PICARRO

L2140-i and L2130-i Isotopic Water Analyzer and Peripherals Installation and Operation 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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READ BEFORE USING THE MANUAL

This manual includes information on how to install the water analyzer in its most common configuration (Analyzer with Vaporizer). For other configurations (Autosampler, SDM, IM, MCM, CWS), please refer to those manuals directly:

- **A0325 Autosampler User Manual** (PN 40025)
- **A0214 MCM User Manual** (PN 40022)
- **A0213 Induction Module-CRDS Setup User Manual** (PN 40033)
- **A0101 SDM User Manual** (PN 40-0005)
- **A0217 Continuous Water Sampler Installation and User Manual** (PN 40-0003)

Please note that the High Throughput Vaporizer was discontinued in December 2013. Picarro continues to support these vaporizers in the field, but they are no longer manufactured. If you require installation instructions for the High Throughput Vaporizer, please refer to an older version of this manual.

For information on Picarro's measurement technology, see the section; **INTRODUCTION TO TECHNOLOGY**

Be selective when following the manual by only referring to the sections that refer to the configuration of your interest. To start, choose one of the setups in the table below based on your configuration.

Refer to **Table of Contents** to find the location of any of the chapters described below.

SETUP	USE CASE	SETUP CHAPTER
Basic Water Analyzer	This mode is used to measure ambient vapor which does not require any calibration with liquid standards.	See **Setup Configuration | Basic Water Analyzer Setup.** This setup requires a CRDS analyzer.
Dual Mode	This mode is used for measurement of ambient vapor coupled with automated injection of liquid calibration standards. The measurement mode alternates between analyzing ambient vapor and liquid standards based on a user defined sequence.	See **Setup Configuration | Dual Mode Setup.** This setup requires A0211 High Precision Vaporizer, A0912 Dual Mode Configuration hardware and software for vapor calibration and an Autosampler. The mode uses high precision method for liquid calibration. Each injection cycle takes 9 minutes.
Manual Mode	This mode is used for semi-automated measurement of liquid water samples with maximum precision.	See **Setup Configuration | Manual Mode Setup.** The setup requires an A0211 High Precision Vaporizer and A0322 Syringe Guide. User manually injects samples after prompt. The control of the vaporizer and the analysis of liquid samples are automated. Each injection cycle takes 9 minutes.
Picarro Autosampler and High Precision Vaporizer (A0211)	This setup is used for automated injection of liquid waters. It consists of two modes that utilize the same hardware: High Precision Mode and High Throughput Mode.	See **Setup Configuration | Picarro Autosampler – High Precision Vaporizer (A0211) Setup.** The setup can operate in five measurement modes: High Precision, High Throughput, Standard*, Express*, and Survey*. ● **High Precision*:** Measures liquid water samples with maximum precision. Liquid samples are automatically injected and analyzed. Each injection cycle takes 9 minutes. ● **High Throughput*:** Used for faster measurement of liquid water samples with good precision. Liquid samples are automatically injected and analyzed. Each injection cycle takes 4 minutes. High Precision and High Throughput Coordinator Modes operate in the exact same fashion except that the steps of sample preparation and

		analysis are faster in the high throughput coordinator mode. ● **Standard**:** Used to measure liquid water samples with maximum precision. This coordinator must be run in either the “iH2O N2” mode or the “iH2O Air” mode. Automatically injects and analyzes liquid samples. Each injection cycle takes 9 minutes. ● **Express**:** Used for faster measurement of liquid water samples with good precision. This coordinator must be run in either the “iH2O N2” mode or the “iH2O Air” mode. Automatically injects and analyzes liquid water samples. when using the Express coordinator, we recommend 10 injections, the first 6 injections take 1.5 minutes each, while the last 4 injections take 5 minutes each. The first 7 injections will be discarded to achieve the optimal memory reduction. ● **Survey**:** Used for super-fast measurements of large sample batches at moderate precision and enables more efficient sample sorting. By manually rearranging samples accordingly, one can reduce the memory effect between adjacent sample. Automatically injects and measures liquid samples. This coordinator must be run in either the “iH2O N2” mode or the “iH2O Air” mode *Only available without Coordinator software upgrade **Only available with Coordinator software upgrade

1. INTRODUCTION TO TECHNOLOGY

Picarro analyzers use time-based, optical absorption spectroscopy of the target gases to determine concentration in a sample. They are based on wavelength-scanned cavity ring-down spectroscopy (WS-CRDS), a technology in which light travels many times through the sample, creating a very long effective path length for the light to interact with the target gas, 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., CO_2, H_2O, H_2S, NH_3) and isotopologue (e.g., $H_2{}^{18}O$, $^{13}CO_2$, $^{15}N^{14}N^{16}O$) 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.

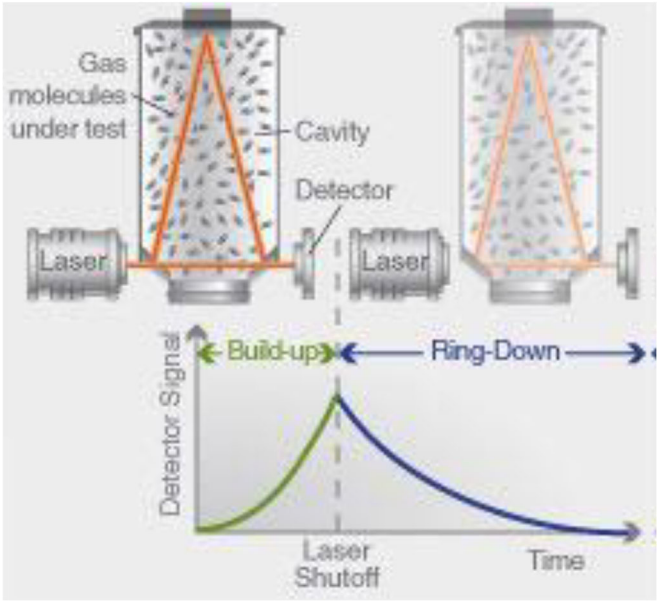
Conventional infrared spectrometers are typically only sensitive enough to detect trace gases at levels in the part-per-million. Cavity Ring-Down Spectroscopy (CRDS), on the other hand, is one thousand to one million more times sensitive.

The increased sensitivity of CRDS is due to the design of the sample cavity and the time-based measurement. In the cavity, a series of mirrors reflects the infrared light through the sample, increasing the path length. For a Picarro cavity of only 25 cm in length, the effective path length of the cavity can be over 20 kilometers.

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.

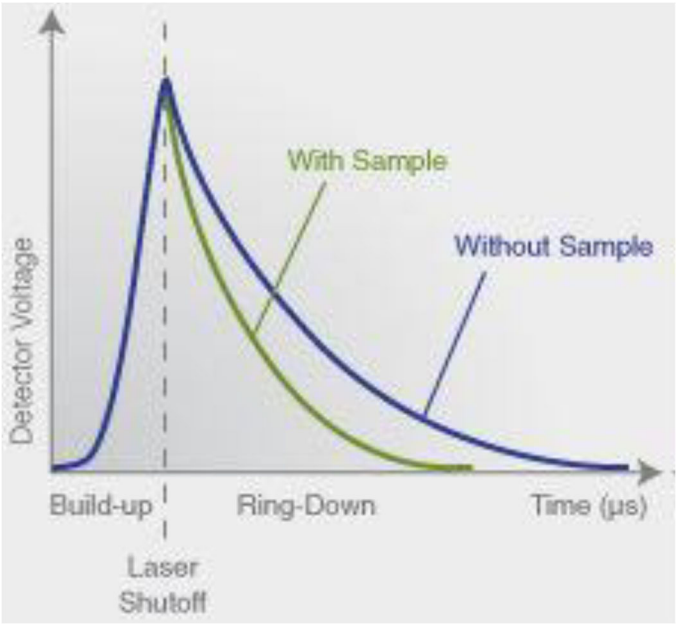
1.2 Relating ring-down time to absorption intensity

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. A cavity can be empty if it contains no gas; it will also appear empty if the molecules of the sample inside the cavity do not interact with the specific wavelength of light.

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

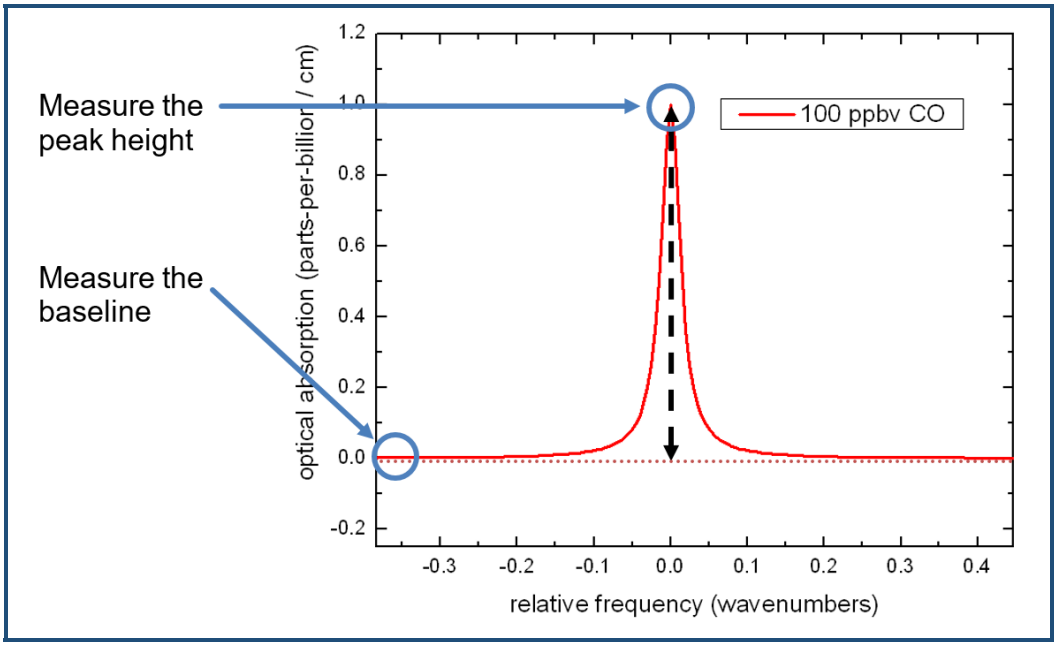


1.3 Converting absorption intensity to concentration

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



However, 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:

- A 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, measured at wavelengths just before peak absorption, at peak absorption, and just after peak absorption, as the absorbance returns to the baseline.

- 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. Small temperature and pressure instabilities can result in large concentration errors due to fluctuating peak heights and baselines. 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.

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

3. ACRONYMS

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

Acronym	Definition
cm	centimeters
CRDS	Cavity Ring-Down Spectroscopy
CWS	Continuous Water Sampler
DAS	Data Acquisition System (the Analyzer)
DIO	Digital Input and Output Between the Analyzer and the Autosampler. DIO Tells the Autosampler to prepare for an injection, and also to do an injection. Additionally, DIO is the place where the autosampler notifies that an injection has been made.
GUI	Graphical User Interface
H_2O	Water
HB	Hotbox
IM	Induction Module
MCM	Micro-combustion Module
mm	millimeters
ppb	Parts Per Billion
ppm	Parts Per Million
SDM	Standards Delivery Module
WB	Warm box
WLM Purge Port	Wavelength Monitor Purge Port. The Port on the Analyzer the dry gas connects to. This keeps the spectroscopy accurate.

Acronym	Definition
” (as in 1/4”)	Inches
°C	degrees Celsius
‰	per mil

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.

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

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.

WARNING

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

CAUTION

The analyzer contains no user serviceable components except the analyzer particulate filter and vaporizer injection port septum. 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.

WARNING

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 and pump weighs 45 lbs (20.4 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.

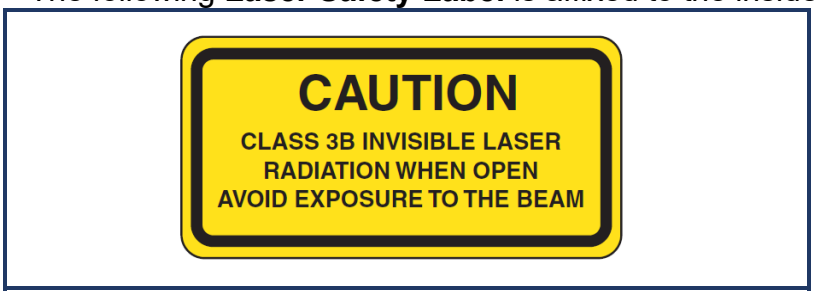
The following Laser Safety Label is affixed to the outer cover of the analyzer.

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



WARNING

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.

NOTE

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

5.2 Unpack the Shipping Boxes

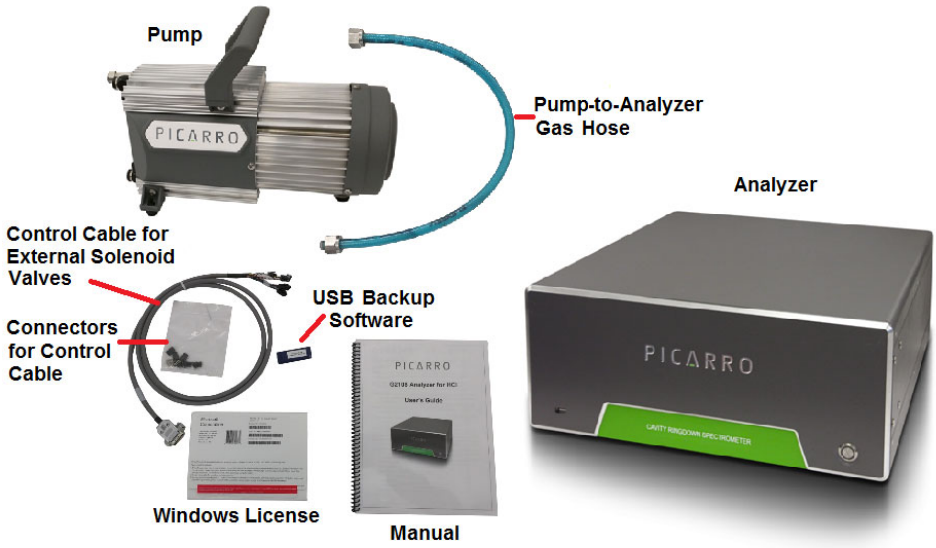
This section describes the contents of the shipping boxes:

- **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.**

WARNING

This analyzer weighs 45 lbs (20.4 kg). Use the technique outlined in the General Safety section on page 19 when lifting or moving the analyzer.

Figure 5: 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. The pump automatically adjusts to local voltage.
Vacuum Hose (1)	Hose to connect the pump to the analyzer.
Pump Manual (1)	Detailed instructions for pump.

6. ANALYZER OVERVIEW

6.1 Intended Use

The L2140-*i* Isotopic Water Analyzer measures concentrations of $\delta^{18}O$, $\delta^{17}O$, δD and ^{17}O-excess using Picarro's patented Cavity Ring-Down Spectroscopy (CRDS).

The L2130-*i* Isotopic Water Analyzer measures concentrations of $\delta^{18}O$ and δD.

The analyzer can be deployed for monitoring applications in a lab or in the field, allowing in-situ analysis of trace and ambient amounts of isotopic water.

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.

6.3 Analyzer Specifications

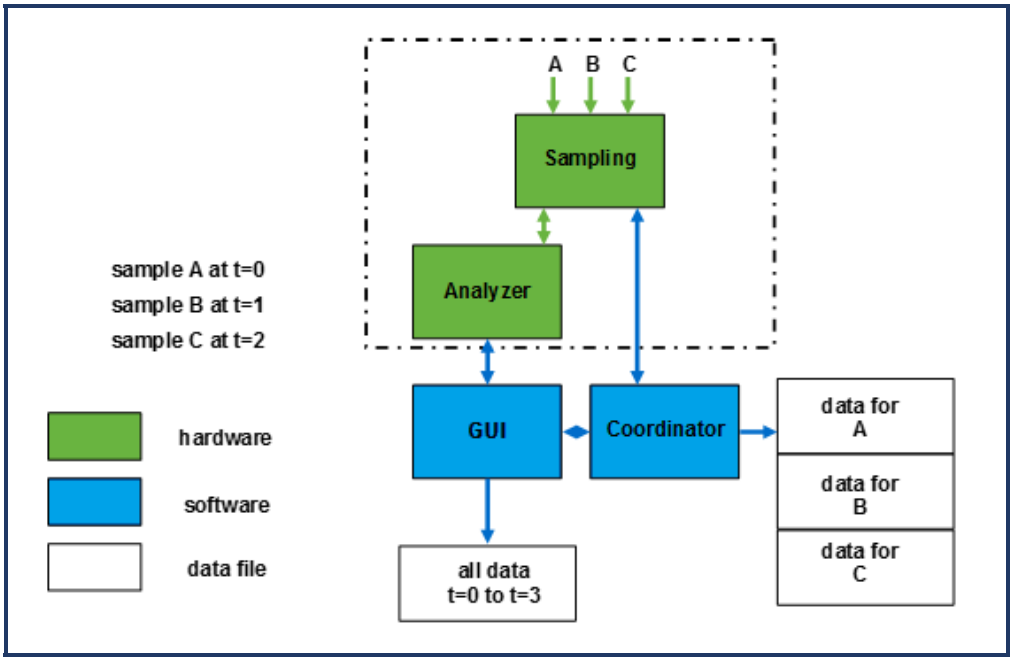
Weight	45 lbs (20.4 kg)
Dimensions	Analyzer: 17" w x 7" h x 17.5" d (43.2 x 17.9 x 44.6 cm), not including 0.5" feet External Pump: 6.1" w x 8.7" h x 13.6" d (15.5 x 22 x 34.5 cm)
Temperature Range	–10 °C to 45°C (vapor sample), 10 to 35°C (liquid sample and system operation) –10 °C to 50 °C (storage)
Sample Pressure	300 to 1000 Torr (40 to 133 kPa)
Sample Flow Rate	~40 sccm at 760 Torr, no filtration required
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 **Startup Power** **Steady-state Power** **Mains Voltage Fluctuation**	100 to 240 VAC; 47 to 63 Hz (auto-sensing) <375 W at start-up (Analyzer and Pump) 120 W (Analyzer), 150 W (Pump) Steady-state operation ±10% of the nominal voltage

Mains supply voltage fluctuation	±10% of nominal voltage
Minimum Rated Circuit Current	10 A @115 VAC, 5 A @230 VAC
Liquid Ingress Protection	None

6.4 Analyzer Operation Flow Diagram

To measure discrete samples (such as individual gas bags) or from multiple locations (when switching valves draw in ambient air from different heights), 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. Figure 9 shows analyzer operation as a flow diagram.

Figure 6: Analyzer Operation Flow Diagram



1. The samples A, B, and C are introduced into the analyzer sequentially.
2. The timing of sample introduction is controlled by coordinator or valve sequencer software.
3. The analyzer measures samples continuously and reports the data to the GUI.
4. The GUI 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, the data is reported as a function of sample.

5. Before shutdown, Picarro recommends flowing clean dry air (CDA) through the analyzer for several minutes. This prevents moist gas in the cavity from condensing on the optics as the analyzer cools.

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

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.

WARNING

Do not connect USB hubs or unauthorized USB devices (except flash drives, mice and keyboards) to the USB ports. Unauthorized USB devices may interfere with the analyzer function.

WARNING

Equipment Damage: 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

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)


WARNING

<u>Equipment Damage</u>: If one accidentally over-saturates the instrument with water, it is very important that one does not turn the instrument off. Rather, let the instrument pull either room air or dry air/N_2 through for a few days to dry out the cavity -- until the instrument can make measurements normally again. If the instrument is turned off right after the accident, water will condense and contaminate the cavity rendering it useless. The cavity repair can be up to 25,000 USD.

7.1 Analyzer and Vacuum Setup

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


WARNING

This analyzer weighs 45 lbs (20.4 kg). Use the technique outlined in the General Safety section on page 19 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

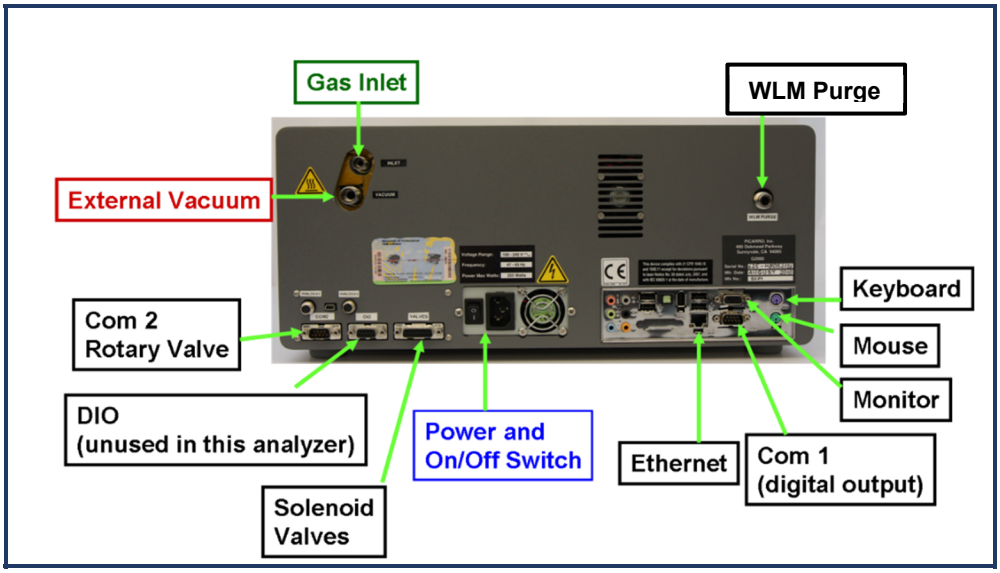
Use the AC power cables supplied with the analyzer or a similarly rated cable. Check with Picarro technical support if you have questions about power cable replacement. An inadequately rated power cable can result in equipment damage.

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 7: Rear panel connections



WARNING

<u>Equipment Damage</u>: Never disconnect the vacuum hose unless the pump and analyzer are OFF. Otherwise, the system may be damaged.

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 Procedure" in Section BASIC OPERATION.

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 8: 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 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.

7.4 Dual Mode Setup

Refer to Figures 9, 10, and 11 below.

1. Inspect the boxes of Picarro products before opening. Carefully unpack the boxes and prepare the facility.
2. Please review the important safety notes before continuing on with the installation. See **Safety**.
3. Install the Analyzer and its External Vacuum Pump (see **Analyzer and Vacuum Setup**).
4. Install the Picarro Autosampler (see Installation | Picarro Autosampler chapter in the **A0325 Autosampler User Manual (PN 40025**).
5. Attach the vaporizer switching valve assembly to the vaporizer inlet ports labelled Purge and Sample 2.
6. Attach the gas line to T section of the vaporizer switching valve assembly.

7. Sampling tubing for measuring ambient water vapor should be connected to the back of the solenoid valve.

Figure 9: Vaporizer Switching Valve Connected to Vaporizer.

