAIL section controls the sending of the data files as e-mail attachments. If the section is not present, e-mail messages are not sent. The key Directory specifies the directory that contains the data files. When the program is run, files in this directory are sent to the specified recipients and the files are deleted. In order to avoid problems with incomplete files, programs that place files into this directory should do so using an atomic operation, such as a rename. The Server key is set to the name of an RFC2821-compliant SMTP server that actually sends the e-mail messages.

The From key is the e-mail address from which the messages are sent. Note that some SMTP servers check that the source is permitted to send mail while others allow any name in this field. The collection of e-mail addresses to which copies of the e-mail is sent is specified by the keys To1, To2, etc. The Subject key is used to fill the subject field in the e-mail header, and may be set to any string. Depending on the SMTP server, it may be necessary to use authentication before e-mails can be sent, as described in RFC2554. If such authentication is not needed, the key UseAuthentication is set to false. If this key is set to true, two additional keys Username and Password must also be specified for the e-mail account.

16.5 Dialup

The DIALUP section is used if a dial-up connection to the Internet needs to be established when the program runs. If the section does not exist, a permanent connection is assumed to be available for carrying out the other tasks specified in the initialization file. The ConnectionName key specifies the name of the dial-up connection to use, as listed under Network Connections in the Control Panel. The values of the keys Username, Password and Number are used to make the connection.

Example of “RemoteAccess.ini” File

[LOGGING]

Logfile=c:/temp/RemoteAccessLog

[NTP]

Server1=time-a.nist.gov

Server2=time-b.nist.gov

Server3=time-a.timefreq.bldrdoc.gov

Server4=time-b.timefreq.bldrdoc.gov

Server5=time-c.timefreq.bldrdoc.gov

Server6=time.nist.gov

Server7=time-nw.nist.gov

UpdateClock=1

[DIALUP]

ConnectionName=Picarro Dialup Access

Username=user

Password=password

Number=14085551212

[EMAIL]

Server=smtp.servername.org

Directory=c:/picarro/mailbox

From=instrument@picarro.com

To1=recipient1@site1.com

To2=recipient2@site2.com

Subject=CRDS data from Silverstone instrument

UseAuthentication=0

17. PERFORMANCE VERIFICATION

17.1 Continuous Gas Samples (analyzer only)

To verify the performance of the isotopic carbon analyzer, attach the inlet of the CRDS analyzer to a cylinder of dry gas with CO₂ concentrations within the specified range of the analyzer. Adjust the outlet pressure of the tank to a range between 3-6 psi and start flowing gas into the analyzer. Collect data for 24 to 48 hours.

To identify the specifications of your analyzer model, refer to the Certificate of Compliance (CoC) that shipped with your instrument.

- For $\delta^{13}\text{C}$ in CO₂: Calculate the standard deviation of data averaged every 5 minutes for one hour. Use gas standards at CO₂ concentrations of 380 ppm.
- For the concentration of CO₂ (at values specified in the CoC): Calculate standard deviation of data averaged every 30 seconds for one hour.
- For drift calculation of CO₂: Calculate 1 hour interval mean of raw data over 24 hours. Determine Peak to Peak (also called minimum to maximum) at concentrations specified in CoC.

17.2 Hyphenated systems (CM-CRDS, AM-CRDS, Aurora-CRDS)

The table below summarizes the steps that the user needs to undertake in order to verify that the performance of the hyphenated CRDS system (CM-CRDS, AM-CRDS, Aurora-CRDS) meets the factory specifications as outlined in the datasheet. Datasheets are available on the Picarro website: www.picarro.com

Step	Description	Specification or action
1.	Install hyphenated system according to relevant Manuals.	Note manual date and revision here
2.	Measure a sample size by solid weight or liquid volume 6 samples will be run.	Record Weight
		1
		2
		3

		4	
		5	
		6	
3.	Weigh out a standard and prepare it for analysis	Record Weight or Volume	
		1	
		2	
		3	
		4	
		5	
		6	
4.	Prepare 2 dummy samples	No action required	
5.	Load autosampler with 2 dummy samples followed by the 6 standards	No action required	
6.	Run samples using instructions in the respective manual	No action required	
7.	Open data file (C:\Picarro\IsotopicData saved with today's date) and export to Excel or other data processing programming. Use standard deviation formula ('stdev' in Excel) to calculate the standard deviation of the 6 samples (omitting dummy samples). If < 0.3 permil (or value specified on datasheet), the instrument passes. If fail, repeat from 2.	Record individual sample results and standard deviation.	
		1	
		2	
		3	
		4	
		5	
		6	
SD			

18. CALIBRATION

The two primary analytical measurements of the instrument are: the concentration of $^{12}\text{CO}_2$ and $\delta^{13}\text{C-CO}_2$. Periodic recalibration with standards of known concentration and/or delta value maintains the accuracy of these quantities. Using the Data Recal Software Utility for calibration enables the calibration constants to be tracked over time, thus enabling the user to follow system performance.

18.1 Calibration and Instrument Performance

All measurements naturally contain a degree of uncertainty. This uncertainty is caused by systematic and random errors from an analytical process. This inherent uncertainty also means that repeated measurements of the same sample will not produce the same value.

However, proper calibration can reduce some of this variation, thus improving instrument performance. During calibration, statistical operations using repeated measurements can be used to estimate the “true value” of the measurement and the amount of uncertainty in that value. When these measurements are performed using a standard of known value, then the statistical operations provide values that can be used to correct data for some systematic errors.

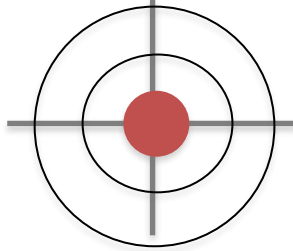
18.2 Statistics, Accuracy and Precision

A set of multiple measurements can be described statistically with two values: the average and the standard deviation. The [average](#) of multiple measurements on the same sample is taken as the “true” value of the measurement, and the [standard deviation](#) of the measurements is reported to express the degree of the uncertainty in that value.

Standard deviation is represented by the Greek letter sigma, σ . It [can be calculated](#) using formulas; many spreadsheet programs can also automatically calculate the standard deviation of set of measurements.

For example, a delta value of $\delta^{13}\text{C}$ in the Vienna PeeDee Belemnite (VPDB) is $-10 \pm 0.3 \text{‰}$. This means the “true” delta value of the standard could range from -10.3‰ to -9.7‰ .

Let's depict this known value and standard deviation as a red circle on a target.

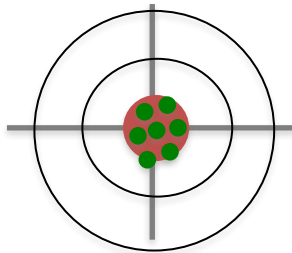


When using an analytical instrument, we are interested in the accuracy and precision of repeated measurements performed on the same sample and under the same conditions.

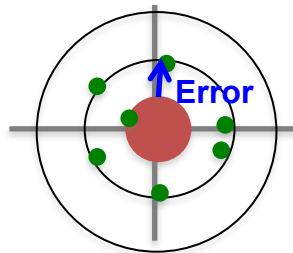
Accuracy refers to how close the measured values are to the “true” value.

Precision refers to how close measured values are to each other.

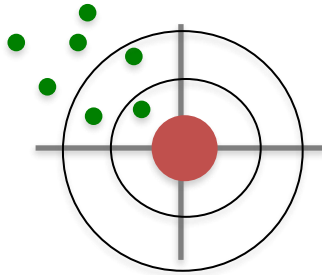
The graph below shows a series of seven measurements that are precise and accurate. The measurements are clustered around a small set of values, and those values are within the standard deviation of the measurement.



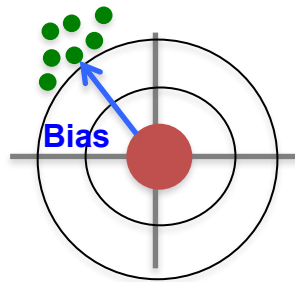
The difference between the “true” value and a measured value is the **error**, shown in the graph below by a blue arrow.



Below is a series of measurements with wide variance. They are neither accurate nor precise.

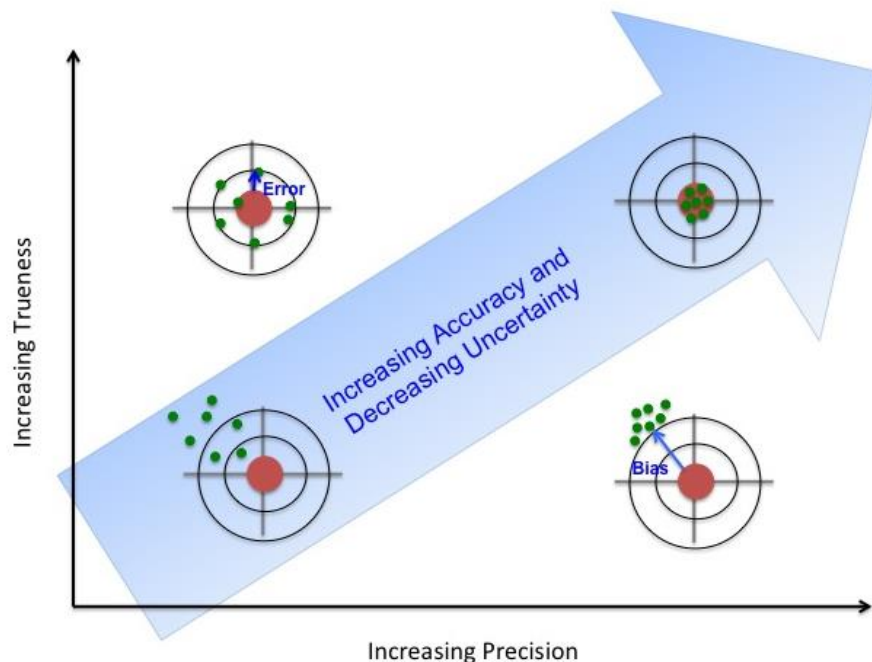


Sometimes measurements differ from the “true” value in a consistent pattern. This difference can be due to **systematic errors** that may be inherent in properties of the instrument or measurement. However, these errors can be accounted for, and the data can be corrected, once an instrument is properly calibrated. **Bias**, represented by the blue arrow in the graph below, can be thought of as the total systematic error.



Also, the measurements shown above are precise, but not accurate. They are precise because they are clustered around a similar value. But they are not accurate because they are far from the “true” value at the center of the graph.

These four graphs can be combined to show the differences between accuracy (trueness) and precision.



There are two other important concepts that describe an instrument's performance:

Repeatability is the precision determined under the same analytical conditions (sample, instrument, method, and instrument operator).

Reproducibility is the precision determined when the different operators use different instruments to measure the same sample with the same method.

18.3 Analyzer versus System Calibration

Picarro CRDS users should pay close attention to the importance of performing a whole system calibration vs. analyzer-only calibration. The analyzer calibration can be performed using standard gases that flow continuously through the CRDS analyzer, while the system calibration requires the use of the appropriate sample form (Gas, Liquid, or Solid) to verify the performance of the front-end + interface + CRDS analyzer.

Calibration Best Practices

- Measure each standard two to three times.
- Always remember to run several “dummy” samples before you start analyzing unknown samples. The role of the dummy samples is to clear the analytical flow path in preparation for the real/actual samples.

18.4 Initial

Initial calibration of the CRDS analyzer and/or of the hyphenated system should be performed upon the receipt of the equipment from the factory. Picarro does not guarantee that the factory isotopic calibration is always accurate.

Calibration Standards

You will need two types of standards: internationally accepted “primary” standards, and a set of working, or “secondary,” standards. The primary standards are used to calibrate the secondary standards, which can be used on a daily basis. We recommend that both the primary standards and the secondary standards bracket the isotope space that you intend to run as unknowns.

Sources for Primary Standards

The $\delta^{13}\text{C-CO}_2$ values for the primary standards are measured against *Vienna Pee Dee Belemnite* (VPDB). These standards can be obtained from:

- National Institute for Standards and Technology (NIST):
<http://www.nist.gov/srm/>
- International Atomic Energy Agency (IAEA):
 - <http://nucleus.iaea.org/rpst/ReferenceProducts/About/index.htm>
 - http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Stable_Isotopes/index.htm
 - http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Stable_Isotopes/13C18and7Li/index.htm
- United States Geologic Survey (USGS):
<http://isotopes.usgs.gov/lab/referencematerials.html>
- Indiana University:
<http://mypage.iu.edu/~aschimme/hc.html>



NOTE

When using gas-phase standards, make sure that the balance (or background) gas of the standard is air, not N₂ or another gas. The balance gas impacts the linewidth of a sample's optical spectrum, and the linewidth precision is key to the high sensitivity of Picarro analyzers.

Standard Reference Material for Organic and Inorganic Carbon Analysis:

The following are recommendations for standards to use with a Picarro CO₂ isotope analyzer that is combined with front-end interface for sample handling.

- **AutoMate-CRDS (AM-CRDS): $\delta^{13}\text{C-CO}_2$ Calibration**

The AutoMate-CRDS can be used to measure dissolved or solid inorganic carbon.

Carbonate isotope standards are available from NIST and the IAEA:

<http://www.nist.gov/srm/>

<http://nucleus.iaea.org/rpst/ReferenceProducts/About/index.htm>

The entire carbon isotopic system is now based on NBS-19 (US National Bureau of Standards). This is a calcite with a defined value of $\delta^{13}\text{C} = +1.95\text{‰}$ versus *Vienna Pee Dee Belemnite* (VPDB).

The simplest calibration would be to load about 0.5mg of this standard into a Labco Exetainer septa top vial and run it using the sequence table on the AutoMate prep device. In this type of run, the atmosphere in the vial is replaced with pure nitrogen, the sample is acidified, and the CO_2 is delivered to the Picarro isotopic analyzer. The Picarro analyzer then provides the measured isotopic value, which you can compare to the internationally recognized value.

There are a series of other solid carbonate material that can be used to prove the isotopic linearity of the AutoMate and the Picarro system. These include:

NIST

<i>Reference material number</i>	<i>Description</i>	<i>$\delta^{13}\text{C}$, ‰, versus VPDB</i>
8543	NBS18 Carbonatite	-5.01
8544	NBS19 Limestone	+1.95
8545	LSVEC-Lithium Carbonate	-46.6

IAEA

<i>Description</i>	<i>$\delta^{13}\text{C}$, ‰, versus VPDB</i>
NBS18 Carbonatite	-5.014
NBS19 Limestone	+1.95
IAEA-CO-1 Marble	+2.492
IAEA-CO-9 Barium Carbonate	-47.321
LSVEC-Lithium Carbonate	-46.6

You can use enriched standards, like IAEA-303, if you are running enriched unknowns. These standards, however, will not be useful for natural abundance unknown samples.

- **CM-CRDS: $\delta^{13}\text{C-CO}_2$ Calibration**

We recommend the use of USGS40 ($\delta^{13}\text{C}_{\text{VPDB}} = -26.389 \text{ ‰}$) and USGS41 ($\delta^{13}\text{C}_{\text{VPDB}} = +37.626$). Both of these are L-glutamic acid standards, which easily combust and can be used to give the user a 2-point calibration.

Another option for the upper end of the isotopic scale is cane sugar (normally around $\delta^{13}\text{C}_{\text{VPDB}} = -10.95 \text{ ‰}$). This $\delta^{13}\text{C}$ value is stable enough that sugar can be used as an internal, or secondary, standard.

Cane sugar (C&H brand, powdered – not granulated) that is available at grocery stores should be fine. You can calibrate the isotopic composition of this sugar via IRMS, if available. It can also be calibrated on your CM-CRDS, using the USGS40 and USGS41 standards. Since sugar generally tends to be hygroscopic, please make sure to store it in a dry place.

Each standard should be analyzed according to the procedure in the CM-CRDS manual with 2-3 replicates analyzed for each standard. You can use the Acetanilide provided with the CM-CRDS starter kit to make “dummy” samples at the beginning of the sequence prior to the start of real samples analysis.

- **Aurora-CRDS: $\delta^{13}\text{C-CO}_2$ Calibration**

With the Aurora-CRDS, you can analyze either Dissolved Inorganic Carbon (DIC) or Dissolved Organic Carbon (DOC). For DIC standards, please refer to the AutoMate-CRDS section above. For DOC standards, you can use either urea or sodium/potassium phthalate. Both standards can be purchased from Indiana University ([website](#) provided above). Each standard should be analyzed according to the procedure in the Aurora manual with 2-3 replicates analyzed for each standard while using “dummy” samples at the beginning of the analysis sequence.

18.5 Periodic

Following the initial calibration of the analyzer and/or system, Picarro recommends using secondary standards to run along with actual samples. If the isotopic carbon system is coupled to a front-end, then the sample sequence should contain standards at these times throughout the run:

1. The beginning, immediately after the “dummy” samples,
2. The end of the sequence, and
3. Every three to four hours between samples.

This practice allows the end-user to correct data for any daily fluctuations and drift that might impact the accuracy of the system.

18.6 Long-Term

The Picarro CRDS analyzer and/or the hyphenated Picarro system should be re-calibrated using primary standards every 3-4 months.

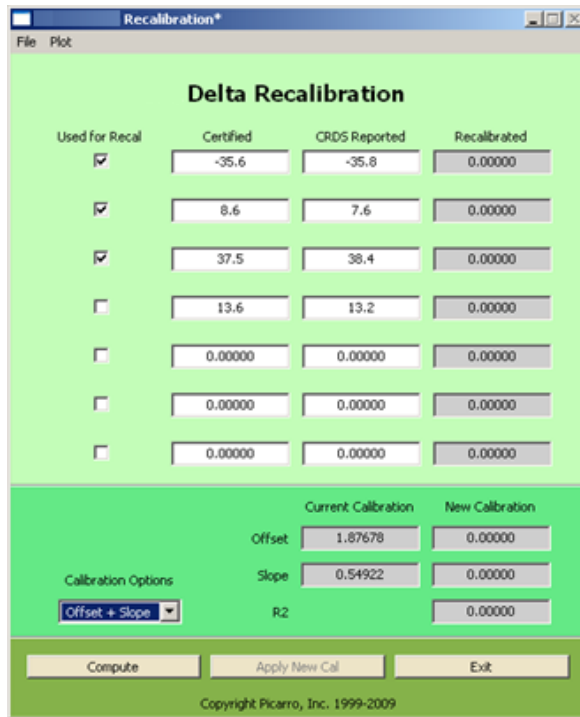
18.7 Data Recal Software Utility

The Data Recal software utility is designed to enable users to perform a routine isotopic calibration or an isotopic calibration verification of Picarro's Isotopic Analyzer via a user-friendly interface.

Data Recal allows the input of ten calibration points. Some of these points can be used for recalibration, while the remaining points can be used as quality control calibrants. In an ideal situation, three isotopically certified standards should be analyzed on the system to generate CRDS-reported values for $\delta^{13}\text{C}$. The standards with isotopic values spanning and encompassing the intended sample analysis should then be used to build a standard calibration curve. Parameters of this curve will then be used to correct the instrument readings so that they match standard values. The other standards will be simultaneously used for quality control, to verify other recalibrated delta values against their certified delta values.

Graphic User Interface (GUI)

The Picarro Data Recalibration (“Data Recal”) software can be found in the “Picarro Utilities” folder in the desktop. The Data Recal software utility can be launched by double-clicking on the Data Recal Icon in the folder. Shown below is a screenshot of the window that will open.

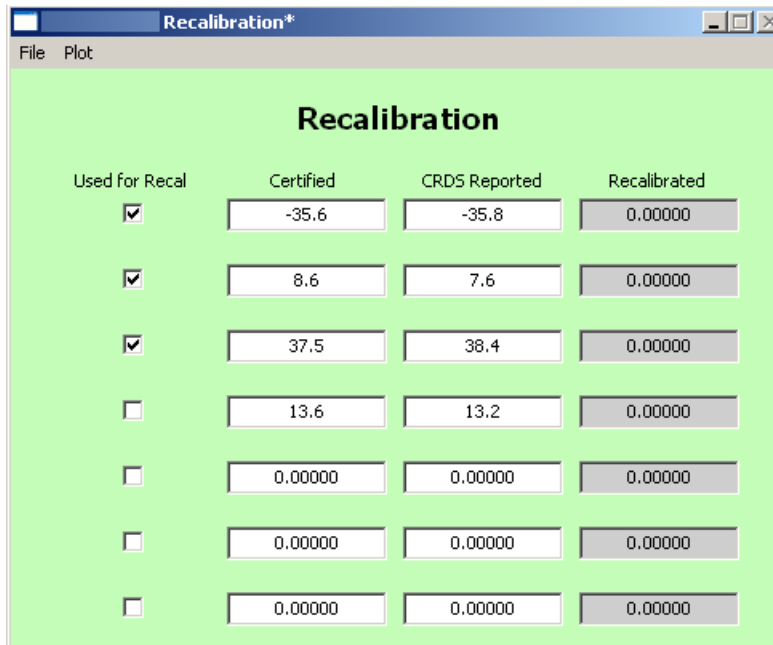


Data Recal Software Utility GUI

The Delta Recal Software Utility comprises three sections:

1. A numerical input and selection section (shown below):

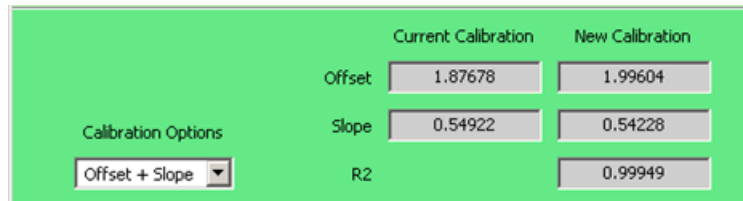
Certified and **CRDS reported** values are entered in the white boxes. Standards that will be used for instrument recalibration are then selected by checking the corresponding box in the first column, labeled “Used for Recal.”



Recalibration section of Data Recal Software Utility GUI

2. Calibration output section (shown below):

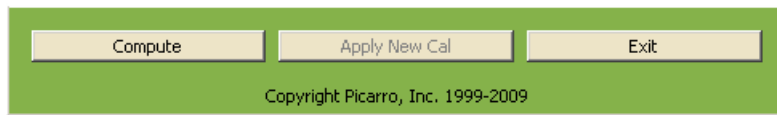
In the “Calibration Options” drop-down menu, you can select either an “offset” or an “offset + slope.” Once the new calibration parameters are calculated, the Data GUI will display the new values under the “New Calibration” column. The parameters that appear here will depend on your initial selection. When the offset+slope option is selected, the program also calculates a goodness-of-fit correlation coefficient (R^2).



Calibration output section of Data Recal Software Utility GUI

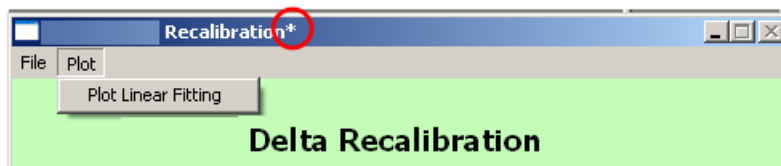
3. Action selection section (shown below):

In this section, the user can click on the compute button to calculate the new calibration parameter(s). The compute button will be grayed out until values have been entered in the **Certified** and **CRDS reported** columns, and at least one pair of **Certified** and **CRDS reported** values selected for the calibration. Once these values are entered or selected, the “Compute” button will be active. Click “Compute” to calculate the new calibration parameters. These parameters will appear in the Calibration output section of the GUI, and an asterisk “*” will be displayed at the end of the window title line, indicating the new change.