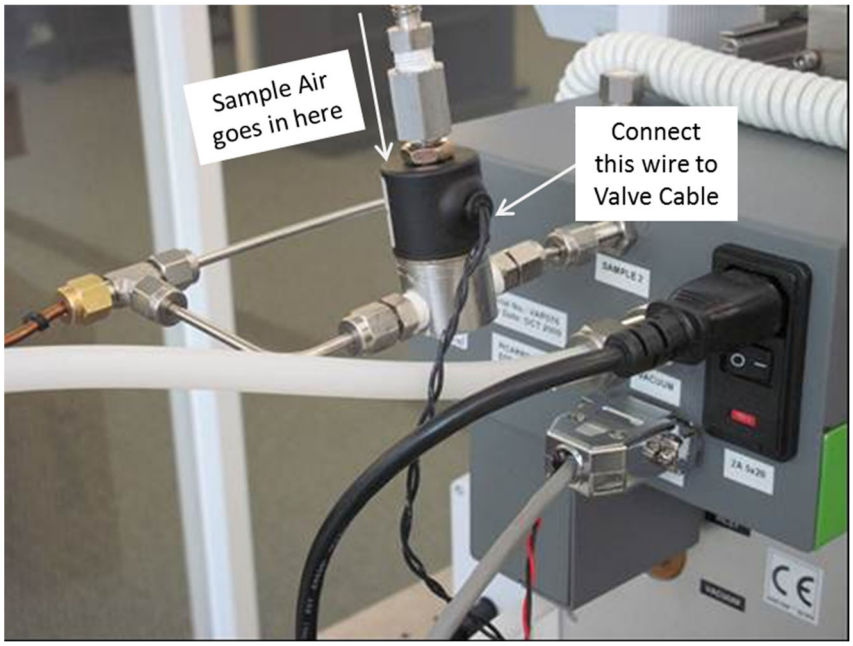


Figure 10: Connections on the back of the vaporizer

8. Supply dry gas to the Analyzer (see **WATER ANALYZER DRY GAS SUPPLY SETUP**). Monitor purge should be at a pressure of *2.5 ± 0.5 psig* (0.17 ± 0.03 bar) from the gas supply/regulator.

9. Make sure all power cables are attached to the power outlets on the analyzer, vaporizer, external pumps and autosampler power block. However, keep the power switch off.
10. Carefully slide the complete system into position. Small movements of the components relative to one another is OK, as the units are well locked. However, do not overly force the system; check for obstacles if the unit does not slide easily.
11. Power up the system: Plug in all the power cables (including the one for the monitor) into the appropriate power supply. Switch ON the components in the following order:
    a) Both external vacuum pumps
    b) Everything else


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 Procedure" in Section BASIC OPERATION.

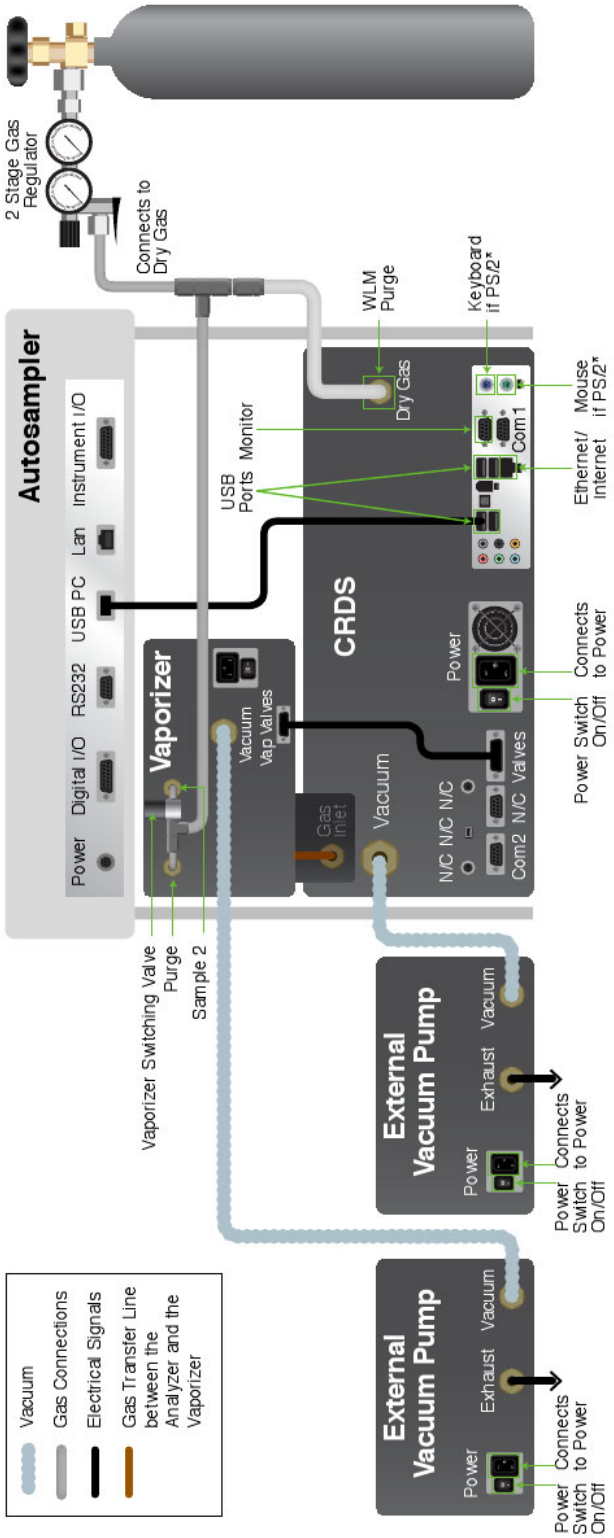

NOTE

As the instrument is starting up, it is normal for there to be a delay in reporting data. This can take several minutes depending on how long it takes for the internal temperature to reach its operating point, and it is normal during this time for some concentration readings to be negative or constant. Additionally, the data selection pull down menus will not be populated with the appropriate items until data is actually being reported in the graph. This is typically less than 30 minutes, but depending on ambient temperature, the analyzer can take up to 2 hours to stabilize.


NOTE

Remember that for the SDM operation, the Vaporizer temperature should be set to 140°C. For all the other coordinator modes, the temperature should be set to 110°C.

Figure 11: Dual Mode Setup



7.5 Manual Mode Setup

Refer to Figures 12, and 13 below.

1. Inspect the boxes of Picarro products before opening. Carefully unpack the boxes and prepare the facility.
2. Please review the important safety notes before continuing on. See **Safety** section.
3. Set up the Analyzer and its external vacuum pump (see **Analyzer and Vacuum Setup**).
4. Place the vaporizer on top of the analyzer using feet of 0.5” (13 mm) thickness to set it to the appropriate height. Align the Inlet port (analyzer) with the delivery port of the vaporizer.
5. Attach a (N_2 or Dry Air) Gas line to the Vaporizer and the Analyzer (see **WATER ANALYZER DRY GAS SUPPLY SETUP**).
6. Find the external vacuum pump for the vaporizer, the hose with fittings attached, and the power cord for the vaporizer. Attach the hose at the vaporizer’s vacuum port and connect it to the External Vacuum Pump. Attach the power cable to the External Vacuum Pump, but keep the power switch off.

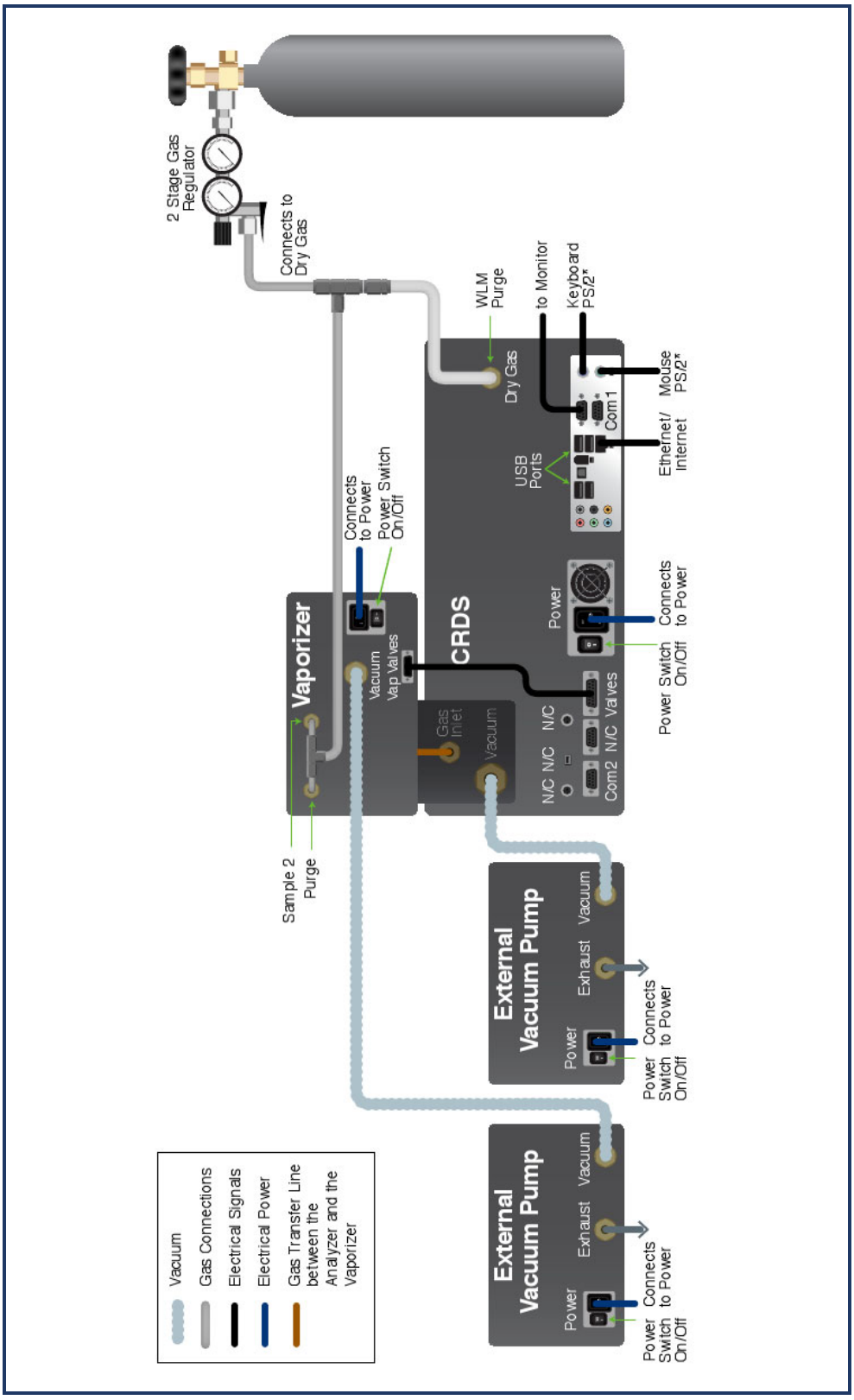
Figure 12: Pump Rear Panel

The pump exhaust port may come with a muffler attached for noise reduction.

7. Connect the Vaporizer and the Analyzer using a Valve Cable and the gas delivery port from the vaporizer (see **VAPORIZER TO ANALYZER CONNECTIONS).**
8. Check the Power Connections to the Machines: Make sure all power cables are attached to the power outlets on the Analyzer, Vaporizer, and two External Vacuum pumps. However, keep the power switch off.

9. Carefully slide the complete system into position: Small movement of the components relative to one another is OK. However, do not overly force the system. Check for obstacles if the unit does not slide easily.
10. Plug all the power cables (including the one for the monitor) into a power supply. Switch ON the components in the following order
    a) External Vacuum Pumps (for the analyzer and the vaporizer).
    b) Everything else.

Figure 13: Manual Mode Setup



7.6 Picarro Autosampler and High Precision Vaporizer (A0211) Setup

Refer to Figure 14 below.

1. Inspect the boxes of Picarro products before opening. Carefully unpack the boxes and prepare the facility.
2. Please review the important safety notes before continuing on with the installation. See **SAFETY.**
3. Install the Analyzer and its External Vacuum Pump (see **Analyzer and Vacuum Setup**).
4. Install the Picarro Autosampler (see Installation | Picarro Autosampler chapter in the **A0325 Autosampler User Manual (PN 40025**).
5. Supply dry gas to the Analyzer (see **WATER ANALYZER DRY GAS SUPPLY SETUP).**
6. Carefully slide the complete system into position: Small movement of the components relative to one another is OK, as the units are well locked. However, do not overly force the system: check for obstacles if the unit does not slide easily.
7. Power up the system: Plug in all the power cables (including the one for the monitor) into the appropriate power supply. Switch ON the components in the following order:
    a. Both external vacuum pumps
    b. Everything else

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 Procedure" in Section BASIC OPERATION.

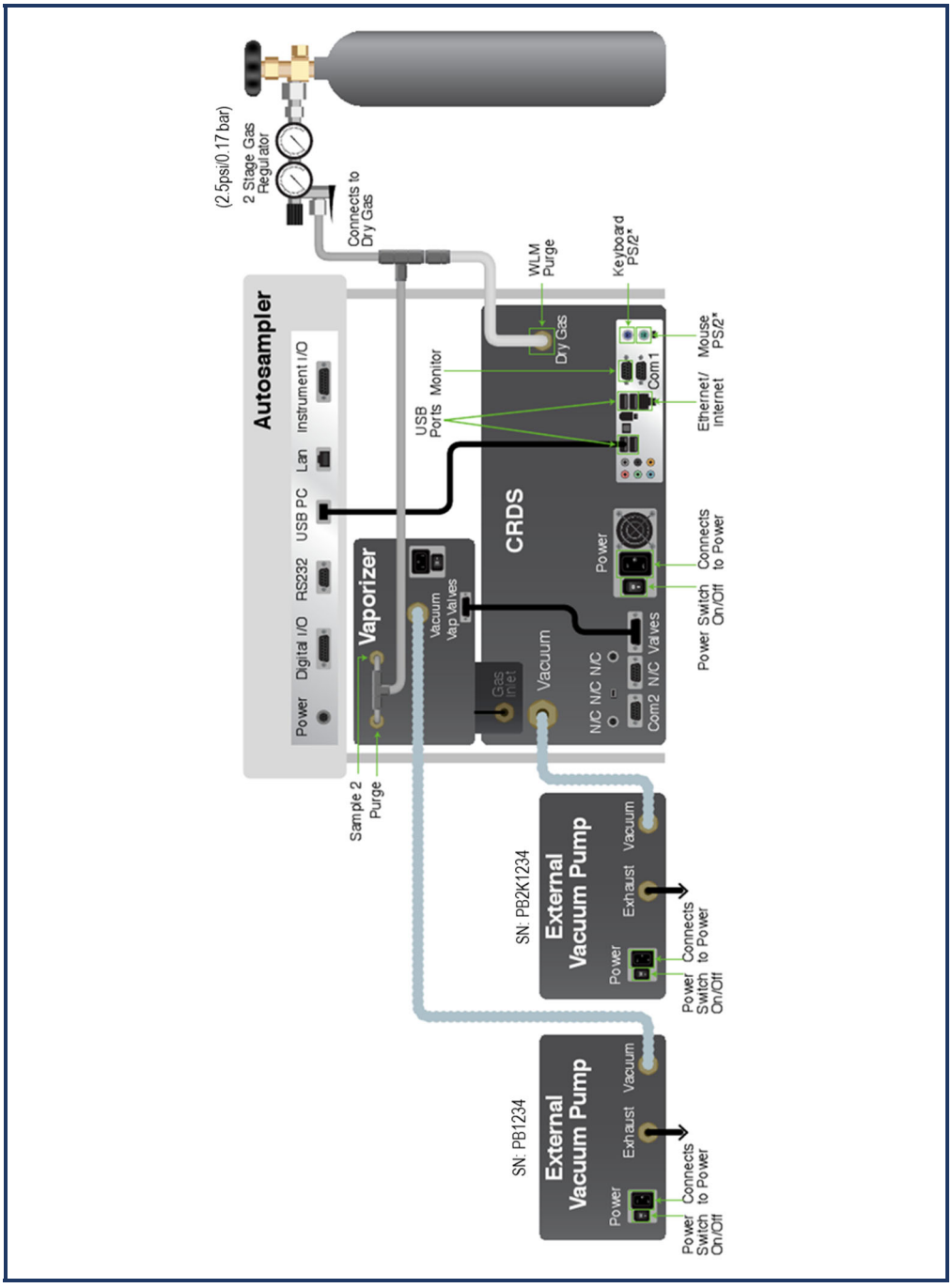
NOTE

As the instrument is starting up, it is normal for there to be a delay in reporting data. This can take several minutes depending on how long it takes for the internal temperature to reach its operating point, and it is normal during this time for some concentration readings to be negative or constant. Additionally, the data selection pull down menus will not be populated with the appropriate items until data is actually being reported in the graph. This is typically less than 30 minutes, but depending on ambient temperature, the analyzer can take up to 2 hours to stabilize.

NOTE

Remember that for the SDM operation, the Vaporizer temperature should be set to 140°C. For all the other coordinator modes, the temperature should be set to 110°C.

Figure 14: Picarro Autosampler-High Precision Vaporizer Setup



8. WATER ANALYZER DRY GAS SUPPLY SETUP

The Picarro L2140-*i* and L2130-*i* analyzers each can work in many configurations, allowing a wide application of the analyzer. This chapter describes how to set up the dry gas supply for all these configurations. Find the section in this chapter that relates to your setup and then complete the gas supply installation steps.

- **Manual Mode Setup** → See Dry Gas Configuration A
- **Picarro Autosampler – High Precision Vaporizer (A0211) Setup** → See Dry Gas Configuration A
- **Picarro Autosampler – High Throughput Vaporizer (A0212) Setup** → See Dry Gas Configuration B
- **Basic Water Analyzer Setup** → No dry gas supply necessary
- **Dual Mode Setup** → See Dry Gas Configuration C
- **Induction Module Setup** → See A0213 Induction Module to CRDS Setup User Manual (PN 40039)
- **SDM Setup** → See A0101 Standards Delivery Module CRDS Setup User Manual (PN 40-0005)

8.1 Dry Gas Configuration A

You will need a dry gas supply for the analyzer and the vaporizer. You can purchase the pressure regulator kit #A0921 or A0293 from Picarro. If you have already purchased a dry gas kit from Picarro, you will need the following additional supply.

- **Dry gas supply of 10-60 psi (4 bar), which is stepped down to 2.5 psi before being connected to the CRDS analyzer.**

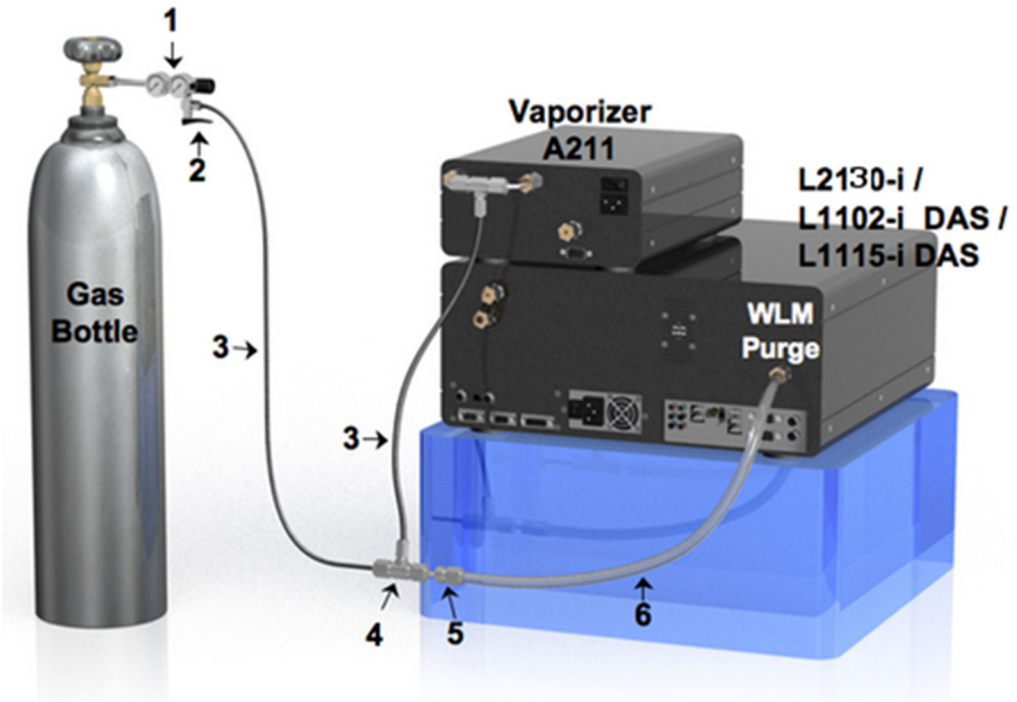
Below, you will find a complete part list and diagram on how to connect dry gas to the water analyzer.

1. Attach the (N_2 or Dry Air) Gas Line to the Analyzer: Attach a Gas line from the “WLM Purge” Port on the Analyzer to the N_2 Regulator, which connects to a (nitrogen or dry air) gas cylinder.
2. To connect 1/4” dry gas tube to the Wavelength Monitor Purge (WLM Purge) Port on the Analyzer, one needs to use the Push

Connector that is attached to the port. The connector is in two pieces: The Outer Flap and the Inner Flap.

3. **To connect the tube to the port**, simply push the tube into the connector and then pull the tube back. If there is a space between the inner flap and the outer flap, this means that the tube is locked to the port. Do not twist and turn**.** To take the tube out of the port, push the Outer Flap in against the Inner Flap, and while doing this, pull out the tube. This will cause the gripping mechanism to release from the tube.

Figure 15: Configuration A



1. Q1-14B-580 Air Liquide Scott Regulator
2. SS-OGM2-S2-A Swagelok Toggle Valve:
3. SS-T2-S-028-20 Swagelok 1/8" OD stainless steel tubing
4. SS-200-3 Swagelok 1/8" stainless steel Tee union
5. SS-400-R-2 Swagelok 1/8" (adapter fitting) to 1/4" (tube fitting) Reducing Union
6. 5033K31 McMaster-Carr 1/4" OD PTFE tubing

Additional tools and parts are required, some others recommended. For the list, please click on the link below which will require you to have a Picarro community account.
https://picarro.box.net/shared/static/r19c3z8etk.pdf

4. Attach the Gas (N_2 or Dry Air) Line to the Vaporizer: Using either output from a (nitrogen or dry air) gas cylinder (should be at a pressure of 2.5 ± 0.5 psig (0.17 ± 0.03 bar)) or from the gas supply/regulator, attach the gas line to the open third leg of the gas line that connects the vaporizer purge and the sample ports (that is shipped connected to the vaporizer).

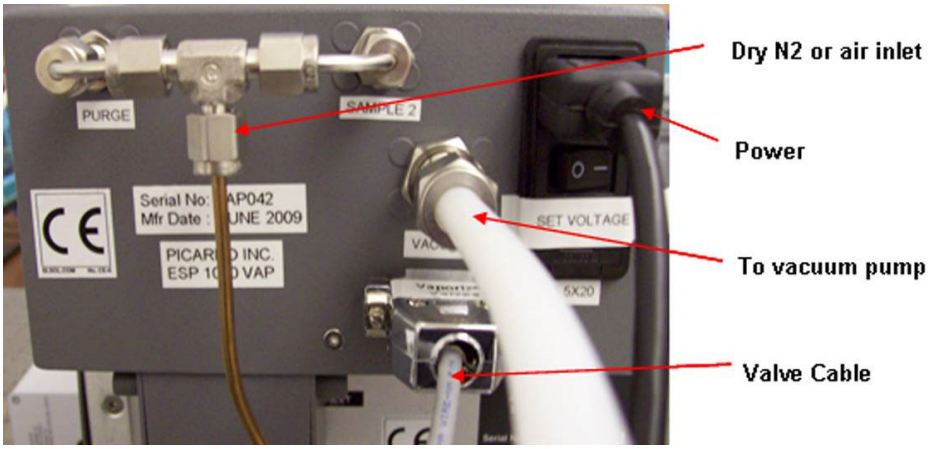
Figure 16: Type description here

Above is an N_2 Regulator: The semi-transparent tube on the left is routed to the 'WLM Purge" Port on the Analyzer. The copper colored tube on the top left comes from the 'Purge' and the 'Sample' ports on the Vaporizer. The copper colored tube on the bottom right goes to the the (N_2 or Dry Air) Gas Cylinder.