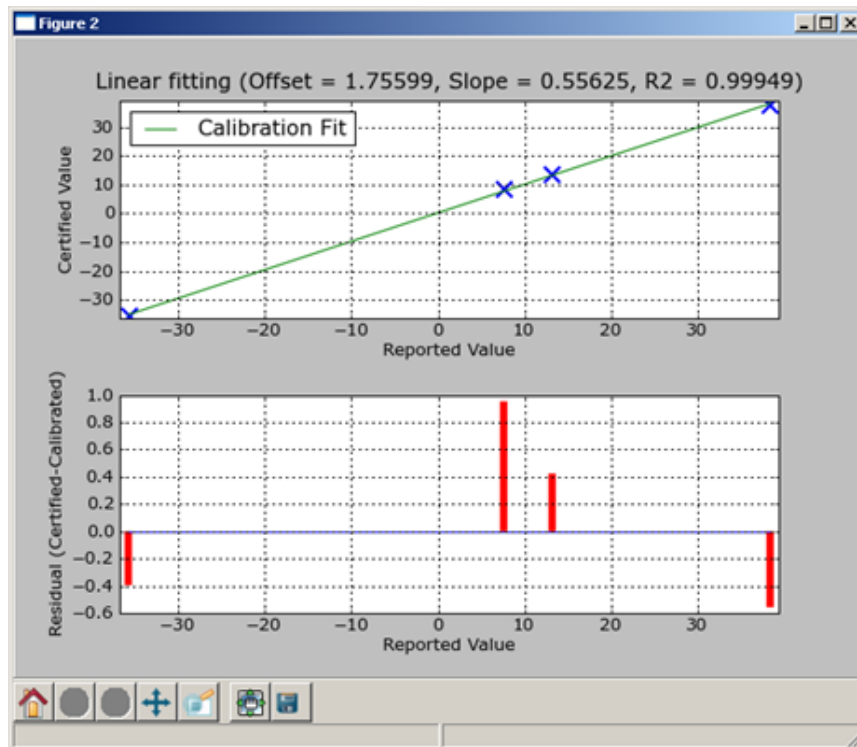


Action selection section of the Data Recal Software Utility GUI

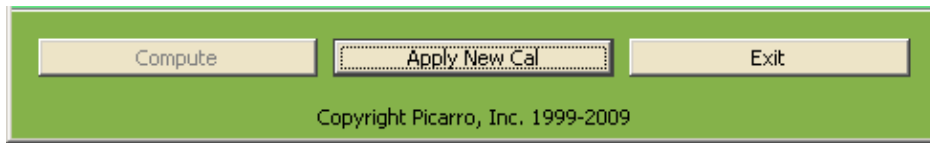
Once the calibration parameters are calculated, you can elect to graphically display the calibration and quality control (QC) standards in a graph. To do this, click “Plot” in the upper left corner of the window, and select “Plot Linear Fitting” from the drop-down menu, as shown below.



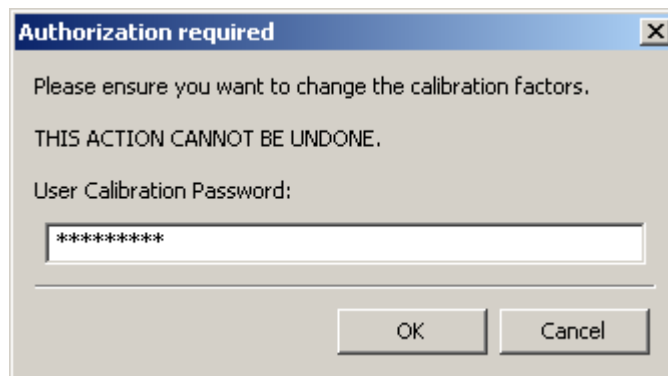
The plot that the utility will generate is shown below; this plot will display two graphs. The top graph presents measurements for the recalibrated standards (calibration and QC), as well as a line fit through those points. The bottom graph shows the residuals, which show how far each measurement is from the best-fit line.



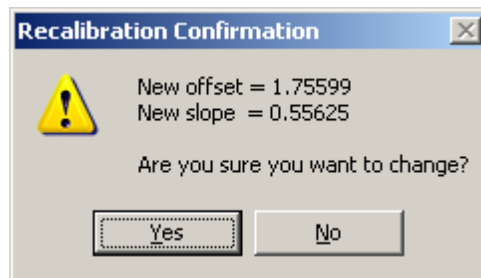
If you decide to accept the new calibration values based on this plot, click on the “Apply New Cal” button.



Then you will be prompted to enter a Calibration Password. **The default Calibration Password is PICARRO.**



Next, a “Recalibration Confirmation” pop-up window will appear, displaying the new offset and slope (when applicable) values. This window will prompt you to confirm your choice to apply these values, in order to avoid any inadvertent mistakes.

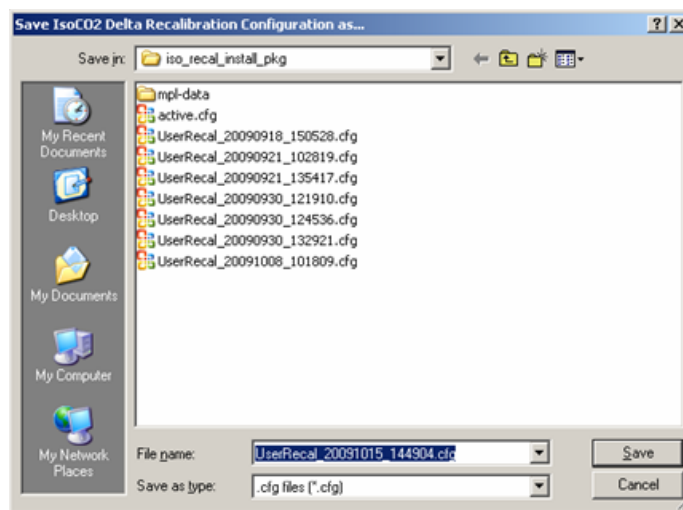


Please note that when you press the “Yes” button, the newly accepted calibration parameters will take effect immediately, without the need for the instrument main GUI to be restarted.

Once you accept the new calibration parameters, the Data Recal Software Utility automatically gives you the option to save the new recalibration file. Saving these files enables you to track the instrument recalibration history. Saved files can be reloaded by clicking “File” in the upper left corner of the window, and selecting “Load Recalibration File.”



Next, select the file that you want to load.



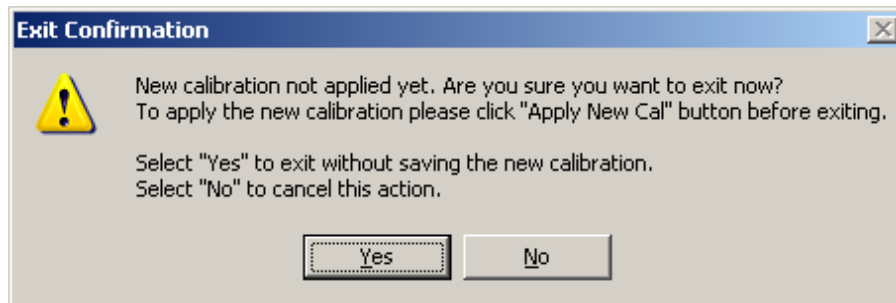
The recalibration file for this example will contain the following information:

-35.6	-35.8	-35.20437	
8.6	7.6	7.64690	
37.5	38.4	38.05748	
cc	1.75599	0.55625	
nc	1.87678	0.54922	0.99949
option	Offset + Slope		

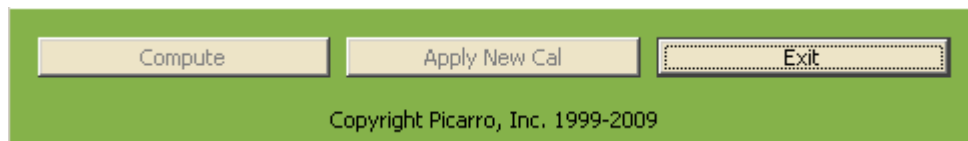
- The first three rows reflect the values from each standard selected for recalibration. The first column in these rows lists the certified values, the second column lists the measured values, and the third column lists the recalibrated values. The number of rows will depend on the number of standards selected to be used for recalibration.

- The cc (**c**urrent **c**alibration) row, read from left to right, lists the current offset and current slope value.
- The nc (**n**ew **c**alibration) row, read from left to right, lists the new offset and new slope values. The third value in this row is the R^2 value, which is only displayed if the calibration option is “offset + slope.”
- The last row displays the calibration option selected.

If you choose to exit the Recal GUI before accepting the new recalibration values, you will be prompted to confirm your choice through a pop-up window. This window contains a warning that continuing to exit will cause the new calibration data to be lost.



When you are finished with the calibration, you can exit the Delta Recal software utility by clicking on the “Exit” button at the bottom part of the Recal GUI.

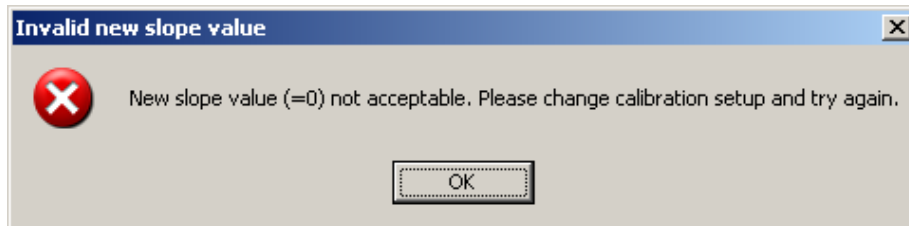




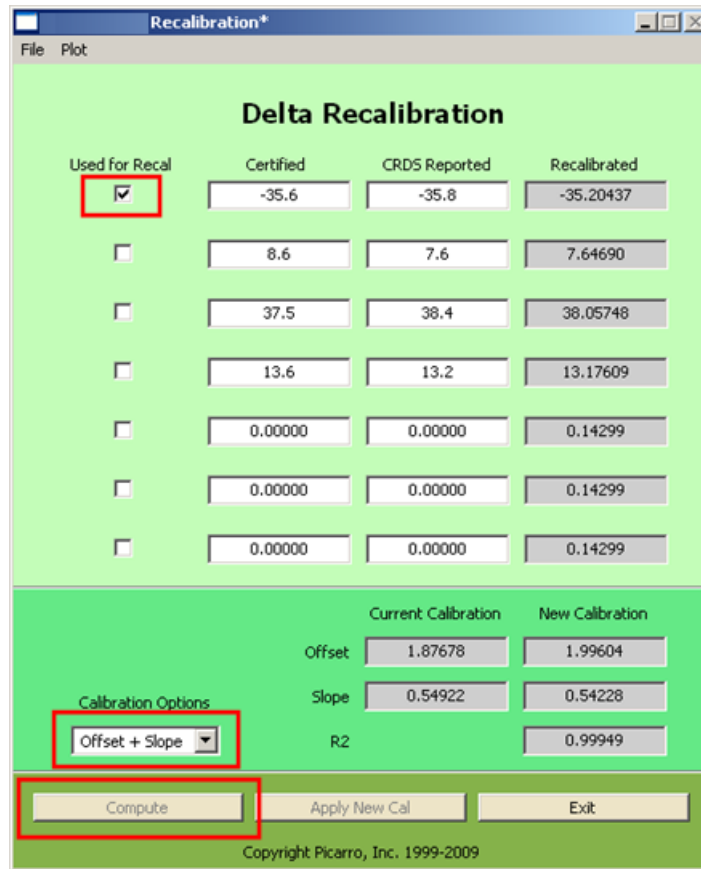
NOTE

Below are explanations of three common issues that might be useful to troubleshoot this GUI.

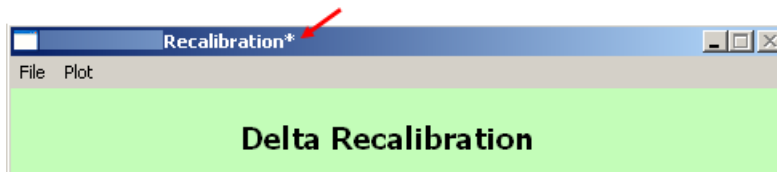
1. The Recal GUI displays an error saying the new slope value is not acceptable. This happens when (1) at least two entries in the **Certified** or **CRDS reported** columns contain zero-value numbers, (2) these entries are selected to be used for recalibration, or (3) the “offset + slope” calibration option is selected. This error occurs because the entered values will lead to an erroneous zero-slope value.



2. The “Compute” button is grayed out when “Offset + Slope” is selected as a calibration option and only **one standard** is selected to be “Used for Recal.” Selecting at least **two standards** by clicking on the appropriate boxes in the “Used for Recal” column will make the “Compute” button active. Both calibration options (“Offset” only and “Offset + Slope”) will also be available.

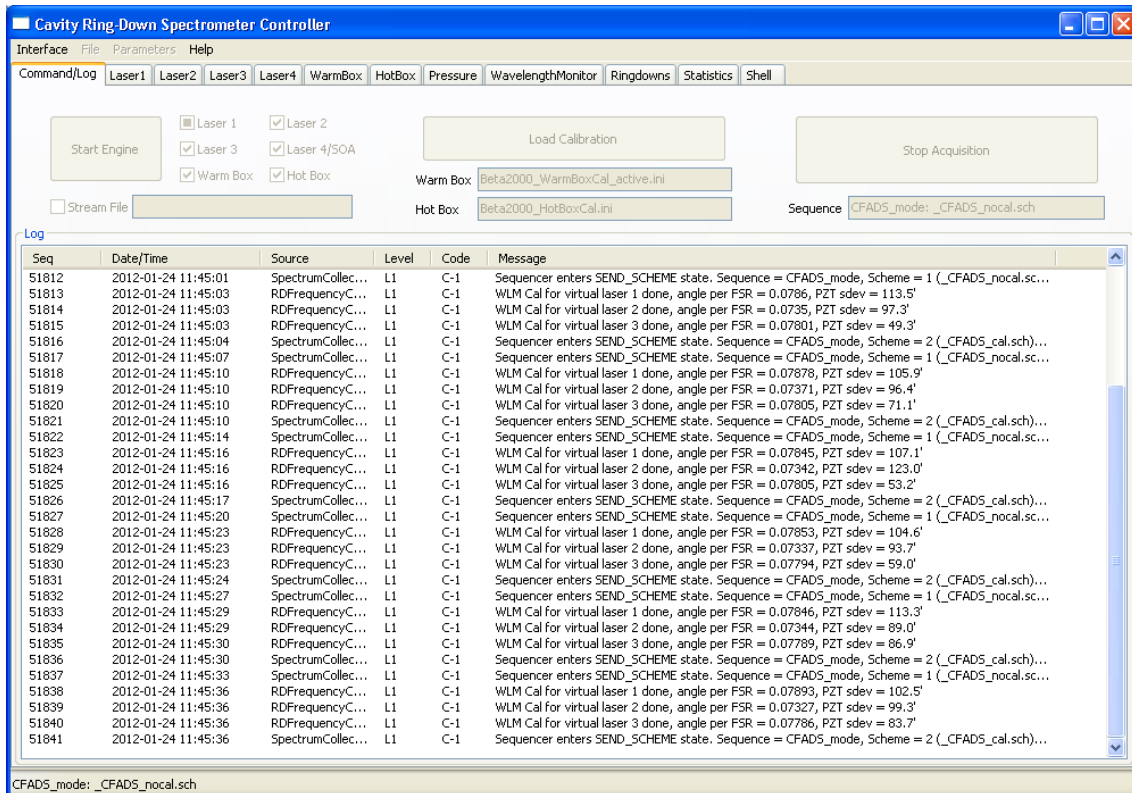


3. Once you click the “Compute” button, the button itself will be grayed out until you change any of the **Certified** or **CRDS reported** values, or until you select new values to be “Used for Recal.” If you make any of these changes, an asterisk “*” will be added to the title line to indicate that something has changed in the configuration. Once the “Compute” button is clicked again, then the “*” will disappear.



19. CAVITY RING-DOWN SPECTROMETER CONTROLLER

On your desktop, there is an icon labeled “Picarro Controller.” Clicking on this icon will open up a useful diagnostics panel (see image below), allowing the user to see the analyzer’s internal temperatures, pressure, and spectroscopy in real time. This program has user-accessible functions, but it cannot change anything related to analyzer functionality. It is intended for diagnostics purposes only.



Cavity Ring-Down Spectrometer Controller Window

20. SETUP TOOL

The Setup Tool can be launched by double clicking on its icon in the desktop folder called Picarro Utilities. This tool allows the user to configure data file saving details, including which data elements are written to data files, digital data output (via serial port or TCP/IP), remote data delivery (via email), and general GUI properties.

Seven tabs of the Setup Tool Window are explained in the next pages. If you have any questions about the Setup tool, please contact Picarro or refer to Picarro Community for further details. - <http://www.picarro.com/community/>



CONFIGURING DATA FILE SAVING DETAILS

The **DATA LOGGER** tab allows the user to configure various data file saving details, including which data elements are written to data files.

Data Columns: Controls which data elements are written to data files.

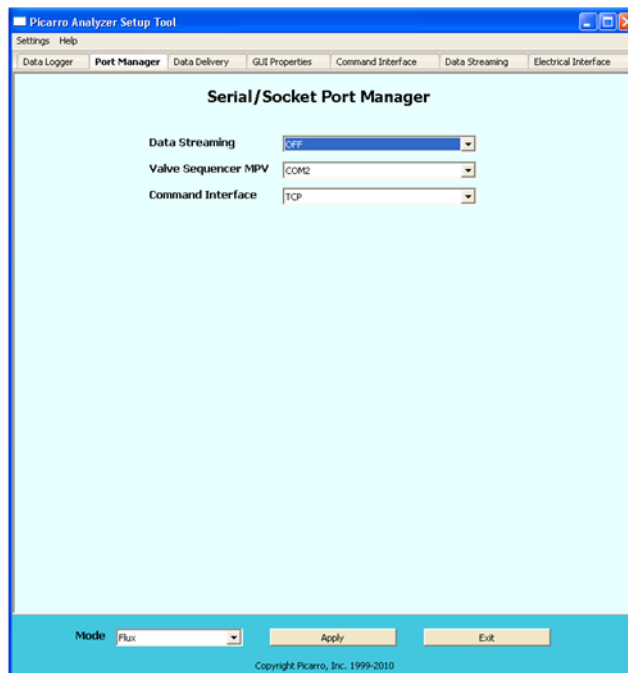
Hours of Each Log File: Controls the size of each data document.

Enable Mailbox Archiving: Enables archiving of data in the mailbox folder – C:\Picarro\G2000\Log\Archive\DataLog_Mailbox

Archived Directory Structure: Specifies part of naming convention for data documents.

Total User Log Storage Size (GB): Specifies the size of storage allowed for User Data (Recent Data).

After making the appropriate edits, click “Apply” to put changes into effect and then “Exit” to close the window.



MANAGING PORTS FOR DIGITAL DATA OUTPUT/INPUT & SERIAL COMMUNICATION

The **PORT MANAGER** tab allows you to control digital data Output/Input via serial port or TCP/IP.

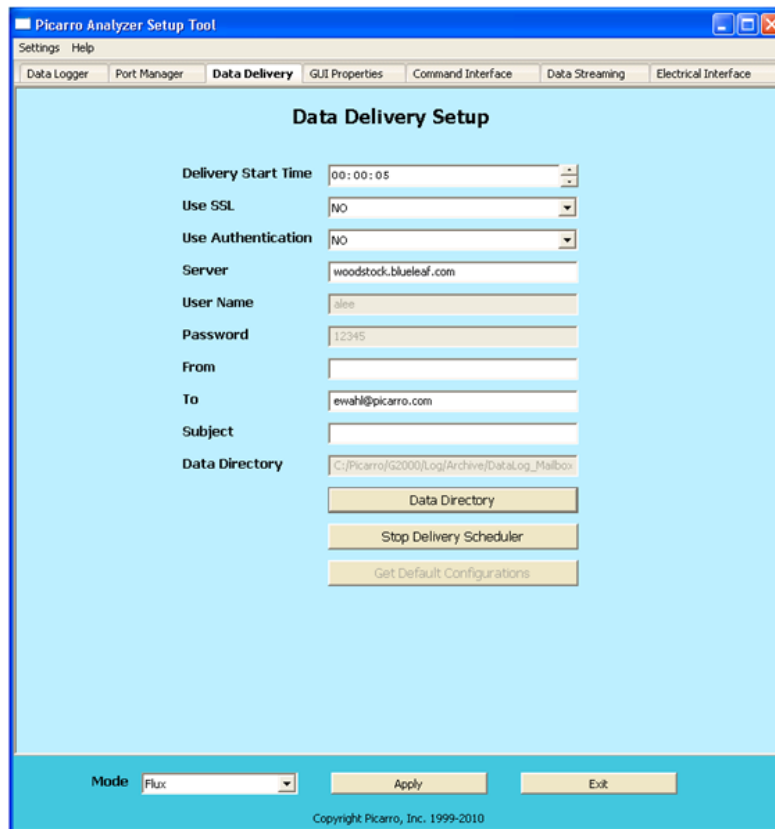
On this window, specify the port you want your data to stream through (COM1/COM2/ Off), the port you want to connect your Valve Sequencer to (COM1/COM2/Off), and/or your desired Command Interface (COM1/COM2/ TCP/Off).

Make sure there are no COM port conflicts before clicking “Apply.”

After making the appropriate edits, click “Apply” to put changes into effect and then “Exit” to close the window.

See below to learn more about Serial Communication in Picarro Analyzer, and also see “External Valve Sequencer” section of this manual to learn more about valve sequencer.

SERIAL COMMUNICATION: The analyzer supports an RS-232 physical command interface, which can be used to control the instrument and to retrieve concentration data. Not all features of the instrument are available on the serial interface. For details on how to use the serial command interface, please see the Programming Guide (included in pdf format on the installation CD). This command set may also be used across a TCP/IP interface through an Ethernet connection.



SCHEDULING REMOTE DATA DELIVERY (EMAIL)

The **DATA DELIVERY** tab allows the user to schedule remote data delivery (email).

Delivery Start Time: Time of the day when data will be sent.

SSL: Depending on the sender's email server, the sender can activate the Secure Sockets Layer (SSL).

Use Authentication: Turning this on will require the receiver to provide a password and a username to access data. Set up the **password & Username** from this window.

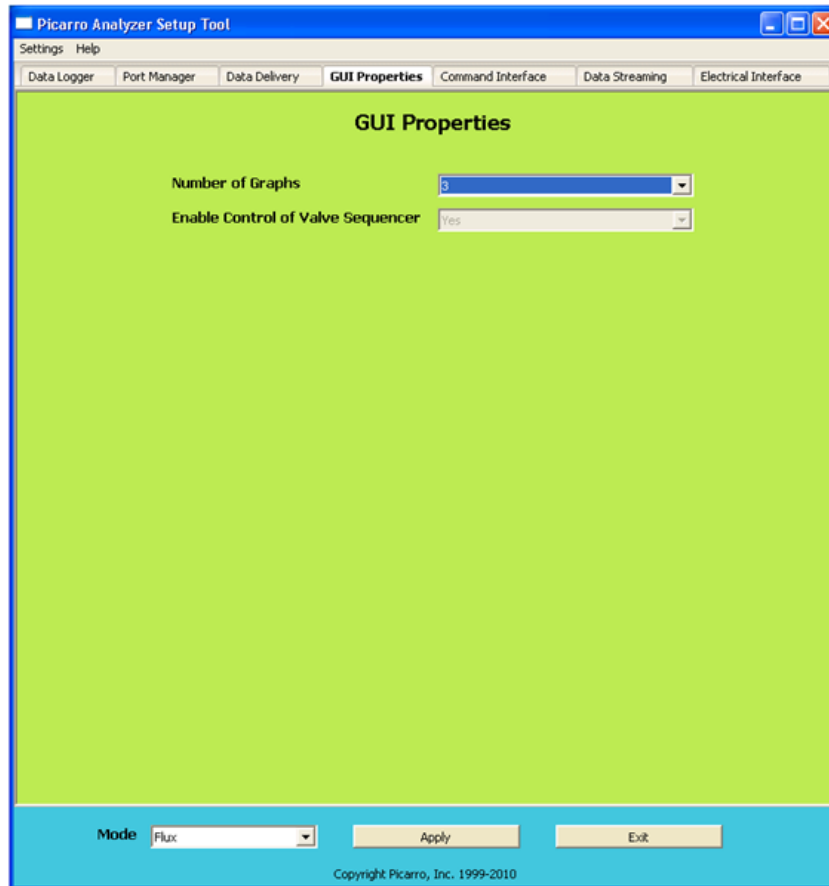
From: Sender's email

To: Receiver's email.