Figure 17: Vaporizer and Analyzer Connections

WLM Purge port back of the analyzer.

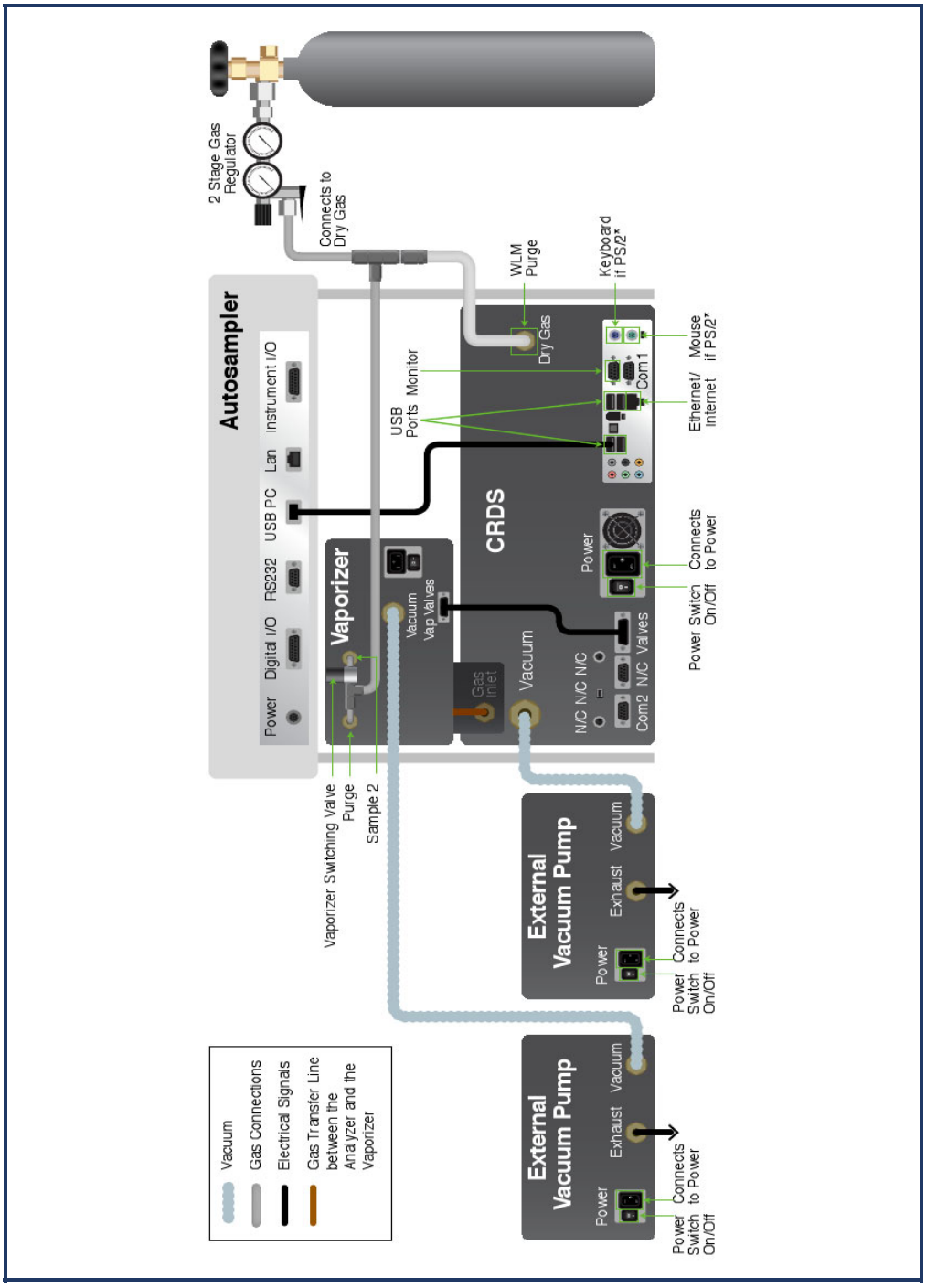
Gas and electrical connections at rear of vaporizer



8.2 Dry Gas Configuration B

The gas connection for the **Dual Mode** setup is very similar to the Dry Gas Configuration A except that it also has a Vaporizer Switching Valve. Follow the Dry Gas Configuration A, but also connect the Vaporizer Switching Valve back of the Vaporizer according to the schematic and images below.

Figure 18: Dry Gas Configuration B



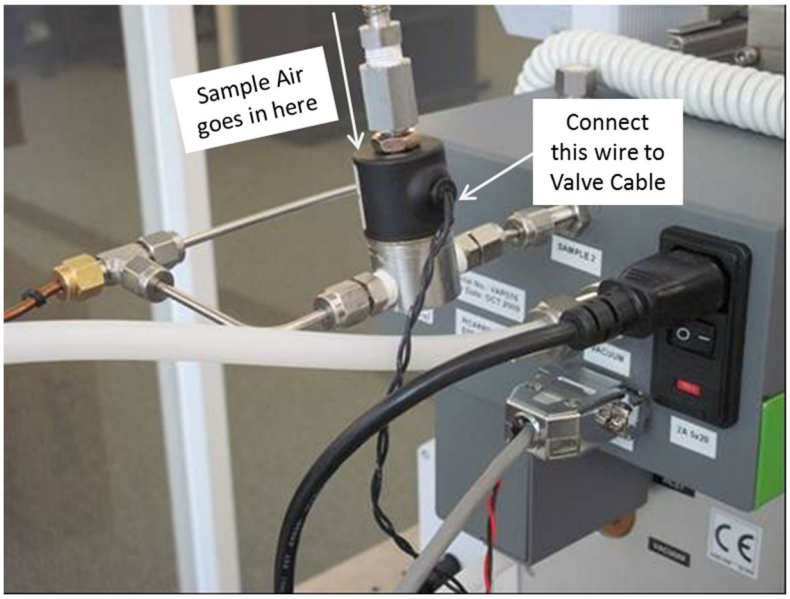
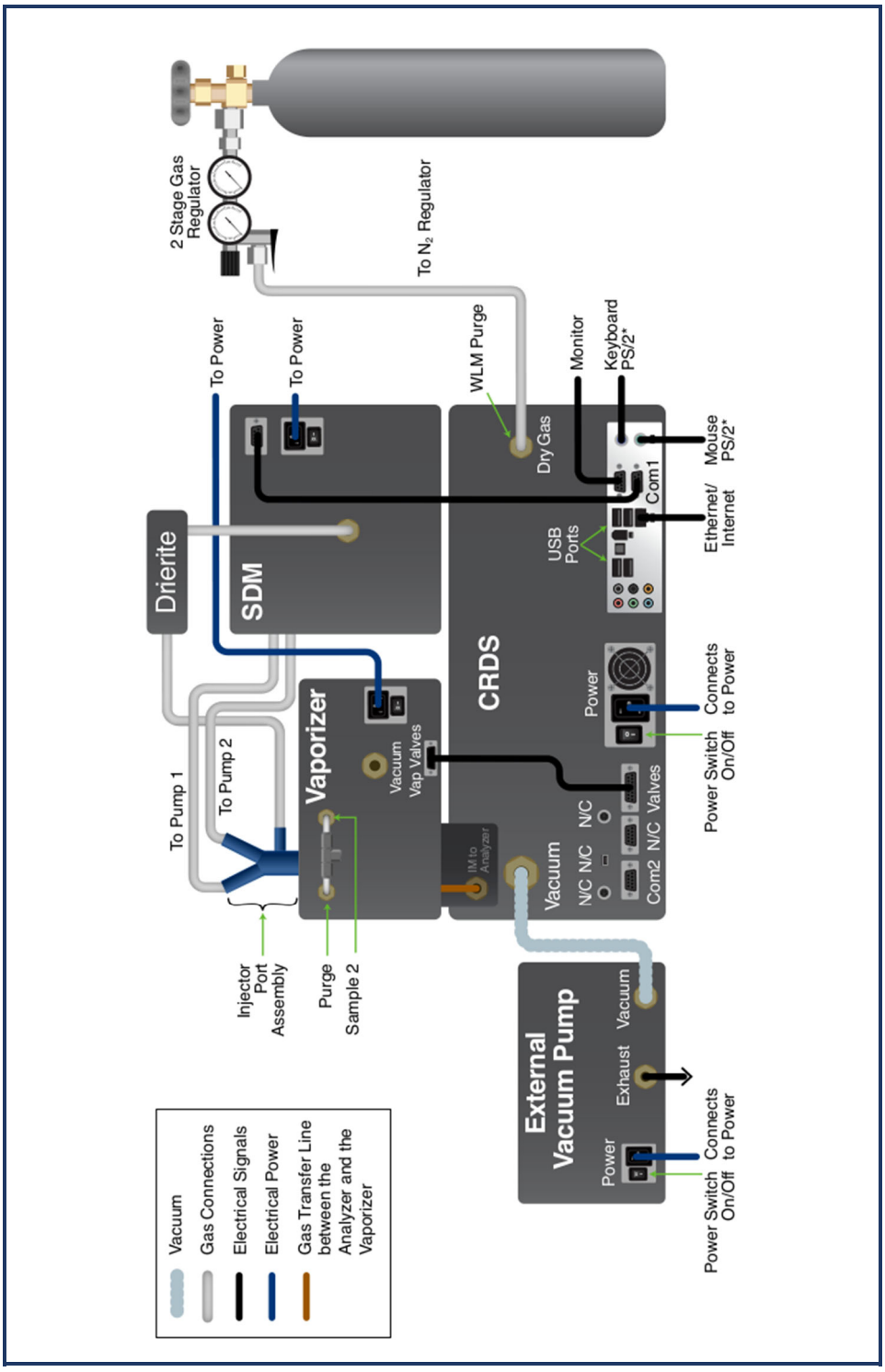


Figure 19: Vaporizer Switching Valve Connected to Vaporizer.

8.3 Dry Gas Configuration C

For the **SDM** setup, you only need to supply dry gas to the CRDS analyzer. (Figure 20).

Figure 20: Dry Gas Configuration C



To connect a 1/4” dry gas tube to the Wavelength Monitor Purge (WLM Purge) Port back of the Analyzer, use the Push Connector attached to the port.

The connector is in two pieces: The Outer Flap and the Inner Flap. To connect the tube to the port, simply push the tube into the connector and then pull the tube back.

If there is a space between the inner flap and the outer flap, this means that the tube is locked to the port. *Do not twist and turn***.** To take the tube out of the port, push the Outer Flap in against the Inner Flap, and while doing this, pull out the tube. This will cause the gripping mechanism to release from the tube.

Wavelength Monitor Purge

Why do the Picarro isotopic water analyzers (L21x0-*i*) have a wavelength monitor (WLM) purge?

The WLM purge acts to fill the warm box of your analyzer with dry gas. The warm box houses the WLM which is part of the analyzer’s laser targeting control loop. The WLM itself enables us to precisely control the wavelength of light being injected into the cavity. Within the warm box there is a distance of about 10 cm which is open path, i.e., the laser light is seeing the ambient atmosphere at 45°C (the temperature at which the warm box is held). Because water is such a strong absorber, and in the case of our isotopic water systems, the laser is specifically tuned to a frequency of water absorption, this open path segment may result in decay of the light prior to entering the WLM. As a result, the performance of the WLM could vary as ambient conditions change. We elect to dry the gas seen by the laser in the warm box such that any potential decay due to water absorption is limited.

Should I always have dry gas purging the WLM or can I leave it open?

At ambient temperature and pressure, drying the gas that enters the WLM is not essential, but we do recommend it. If you have access to a zero air or N_2 tank, such as the tank being used as the dry gas source for your vaporizer (High Precision or High Throughput Vaporizer), we recommend adding a T to the line and feeding both your vaporizer and WLM purge with the same dry gas source. You can also purchase a dry gas kit from us with the necessary regulator and fittings to connect a N2 tank (part # A0921) or zero air tank (part # A0923) to your system. If you are operating your analyzer in a very humid environment, such as above 3% water content (30,000 ppm), we always recommend dry gas be supplied to your WLM

purge. Without this dry gas supply, you may experience more drift in the analyzer.

Does the gas used for the WLM purge need to be the same as matrix gas for the cavity?

No, the gas that is used to purge the WLM can differ from the matrix gas seen by the cavity. Picarro isotopic water analyzers have two modes of operation; air and N2 (use the “Picarro Mode Switcher” to switch between the two). If, for example, you are using the SDM and operating in air mode, you can use N2 to purge the WLM. The opposite is also fine. If you’re running from a tank, you’ll typically use the same gas for convenience.

9. VAPORIZER TO ANALYZER CONNECTIONS

Valve Controller Cable

Attach the 15 pin end of the grey valve cable to the port labelled **Vap Valves** on the vaporizer and connect to the port labelled **VALVES** on the analyzer (third connector from the left at the bottom row of the Analyzer).

Gas Line

1. Carefully align the analyzer and the autosampler relative to each other such that the gas delivery line hanging from the vaporizer is aligned with the inlet port of analyzer. *Do not bend the delivery port in the process.* If the delivery port is not horizontally aligned with the analyzer inlet port, gently move the position of the vaporizer on the autosampler by loosening the clamps and retightening them after alignment.
2. Follow the images below to connect the gas line from the vaporizer to the analyzer. Once the vaporizer is connected to the analyzer, carefully push the autosampler and vaporizer forward so that there is no gap between the insulation around the vaporizer outlet and the analyzer.

Figure 21: Type description here

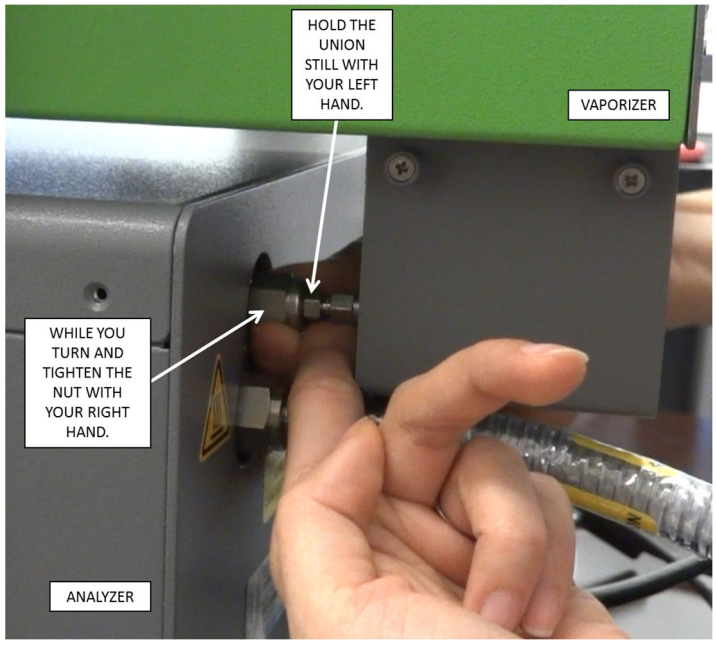
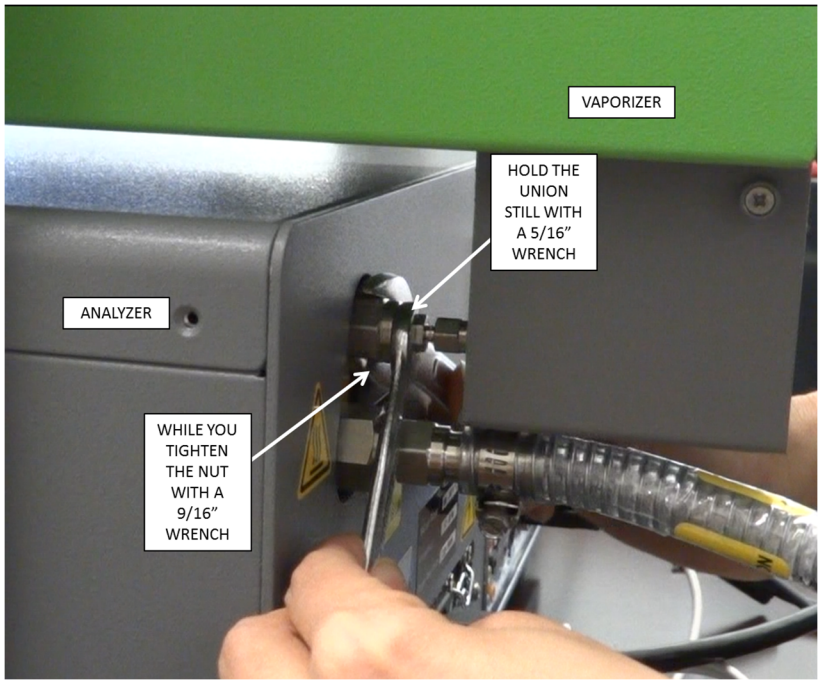


Figure 22: Type description here

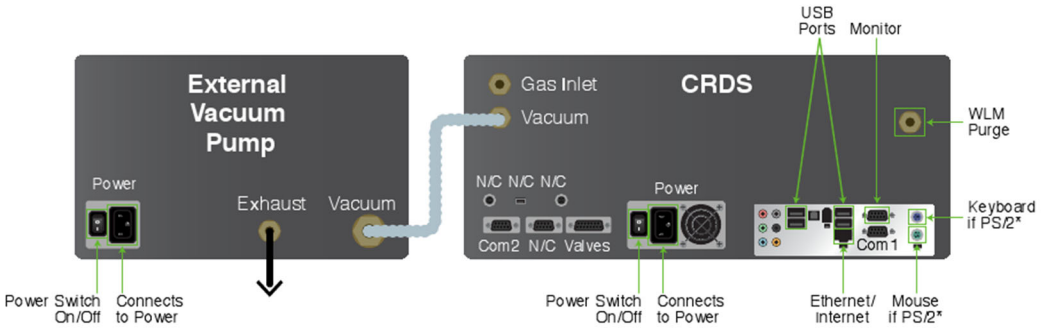


10. BASIC OPERATION

10.1 Start Up

Picarro Analyzers are designed to start up upon receiving mains power. First, make sure the basic analyzer hardware was installed per the instructions in this manual.

Figure 23: Analyzer Setup



The CRDS analyzer and the Vaporizer each have a vacuum pump. Make sure that the vacuum pump being installed is for the CRDS analyzer.

The exhaust port of the External Vacuum Pump will have a muffler attached for noise reduction.

Once the hardware is installed the mains power switch can be turned to ON (O/I switch on rear of analyzer should be depressed to position “I”). At this point, the computer and CRDS software will start up automatically. The following status window will demonstrate that the CRDS software is loading.

Figure 24: Startup; Software Loading Sequence

Once the CRDS software has been launched, the Analyzer will move towards obtaining its highly controlled temperature and pressure set points. In the case of the water analyzer, these are 80°C and 50 Torr. Warm up typically takes about one hour. By design, the cavity pressure will not start to decrease until the cavity temperature is close to its set point. Ideally, the Analyzer is open to room air during the warm up, i.e., there is nothing attached to the “Gas Inlet” on the rear of the Analyzer. This is desired because ambient water vapor will provide a good signal for the Picarro Wavelength Monitor (WLM) which provides the frequency control for the spectral measurement.

If the Analyzer is without a signal for a long period of time (i.e., it is left on dry gas for multiple hours to days), the frequency axis of the Analyzer can

get lost resulting in incomplete spectra. If you notice an increase in measurement interval or data drop outs after a period of idle time on dry gas, simply disconnect or turn off your dry gas source. The instrument will stabilize after a period of measuring room air.

10.2 Shut Down

Before proceeding to turn off the analyzer, note the following warnings.


CAUTION

Equipment Damage: A flow of clean, relatively dry gas should always be directed through the instrument for several minutes prior to shut 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

FOR ALL USERS: Do not turn off the pump or disconnect the vacuum line while the instrument is operating.


CAUTION

FOR G2000 SERIES ANALYZER USERS: If you have trouble turning off the analyzer software, do not kill process(es) in the task manager. Instead, double-click on the "Stop Instrument" icon in the "Diagnostics" folder on your desktop.


CAUTION

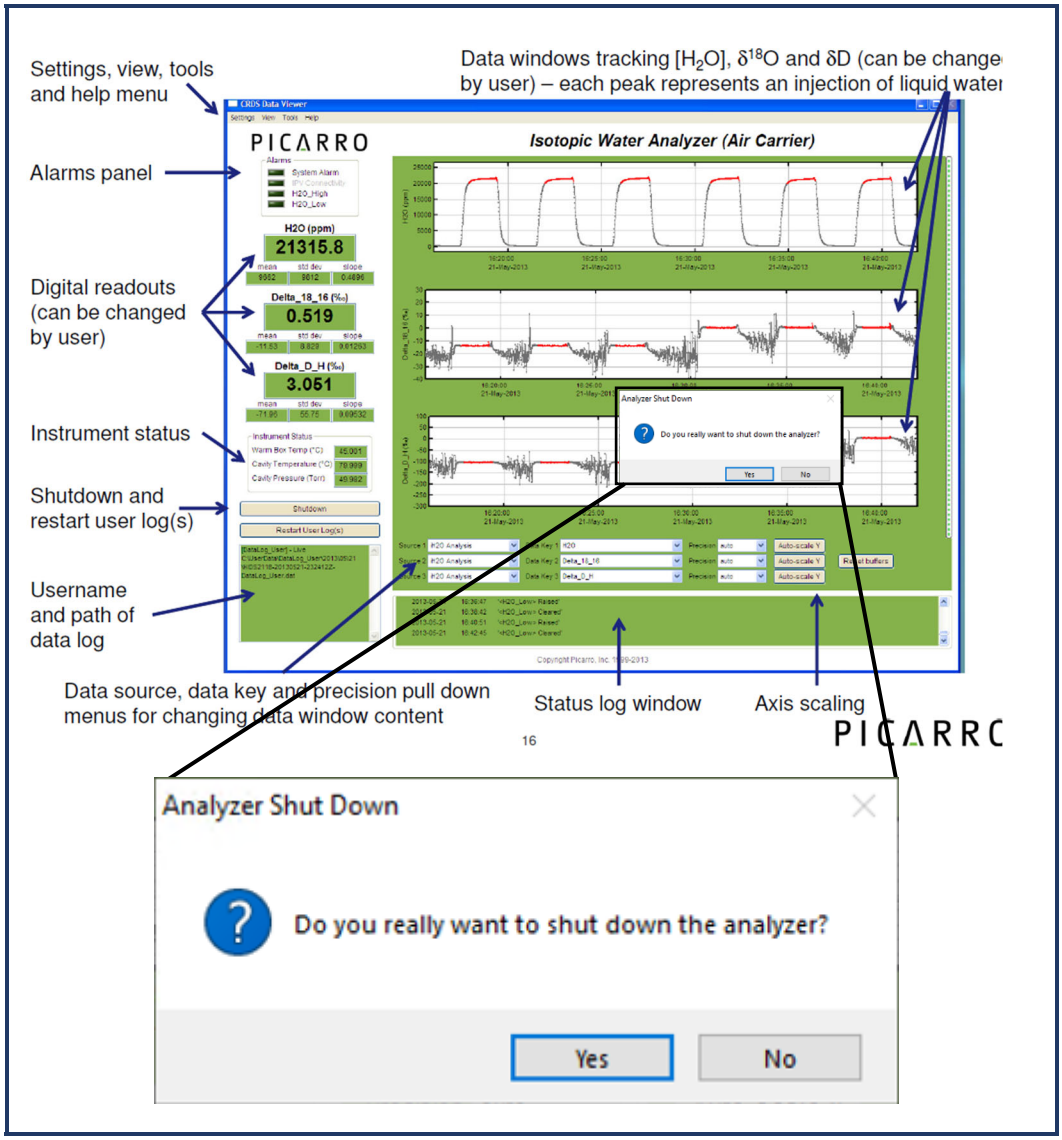
Equipment Damage: If you accidentally over-saturate the instrument with water, it is very important that you do not turn the instrument off. Instead, let the instrument pull either room air or dry air/N2 through for a few days to dry out the cavity - until the instrument can make measurements normally again. If the instrument is turned off right after the accident, water will condense and contaminate the cavity rendering it useless. The cavity repair can cost up to $25,000 (USD).