Subject: subject line of the email.

Data Directory: Location of the data you want email.

After making the appropriate edits, click "Apply" to put changes into effect and then "Exit" to close the window.



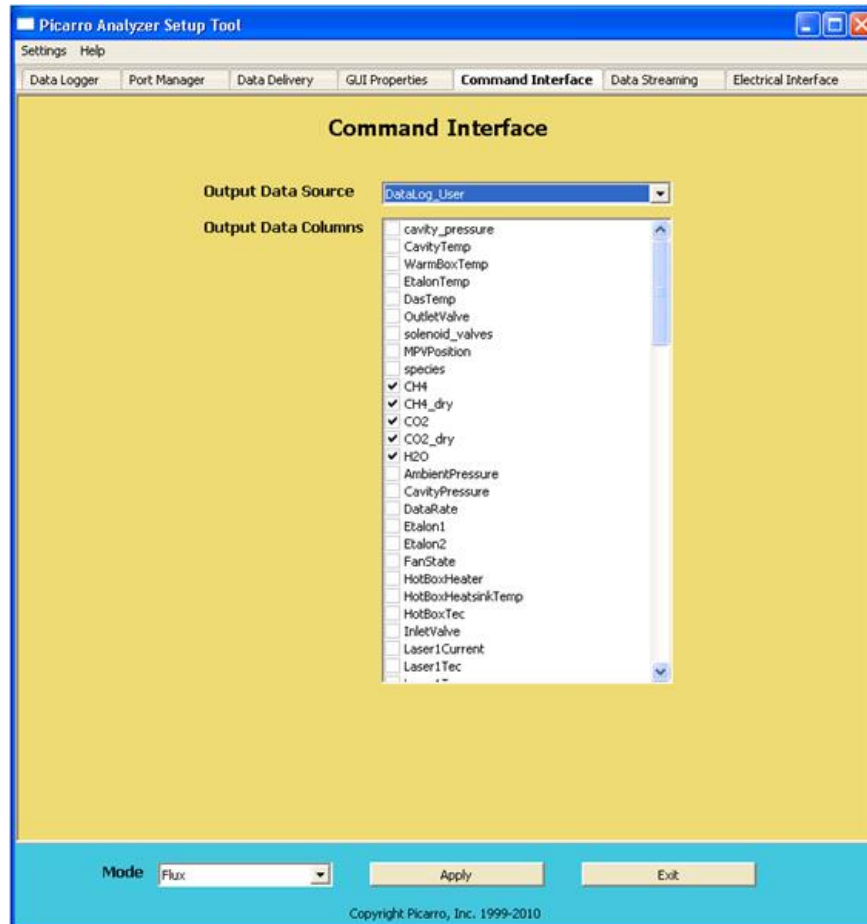
EDITING THE MAIN GUI'S PROPERTIES

The **GUI PROPERTIES** tab allows you to set the number of line graphs visible on the main GUI. It also allows you to enable the control of Valve Sequencer from the main GUI.

To make the Valve Sequencer menu item visible under the “Tools” menu of the main GUI:

1. Click on “Settings” of the “Setup Tool” window, and then “Switch to Service” mode.
2. Choose “Yes” next to “Enable Control Valve Sequencer” drop down menu on the “GUI Properties” tab.
3. Click “Apply” to put changes into effect and then “Exit” to close the window.

You should now be able to access the “Show/Hide Valve Sequencer GUI” menu from the main GUI under “Tools.”



SPECIFYING DIGITAL DATA OUTPUT FOR COMMAND INTERFACE

The **COMMAND INTERFACE** tab allows you to specify the data elements that are sent via COM port/TCP (specified in the PORT MANAGER tab).

To output data, the Command Interface needs to be sent commands.

After making the appropriate edits, click “Apply” to put changes into effect and then “Exit” to close the window.

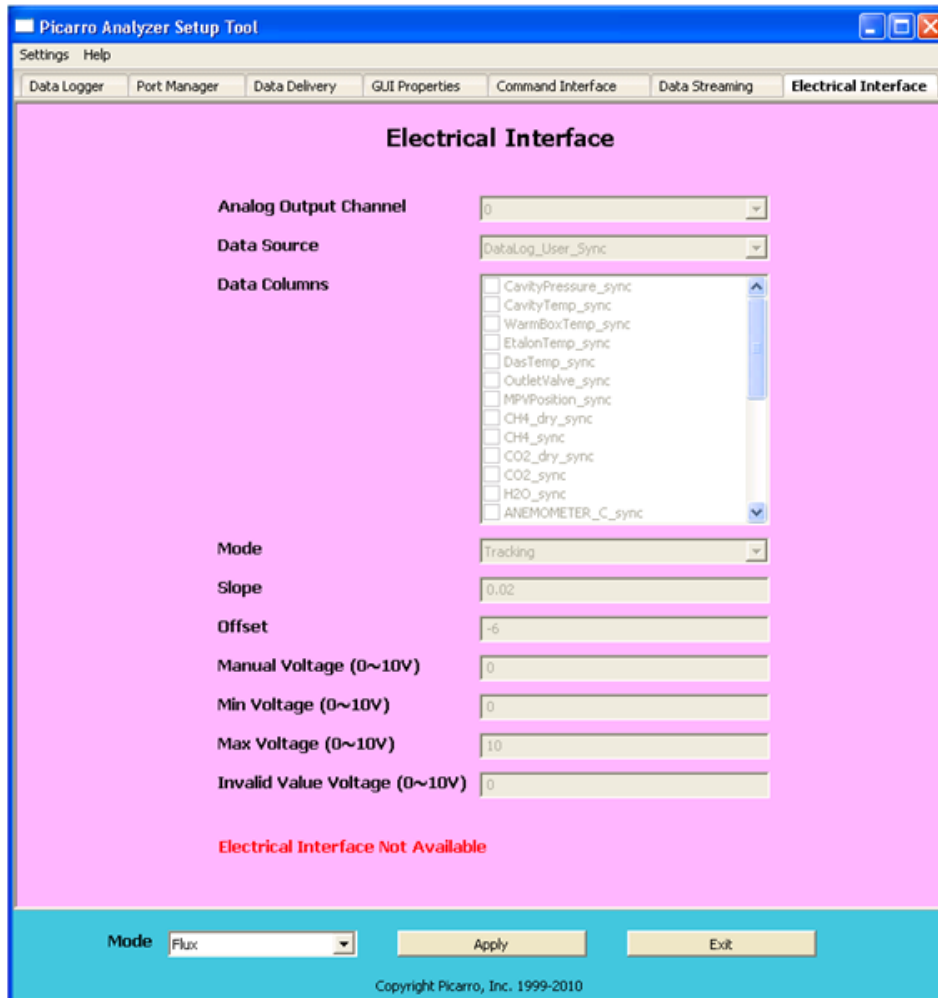


SPECIFYING DIGITAL DATA OUTPUT FOR DATA STREAMING

The **DATA STREAMING** tab allows you to specify the data elements that you want to send via COM port (specified from the PORT MANAGER tab).

Data Streaming outputs data continuously, whereas the Command Interface needs commands to output data.

After making the appropriate edits, click “Apply” to put changes into effect and then “Exit” to close the window.



CUSTOMIZING ANALOG OUTPUT CHANNELS

The Picarro analyzer may be optionally configured with an Electrical Interface Card (EIC) that provides up to 8 analog signals available to the user for monitoring various measurements results and analyzer parameters.

The **ELECTRICAL INTERFACE** tab allows you to customize each analog output channel.

After making the appropriate edits, click “Apply” to put changes into effect and then “Exit” to close the window.

This tab will be disabled if your analyzer was not configured to work with an analog peripheral.

21. BEST PRACTICES AND TIPS AND TRICKS

21.1 Sample Drying

The best measurement results can be achieved if the sample is dried prior to its admission to the CRDS analyzer. The use of a Nafion[®]-based drying method is highly recommended. One way of implementing a Nafion[®]-based drying system is to recirculate a portion of the dried sample gas to the outer shell side of the dryer, creating both a gradient in the water partial pressure and total gas pressure across the Nafion[®] membrane. This allows the dryer to function without needing a separate supply of clean dry air, as is typically required for Nafion[®]-based drying systems. If a source of clean dry air is available, a standard Nafion[®] drying system may be used. Such systems are commercially available from Perma Pure (www.permapure.com).

21.2 Rigorous Calibration for Highest Performance Measurements

A rigorous calibration procedure will result in the highest accuracy of the isotopic carbon measurements. For information about a more rigorous calibration procedure to improve the stability of carbon isotope measurements, please refer to the webinar Picarro delivered in 2015:

http://www.picarro.com/resources/webinars/improving_the_stability_of_carbon_isotope_measurements_in_carbon_dioxide_and_meth

This webinar explains the rationale behind this calibration procedure, and it outlines the steps recommended to achieve it.

21.3 Diluting High Concentration Standard Tanks

Often, calibration gas standards are only available in either pure form or in high concentration form. It is crucial, however, to make sure that the balancing gas of the high concentrated gas standard – and of any intended dilution thereafter – matches the CRDS analyzer mode chosen.

In most cases, the balancing gas should be synthetic air (Zero-Air), which is made up of 80% N₂ and 20% O₂. This balance gas is especially useful if the CRDS analyzer is used for atmospheric measurements. However, if the CRDS analyzer is interfaced to one of the Picarro front-ends (CM-CRDS, AM-CRDS, Aurora-CRDS), the carrier gas of choice is N₂. Therefore, the calibration gas standards intended for these hyphenated systems should strictly use N₂ as a balancing gas. The use of zero-air or a mixture of N₂ and zero-air gases will severely compromise the accuracy of the isotopic measurements.

To properly dilute standards, you will need to employ a set of mass flow controllers (MFC), one on each of the stock standard tank and one on the appropriate balancing gas tank (Zero-Air in most cases). These controllers help you measure the flow out of the stock gas standard tank and the appropriate balancing gas tank so that a known amount of diluting gas is added into the mixing volume. Great care should be taken in order to avoid any potential fractionation in isotopic composition of the standard gas, especially if it will be used concurrently as an isotopic standard. The mixing setup shown in the **Working With ^{13}C -Enriched Standards** section can be emulated for the concentration standard mixing purpose.

21.4 Working With ^{13}C -Enriched Standards

To prepare a series of less enriched ^{13}C gas standards from a stock ^{13}C -enriched gas standard lecture bottle for your multipoint calibration purposes, please follow the procedure below. For reference, the $^{13}\text{CO}_2$ -Enriched standard was purchased from Isotec, Inc., a division of Sigma-Aldrich (phone: 1-800-448-9760). The lecture bottle used here is at 99 atom % $^{13}\text{CO}_2$ enrichment:

1. Evacuate manifold and 3.8L mixing tank, as shown below.
2. Fill 25cc chamber with >99% $^{13}\text{CO}_2$ (10 – 75 Torr)
3. Open valve to 3.8L mixing tank
4. Fill 3.8L mixing tank with standard abundance CO_2 gas to 5 bar gauge
 - **Note:** Make sure that the standard abundance CO_2 is in a balance gas that matched the operating mode of the Picarro analyzer (Air in most cases, or N_2 in other cases)
5. Use as source for concentration and humidity testing
6. Obtain intermediate delta by subsequent dilution with standard abundance CO_2



22. SERVICE AND MAINTENANCE

The advanced, rugged design of Picarro analyzers provides stable, long-term operation with minimal service or maintenance. With the exception of the particulate filter, the analyzer is not user serviceable. Should it appear to malfunction, please refer to the **Troubleshooting** section or contact Picarro.

22.1 Particulate Filter

There are two in-line, sub-micron particulate filters before the measurement cavity. The first is user-replaceable. Replacement filters can be purchased from Picarro and installed by the user. **It is important to NEVER remove the second filter, which is directly attached to the cavity. Only change the filter immediately following the inlet at the back of the analyzer. Refer to the filter replacement procedure in this document for further details.**

The symptoms of a clogged filter can be analyzer reporting “pressure low,” or there being no flow into the instrument, causing unusual measurements. Filters can become clogged after years of use in dirty environments. If liquid water is accidentally sucked into the inlet line, it will clog the filter and impede the flow (usually for a few days) until it evaporates. If this occurs, it is important to NOT turn off the analyzer or replace the filter until it is dry. The reason for this is that the increased humidity due to liquid water in the filter can cause condensation on the optics if the analyzer is allowed to cool from its operating temperature. Often, after the filter dries, the analyzer will begin functioning normally, and a filter replacement is not necessary.

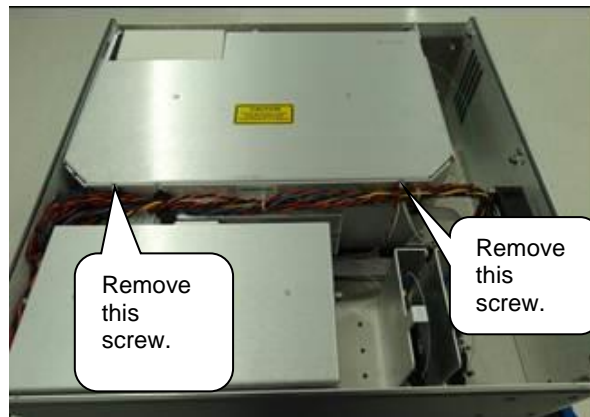
Picarro Analyzer Replacement Procedure for User-Serviceable Particulate Filter

Tools Required:

- 2 mm hex driver
- 9/16” open-end wrench
- 5/8” open-end wrench
- 11/16” open-end wrench

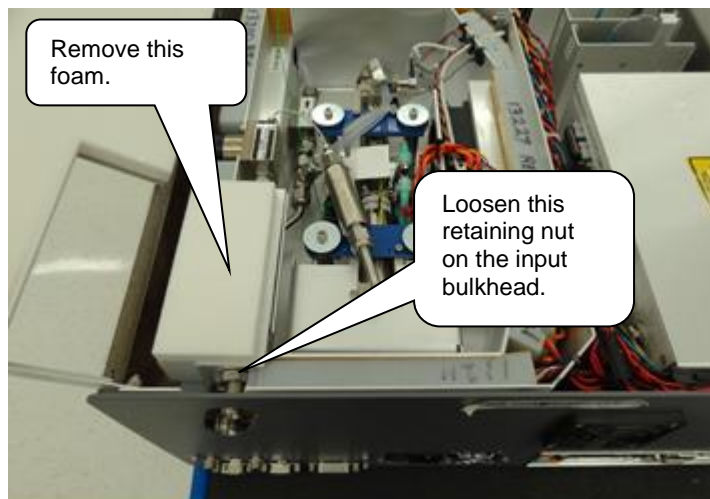
Removing the Old Particulate Filter

1. Move the analyzer to a clean work environment.
2. Using a 2 mm hex driver, remove the top lid of the analyzer by removing six M3 x 6mm socket flathead screws.
3. Loosen and remove the 2 screws on the inner long side of the bigger box. Open the lid (see below).



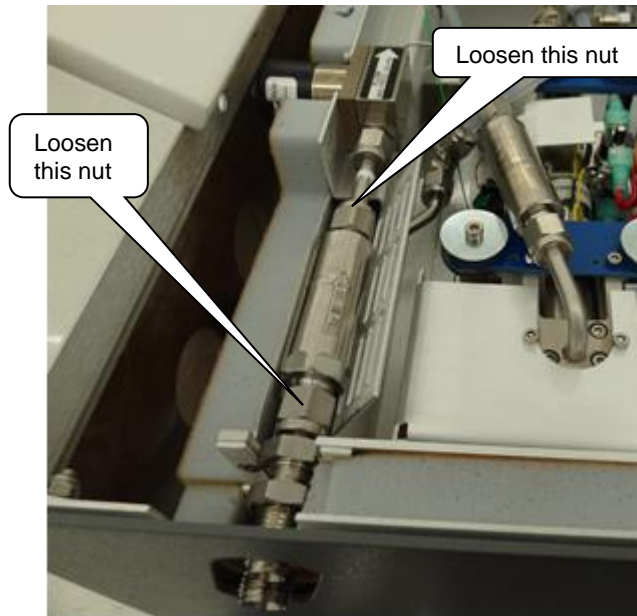
Remove 2 screws and open the lid of the bigger inner box within the analyzer.

4. Using a 5/8" wrench, loosen the retaining nut on the input bulkhead (about 1 full turn should be enough) (see picture after step 5).
5. Slide the foam towards left side of the analyzer (from the back of the analyzer) to remove it (see below).

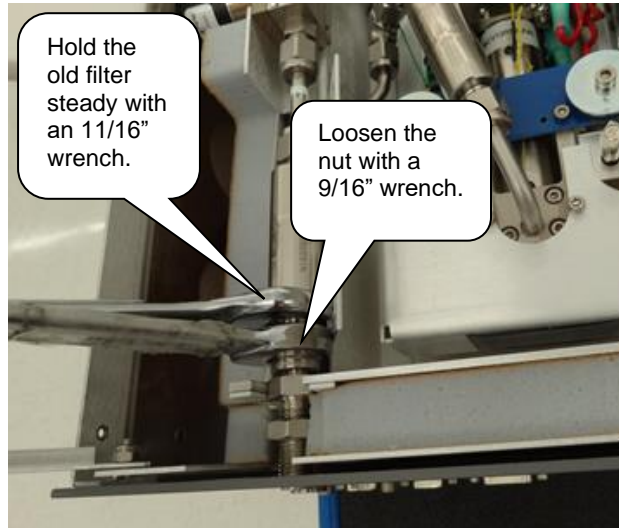


Remove the foam.

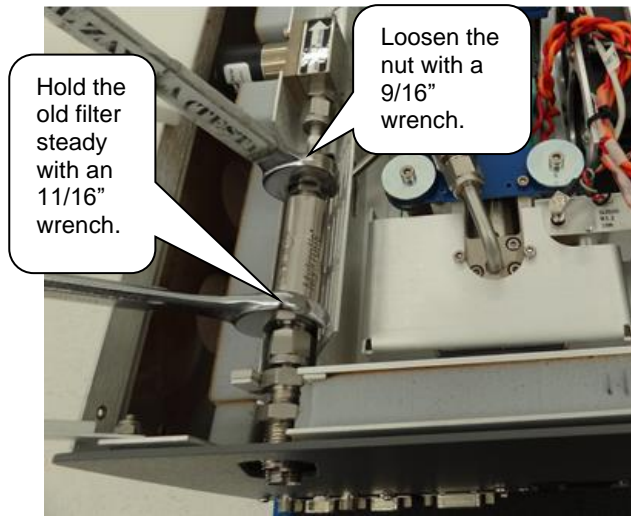
- Using the 9/16" and 11/16" wrenches, loosen two nuts that are connecting the filter to the analyzer (see next three pictures).



Loosen 2 nuts to remove the filter



Loosen the First Nut

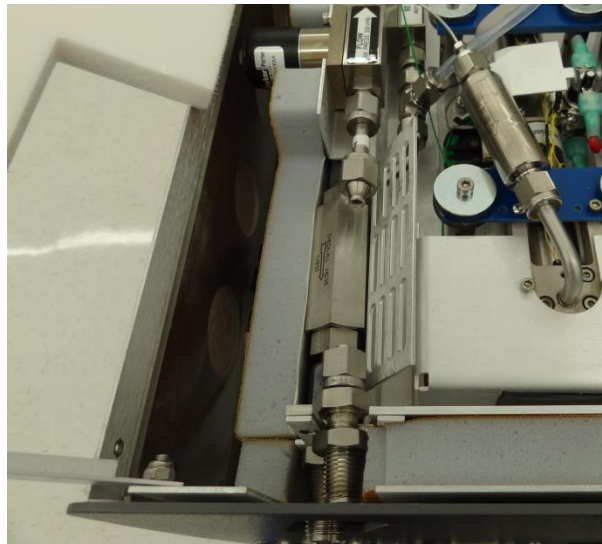


Hold the old filter steady with an 11/16" wrench.

Loosen the nut with a 9/16" wrench.

Loosen the Second nut

7. Slide the filter slightly towards the back of the analyzer and lift it out (see below).



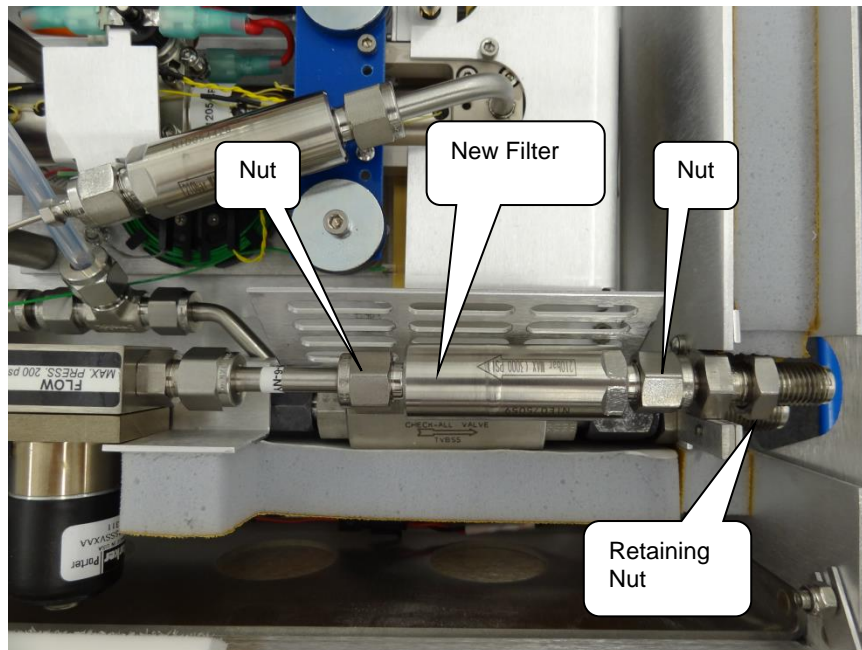
Remove the old filter

Installing the New Filter



Note: When re-attaching 1/4" Swagelok fittings, the nut should be hand-tightened and then turned an additional 1/8 of a turn using a wrench.

1. Remove the filter from its packaging.
2. Using the 9/16" and 11/16" wrenches, attach it to the two nuts. The arrow on the filter needs to point away from the back of the analyzer.



New filter attached. Make sure the arrow is pointing in the correct direction.

3. Using a 5/8" wrench, reposition the filter foam cover and tighten the retaining nut on the bulkhead fitting. The metal edge of the filter cover should be under the foam.
4. With a 2 mm hex driver, reattach the analyzer's top with 6 screws.

22.2 Cleaning

Clean the outside of the analyzer with a clean dry cloth. Only certified service technicians should access or clean the inside of the analyzer.

23. TROUBLESHOOTING

The following section lists problems that may be encountered during installation and operation of the analyzer. The corresponding step-by-step procedures provide resolution in most cases. If, after attempting these procedures, the problem remains unresolved, please contact Picarro Customer Service at (408) 962-3900 or support@picarro.com.

23.1 Power LED on Analyzer Does Not Illuminate

Context: Turning on the analyzer by momentarily depressing its front panel power switch should apply power. The green power LED is illuminated when it detects the correct power levels.

- (a) Check that the AC power cord is attached and plugged into a working outlet.
- (b) Check that the rear on-off switch near the AC power cord is in the on position.
- (c) Press and hold the front panel power switch for at least 5 seconds, as the analyzer may take several seconds to respond.

23.2 User Interface Program Does Not Start

Context: The computer may be configured to start the instrument and the associated user interface program automatically after it completes its boot-up sequence, or the program may be launched using the “Start instrument” icon on the desktop.

- (a) Communications problems with the analyzer may occur if the analyzer fails to initialize correctly on power up. Should the analyzer initialization process not complete correctly, shut down the instrument by shutting down the Windows operating system on the control computer: use the Start menu, select the red Shut down button and select “Shut down” in the drop-down box under “What do you want the computer to do?” Wait for the shutdown to complete normally and for the computer and analyzer to turn off completely. After a few seconds, restart the computer by momentarily depressing the power button.



NOTE: Do not simply restart Windows, since this does not cycle the power to the analyzer.