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 (Figure 24) 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).

Figure 25: Shutdown Dialog



10.3 In case of an electrical power outage

If power to the analyzer is cut off for any reason, the analyzer will cease operation. When the power is reapplied, the analyzer will restart automatically. The Picarro software tools will 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. The Analyzer will not restart any active Coordinators that were operating before the power outage.

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

10.4 Dual Mode Setup

Dual mode is used for measurement of ambient vapor coupled with automated injection of liquid calibration standards. This setup requires A0211 High Precision Vaporizer, A0912 Dual Mode Configuration hardware and software for vapor calibration, and an Autosampler. Each injection cycle takes 9 minutes.

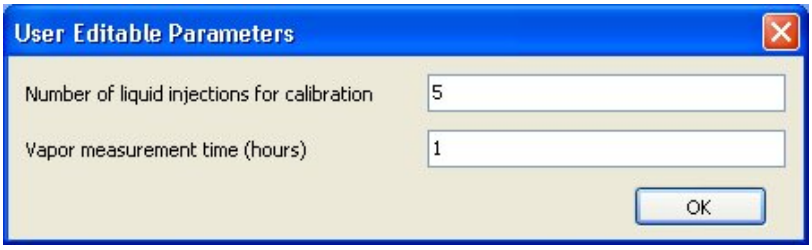
OPERATION

1. Before continuing, review the important safety notes in the **SAFETY** section.
2. Make sure the hardware setup is complete and the system turned on in the correct sequence.
3. Once turned on, the main CRDS Data Viewer of the analyzer will open automatically on the desktop screen. To understand all the functions of the main CRDS Data Viewer, see **CRDS Data Viewer**. A sequence of start-up messages will also appear in the Status Log Message window of the main CRDS Data Viewer. For definition, see **Common Status Log Messages**.
4. Make sure the temperature of the High Precision Vaporizer stabilizes at 110°C by viewing the read out on the front of the vaporizer.

Before starting measurements, ensure you are in the correct measurement mode. Select the measurement mode that matches the dry gas supplied to your Vaporizer (either N2 or zero air). See section Switching between Measurement Modes for instructions.

5. Make sure the Picarro Autosampler software is running, that the Autosampler has been trained, methods and jobs defined, and samples loaded. Refer to the **Picarro A0325 Autosampler User Manual** (PN 40025) for detailed setup instructions.
6. Double click on the Coordinator Launcher icon on the analyzer's desktop. The coordinator software allows the analyzer to take measurements from multiple samples and is used to control the sample source and match the corresponding real time read out with the sample source. To learn more about the coordinator software (running the software, loading sample description, functions of the coordinator window), see **Coordinator Software.** Choose and launch an appropriate coordinator mode from the choices in the drop down menu of the coordinator launcher window. The Dual Mode Setup can operate in one coordinator mode.
7. Once launched, before the Coordinator window opens up, the User Editable Parameters window will pop up (as shown below):

Figure 26: User Editable Paramters Window



This allows measurement of liquid isotopic water standards at fixed time intervals during the measurement of the vapor phase to verify calibration. The analyzer will run the parameters specified in a continuous loop until exiting from the program (i.e., measure 5 liquid injections, 1 hour of vapor, 5 liquid injections, 1 hour of vapor, etc.). Measurement will always start with liquid injections.

- **If no liquid samples are to be measured then enter '0' in the field for liquids. It will then measure the vapor continuously.**
- **If no vapor samples are to be measured then enter '0' in the field for vapors. It will then run only the liquid samples specified in the Autosampler job (see later section for details).**

- **If the analyzer is already running and these parameters need to be changed it will require exiting and restarting the Picarro coordinator software.**

Analysis of liquid samples requires that both the coordinator software and autosampler job be started. Be sure to start the Autosampler Controller software before launching the Dual Mode Coordinator. Once the Autosampler Controller software is open, you may start the Dual Mode Coordinator. Once open, click "Run" on the Autosampler Controller software.

Picarro highly recommends matching the "Number of liquid injections for calibration" to the injection count set in the Autosampler job. This ensures one sample vial is analyzed completely before returning to vapor measurements. If two or more liquid calibration standards are used then "number of liquid injections for calibration" can also be an integer multiple of the injection count set in the Autosampler job.

For example, if eight injections each of two liquid standards are to be run every 6 hours during vapor measurements then enter 16 (8 injections * 2 standards) in the first field and 6 in the second field.

Be sure there are sufficient liquid standards available because once all the liquid samples specified in the Autosampler job have been run and the current vapor measurement is complete, the analyzer will wait indefinitely or until a new Autosampler job is started.

To calculate the time to complete the autosampler job use the follow formula:

Cycle time = number injections * 9 min + vapor measurement time

---

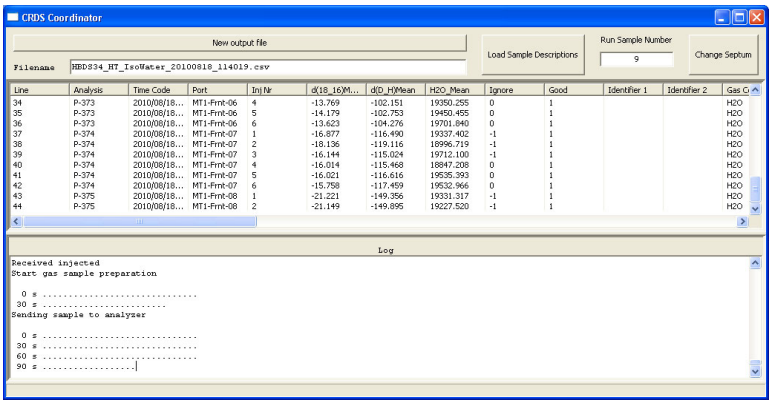
Assuming 1 standard per cycle, 8 injections, and 6 hours vapor measurement: the total cycle time is 432 minutes and consumes 1 vial. The Picarro Autosampler has a tray for up to 105 vials. Therefore, one full tray of 105 vials will last 432 * 105 = 45360 minutes or 31.5 days. Thus, plan on one tray lasting for one month of measurements when calibrating every 6 hours.

Once the injection number and vapor measurement duration parameters have been entered, and the 'OK' button is clicked, the coordinator window will pop up on your desktop. The different software element will indicate whether liquid or vapor is being measured.

8. Once launched, the coordinator will automatically start collecting data. The data will also be available in the GUI as pulses. To customize pulse analysis or to adjust the peak of pulse data, please see **Pulse Customization.**

Figure 27: Coordiator Launcher

Coordinator Launcher Window



Coordinator Window

DATA

To learn where to retrieve the data, and to set the frequency of file archival and automatic deletion of old files, see **Data Files.** To access one's data remotely, see the section, **REMOTE DATA ACCESS.**

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, click on the Setup Tool icon in the Picarro Utilities folder in the desktop.

The Picarro Water Analyzers allow users to archive data using a compressed, binary "HDF5" or "h5" format. **THE DATA FILE VIEWER** program, which comes installed with the hardware, allows one to open and

convert h5 files, as well as viewing the h5 files as graphs. For more information, see **THE DATA FILE VIEWER.**

The Picarro Water Analyzers come preinstalled with the ChemCorrect software which allows one to screen and quantify contamination in isotopic water samples. To post process data using ChemCorrect Software, see **ChemCorrect Software: Analysis of Coordinator Files.**

One many need to adjust the sample injection volume to improve the quality of one's data. See **Adjusting Injection Volume** for more information.

10.5 Manual Mode Setup

OPERATION

1. Before continuing, review the important safety notes in **SAFETY.**
2. Make sure the hardware setup is complete and the system turned on in the correct sequence.
3. Once turned on, the main CRDS Data Viewer of the analyzer will open automatically on the desktop screen. To understand all the functions of the main CRDS Data Viewer, see **CRDS Data Viewer**. A sequence of start-up messages will also appear in the Status Log Message window of the main CRDS Data Viewer. For definition, see **Common Status Log Messages**.
4. Make sure the temperature of the High Precision Vaporizer has stabilized to 110 °C.

Before starting measurements, ensure you are in the correct measurement mode. Select the measurement mode that matches the dry gas supplied to your Vaporizer (either N2 or zero air). See section Switching between Measurement Modes for instructions.

5. Double click on the Coordinator Launcher icon on the desktop. The coordinator software allows the analyzer to take measurement from multiple samples and is used to control the sample source and match the corresponding real time read out with the sample source. To learn more about the coordinator software (running the software, loading sample description, functions of the coordinator window), see **Coordinator Software.** Choose and launch an appropriate coordinator mode from the choices in the drop down menu. The coordinator window will pop up.

The Manual Mode Setup can operate in one coordinator mode in the **L2130-*i***.

- **Manual Inject:** Used for semi-automated measurement of liquid water samples with high precision. Requires A0211 High Precision Vaporizer and A0322 Syringe Guide. User manually injects samples after prompt. The vaporizer control and the analysis of liquid samples are automated. Each injection cycle takes 9 minutes.

The Manual Mode Setup can operate in two coordinator modes for the **L2140-*i*.**

- **O^{17} Manual Inject:** Used for semi-automated measurement of liquid water samples for $\delta^{18}O$, $\delta^{17}O$, δD and ^{17}O-excess. Requires A0211 High Precision Vaporizer and A0322 Syringe Guide. User manually injects samples after prompt. The vaporizer control and the analysis of liquid samples are automated. This coordinator must be run in either the “iH2O N2 O-17” mode or the “iH2O Air O-17” mode. In this mode the coordinator will output $\delta^{17}O$ and ^{17}O-excess. Each injection cycle takes 9 minutes.
- **Manual Inject:** Used for semi-automated measurement of liquid water samples with high precision on $\delta^{18}O$ and δD. Requires A0211 high precision vaporizer and A0322 Syringe Guide. User manually injects samples after prompt. The vaporizer control and the analysis of liquid samples are automated. Each injection cycle takes 9 minutes.

To learn about all the other coordinator modes supported by the Picarro water analyzer (in different setups), see **Coordinator Modes Available On a Picarro Water Isotope Analyzer**.

6. Once launched, the coordinator will direct the user on when to manually inject samples and it will automatically start collecting data. The data will also be available in the GUI as pulses. To customize pulse analysis or to adjust the peak of one’s data pulses, see **Pulse Customization**.
7. The status bars at the bottom of the Coordinator window will allow one to know if the analyzer is ready for a manual injection or not. If ready, the sample description (if preloaded) will appear. If not loaded, a description can be added. Manually inject the sample and then press the Injected button in the lower right corner of the Coordinator window. The coordinator software will prepare the

sample in the vaporizer in high precision mode. It will take approximately 9 minutes until it is ready for the next injection.

DATA

To learn about different types of data produced by one's system and to set file archival and automatic deletion of old files, see **Data Files.** To access one's data remotely, see **REMOTE DATA ACCESS.**

The Picarro Water analyzers allow users to archive data using a compressed, binary "HDF5" or "h5" format. The Data File Viewer program, which comes installed with the hardware allows one to open and convert h5 files, as well as viewing the h5 files as graphs. For more information, see **THE DATA FILE VIEWER.**

The Picarro Water Analyzers come preinstalled with the ChemCorrect software which allows one to screen and quantify contamination in isotopic water samples. To post process data using ChemCorrect Software, see **ChemCorrect Software: Analysis of Coordinator Files.**

One many need to adjust the sample injection volume to improve the quality of data. See **Adjusting Injection Volume** for more information.

10.6 Picarro Autosampler and High Precision Vaporizer Setup

OPERATION

1. Before continuing, review the important safety notes in **SAFETY.**
2. Make sure the hardware setup is complete and the system is turned on in the correct sequence.
3. Once turned on, the main CRDS Data Viewer of the analyzer will open automatically on the desktop screen. To understand all the functions of the main CRDS Data Viewer, see **CRDS Data Viewer**. A sequence of start-up messages will also appear in the Status Log Message window of the main CRDS Data Viewer. For definition, see **Common Status Log Messages**.
4. Make sure the temperature of the High Precision Vaporizer has stabilized at 110°C by viewing the read out on the front of the vaporizer.

Before starting measurements, ensure you are in the correct measurement mode. Select the measurement mode that matches the dry

gas supplied to your Vaporizer (either N2 or zero air). See section Switching between Measurement Modes for instructions.

5. Make sure the Picarro Autosampler software is running, that the Autosampler has been trained, methods and jobs defined, and samples loaded. See **A0325 Autosampler User Manual (PN 40025**.
6. Double click on the Coordinator Launcher icon in the analyzer's desktop. The coordinator software allows the analyzer to take measurements from multiple samples and is used to control the sample source and match the corresponding real time read out with the sample source. To learn more about the coordinator software (running the software, loading sample description, functions of the coordinator window), see **Coordinator Software.** Choose and launch an appropriate coordinator mode from the choices in the drop down menu of the coordinator launcher window. The coordinator window will pop up.

   The Picarro Autosampler – High Precision Vaporizer Setup can operate in following coordinator modes:

For the L2140-*i*:

- **High Precision:** For interfacing with an autosampler for highest precision measurements of $\delta^{18}O$ and $\delta^{2}H$. This coordinator must be run in either the iH2O N2 mode or the iH2O Air mode. In this mode the coordinator *will not* output $\delta^{17}O$ and ^{17}O-excess. Each injection cycle takes 9 minutes.
- **High Throughput:** For interfacing with an autosampler for faster measurements of $\delta^{18}O$ and $\delta^{2}H$ with good precision. This coordinator must be run in either the iH2O N2 mode or the iH2O Air mode. In this mode the coordinator *will not* output $\delta^{17}O$ and ^{17}O-excess. Each injection cycle takes 4 minutes.
- **O^{17} High Precision:** For interfacing with an autosampler for highest precision measurements of $\delta^{18}O$, $\delta^{17}O$, δD and ^{17}O-excess. This coordinator must be run in either the "iH2O N2 O-17" mode or the "iH2O Air O-17" mode. In this mode the coordinator *will* output $\delta^{17}O$ and ^{17}O-excess.
- **Express*:** Used for faster measurement of liquid water samples with good precision. This coordinator must be run in either the "iH2O N2" mode or the "iH2O Air" mode. Automatically injects and analyzes liquid water samples. when using the Express coordinator, we recommend 10 injections,

the first 6 injections take 1.5 minutes each, while the last 4 injections take 5 minutes each. The first 7 injections will be discarded to achieve the optimal memory reduction.

- **Standard*:** Used to measure liquid water samples with maximum precision. This coordinator must be run in either the “iH2O N2” mode or the “iH2O Air” mode. Automatically injects and analyzes liquid samples. Each injection cycle takes 9 minutes.
- **Survey*:** Used for super-fast measurements of large sample batches at moderate precision and enables an efficient sample sorting. Automatically injects and measures liquid samples. This coordinator must be run in either the “iH2O N2” mode or the “iH2O Air” mode.

  Survey mode has two use cases:

  1. **Sample Sorting and Rearrangement:** Survey large sample batches and use the output values to manually rearrange samples. This will result in reducing the memory effect of followed measurements (either by Express mode or by Standard mode). In this use case we recommend doing 1 injection per sample, with sample volume of 2.5 µl. Using these parameters, measurement time is 95 seconds per sample.
  2. **Sample Measurement with Moderate Precision**: Use the survey mode to quickly measure samples with moderate precision. Here we recommend 6 injections with sample volume of 2.5 µl. The first 3 injections should be discarded to achieve the acceptable levels of memory. Using these parameters, measurement time is reduced to 9.5 minutes per sample.

     *only available with Coordinator software upgrade

For the L2130-*i*:

- **High Precision:** Used to measure liquid water samples with maximum precision. This coordinator must be run in either the “iH2O N2” mode or the “iH2O Air” mode. Automatically injects and analyzes liquid samples. Each injection cycle takes 9 minutes.
- **High Throughput:** Used for faster measurement of liquid water samples with good precision. This coordinator must be run in either the “iH2O N2” mode or the “iH2O Air” mode. Automatically injects and analyzes liquid water samples. Each injection cycle takes 4 minutes.
- **Express*:** Used for faster measurement of liquid water samples with good precision. This coordinator must be run in either the “iH2O N2” mode or the “iH2O Air” mode. Automatically injects and analyzes liquid water samples. when using the Express coordinator, we recommend 10 injections, the first 6 injections take 1.5 minutes each, while the last 4 injections take 5 minutes each. The first 7 injections will be discarded to achieve the optimal memory reduction.
- **Standard*:** Used to measure liquid water samples with maximum precision. This coordinator must be run in either the “iH2O N2” mode or the “iH2O Air” mode. Automatically injects and analyzes liquid samples. Each injection cycle takes 9 minutes.
- **Survey*:** Used for super-fast measurements of large sample batches at moderate precision and enables an efficient sample sorting. Automatically injects and measures liquid samples. This coordinator must be run in either the “iH2O N2” mode or the “iH2O Air” mode.

  Survey mode has two use cases:

  1. **Sample Sorting and Rearrangement:** Survey large sample batches and use the output values to manually rearrange samples. This will result in reducing the memory effect of followed measurements (either by Express mode or by Standard mode). In this use case we recommend doing 1 injection per sample, with sample volume of 2.5 µl. Using these parameters, measurement time is 95 seconds per sample.

2. **Sample Measurement with Moderate Precision:** Use the survey mode to quickly measure samples with moderate precision. Here we recommend 6 injections with sample volume of 2.5 µl. The first 3 injections should be discarded to achieve the acceptable levels of memory. Using these parameters, measurement time is reduced to 9.5 minutes per sample.

   *only available with Coordinator software upgrade

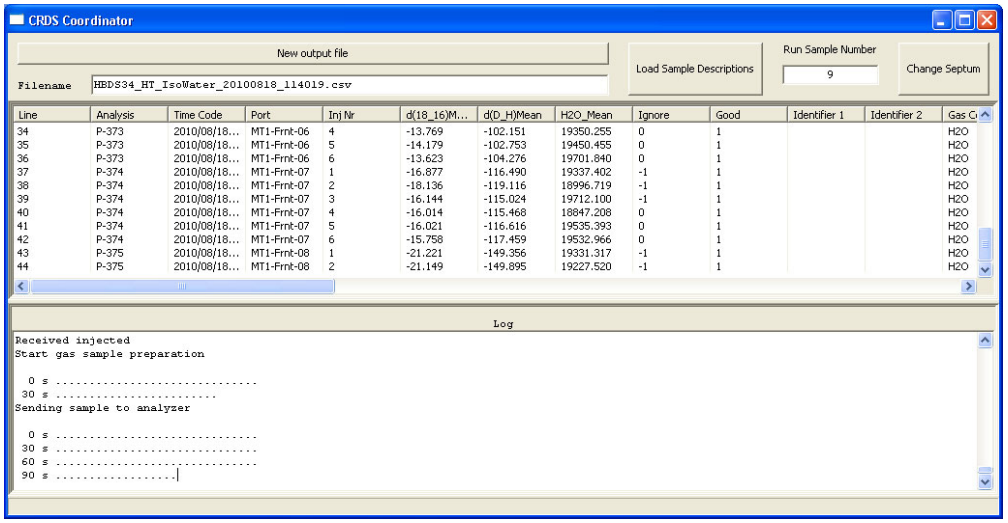
Analysis of liquid samples requires that both the coordinator software and autosampler job be started. Be sure to start the Autosampler Controller software before launching the Dual Mode Coordinator. Once the Autosampler Controller software is open, you may start the Coordinator. Once open, click "Run" on the Autosampler Controller software.

7. Once launched, the coordinator will automatically start collecting data, assuming the Autosampler job has been started. The data will also be available in the GUI as pulses. To customize pulse analysis or to adjust the peak of pulse data, please see **Pulse Customization.**

Figure 28: Coordinator Launcher

Coordinator Launcher Window for the L2140-i

Figure 29: Coordinator Window



DATA

To learn where to retrieve the data from, and to set the frequency of file archival and automatic deletion of old files, see **Data Files.** To access one's data remotely, see **REMOTE DATA ACCESS.**

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, click on the Setup Tool icon in the Picarro Utilities folder in the desktop.

The Picarro Water analyzers allow users to archive data using a compressed, binary "HDF5" or "h5" format. The Data File Viewer program, which comes installed with the hardware, allows one to open and convert h5 files, as well as viewing the h5 files as graphs. For more information, see **THE DATA FILE VIEWER.**

The Picarro Water Analyzers come preinstalled with the ChemCorrect software which allows one to screen and quantify contamination in isotopic water samples. To post process data using ChemCorrect Software, see **ChemCorrect Software: Analysis of Coordinator Files.**

One many need to adjust the sample injection volume to improve the quality of one's data. See **Adjusting Injection Volume** for more information.

10.7 Picarro Autosampler and High Throughput Vaporizer Setup

Picarro removed the High Throughput Vaporizer (part number A0212) from the price list in December 2013. Since that time, we have not shipped new High Throughput Vaporizers; however, we do continue to support High Throughput Vaporizers that are in the field. If you own a High Throughput Vaporizer, please contact support@picarro.com for operational instructions. They will refer you to an older version of this manual.

11. PICARRO SOFTWARE

11.1 Desktop Icons and Folders

On the Window's desktop, the following icons and folders may be present. The options available will vary depending on the configuration of your analyzer.