23.3 Sample Pressure Cannot Be Controlled To the Appropriate Value for Concentration Measurements

Context: Under normal operation, the cavity pressure is automatically locked to the correct value by means of electronically controlled inlet and outlet valves. The message “Pressure Locked” on the front panel display and the user interface indicates that the cavity pressure is at the appropriate value. Should either of the messages “Pressure high” or “Pressure low” be displayed, the cavity pressure is out of its correct operating range.

- (a) The “Pressure low” message indicates that there is insufficient gas available at the inlet of the analyzer. Check the inlet plumbing to the analyzer and ensure that the pressure at the inlet is within the specifications.
- (b) The “Pressure high” message indicates that gas cannot be removed from the analyzer at a sufficient rate. Check the vacuum line between the analyzer and the power vacuum unit for leaks. Failure of the vacuum pump, injecting dilution gas at excessive pressure, or excessive pressure at the inlet can also cause this problem.

23.4 User Interface Program “Freezes” and Does Not Update Graphs as Data are Collected

Context: The computer may become unresponsive causing the programs that control the analyzer to stop functioning. The computer and analyzer should be shut down and restarted.

- (a) Re-setting the computer and the instrument requires that the computer be shut down and restarted. If the computer responds to the mouse, a normal Windows shutdown may be carried out: use the Start menu, select the red Shut down button and select “Shut down” in the drop-down box under “What do you want the computer to do?” Wait for the shutdown to complete normally and for the computer and analyzer to turn off completely. After a few seconds, restart the computer by momentarily depressing the power button.
- (b) If the computer does not respond to the mouse, hold down the power switch on the front panel for a few seconds until the computer and the instrument turn off. After another few seconds, restart the analyzer by momentarily depressing the power button.

24. TRANSPORTATION & STORAGE

In the event that the instrument will be transported or stored, the following procedure can be used to prepare the instrument and repack it into the original carton.

24.1 Packing the Analyzer

1. Shutdown the instrument using the shutdown button, using the “prepare for shipment” option. Clean dry gas should be attached to the instrument prior to shutting down. This prevents condensation inside the system during storage or shipment.
2. Disconnect all tubing and electrical connections from the analyzer.
3. To prevent contamination and possible damage to the connector threads, place caps on all gas connections.
4. Place the analyzer in a plastic bag with a package of desiccant. Seal the bags with tape.
5. Pack the analyzer in the original shipping container ensuring that all of the foam pieces are in place to protect the analyzer during shipping.



CAUTION

When shipping or relocating the analyzer, it is important to protect it from mechanical shocks. Failure to do so can compromise its performance. When shipping the analyzer, use its original packaging only.

25. WARRANTY CLAIMS

In order to track incidents, and enable our customers to follow progress using the online Picarro Support Community, Picarro has adopted a case number structure for service requests. If you need help from Picarro, please contact us in accordance with these instructions.

1. Contact Technical Support to be assigned a case number.

Please call: +1 408 962 3991

Or email: support@picarro.com

To help us assist you, please provide the following information:

- Analyzer Serial Number
 - Your Institution
 - A description of the symptom, including error codes when relevant. This will, for example, help us understand whether the problem is related to hardware, software or sample handling.
 - Screen captures, data and photos can also help us.
 - We have a number of tools to help customer online and an internet connection will be extremely useful.
2. In some cases, Picarro is unable to resolve the situation remotely and a return is necessary. We will do our best to make this as painless as possible. The first step in the process is to secure a Return Material Authorization number. Your Technical Support representative will email a link to complete and submit our RMA form online. Upon completion of the form, the RMA number will be sent, automatically, as well as additional information regarding the return process, such as appropriate packing, insurance. Units returned without a valid RMA number will not be worked on until the RMA process is complete.

26. TECHNICAL SUPPORT

We are committed to helping our customers! Following the steps below will help us get to your problem faster.

- **Visit our popular Community forum at www.picarro.com/community.** It offers a wealth of information with answers to thousands of questions from our customers as well as useful links and updates to operate your analyzer optimally. If this is your first time visiting this forum, you will be asked to login using your username and password, which can be created easily with a special email invitation from Picarro. These invitations are automatically emailed to current customers upon purchase as well as to interested individuals; otherwise, please email us to request an invitation to community.
- **Email us at support@picarro.com.** We will get back to you right away. We highly recommend that you attach data and/or screen shots that you feel might help us diagnose your problem to your email.
- **Please activate the LogMeIn software before emailing us (see tutorial below).** This activation allows our technical engineers to get access to your analyzer's desktop remotely, allowing us to find and solve your problem quickly. This access can easily be turned off by the user.
- Call us at +1.408.962.3991

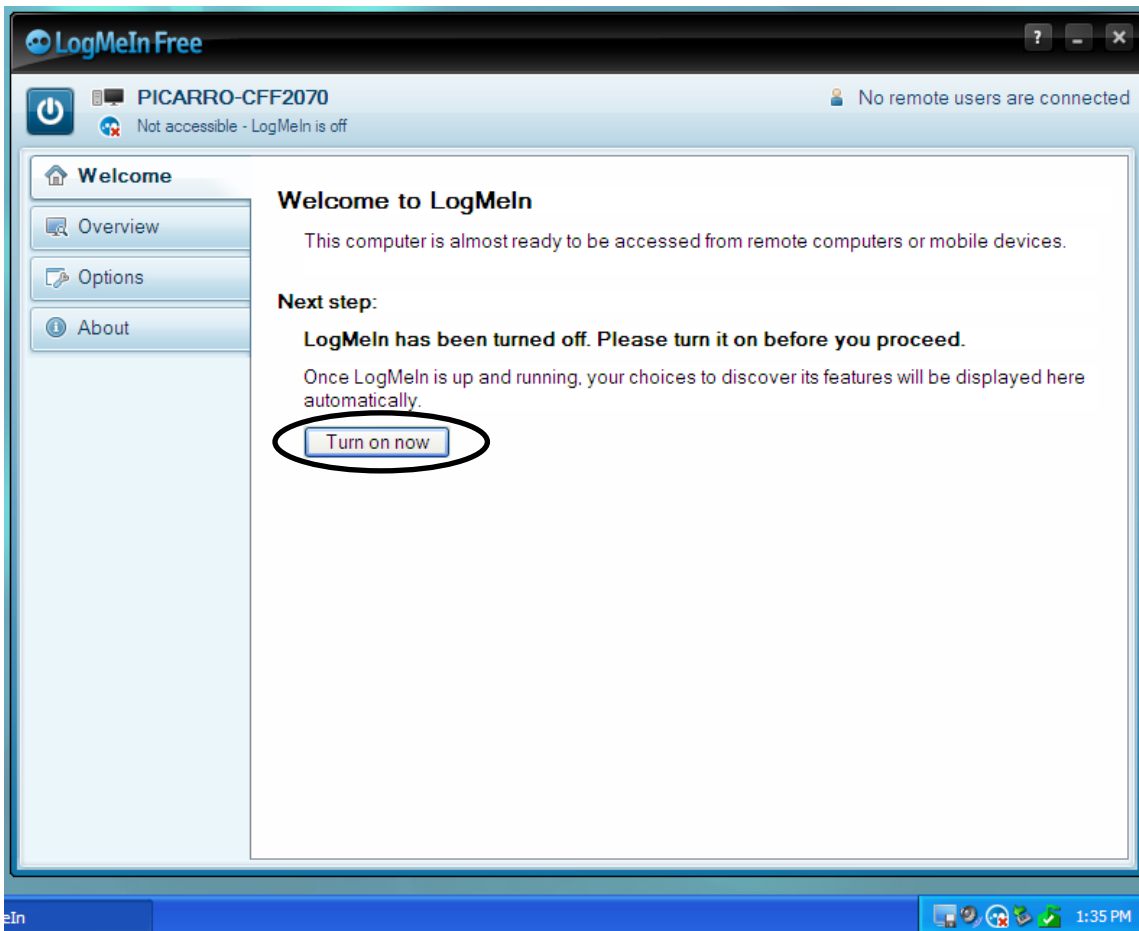
Picarro's website also offers links to application notes, customer conference presentations and posters, whitepapers, datasheets, and so much more. Please visit us at www.picarro.com.

To Activate the LogMeIn Software

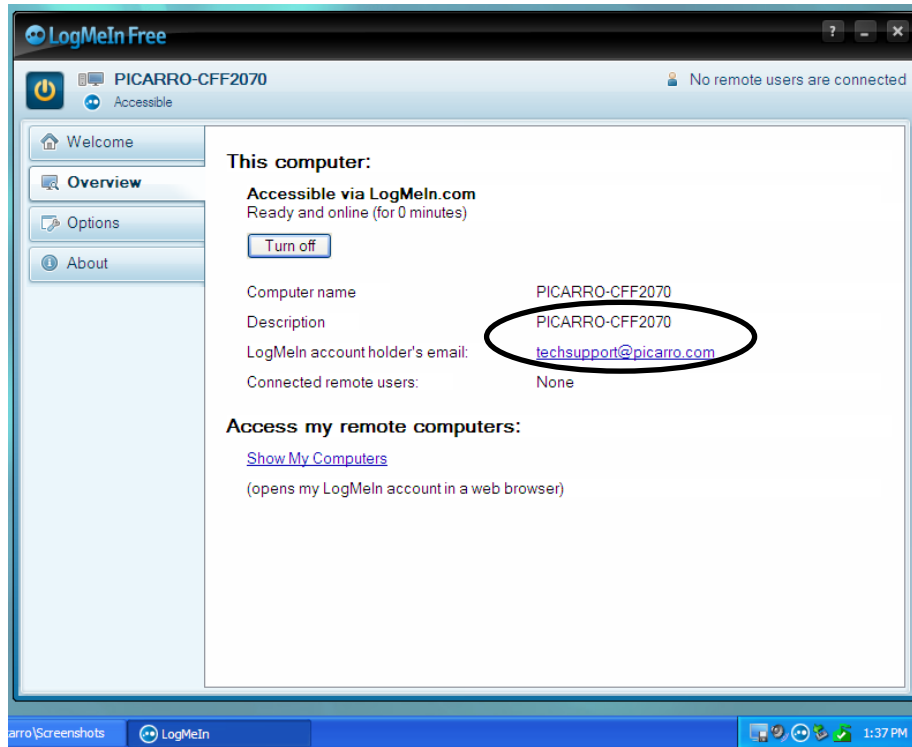
1. Click on the “LogMeIn” icon in the Windows task bar at the lower right hand corner. The “LogMeIn Free” window will pop up.



2. Click the “Turn on now” button.



3. Send both the “Description” and “LogMeIn account holder’s email” entries to Picarro, including a description of your problem. The “LogMeIn account holder’s email” shows the account that the instrument is currently on (default is an @picarro.com email).



4. After your problem has been solved, you can turn off Picarro’s access to your desktop by clicking on the “Turn off” button (shown on screenshot above).

27. APPENDIX A – UNDERSTANDING THE G2121-*i* ISOTOPIC CARBON DATA LOG

Picarro analyzers use cavity ring-down spectroscopy to measure the optical absorption of species like CO₂, CH₄, CO and H₂O (for more details on this process, see the section called **Cavity Ring-Down Spectroscopy**). The software uses the absorption measurements to generate an optical spectrum of species absorption at particular wavelengths of light.

Algorithmic fitting of this optical spectrum generates information that can be used to calculate species concentration and isotopic abundance. The information in this section first provides more detail about the computations that convert CRDS absorption measurements to isotopic ratio anomalies in delta notation. Then it explains what information is recorded in the data log and how to reconstruct (insofar as this is possible) the sequence of calculations leading from the outputs of the spectroscopic fitter to the final delta values. Understanding this process may be of use in diagnosing anomalous or unexpected results.

This discussion will be in the context of absorption measurements for ¹²C¹⁶O₂ and ¹³C¹⁶O₂ and the corresponding isotopic abundance ratio, δ¹³C.

27.1 Relationship between Absorption and Isotopic Abundance

The analysis software for Picarro isotopic CO₂ analyzers arbitrarily labels absorption values for ¹²C¹⁶O₂ and ¹³C¹⁶O₂ as “Peak87” and “Peak88,” respectively. To a first approximation, the ratio of the peak absorption values is proportional to the ratio of isotopic abundances.