1. **Start Instrument**: When clicked, the analyzer will start measuring in the configuration that it was last in when the software/analyzer was shut down.
2. **Coordinator Launcher: Depending on the system's configuration, the coordinator program may or may not be included.** Clicking on this icon will lead you to a window which will allow you to select the appropriate mode for coordinator output, for example using the high precision vaporizer or the standards delivery module.
3. **Picarro Mode Switcher: Depending on the system's configuration, the Mode Switcher Software may or may not be included.** When clicked, you will be led to a window which will allow you to switch between various measurement modes. For the L2140-*i* this is how you switch between the normal mode for measuring only $\delta^{18}O$ and δD, and the ^{17}O mode for measuring $\delta^{18}O$, $\delta^{17}O$, δD and ^{17}O-excess. For all water isotope analyzers, this is how you switch between measuring water in an air or pure nitrogen matrix.
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 certain aspects are password protected to avoid inadvertent changes related to analyzer functionality. Password protested functionalities are intended for diagnostics purposes only and should only be accessed by members of Picarro's Technical Support Team.
5. **Picarro Utilities Folder:**
   - **THE DATA FILE VIEWER: When clicked, you will be led to a window which will allow you to convert between *.dat and H5 data files and to make various graphical representations of your data.**
   - **Data Recal: When clicked, you will be led to a window which will allow you to recalibrate your data based on known, certified data.**

- **Setup Tools: When clicked, you will be led to a window which will allow you to edit various settings for your analyzer (See the "Setup Tools" in the Desktop Icons and Folders section of this manual).**

6. **PostProcess ChemCorrect:** The ChemCorrect software is now included on all Picarro water isotope analyzers. The software allows post acquisition analysis of discrete sample data generated by the coordinator. See section entitled **ChemCorrect Software**.
7. Diagnostic Folder
   - **Stop Instrument: When clicked, you will be led to a window (see below) which 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 the Shutdown section of this manual to shut down the analyzer in normal circumstances.**

Figure 30: Stop CRDS Window

11.2 Switching Between Measurement Modes

1. The Picarro Mode Switcher allows users to operate the analyzer in various modes. Switching between measurement modes is accomplished with a few easy steps:
2. Activate the user interface by double-clicking the Picarro Mode Switcher icon on the desktop.
3. To switch modes, click the drop-down menu, select the desired measurement mode, and then click the launch button.

Figure 31: Picarro Mode Switcher

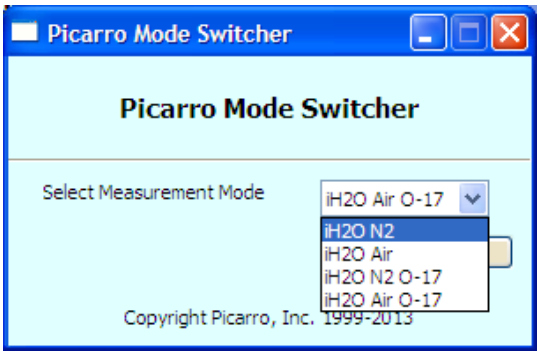
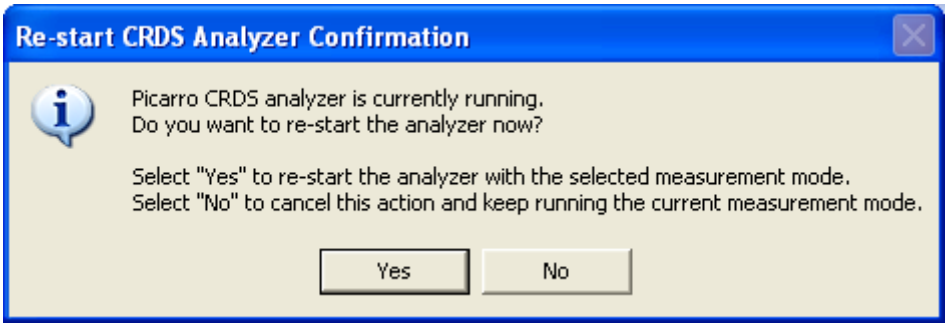


Figure 32: Restart CRDS Confirmation

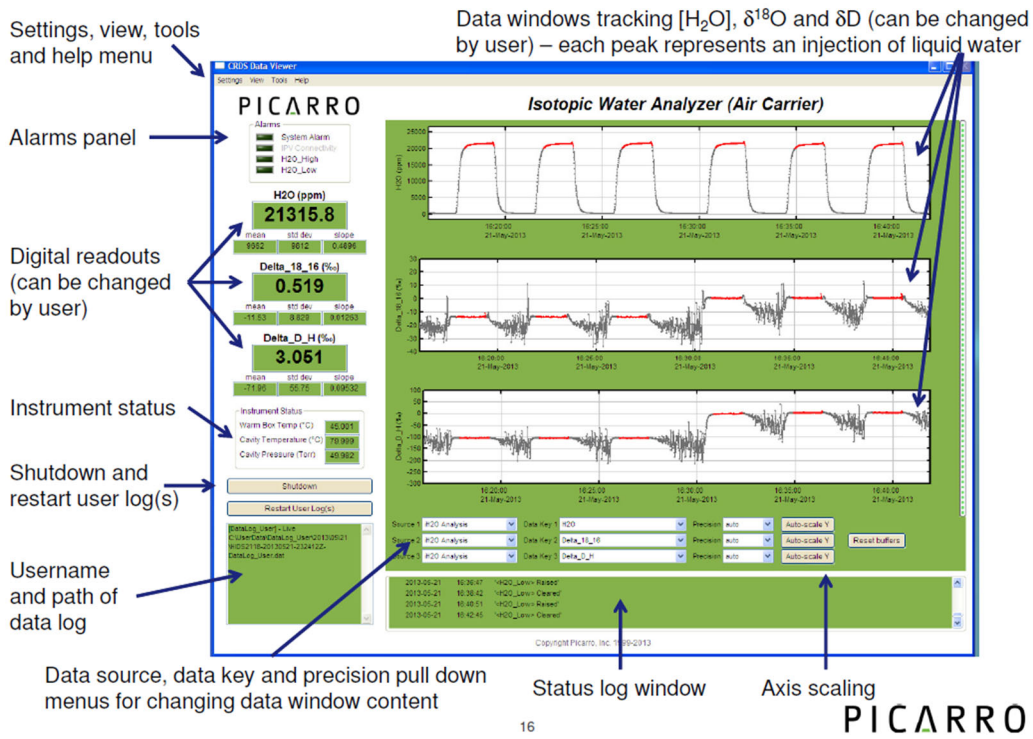


4. Confirm your selection when prompted by the confirmation dialog box.
5. The analyzer software will then re-start in the new measurement mode. There is no need to turn off the vacuum pump or any other peripherals during this process.

11.3 CRDS Data Viewer

The Picarro analyzer GUI has many features. See below for more information.

Figure 33: Data Viewer Layout



Layout of the Picarro CRDS Data Viewer. Types of data shown in the main GUI will differ between different analyzer configurations.

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:

- **Lock/Unlock time axis when zoomed: When locked, forces the two graphs to display the same time scale during zoom.**

- **Show/hide statistics: Toggles the measurement statistics display, see Digital Readout section below.**
- **Show/hide instrument status: Toggles the instruments status display. See Instrument Status section below.**
- **Tools Menu**

  This menu item has one entry:

- **User Calibration: Opens the user calibration window (default password is "picarro"). The calibration slope and intercept can be entered and their effects immediately seen in the data. Please refer to the Calibration section of this manual to learn more. The password can be reset in the QuickGui.ini file in the instrument directory: "C:\Picarro\G2000\AppConfig \Config\QuickGUI\" under the section: [Authorization] UserCalPassword = Picarro Show/Hide Valve.**
- **Help Menu**

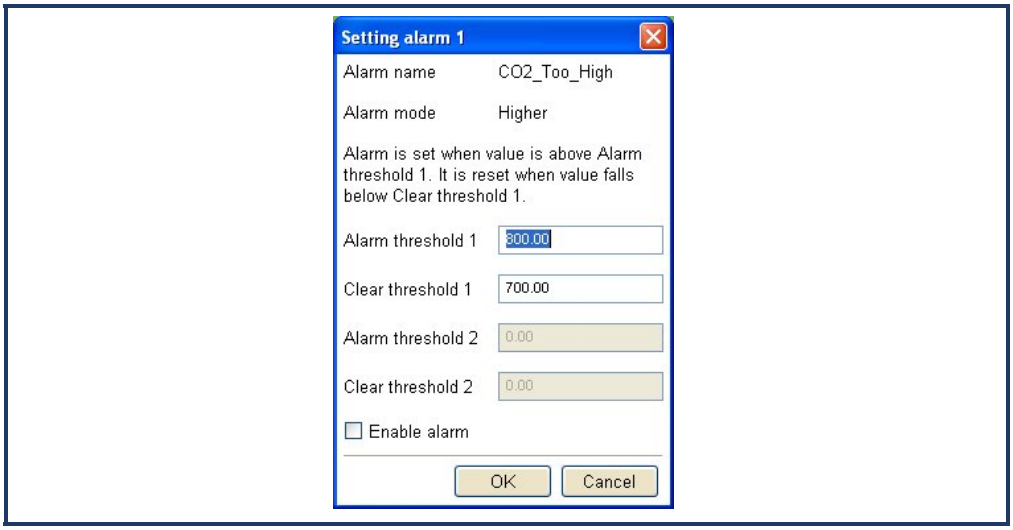
  "About" displays the version number of the instrument.

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 (i.e., "CO_2 Too High/Low"). The gas concentration alarm LEDs are off (grayed out) 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. The user can either enable the alarm or change the set point.

Figure 34: Alarm Settings Dialog



To change the set point, type the value you wish to set the alarm to and click the “OK” button to confirm. If you do not wish to change the alarm value anymore, press “cancel.” If you do nothing, the dialog box will eventually disappear, and the alarm value will remain unchanged.

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.

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.

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.

Data Window

The data window displays a graph of any stream of data vs. the computer's 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.

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.

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 wavelength monitor, indicated as "warm box temp."

The "DAS temp" sensor is located on the main electronics board. It is commonly 5-10°C above ambient temperature.

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.

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 front panel display.

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.

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.

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.

Common Status Log Messages

Temperature Locked: WB/HB (normal startup)

The system waits for the warm box (“WB” – the wavelength monitor chamber) to reach operating temperature. Similarly, the temperature of the hot box (“HB” – the 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 (normal startup)

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 (normal startup)

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

Measuring (normal startup)

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

Pressure High – check vacuum pump (error)

There is unusually high pressure. The pump is either weak or dying or the vacuum hose has a leak. See Troubleshooting section.

11.4 Coordinator Software

In order to measure discrete samples or to control external peripherals and accessories a separate software tool (Coordinator) is used to control the sample source and match the corresponding real time read out with the sample source. **The Coordinator programs that are accessible to a user, are dependent on the system configuration.**

Although this section will provide an overview to the concept of Coordinators, it does not necessarily provide the detail on all Coordinators available on a Picarro water isotope system. Instead, refer to the separate User Manual provided with your Picarro accessories, for example:

- SDM User Manual
- IM User Manual
- MCM User Manual
- CWS User Manual

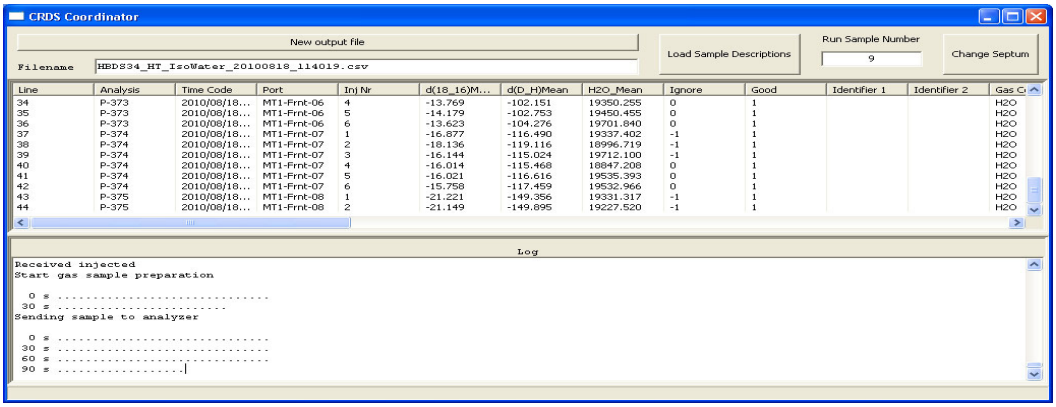
How to Run Coordinator Software:

1. First, make the required hardware connections for your system of interest. Afterwards, turn on the analyzer and wait for the CRDS Data Viewer of the analyzer's software to open up automatically on

your desktop screen. Next, launch the coordinator software by double clicking on the ‘Coordinator Launcher’ icon on your desktop.

2. After double clicking on the ‘Coordinator Launcher’ icon, a window will appear. Choose the appropriate coordinator from the drop down menu, and then click on the ‘Launch’ button. Make sure that the chosen coordinator is supported by your hardware connections and that samples are ready to be analyzed.

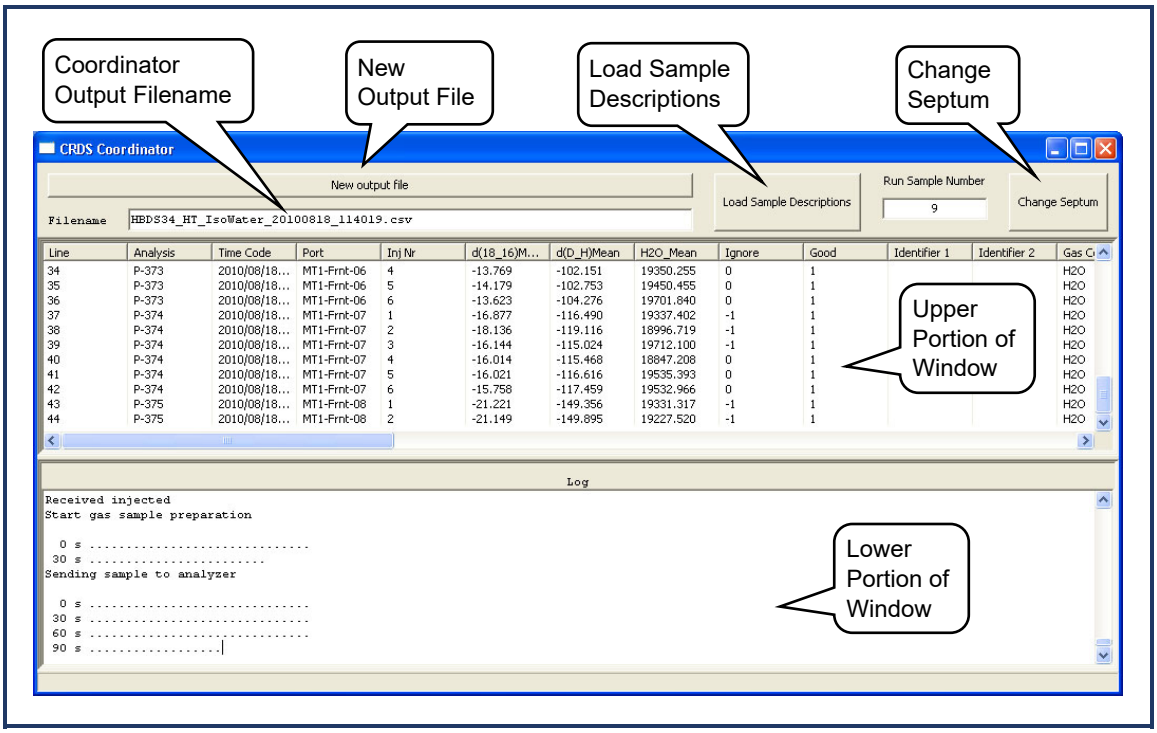
Figure 35: Coordinator Launcher and Window



Coordinator window. The look of the window may vary depending on the configuration of your analyzer.

3. After clicking on the “Launch” button, the coordinator window will pop up (depending on the coordinator mode chosen, you may or may not be asked to set parameters for your analysis). From the Coordinator window, you will be able see results from sample analysis, see the current status of your analyzer, and load sample descriptions.

Figure 36: Coordinator Window Description



Coordinator Window Descriptions

1. **Change Septum Button**: Used to pause the Autosampler and the vaporizer in the middle of an analysis to physically change the septum on the vaporizer.
2. **Load Sample Descriptions Button**: Located around the upper right corner of the Coordinator Window. The button allows the user to include a description for each vial in the data file output on the coordinator window.

   In order to load the sample description file, press the button labeled 'Load Sample Descriptions'. If you are using the CTC PAL Autosampler, two file dialog boxes will appear in sequence, the first for the front tray and the second for the rear tray. For the Picarro Autosampler, only one dialog box will appear. Select the sample description file, and then click to 'Open'. If a certain tray (front or rear) is not being used, use the 'Cancel' button to dismiss the dialog.
3. **New Output File Button**: Clicking on this button will save the data that you see on the coordinator window into a file, and then clear the data from the Coordinator Window.
4. **Upper Portion of The Window**: Each row represents the analysis results from a single injection. The types of columns are pre-selected by Picarro to include the most useful values for isotopic water analysis and for diagnostic indications.

The values for the columns, unless otherwise noted, are the average value for time period of the injection, which was marked in red on the CRDS Data Viewer. Values of the form *_SD are standard deviations for that same time period. The time period is selected by trigger thresholds based on the water vapor concentration. The analyzer is characterized and specified based on the factory default trigger thresholds—changing these values is not recommended, please contact Picarro if you feel this is necessary.

5. **Lower Portion Of The Window** (labeled Log): This window displays the action that is currently taking place. For those actions that take some time to complete, a period is displayed each second and a new line is started every thirty seconds to show progress.
6. **Coordinator Output Filename**: Can be seen in the upper left of the Coordinator window. It follows an automated convention of:

   model, serial number, mode, year, month, date, and time. For example:

   HBDS34_HT_IsoWater_20190818_114019.csv

   This means the coordinator file output was taken using analyzer HBDS34 in high throughput isotopic water analysis starting on 18 August 2019 at 11:40:19 am.

How to Make the Sample Description File:

The sample description file should be in CSV (comma separated value) format. Use the supplied NotePad++ software. Write the sample descriptions in the format as shown below.

Tray,Vial,Identifier 1,Identifier 2

1,1,Picarro 00,standard

1,2,Picarro 11, standard

1,3,Picarro 22, standard

1,4,WA 1,first sample from Washington

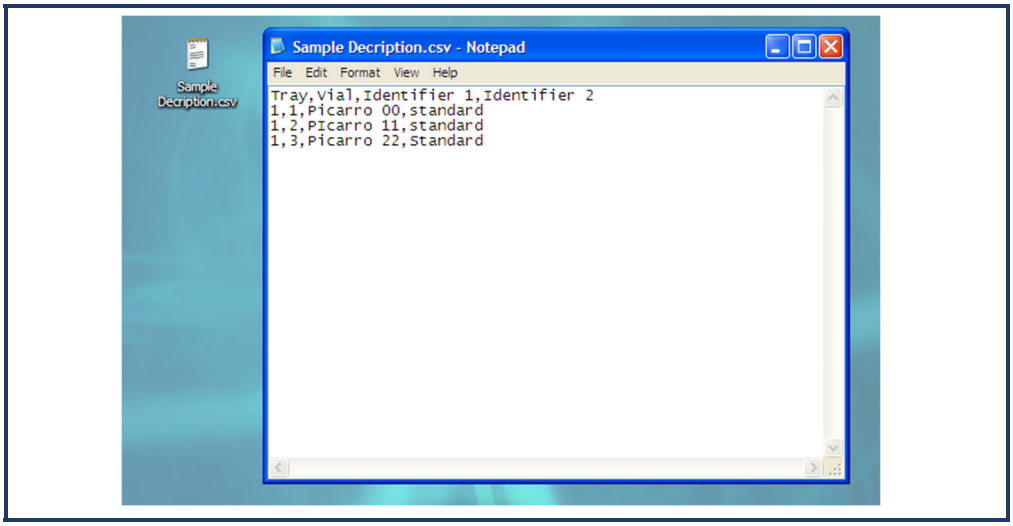
1,5,WA 2,second sample from Washington

1,6,CA 1, first sample from California

1,7,CA 2, second sample from California

1,8,Picarro 00, standard

Figure 37: Sample Description Example



After the first line (which should contain the column heading), each line should represent a sample description for the analysis results from a single injection. The lines in the file may be arranged in any order. The capitalization and spacing of the first line must exactly match the provided example. MS Excel can be used if the file is saved in CSV format. It is recommended to generate the file using Windows operating systems (as on the analyzer) as there are differences in CSV format between different operating systems. It is permissible to load the sample description files at any time during the data collection. The output file is rewritten to use the new sample descriptions, so that the most recently loaded descriptions are always used.

11.5 Parameters Recommended for Standard, Express, and Survey Modes

The widely accepted standard protocol for water isotope analysis is to run 6 injections of the sample, and average only the last 3 data points to obtain the isotopic values of the sample.

Using the **Express** mode, Picarro recommends running 10 injections per sample, and in similarity to the standard mode, average only the last 3 data points to obtain the isotopic values of the sample stage.

Before launching the Express coordinator, please set number of injections to 10, and volume of sample to 1.8 µl, in the Autosampler user interface.

Using the **Survey** mode requires only one injection.

Before launching the Survey coordinator, please set number of injections to 1, and volume of sample to 2.5 µl, in the Autosampler user interface.

The following table summarizes Picarro's recommendations for processing samples.

Coordinator	Number of Injections*	Sample Volume* (µl)	Number of Injections to Discard**
Standard	6	1.8	3
Express	10	1.8	7
Survey	1	2.5	0

*Edits are done to the autosampler software method tab.

**Edits are done to the ChemCorrect post processing parameters.

When using samples with large isotopic range, more injections can be added to help reduce the memory effect.

11.6 Coordinator Modes Available On a Picarro Water Isotope Analyzer

The CRDS analyzer needs to be equipped with the appropriate hardware to support a coordinator mode.

Hardware	Associated Coordinator(s)
High Precision Vaporizer (A0211) CRDS Analyzer (L21x0-i)	Manual Injection
High Precision Vaporizer (A0211) Autosampler (A0325) CRDS Analyzer (L21x0-i)	**L2130-*i*:** • High Precision** • High Throughput** • Standard* • Express* • Survey* **L2140-*i*** • High Precision • High Throughput • High Precision ^{17}O • Express* • Survey* *Only available with Coordinator software upgrade ** only available without coordinator upgrade
High Precision Vaporizer (A0211) Autosampler (A0325)	Dual Mode Dual Mode ^{17}O (if L2140-*i*)

Hardware	Associated Coordinator(s)
CRDS Analyzer (L21x0-i) Vaporizer Switching Valve (A0912)	
High Precision Vaporizer (A0211) Standards Delivery Module (A0101) CRDS Analzyer (L21x0-i)	Standards Delivery Module (SDM)
High Precision Vaporizer (A0211) Micro Combustion Module (A0214) Autosampler (A0325) CRDS Analyzer (L21x0-i)	MCM High Precision MCM High Throughput MCM Manual Mode
Induction Module (A0213) CRDS Analyzer (L21x0-i)	Induction Module
Continuous Water Sampler CRDS Analyzer (L2130-*i* or L2140-*i*)	Continuous Water Sampler

Description of Different Coordinator Modes:

1. **High Precision:** Used to measure liquid water samples with maximum precision. Automatically injects and measures liquid samples. Each injection cycle takes 9 minutes. High Precision and High Throughput Coordinator Modes operate in the exact same fashion except that the steps of sample preparation and analysis are faster in the high throughput coordinator.
2. **High Throughput:** Used for faster measurement of liquid water samples with good precision. Automatically injects and measures liquid samples. Each injection cycle takes 4 minutes. High Precision and High Throughput Coordinator Modes operate in the exact same fashion except that the steps of sample preparation and analysis are faster in the high throughput coordinator.
3. **Standard*:** Used to measure liquid water samples with maximum precision. Automatically injects and measures liquid samples. Each injection cycle takes 9 minutes.
4. **Express*:** Used for faster measurement of liquid water samples while retaining high precision. Automatically injects and measures liquid samples. Here we recommend 10 injection the first 6 injections take 1.5 minutes while the last 4 injections take 5 minutes. The first 7 injections will be discarded to achieve the optimal memory reduction.
5. **Survey*:** Used for super-fast measurements of large sample batches at moderate precision and enables an efficient sample sorting. By rearranging samples accordingly, we can reduce the

memory effect between adjacent sample. Automatically injects and measures liquid samples. Each injection cycle takes 95 seconds. For best practice, we recommend 1 injection per sample followed by manual sorting of samples according to survey results.

*Only available with Coordinator software upgrade.

6. **Manual Inject:** Used for semi-automated measurement of liquid water samples with maximum precision. Requires A0211 High Precision Vaporizer and A0322 Syringe Guide. User manually injects samples after prompt. The vaporizer control and the analysis of liquid samples are automated. Each injection cycle takes 9 minutes.
7. **Dual Liquid/Vapor:** Used for measurement of ambient vapor coupled with automated injection of liquid calibration standards. Requires A0211 high precision vaporizer, A0912 Dual Mode Configuration hardware and software for vapor calibration and Autosampler. Alternates between analyzing ambient vapor and liquid standards based on user defined sequence. Uses high precision method for liquid calibration. Each injection cycle takes 9 minutes.
8. **Standards Delivery Module (SDM):** Used for measurement of ambient vapor coupled with automated injection of liquid calibration standards. Requires A0211 High Precision Vaporizer and A0101 standards delivery module. Alternates between analyzing ambient vapor from multiple points and a continuous stream of vaporized standard. The alternation is based on user defined sequence. A calibration measurement takes approximately 20 minutes per concentration/standard. Before operating in SDM mode, set the vaporizer temperature to 140°C**.**
9. **IM CRDS (Induction Module)**: Requires the IM. Used for isotopic analysis of extracted water from samples such as soil, plants, or tissues and allows the isotopic analysis of the extracted water. This requires the Induction Module.
10. **Micro Combustion Module (MCM)**: Used to measure liquid water samples while destructively removing potential contaminants with maximum precision. Requires A0211 High Precision Vaporizer, A0214 Micro Combustion Module and Autosampler. Automatically injects and measures liquid samples. Each injection cycle takes 9 minutes. In addition to controlling the valve sequence for injection liquid water samples, the MCM coordinator also control the heating of the MCM to ensure removal of interfering organics.
11. **Continuous Water Sampler (CWS):** Used for continuous, real-time measurements of water. Requires A0217 Continuous Water

Sampler. No discrete sampling is required. Automatically switches between calibration standards and samples using four inlet ports.

IMPORTANT NOTE: The L2140-i can operate in four instrument modes (iH2O N2, iH2O Air, iH2O N2 O-17 and iH2O air O-17). Due to the high precision demands of 17O-excesss science, only the 'High Precision', 'Dual Mode' and 'Manual Inject' coordinator modes will work for the two O-17 instrument modes.

Description of Column Headers Used in Coordinators:

The following table provides information regarding the column headers presented in the Coordinator output files available on a Picarro water isotope analyzer. The table includes the header for the following coordinators:

- **High Precision**
- **High Throughput**
- **Standard**
- **Express**
- **Survey**
- **Dual Mode**

The table covers all variations of the coordinators. Coordinators vary by analyzer product number, therefore not all columns will be visible on an individual analyzer.

Item	Description
Line	Line counter. Each line represents a single injection or data point (for vapor measurements in the dual mode).
Analysis	Sequential number of the sample run over the history of the analyzer.
Time Code	Time the line was recorded in "Year/Month/Day Hours:Minutes:Seconds". This time stamp is linked the local time of your computer's clock.
Port	Reports the vial position on the tray where the autosampler is sampling from.
Inj Nr	Sequential injection number from the port (vial).

Item	Description
d(17_16)Mean	The average $\delta^{17}O$ value, in per mil (‰), measured at that interval (Line). The typical raw data acquisition rate on a L2140-*i* is ~ 1 Hz, therefore this represents the average of 1 Hz data points across the water pulse. The averaging window is shown in red on the CRDS Data Viewer. The reported delta values are not calibrated. Post-processing is required for calibration. Only available on a L2140-*i*.
d(18_16)Mean	The average $\delta^{18}O$ value, in per mil (‰), measured for that injection (Line). The typical raw data acquisition rate on a L21x0-*i* is ~ 1 Hz, therefore this represents the average of 1 Hz data points across the water pulse. The averaging window is shown in red on the CRDS Data Viewer. The reported delta values are not calibrated. Post-processing is required for calibration.
d(D_H)Mean	The average $\delta^{2}H$ value, in per mil (‰), measured for that injection (Line). The typical raw data acquisition rate on a L21x0-*i* is ~ 1 Hz, therefore this represents the average of 1 Hz data points across the water pulse. The averaging window is shown in red on the CRDS Data Viewer. The reported delta values are not calibrated. Post-processing is required for calibration.
E17_Mean	The average ^{17}O-excess value, in per mil (‰), measured for that injection (Line). ^{17}O-excess is the deviation the expected relationship between $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios and is defined by: E17_Mean = ln[d(17_16)Mean + 1] – 0.528ln[d(18_16)Mean + 1] The typical raw data acquisition rate on a L2140-*i* is ~ 1 Hz, therefore this represents the average of 1 Hz data points across the water pulse. The averaging window is shown in red on the CRDS Data Viewer. The reported delta values are not calibrated. Post-processing is required for calibration. Only available on a L2140-*i*.
H2O_Mean	The average water concentration, in ppm, measured for that injection (Line). The typical raw data acquisition rate on a L21x0-*i* is ~ 1 Hz, therefore this represents the average of 1 Hz data points across the water pulse. The averaging window is shown in red on the CRDS Data Viewer. The reported delta values are not calibrated.
Ignore	-1 or 0: -1 indicates the measurement should be ignored and is based on the first three injections from each sample vial being ignored due to sample-to-sample isotopic memory.
Good	0 or 1: 1 indicates that the mean H_2O concentration is within the required range. 0 indicates that the mean H_2O concentration is outside the required range.

Item	Description
Vapor d(17_16)	Only reported when operating in the Dual Mode. Populated when the Dual Mode is measuring ambient vapor. Raw $\delta^{17}O$ output from the Analyzer with no averaging. The typical raw data acquisition rate on a L2140-*i* is ~ 1 Hz, therefore during the vapor measurement phase a line will be created every ~ 1 second. Only available on a L2140-*i*.
Vapor d(18_16)	Only reported when operating in the Dual Mode. Populated when the Dual Mode is measuring ambient vapor. Raw $\delta^{18}O$ output from the Analyzer with no averaging. The typical raw data acquisition rate on a L21x0-*i* is ~ 1 Hz, therefore during the vapor measurement phase a line will be created every ~ 1 second.
Vapor d(D_H)	Only reported when operating in the Dual Mode. Populated when the Dual Mode is measuring ambient vapor. Raw $\delta^{2}H$ output from the Analyzer with no averaging. The typical raw data acquisition rate on a L21x0-*i* is ~ 1 Hz, therefore during the vapor measurement phase a line will be created every ~ 1 second.
Vapor E17	Only reported when operating in the Dual Mode. Populated when the Dual Mode is measurement ambient vapor. Raw ^{17}O-excess output from the Analyzer with no averaging. The typical raw data acquisition rate on a L21x0-*i* is ~ 1 Hz, therefore during the vapor measurement phase a line will be created every ~ 1 second. Only available on a L2140-*i*.
Vapor H2O	Only reported when operating in the Dual Mode. Populated when the Dual Mode is measurement ambient vapor. Raw H_2O concentration output from the Analyzer with no averaging. The typical raw data acquisition rate on a L21x0-*i* is ~ 1 Hz, therefore during the vapor measurement phase a line will be created every ~ 1 second.
Identifier 1	First identifier of the sample. Only populated if a sample description file is loaded when the coordinator is open.
Identifier 2	Second identifier of the sample. Only populated if a sample description file is loaded when the coordinator is open.
Gas Configuration	Indicates the type of gas being measured. Water isotope analyzers measure water vapor sample.
Timestamp Mean	Unix timestamp.
d(17_16)_SD	Standard deviation of the measured $\delta^{17}O$ across an injection's averaging window. The averaging window is show in red on the CRDS Data Viewer. Only available on a L2140-*i*.
d(18_16)_SD	Standard deviation of the measured $\delta^{18}O$ across an injection's averaging window. The averaging window is show in red on the CRDS Data Viewer.

Item	Description
d(D_H)_SD	Standard deviation of the measured δ^2H across an injection's averaging window. The averaging window is show in red on the CRDS Data Viewer.
H2O_SD	Standard deviation of the measured H_2O concentration across an injection's averaging window. The averaging window is show in red on the CRDS Data Viewer.
E17_SD	Standard deviation of the measured ^{17}O-excess across an injection's averaging window. The averaging window is show in red on the CRDS Data Viewer. Only available on a L2140-*i*.
d(18_16)_Sl	Slope of the measured $\delta^{18}O$ across an injection's averaging window. The averaging window is show in red on the CRDS Data Viewer.
d(D_H)_Sl	Slope of the measured δ^2H across an injection's averaging window. The averaging window is show in red on the CRDS Data Viewer.
H2O_Sl	Slope of the measured H_2O concentration across an injection's averaging window. The averaging window is show in red on the CRDS Data Viewer.
baseline_shift	The average value for baseline shift, in ppb/cm, measured for that injection (Line). Baseline_shift is a spectral term that is measured on the L2130-*i* and L2140-*i*. It is the change in the constant term of the fitted baseline, relative to an empty cavity baseline which is measured at the Picarro factory. This column can be used to track potential spectral interference and data integrity. See **ChemCorrect** section.
slope_shift	The average value for slope shift, in ppb/cm, measured for that injection (Line). Slope_shift is a spectral term that is measured on the L2130-*i* and L2140-*i*. It is the change in the linear term of the fitted baseline, relative to an empty cavity baseline which is measured at the Picarro factory. This column can be used to track potential spectral interference and data integrity. See **ChemCorrect** section.
residuals	The average value for residuals, in ppb/cm, measured for that injection (Line). Residuals is a spectral term that is measured on the L2130-*i* and L2140-*i*. This term represents the root mean squared residual of the least-squares fit of the measured spectra versus the expected spectra. This column can be used to track potential spectral interference and data integrity. See **ChemCorrect** section.

Item	Description
baseline_curvature	The average value for baseline curvature, in ppm*cm, measured for that injection (Line). Baseline_curvature is a spectral term that is measured on the L2130-*i* and L2140-*i*. This term represents the quadratic term in the fitted baseline. This column can be used to track potential spectral interference and data integrity. See **ChemCorrect** section.
interval	Average of the elapsed time between each fitted spectrum for an injection's averaging window.
ch4_ppm	The average methane concentration, in ppm, measured for that injection (Line). This column can be used to track potential spectral interference and data integrity. Methane concentration is not calibrated and should not be used directly to determine the methane concentration in the water source.
h16od_adjust	This term represents an adjustment applied to WLMh16od_offset, a filtered and scaled frequency error derived from least-squares fit. h16od_adjust is only reported on the L2130-*i* and L2140-*i*. This column may be used to the Picarro Technical Support team in diagnosing wavelength locking.
h16od_shift	This term represents an adjustment applied to WLMh16od_offset, a frequency error derived from least-squares fit. h16od_shift is only reported on the L2130-*i* and L2140-*i*. This column may be used to the Picarro Technical Support team in diagnosing wavelength locking.
n2_flag	Flag for reported the measurement mode at the time of measurement. n2_flag will equal 1 for operation in the N_2 mode, and equal to 0 for operation in the Zero Air mode.
DAS Temp	Temperature measured at the DAS board in the Picarro Analyzer.
Tray	Tray number. Relevant for CTC Autosampler (Picarro Part Number A0321).
Sample	Vial sample number.
Job	Line in the autosampler job queue.
Method	Autosampler method that is associated with the autosampler sequence.
Error Code	Error code associated with Autosampler operation.

11.7 Data Files

During operation, the analyzer generates ASCII format text output file that is updated after each batch of concentration measurement is complete. 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 and Archived 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*
    - CFHADS2007: 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 and the local computer's time).

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 which 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\Year\Month\Day**

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 clock[1]. 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-
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	ms

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

Variable Name	Description	Units
	Example: at 3:00:00 PM on January 12 the value is 63556671600000	
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 GMT[2] (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 calculators[3] that convert Epoch Time to local time at any time zone, as well as many functions in commonly used data analysis p

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

[3] For example, http://www.epochconverter.com

11.8 ChemCorrect Software

Principle of Operation

Picarro CRDS has become a *de facto* standard for many water sample research areas, such as ice core, watershed, and aquifer studies. For various reasons, samples can contain a variety of chemical contaminants, which in some cases can lead to spectral interference that can degrade the accuracy of results. It is difficult to eliminate these contaminants from water samples without fractionating the isotope ratios and diminishing sample fidelity.

Proprietary software, called ChemCorrect™, comes pre-loaded on your Picarro water isotope analyzer. This program solves the problem of data degradation and fidelity resulting from water samples contaminated with trace hydrocarbons. In addition, ChemCorrect™ can be used to correct data an isotope reference scale (typically VSMOW-SLAP for water isotopes). The software makes the *a priori* assumption that your standards are clean waters that do not contain any contamination. Then the program compares a number of features in the spectra from the samples and the standards, applies a statistical test to see if the samples are different from the standards, and assigns flags based the statistical differences. These flags alert you to artifacts, potentially from contamination, that may affect the accuracy of your results. Finally, the software using a linear regression to correct your samples to an isotope reference scale by comparing the measured values of your standards to their accepted values.

How Contaminants Impact The Optical Spectrum

Contaminants fall into one of the following three categories, based on the nature of the distortion to the optical spectrum:

1. Compounds that do not affect the spectrum (at concentrations up to 10-20% of the water sample). Most compounds fall into this category. In the presence of these contaminants, Picarro analyzers will report accurate and precise isotope values without bias or increase in noise.
2. Large compounds (with more than about 6-8 atoms) contribute a broad, spectrally unresolved absorption baseline beneath the target molecules. To first order, this baseline will cause no systematic bias to the reported values. Because optical absorption is a linear, additive process, the water vapor spectrum will ‘float’ on top of the contaminant baseline. The linearity and wide dynamic range of CRDS makes the technique particularly insensitive to these baseline offsets.

In some cases, however, this baseline offset is accompanied by a tilt of the spectrum with wavelength. This larger offset, if uncorrected, can cause bias in the measurements and degrade the precision of the instrument.

3. Small compounds (with fewer than 6-8 atoms) have spectrally resolved absorption lines that can interfere with the lines from the observed water vapor. This can lead to systematic errors in the reported isotope ratios. One example of such a molecule is methanol, which has a particularly complex absorption spectrum in this spectral region.

   The ChemCorrect™ software uses known spectral interferences or general spectral patterns to identify trends due to contamination.

ChemCorrect™ on the L2130-i and L2140-i:

The L2130-*i* and L2140-*i*, when operating in 'normal' measurement mode ($\delta^{18}O$ and δD), also measure spectral indicators that can be used to determine the integrity of the spectra and resulting data.

Using the spectral indicators listed below, the ChemCorrect™ software performs statistical tests to determine how those spectral features differ between the samples and the standards.

- **RESIDUAL: the root mean squared residual of the least-squares fit to a spectra, in units of ppb/cm, is used to screen for potential small molecule contaminants, e.g., methanol.**
- **BASELINE SHIFT: the spectral baseline is a good early indicator of a potential issue with a sample. The baseline shift term is a change in the constant term of a fitted baseline, in units of ppb/cm.**
- **BASELINE CURVATURE: the spectral baseline is a good early indicator of a potential issue with a sample. The baseline curvature team is a change in the quadratic term of a fitted baseline, in units of ppb*cm.**
- **SLOPE SHIFT: the slope of the spectral baseline or change in the linear term of the fitted baseline, in units of ppb/cm, although not unique is also a useful indicator for moderately-sized molecules, e.g., ethanol that can interfere with nearby spectral features.**

The software flags these indicators if they deviate from the thresholds set in ChemCorrect.

For example, a red flag can be triggered by any of the following:

- **the sample residual being 1.5 σ away from the mean of the standards residual**
- **the sample baseline shift being 18 σ away from the mean of the standards baseline shift**
- **the sample baseline curvature being 3 σ away from the mean of the standards baseline curvature**

Sometimes the software generates false positives by flagging features that do not arise from contamination. To reduce the number of false positives, the notification thresholds can be changed to be less stringent. This can be done by editing the ChemCorrect™ Instruction Set. If a user edits the Instruction Sets, we recommend changing the name of the Instruction Set so that it is possible to revert to the original set supplied by Picarro.

If a flag is raised, a number of things can be done. First, try some offline sample treatment methods, such as the use of activated charcoal. Second, if you suspect alcohols may be present in your samples, you can utilize Picarro's Micro Combustion Module (MCM) to remove those artifacts. Third, and as a last resort, you can analyze your samples using an alternative technique, such as Isotope Ratio Mass Spectrometry (IRMS). IRMS is not susceptible to spectral interference from alcohols; it can, however, introduce other analytical artifacts and have other interferences, such as mass interference, that can affect accuracy.

Analysis of Coordinator Files

The following Coordinator output files can be post-processed using ChemCorrect™:

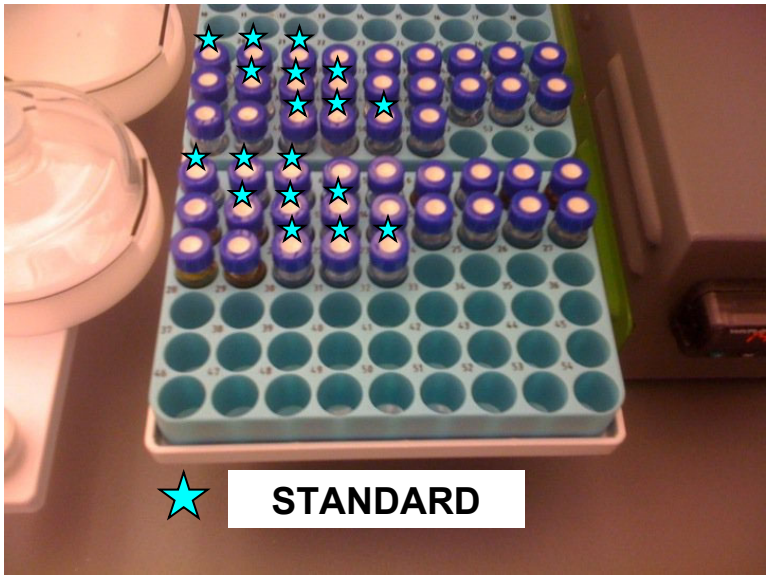
- **High Precision**
- **High Throughput**
- **Manual Injection**
- **Standard**
- **Express**
- **Micro Combustion Module**

ChemCorrect™ cannot be applied to data $\delta^{17}O$ and ^{17}O-excess data. Nor can it be applied to Coordinators generated during SDM, IM, Dual Mode or Continuous Water Sampler Setups.

Preparing the Run Sequence:

1. Each run needs at least 2 standards (3 is recommended but more is better) with known $\delta^{18}O$ and δD values. These values create a linear fit, which is used in calibration of the samples.
2. The standards must be run one after another at the beginning of each tray to be analyzed. The post processing software works sequentially and therefore requires the linearity of the known standards before it can correct the unknown values of the samples. It is recommended to include standards in the middle and end of the sample set as controls. An example is shown below, vials with the CYAN stars being the standards:

Figure 38: Run Sequence with Standards



3. Due to memory, the first two to three injections of each vial should be ignored. Because of this, a minimum of six injections should be run per vial. The number of injections is set using the Autosampler Controller software (A0325) or the external control pad of the CTC Autosampler (A0321) prior to the run.

Files Required to Run ChemCorrect™:

ChemCorrect™ requires a *standards file*, an *instruction set*, and a *source file* (data output from the coordinator software that is in C:\IsotopeData). Each of these files are provided in .csv formats. To ensure the standards

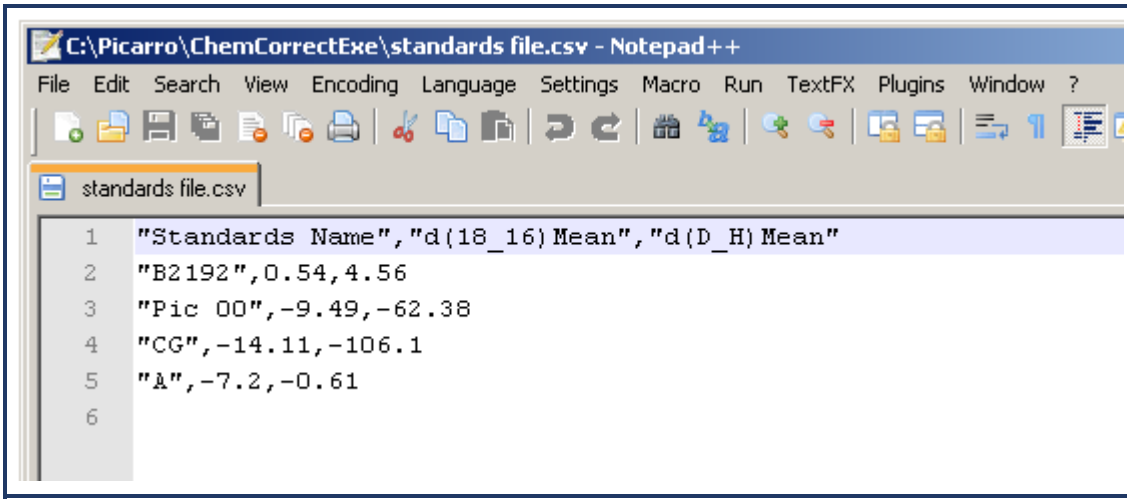
file format is preserved, Picarro recommends editing the file using Notepad++ which is provided with the analyzer.

A sample data file along with the standards and instruction files can all be found in the ChemCorrect™ main folder C:\Picarro\ChemCorrectExe.

Standards File:

The standards.csv file must contain the name and known $\delta^{18}O$ and δD values of each standard (relative to an isotope reference scale, typically VSMOW-SLAP for water isotopes). The names in the standards.csv file must match (case-sensitive) the names in the source file under "Identifier 1". If they do not match, standards will be treated as samples.

Figure 39: Standards CSV File Example



Instruction Set:

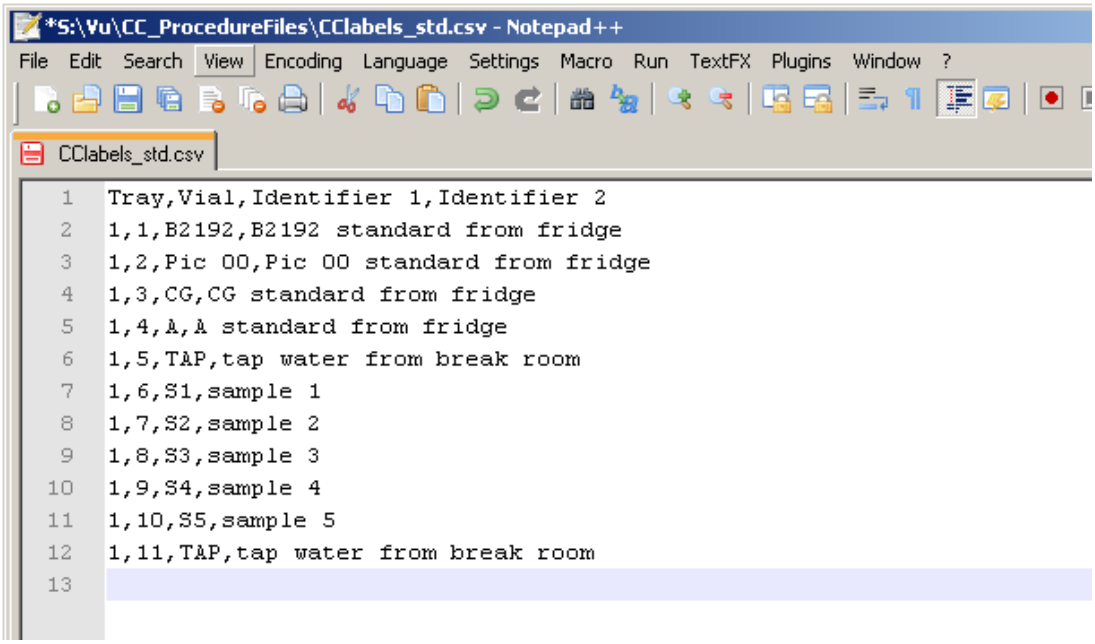
The instruction set is provided by Picarro.