Isotopic abundance is typically expressed in delta notation of the least abundant isotope, δ. The relationship between measured absorption values (denoted for now as α₈₇ and α₈₈), and delta is a linear one:

$$\delta^{13}\text{C (in permil)} = A (\alpha_{88} / \alpha_{87}) + B. \tag{1}$$

Ideally, the constant B would be equal to -1000; however, real instruments have offsets that result in B deviating slightly from that value. The constant A lumps together many spectroscopic parameters, as well as the nominal ¹³C/¹²C abundance ratio. In practice, A and B must be determined from calibration standards. For instructions on how to calibrate the instrument, see the **Initial Analyzer Calibration** section.

27.2 Computation of $\delta^{13}\text{C}$ From the Spectroscopic Data Recorded by the G2121-i: The Case of CO_2

Algorithms in Picarro analysis software determine best-fit peak absorption. They also account for spectral features generated by other species in the sample that directly or indirectly alter the desired spectrum. For example, methane contributes weakly to the absorption at the frequency of our Peak88, and water vapor contributes to the absorption at the frequency of our Peak87. Water vapor also contributes an indirect interference: it changes the shape of measured spectral lines, which affects the proportionality of the relationship between absorption and molecular abundance.

The effects of these interferences are small compared to the absorption values that we measure, but they are not negligible when computing isotope ratios at the permil level and below. The best approach we have found for dealing with interferences is to make auxiliary measurements of the interfering species at frequencies where they absorb strongly enough to be measured well. Then we use this information to correct the peak values reported by the algorithmic fit of the CO_2 spectrum. The magnitude of the correction is determined empirically, by measuring the spectrum of a sample containing CO_2 from a cylinder, with invariant isotopic composition, while changing the concentration of the interfering species.

All of the outputs from the algorithmic analysis, as well as derived quantities such as $\delta^{13}\text{C}$, are stored in “private” data log files in the directory tree `C:\Picarro\G2000\Log\Archive\DataLog_Private`.

Columns in the private data log can be used to follow how the algorithmic outputs are converted to an isotopic ratio. The starting places for tracking these calculations are the best-fit absorption values for water vapor, $^{12}\text{C}^{16}\text{O}_2$, methane, and $^{13}\text{C}^{16}\text{O}_2$. These values are entered in the log columns `peak75`, `peak87_baseave`, `ch4_splinemax_for_correction`, and `peak88_baseave`, respectively.

The water vapor concentration is derived directly from `peak75` without any further correction.

The $^{12}\text{C}^{16}\text{O}_2$ peak is corrected for direct water interference to give a “spectroscopic” peak value:

$$\text{peak87_baseave_spec} = \text{peak87_baseave} + \text{C87_water} * \text{peak75}. \quad (2)$$

The methane peak is also corrected for water interference:

$$\text{ch4_splinemax_spec} = \text{ch4_splinemax_for_correction} + C_{\text{ch4_water}} * \text{peak75}. \quad (3)$$

Finally, the weak $^{13}\text{C}^{16}\text{O}_2$ peak is corrected for instrumental offset, direct interferences from methane and water vapor, and the indirect interference that arises from the humidity dependence of the absorption line width:

$$\begin{aligned} \text{peak88_baseave_spec} = & \text{peak88_baseave} + C_{88_offset} \\ & + C_{88_ch4_linear} * \text{ch4_splinemax_spec} \\ & + C_{88_ch4_h2o_bilinear} * \text{ch4_splinemax_spec} * \text{peak75} \\ & + C_{88_water_linear} * \text{peak75} \\ & + C_{88_bilinear} * \text{peak75} * \text{peak87_baseave_spec} \\ & + C_{88_quad_linear} * \text{peak75} * \text{peak87_baseave_spec}^2 \end{aligned} \quad (4)$$

The coefficients C_{xxx} appearing in Equations (2 - 4) are stored in the file C:\Picarro\G2000\InstrConfig\Calibration\InstrCal\FitterConfig.ini with names that basically match the subscripts appearing in Eq. (4).

The “spectroscopic” peak values $\text{peak87_baseave_spec}$ and $\text{peak88_baseave_spec}$ are substituted for α_{87} and α_{88} in Eq. (1) to produce the “raw”, i.e. not averaged, value of $\delta^{13}\text{C}$, which is reported as Delta_Raw . **Note:** α_{88} is actually the average of two measurements of $\text{peak88_baseave_spec}$. For more information on this averaging, see the section **Sequence of spectroscopic measurements for the G2121-i algorithm** below.

The only further processing of the isotopic ratio is time averaging. For example, each reported value of Delta_5min is the simple average of all reported values of Delta_Raw in the 5-minute interval ending with the current measurement.

The final isotopic ratio and the quantities that appear in Eq. (4) – but not all of the uncorrected fitter outputs that go into the computation of the quantities in Eq. (4) – are reported in the user data logs in the directory tree C:\UserLog\DataLog_User.

The calibration constants A and B in Eq. (1) are stored in the file C:\Picarro\G2000\InstrConfig\Calibration\InstrCal\InstrCal.ini, where they are labeled $\text{concentration_iso_slope}$ and $\text{concentration_iso_intercept}$, respectively.

The absorption of the $^{12}\text{C}^{16}\text{O}_2$ line is also used to report the “concentration” (more properly, mole fraction) of $^{12}\text{C}^{16}\text{O}_2$, through the following sequence of transformations.

Provisional concentrations are reported as:

$$\text{CO2_12_ppm_wet} = 1.68307 * \text{peak87_baseave_spec} \quad (5)$$

and

$$\text{CO2_12_ppm_dry} = \text{CO2_12_ppm_wet} / \text{wd_ratio}, \quad (6)$$

where

$$\text{wd_ratio} = 1 + (0.01002 * \text{peak75}) * [-0.0141 - 3.065 \times 10^{-4} * (0.01002 * \text{peak75})] \quad (7)$$

is an empirical correction factor that relates the dry mole fraction to the mole fraction measured in moist air by accounting for dilution and the effect of water vapor on the line width.

The calibrated $^{12}\text{C}^{16}\text{O}_2$ mole fraction is reported as:

$$12\text{CO2_dry} = A_{12} * \text{CO2_12_ppm_dry} + B_{12} \quad (8)$$

where the coefficients A_{12} and B_{12} are stored in the file C:\Picarro\G2000\InstrConfig\Calibration\InstrCal\InstrCal.ini, and labeled concentration_c12_gal_slope and concentration_c12_gal_intercept, respectively.

The quantities 12CO2_dry and Delta_Raw are the primary analytical quantities reported by the instrument. They are also the quantities that are suitable for practical user calibration. For instance, traceable primary standards of $\delta^{13}\text{C}$ are maintained by national standards laboratories, whereas there are no primary standards for $^{13}\text{C}^{16}\text{O}_2$ mole fraction. We recommend that the users of the G2121-i consider only $^{12}\text{C}^{16}\text{O}_2$ mole fraction and $\delta^{13}\text{C}$ as primary, calibrated quantities.

Other quantities, such as $^{13}\text{C}^{16}\text{O}_2$ mole fraction and the abundance ratio of ^{13}C to ^{12}C should be regarded as derived quantities, computed from the $^{12}\text{C}^{16}\text{O}_2$ mole fraction, $\delta^{13}\text{C}$, and the relation

$$\delta^{13}\text{C} \text{ (in permil)} = 1000 \times [(R_{\text{sample}}/R_{\text{reference}}) - 1] \quad (9)$$

where R_{sample} and $R_{\text{reference}}$ refer to the isotopic $^{13}\text{C}/^{12}\text{C}$ ratios of the sample and reference, respectively. If the delta scale is calibrated according to the VPDB scale, then $R_{\text{sample}} = R_{\text{reference}} = 0.0111802$ (see, for instance, Werner and Brand, "Referencing strategies and techniques in stable isotope ratio analysis," *Rapid Commun. Mass Spectrom.* 2001; **15**: 501—519). Note also that frequent calibration with accurate concentration and isotopic ratio standards should be performed to obtain the most accurate results. Entries in the data log for $^{13}\text{C}^{16}\text{O}_2$ mole fraction ^{13}C to ^{12}C ratio are approximate values only and should not be used in place of Eq. (9).

27.3 Ordering of Entries in the Data Log

This section provides more details about the organization of the data logs and the sequence in which new data is entered in the logs.

To understand the structure of the data log, we must first understand the sequence of measurements that the analyzer makes to acquire the complete data set needed for the calculation of delta. The CRDS spectrometer acquires spectra of the molecular lines of interest in an endlessly repeating series of measurements. For a given instrument, these measurements always follow the same sequence. In the case of the isotopic CO_2 analyzer, species measurements alternate between $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$, with less frequent measurements of water vapor and methane. The sequence of spectra gathered is: $^{13}\text{C}-^{12}\text{C}-^{13}\text{C}-^{12}\text{C}-^{13}\text{C}-\text{CH}_4-^{13}\text{C}-^{12}\text{C}-^{13}\text{C}-^{12}\text{C}-^{13}\text{C}-\text{H}_2\text{O}$.

For each spectrum acquired, the analysis algorithm also reports an identification that specifies which spectral region was measured. These identification numbers are labeled SpectrumID in the .dat files. (See **File Management** section to learn more about these files.)

In this case, SpectrumID=105, 106, and 11 designate the $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, and H_2O regions, respectively. The methane region has two spectrum identification numbers, 25 and 29, corresponding to two different data sets that the analyzer can acquire. The first is designed for high precision measurements of low methane concentrations (< 15 ppm approximately), and the second permits measurement of higher methane concentration but with poorer precision.

Each of these measurements results in data that is needed for the delta calculation, but not every measurement results in an immediate entry in the data log. Data that is not immediately logged is not lost; rather, it is stored and logged at a later time.

In the case of this analyzer, data is logged after a $^{12}\text{CO}_2$, methane, or water vapor measurement, but not after a $^{13}\text{CO}_2$ measurement. Instead, the $^{13}\text{CO}_2$ fit outputs are entered together with the results of the next spectrum to be acquired. The sequence of measurements and data log entries is indicated schematically in the table below.

SpectrumID	106	105	106	105	106	25/29	106	105	106	105	106	106	11
Species	$^{13}\text{CO}_2$	$^{12}\text{CO}_2$	$^{13}\text{CO}_2$	$^{12}\text{CO}_2$	$^{13}\text{CO}_2$	CH_4	$^{13}\text{CO}_2$	$^{12}\text{CO}_2$	$^{13}\text{CO}_2$	$^{12}\text{CO}_2$	$^{13}\text{CO}_2$	$^{13}\text{CO}_2$	H_2O
New log entry	NO	YES	NO	YES	NO	YES	NO	YES	NO	YES	NO	NO	YES
New delta	NO	YES	NO	YES	NO	NO	NO	YES	NO	YES	NO	NO	NO

27.4 Sequence of Spectroscopic Measurements for the G2121-I Algorithm

The $^{13}\text{CO}_2$ fit outputs are entered with the next $^{12}\text{CO}_2$ spectrum acquired to account for concentration differences between measurements. If total CO_2 concentration changes between absorption measurements of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$, then those absorption values cannot be used to calculate delta ratio. Concentration impacts the reported delta value, and this means that change of concentration could be misinterpreted as a change in delta.

To deal with variable total CO_2 concentration, Picarro uses linear interpolation to derive $^{13}\text{CO}_2$ absorption at the time of a $^{12}\text{CO}_2$ measurement. The analysis software averages two measurements of $^{13}\text{CO}_2$ absorption and computes the ratio of this average to the $^{12}\text{CO}_2$ absorption measured between the ^{13}C measurements. This removes any spurious effect of a linear change in concentration on the reported isotopic ratio.

Picarro refers to the averaging of $^{13}\text{CO}_2$ measurements, and subsequent comparison to $^{12}\text{CO}_2$ absorption, as “bookending.” The logging scheme explained at the end of the previous section means that every line of the data log with SpectrumID = 105 (i.e. $^{12}\text{CO}_2$) contains a new, properly bookended value of delta. However, because no entry is recorded for the $^{13}\text{CO}_2$ measurements immediately following the measurements of methane and water vapor, not enough information is preserved to completely reconstruct the bookending procedure. That is, one of the values of peak88_baseave_spec that was used to compute the first value of α_{88} following a water or methane measurement is not retained in the log.