- **L2130-*i* / L2140-*i* Instruction Set: chemcorrect_inst avg_orgeval_10.csv**

Source File:

This is the output file from the Coordinator (stored in C:\IsotopeData). Before closing the Coordinator at the end of an Autosampler Sequence, it is advised to load the sample description file. Below is an example of a sample description file. Ensure that the "Identifier 1" for standards is identical to the "Standards Name" list in the standards file.

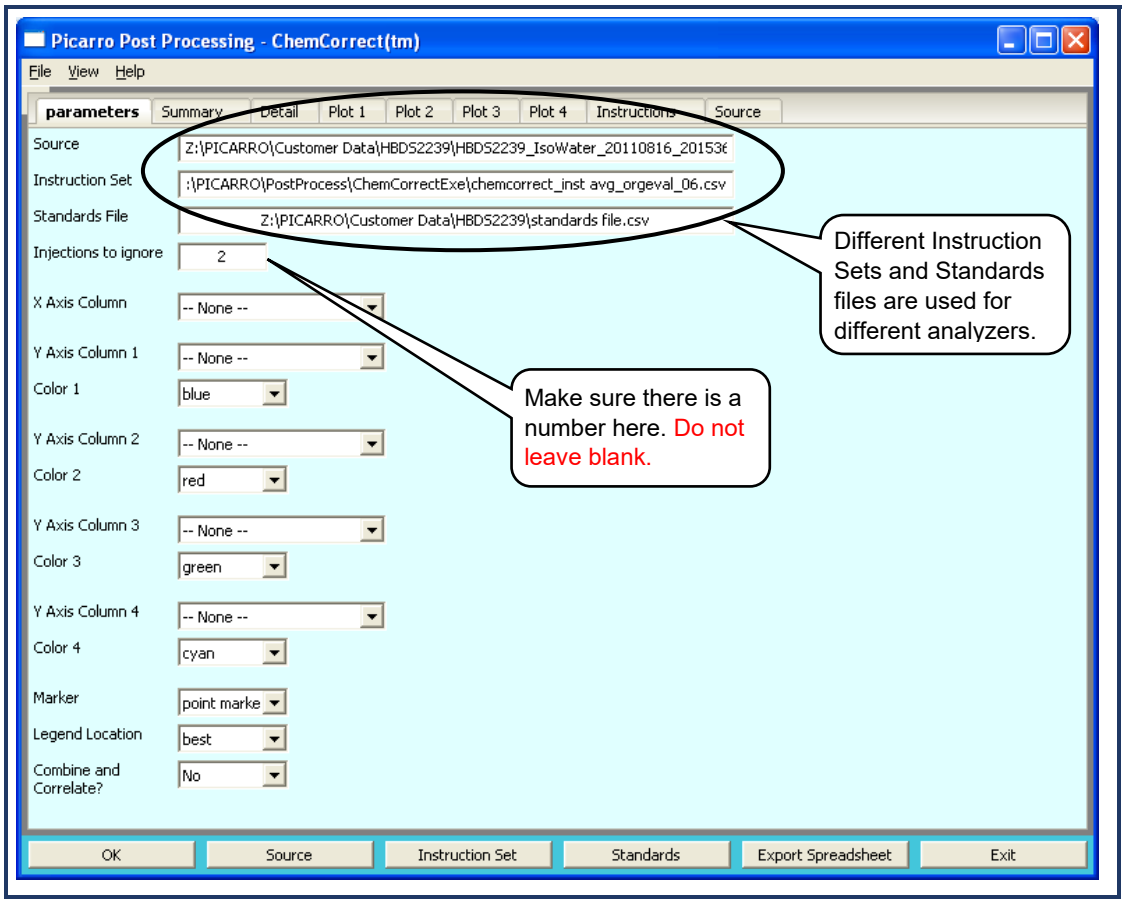
Figure 40: Sample Description File



Running ChemCorrect™:

1. Double-click the ChemCorrect™ icon on the analyzer desktop. The ChemCorrect™ program will now open.
2. The top four boxes are the required fields: the most recent *Source* file name (sometimes empty), *Instruction Set* name, *Standards File* and the number of *Injections to Ignore*. You also have an option to plot additional graphs for other parameters.
3. To choose a different source file to be analyzed, click the “Source” button located on the bottom of the window. Then use the finder window to locate the desired raw data file and click “Open.”
4. To select a different instruction file than the one displayed, click the “Instruction Set” button located on the bottom of the window. Then use the finder window to locate the desired instruction file and click “Open”.
5. To change the number of injections to be ignored, highlight the existing number and type in the preferred one (required 2 but 3 is recommended). *Do not leave this field blank.*
6. When the correct source and instruction files are shown, click the “OK” button at the bottom of the window to start the ChemCorrect™ analysis.

Figure 41: ChemCorrect Window



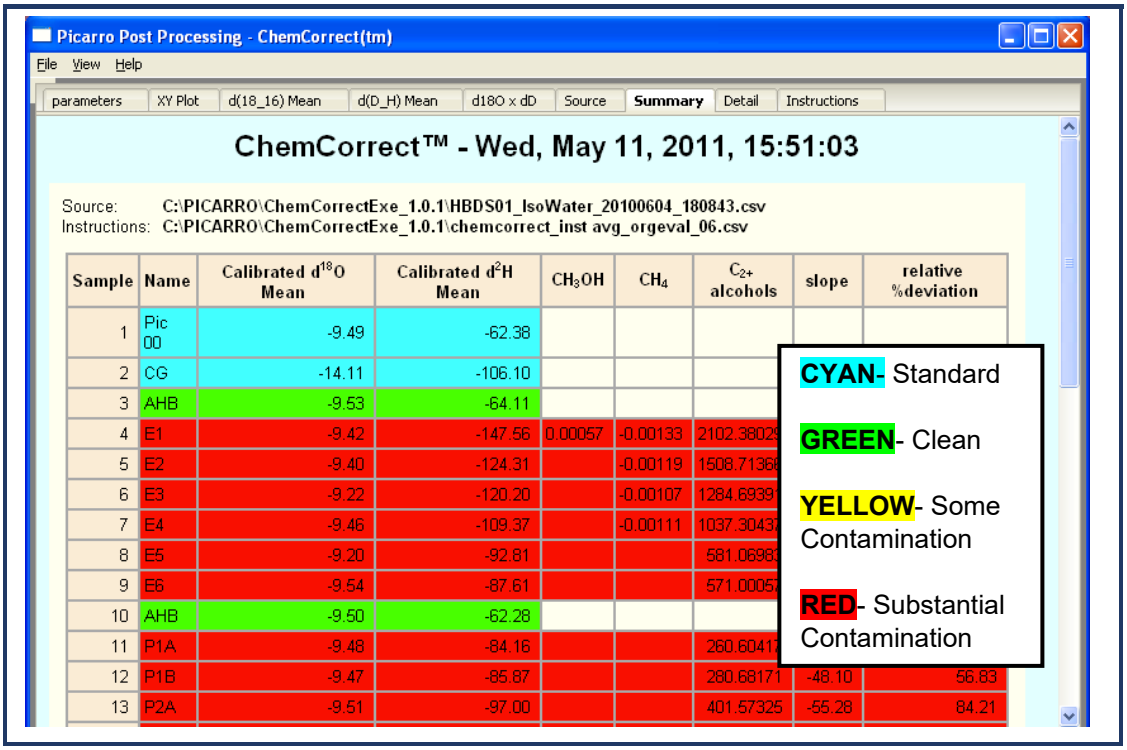
Example Analysis:

See the figure below.

1. Select “HBDS01_IsoWater_20100604_180843.csv” (which Picarro has provided in the main folder) as the source, and “chemcorrect_inst avg_orgeval_06.csv” as the instruction file. Then click “OK.”
2. The first display is called the “Summary.” Contained here are: the calibrated isotope values and visual indicators as to the severity of contamination by sample.
3. The CYAN rows are standards.
4. The GREEN rows are samples that have been determined to have little to no contamination.
5. The YELLOW rows are samples that contain trace values of contamination that may slightly shift the isotope values.
6. The RED rows are samples with severe contamination leading to inaccurate δ^2H and $\delta^{18}O$ readings.

7. A star next to a sample indicates a problem, e.g. missing rows in the source file resulting in an inaccurate calculation.
8. Red/yellow rows display relative contamination due to methane, methanol, or “other” hydrocarbons in the respective columns on the right.

Figure 42: ChemCorrect Analysis



9. There are other tabs that can be accessed by clicking on them in the top left corner of the window.
10. Detail: Summons a list of summarized charts by injection and sample chronologically. The un-calibrated and calibrated values, as well as the measurements taken to calibrate the values are included per injection. Below each chart is a summary.
11. Source: Displays the original raw data file without any changes or calibration.
12. Instructions: Displays the raw instruction file used by ChemCorrect™ as well as comments on the far right of each instruction.
13. Additional plots for visualizing your data.
14. At the bottom of the ChemCorrect™ window are additional buttons “OK”, “Export Spreadsheet,” and “Exit” buttons.
15. OK: each time you reloaded the source and instruction sets, you can click “OK” again to process more data without closing and re-

opening ChemCorrect™. Once you make your edits, export the result to save your processed data.

16. Export Spreadsheet: Creates an excel spreadsheet complete with all the information contained in the four tabs in the ChemCorrect™ main window as well as all the data sets and formulas used to calibrate the isotope values.
17. Exit: Quits ChemCorrect™.
18. The standards.csv file can be amended if needed, but the format must remain the same. To edit, simply open the file, make the desired changes, and hit save. For the changes to be reflected in ChemCorrect™, hit the "OK" button at the bottom of the ChemCorrect™.
19. For more advanced users, *Instruction Sets* can be edited to perform your required calculations. If editing the Instruction Set, we recommend changing the name of the Instruction Set so that it is possible to revert to the original set supplied by Picarro.

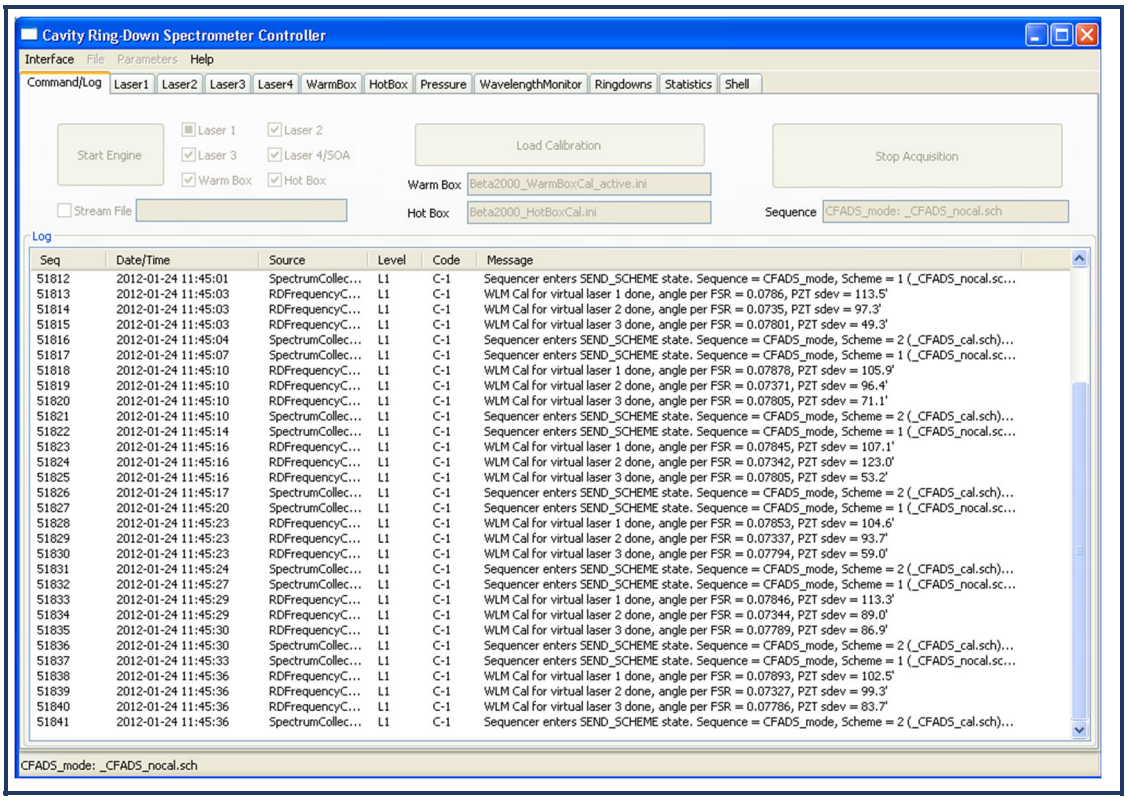
Picarro recommends running the post processing within 7 days of initially acquiring the data. If a sample is flagged as contaminated, the post processing software will automatically set aside the associated spectral files. These files can be sent to Picarro for further analysis and spectral library development. Once set aside, these files will not be affected by the automatic file management software which is running on the analyzer.

Due to the large amount of data generated by the analyzer a buffer of approximately 10 GB of spectral files are kept, after which point, they are erased. This corresponds to approximately 2 weeks of operation. Running the post processing ensures that any spectra associated with contamination are not erased.

11.9 Cavity Ring-Down Spectrometer Controller

On your desktop, there is an icon labelled "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 cannot change anything related to analyzer functionality and is intended for diagnostics purposes only.

Figure 43: CRDS Controller



12. PERFORMANCE VERIFICATION

12.1 Drift and Precision Testing

Precision and drift tests for $\delta^{18}O$ and $\delta^{2}H$ (δD) are recommended every 6 to 12 months throughout an analyzer's lifetime. This will allow you to verify a new installation, track performance as the instrument ages, determine if it is time for a Factory Refresh, and perhaps identify a small problem before it becomes a major setback. These tests can also be performed when data quality suddenly and inexplicably deteriorates.

Here are the testing procedures for each analyzer:

L2130-i and L2140-i:

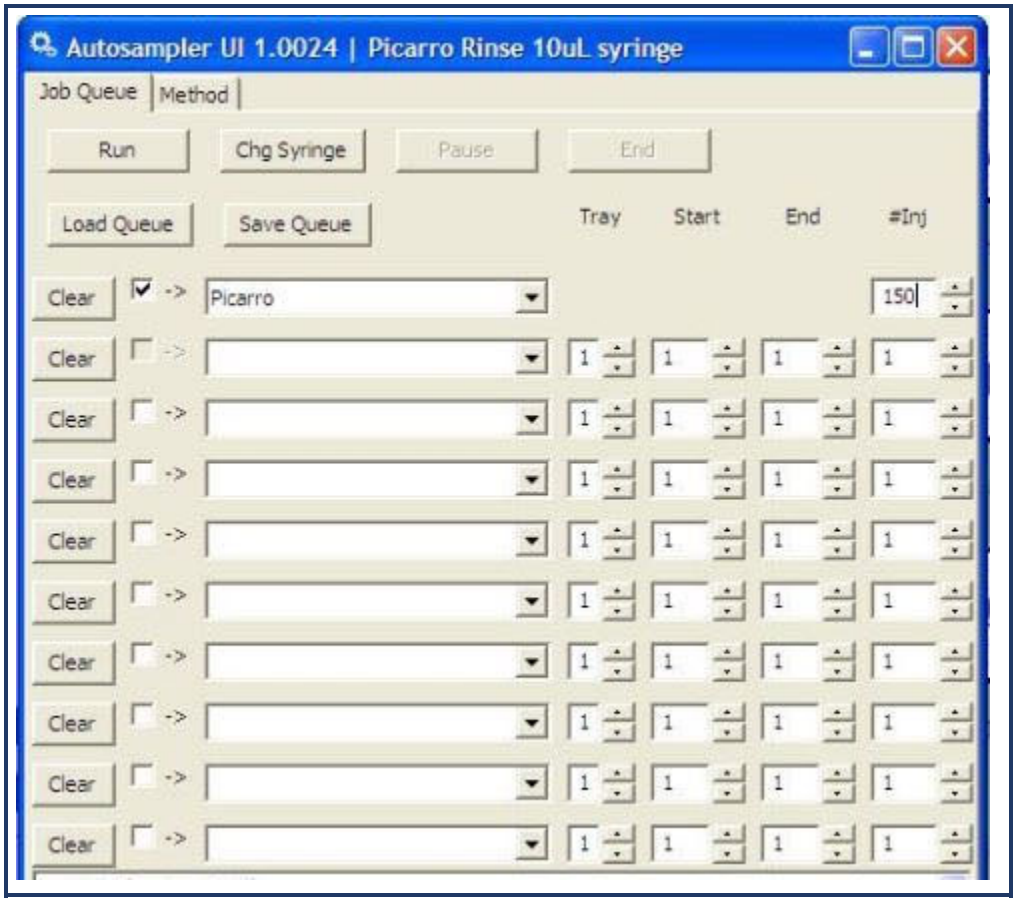
The drift and precision test for a L2130-*i* and L2140-*i* is conducted by measuring water from the wash station, instead of vials. These analyzers are precise enough to detect small variability in the composition of water from individual vials, even if it was sourced from the same supply. By running the drift and precision test from the wash station, vial to vial noise is avoided.

The following instructions are written for the Picarro Autosampler (part number A0325). If you are using a CTC-style Autosampler (part number A0321), please consult the following Community post for additional information: https://www.picarro.com/support/community/using-autosampler-inkwell-wash-station-sample-precision-test-water-analyzer.

1. Fill a wash station jar with water and screw on the cap. The water should be pure deionized water, with no organics or salts, although tap water, bottled water, or one of your secondary standards can also be used. Because of the large volume required, we do not recommend using primary standards for this test. The water should be pure deionized water, with no organics or salts. The sample should be filtered if it contains particulate matter.
2. Load the wash station into the rear wash station (Wash Station 1) holder on the Autosampler.
3. Double-click on the desktop icon 'Autosampler Control.' This will open the program that controls the Autosampler.
4. In the top row of the sample list, check the box to the right of the button 'Clear.' Then use the keyboard command 'Ctrl + i' to switch to the wash station test mode. This is a run sequence that will only draw water out of wash station 1. Select the method 'Picarro' from

the drop down list and enter 150 into the box underneath the column '#Inj.'. This will set up a run of 150 injections from the wash station.

Figure 44: Autosampler Control Window



5. Minimize the Autosampler window and double-click on the desktop icon 'Coordinator Launcher.' This will open the window 'Picarro Coordinator Launcher' with a dropdown menu 'Select Coordinator.' Select 'High Precision' and click 'Launch.' Once the 'CRDS Coordinator' window is open, it will start to run through a series of checks, which include cleaning the vaporizer by opening and closing valves.
6. Return to the Autosampler window and click 'Run.'
7. Once the vaporizer cleaning has finished, the Coordinator will initiate the first injection from the Autosampler. Then it will run through the entire Autosampler queue that was set up in step 5. The complete Autosampler queue will include 150 injections and it will take approximately 24 hours. You can monitor the progress of the run in the 'CRDS Coordinator' window. Please check to ensure that H_2O concentrations of the first few injections fall within about 17,000 to 23,000 ppm, and that the injection concentrations are within about ± 1,000 ppm of each other. You can now leave the system to

run for 24 hours, during which time it will collect the necessary data to test the precision and drift of the instrument.

8. When the run is complete, navigate to the file C:\IsotopeData and identify the Coordinator output file. The correct file name can be found in the CRDS Coordinator window in the 'Filename' box, and the file will have the format .csv (comma-separated values). Move this file to another computer with Microsoft Excel or similar spreadsheet program.

9. Open the .csv Coordinator output file. Then copy and paste data from the columns labeled 'd(18_16)Mean' and 'd(D_H)Mean' into a drift and precision test analysis spreadsheet that can be downloaded here: https://picarro.box.com/s/20dfkjs0szvl6mftg8cg.The spreadsheet is set up to calculate precision and drift and record the values in table provided. Within the spreadsheet, you will find a table labeled 'Report.' Review this table and check the cells underneath the column 'State.' If these cells read 'pass,' the instrument passed the standard drift and precision test. If any boxes are labeled 'fail,' you should contact Picarro's Technical Support team at support@picarro.com. Please provide the serial number of your analyzer.

12.2 Leak-Free Operation with a High Precision Vaporizer (A0211)

Following an injection of liquid into the water isotope analyzer, the shape of the square "pulse" in the water concentration versus time graph provides information about the quality of the injection and any potential problems that can lead to poor data.

One potential problem is a leak between the vaporizer and the analyzer. These leaks can be detected by plotting the water concentration along with the “outlet proportional valve” setting during the analysis. The outlet valve performance provides a way to identify unexpected pressure changes in the system, and it is useful indicator of vaporizer performance. Here’s why: The vaporizer converts a liquid sample into gas. At the beginning of sample analysis, one of the vaporizer valves is opened to the analyzer to allow gas to pass from the vaporizer into the analyzer cavity. During analysis, the pressure in the cavity steadily decreases because the gas is leaving the fixed volume of the vaporizer. To keep the cavity pressure constant, the outlet proportional valve slowly adjusts to compensate for the pressure change at the inlet.

For additional background on the operation of the High Precision Vaporizer, you can review the following Picarro Community post online: http://www.picarro.com/community/picarro_community/vaporizer_a0211_operation_schematic

Viewing the Outlet Valve Position

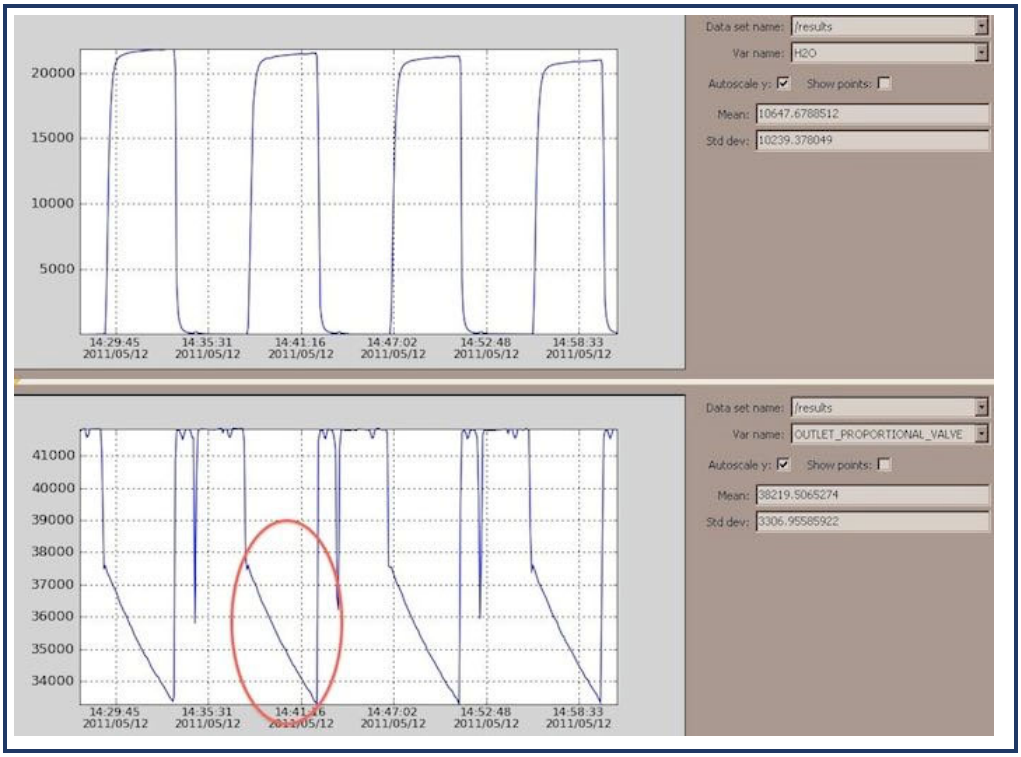
To access the outlet valve position plot within the CRDS Data Viewer GUI, go to Settings > Change GUI Mode. When asked for a password, use the default Picarro password (“picarro”), and press OK. Now you can select the Outlet Proportional Valve plot.

The outlet valve position is also recorded in the Private Data Log files (see **“Archived Data”** section for details on how to access these files). If you would like the data stored in the User Data, you can use the Setup Tool to include the outlet valve in your user data files.

Typical Appearance of Water Concentration and Outlet Proportional Valve Graphs

For all of the following plots, the water concentration is the top graph and outlet proportional valve position is on the bottom**.** Ideally, the water pulse should be square, and the outlet proportional valve position should gradually decrease at the flat top of the water pulse, as shown below. These features correspond to the outlet valve gradually closing during the analysis of the pulse.

Figure 45: Ideal Water Concentration and Outlet Proportional Valve Graphs



For a proper analysis, the concentration of the dry gas (between the pulses) should be < 500 ppm H_2O. The peak height of the pulse should be reproducible (within ± 1,000 ppm) and between approximately 17,000 and 23,000 ppm.

Water Concentration and Outlet Proportional Valve Graph Problems and Potential Causes

Problem: Extra Pulses after the Main Sample Pulse

The image below shows extra little "pulses" after the main sample pulse. Note that the peaks for the main pulses appear normal, and the outlet valve is operating normally. The problem is during the cleanout cycle of the vaporizer, not during sample delivery.

There are three potential causes of this problem:

1. Leaky vaporizer septum. This should be changed after every ~ 300-400 injections.
2. Bad vaporizer vacuum pump. The pump may be starting to fail if it has more than 10,000 hours of use.
3. Bad connection between the vaporizer vacuum pump and the vaporizer. Check the tubing and swage connections for cracks near the metal connections. Be careful not to over-tighten the swage fittings.

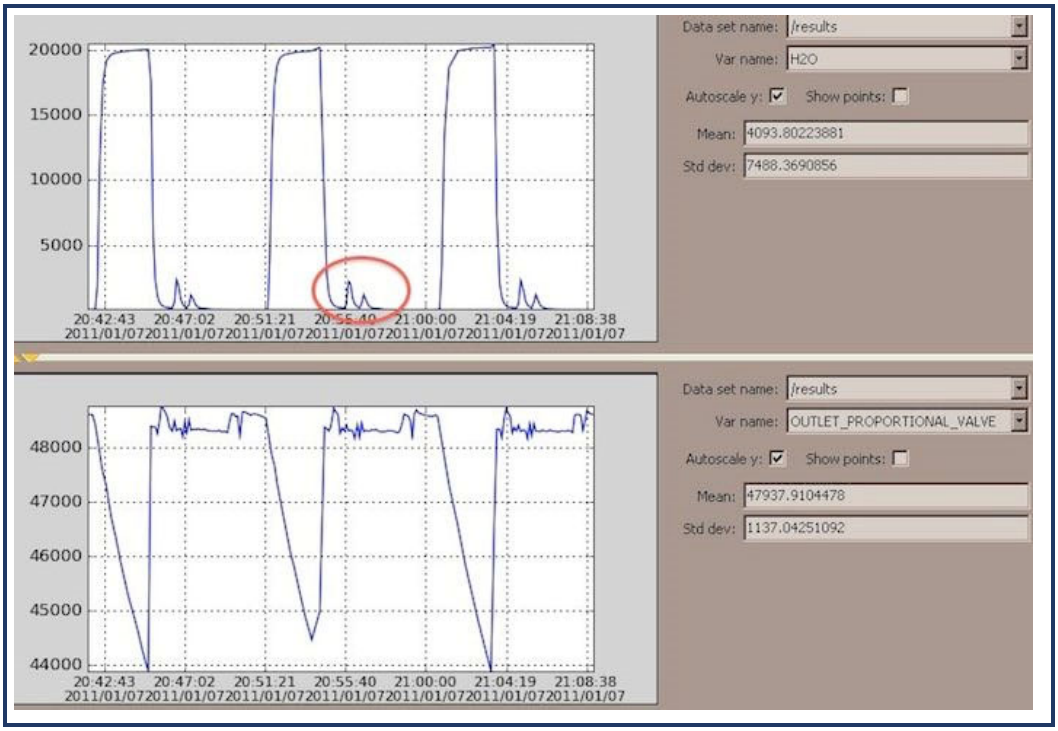


Figure 46: Extra Pulses after the Main Sample Pulse

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.

Problem: Extra Peaks Before and After the Main Sample Pulse

The water concentration graph below has two abnormalities: an extra little peak after the main peak, and a "spike" at the beginning of the main peak. Note also that the outlet proportional valve is flat. This indicates that the outlet valve is constant during the time the analyzer is drawing air from the vaporizer's internal fixed volume. Because the outlet valve is constant, the pressure on the inlet of the analyzer is not changing. This indicates there is a leak between the analyzer and the vaporizer.

The spike at the beginning of the main pulse could be moist ambient air entering through the leak. In this particular example, the spike peaks at ~ 12,000ppm. In a dry environment, a leak might look like a slope going upwards from left to right with a dependence on the ambient conditions relative to the nominal 20,000 ppm concentration of the vaporized sample. A very leaky septum could also look similar.

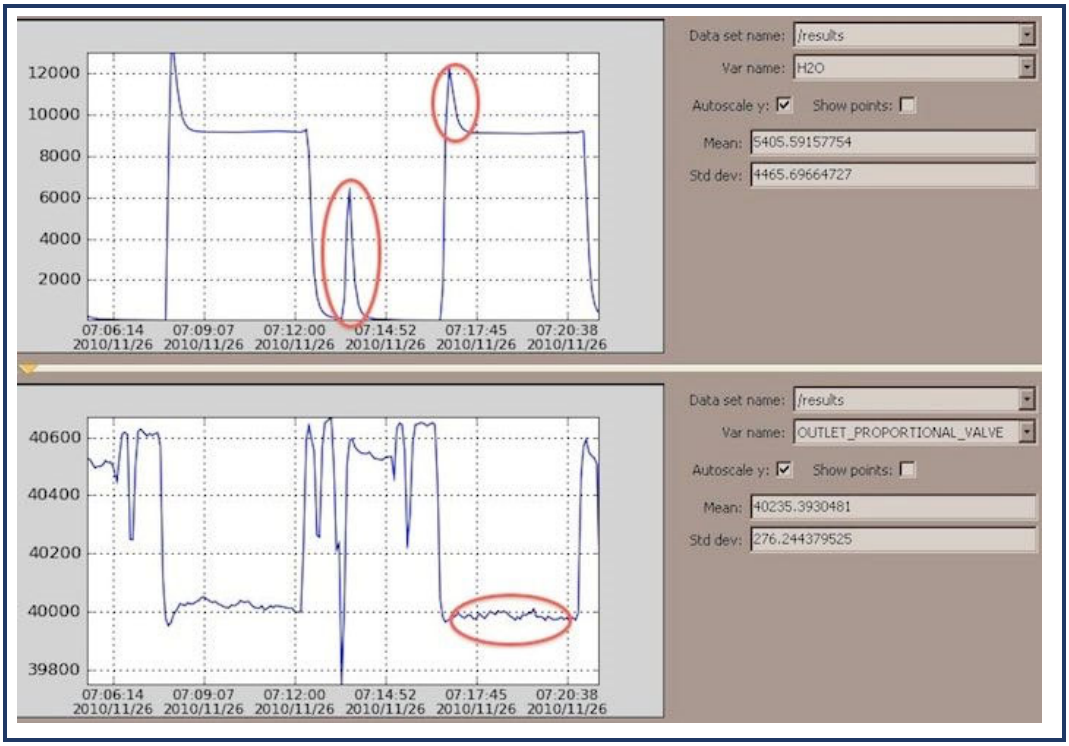
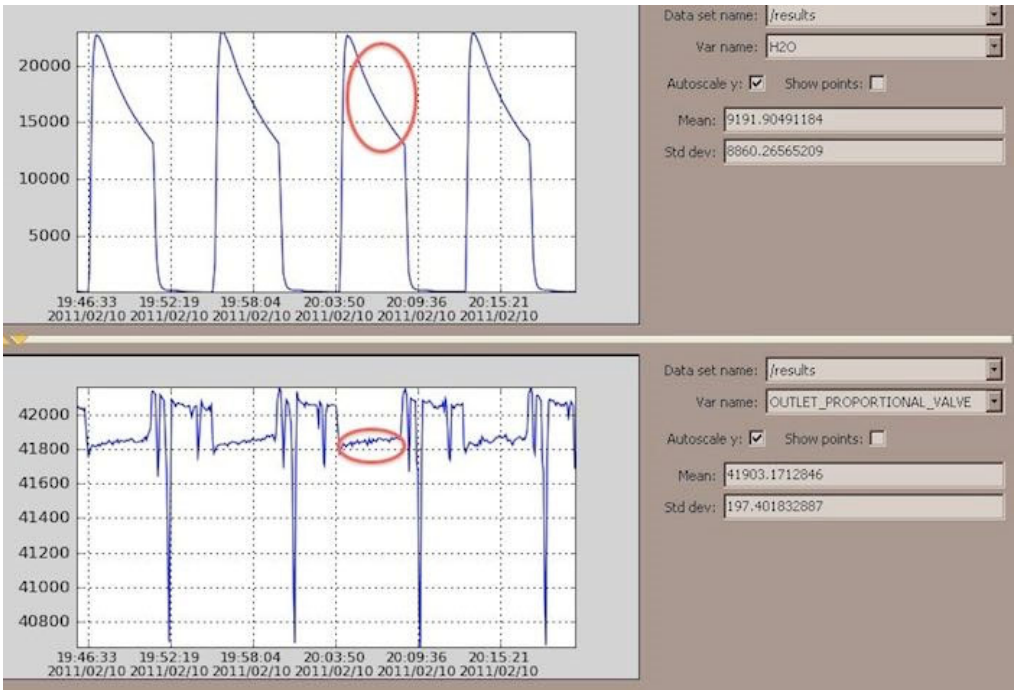


Figure 47: Extra Peaks Before and After Main Sample Pulse

Problem: Decreasing Concentration in the Main Pulse

In this example, the outlet valve is constant during the pulse, but the pulse has a decreasing concentration. This is consistent with a leak of lower-concentration ambient air into the analyzer during analysis. This leak is likely at the connection from the vaporizer to the analyzer.

Figure 48: Decreasing Concentration in Main Pulse



Problem: Water Pulse Is Sloped

The slope of the main pulse in the water concentrations, particularly one going upwards as in the first example shown below, indicates poor mixing inside the vaporizer. This can happen if the valve that injects dry gas into the vaporizer is not working perfectly. In this case, the outlet valve position is basically normal and therefore a leak between the vaporizer and analyzer is excluded as the cause of the problem.

In the second example below, however, note the change in the nominal outlet valve position. This shows the vaporizer is filling to different pressures with each pulse, so there is inconsistent filling of the vaporizer.

If you see either:

- **Variation in the nominal stopping position of the outlet valve, or**
- **Large increases in water concentration during a pulse**

Contact Technical Support (support@picarro.com) and we can help diagnose and repair the fault, if necessary. Please always provide your analyzer and vaporizer serial number when contacting Picarro.

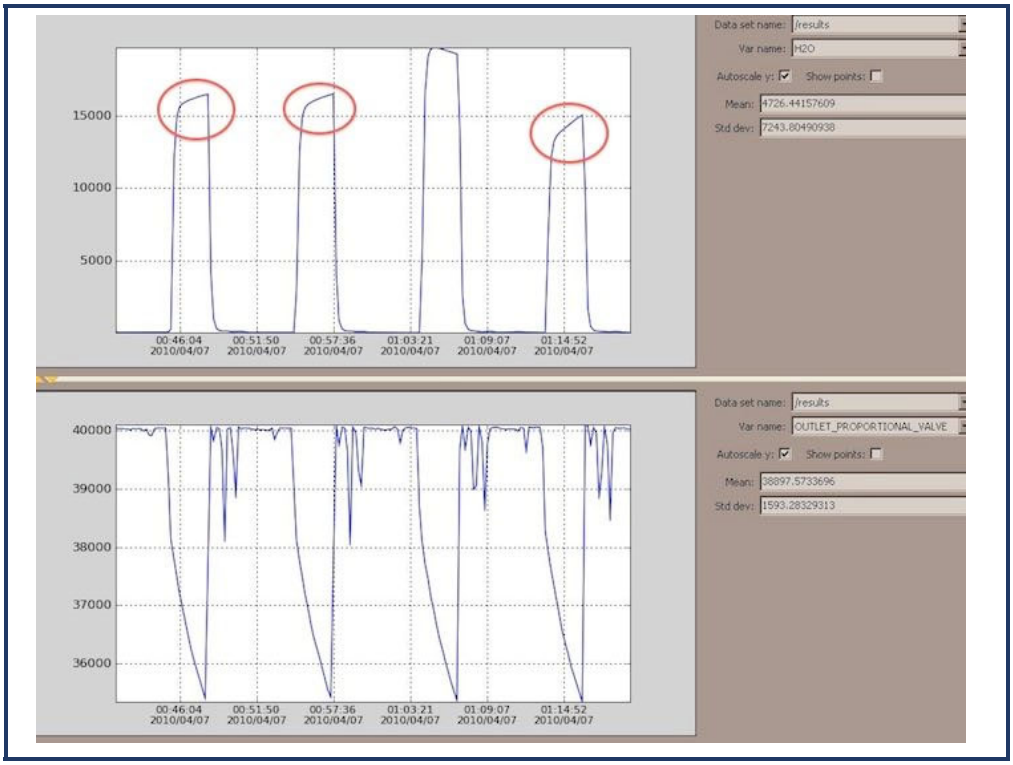
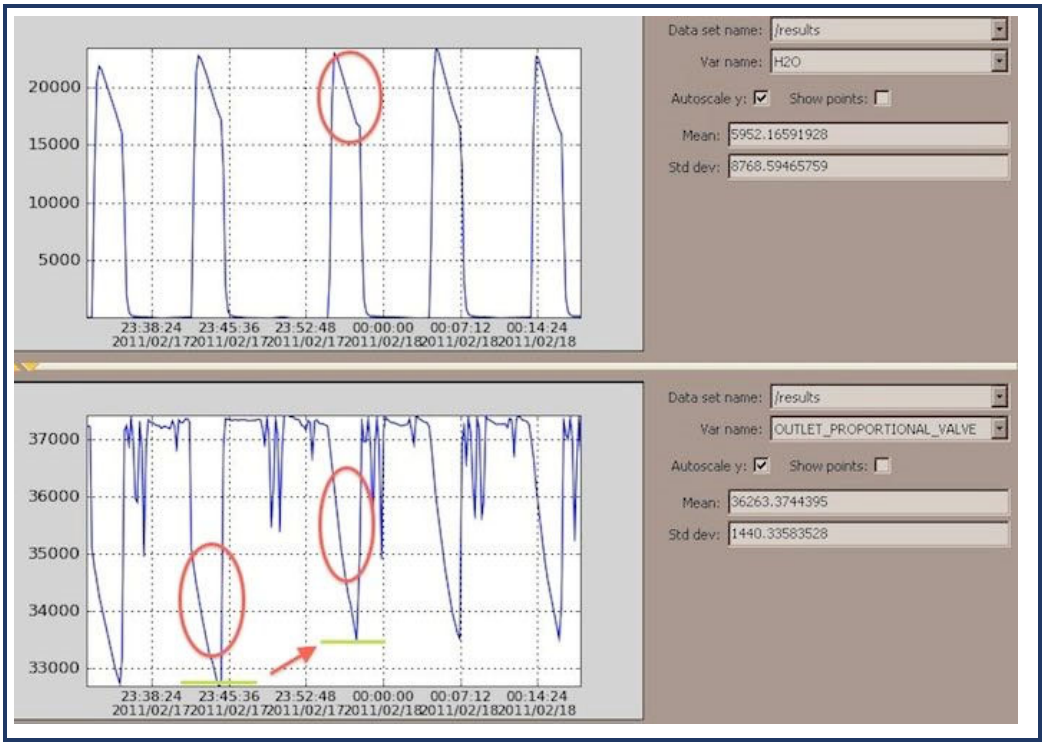


Figure 49: Water Pulse Sloped – Poor Mixing in Vaporizer

Figure 50: Water Pulse Sloped – Inconsistent Filling of Vaporizer



Problem: Variability in Measured Water Concentration

The measured water concentration should consistently be near 20,000 ppm (±1000 ppm). The circled areas in the water graph below shows values that are higher or lower than expected. The outlet valve behavior is normal.

This can happen if the syringe is clogged, causing inconsistencies in the injected volume. Another possible problem is an inconsistent gas supply, perhaps due to a failing regulator or another piece of equipment using the same dry gas supply. This causes inconsistent pressure or flow at the inlet dry gas supply.

Other problems associated with sample delivery are:

- **Overfilling or pressurizing the liquid in the vials**
- **Significant contamination of the samples**
- **Insufficient needle depth resulting in the collection of air, rather than liquid**
- **Variable volume bubble in the syringe**

A test injection is recommended before each run, when you change a syringe, or if water concentrations during the pulse are consistently outside of the ideal ~ 17,000 to 23,000 ppm range. It is possible to scale the injection volume by the appropriate percentage to target the ideal water concentration range (see section Adjusting Injection Volume).

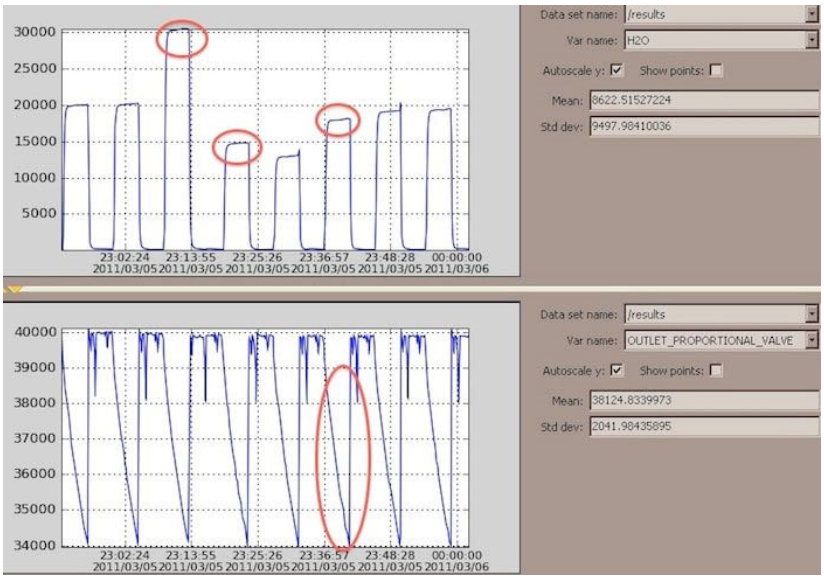
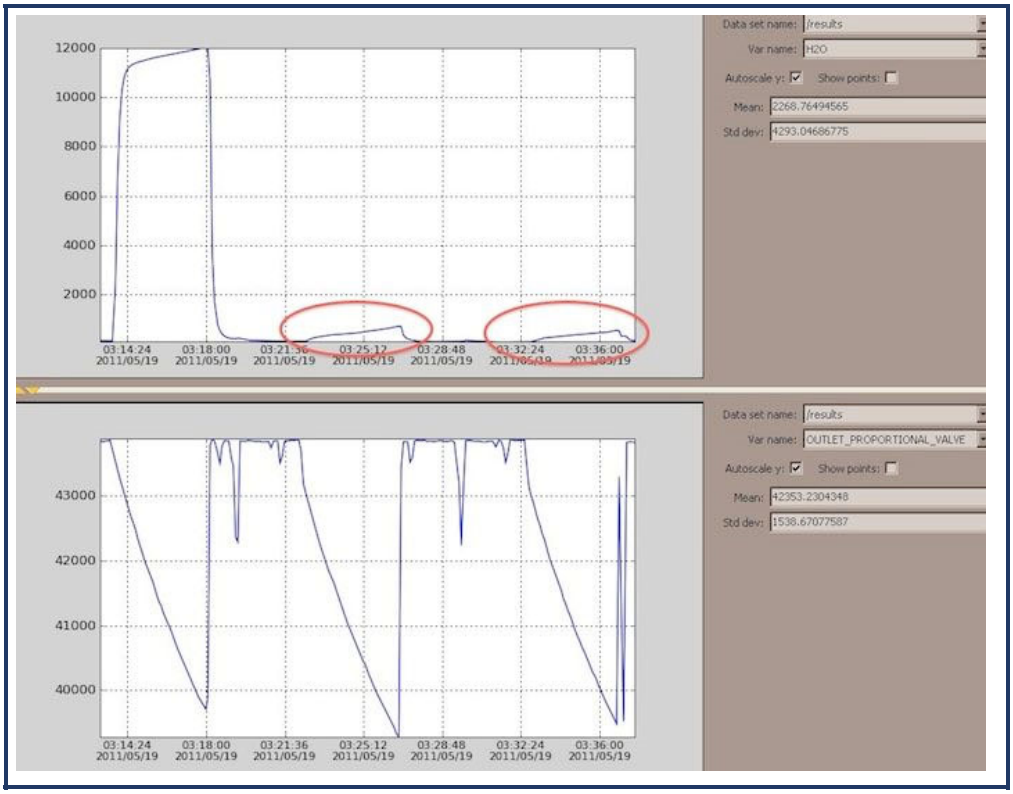


Figure 51: Water Pulse Sloped – Water Concentration Variability

Problem: Water Concentration Suddenly Decreases

In this example, the measured water concentration drops to near the baseline. This can happen if the needle penetration depth into the vaporizer changes and is not deep enough to get the sample into the vaporizer. The tall peak at left is a partial injection, but the subsequent peaks indicate that very little water was injected into the vaporizer.

Figure 52: Water Pulse Sloped – Sudden Decrease in Water Concentration



Problem: Baseline of Water Concentration and Outlet Valve Change

This is what happens when a normal analysis runs out of dry air from the dry air cylinder. The same behavior is also possible if there is a large gas leak in your cylinder. As the cylinder gas pressure goes to zero, the vaporizer is forced to take in moist room air, either from the leak or backwards through the Wavelength Monitor (WLM) purge line. The result is that the nominal dry baseline rises to the level of the room air. Also, the outlet valve position decreases since the vaporizer experiences less pressure from the cylinder gas.

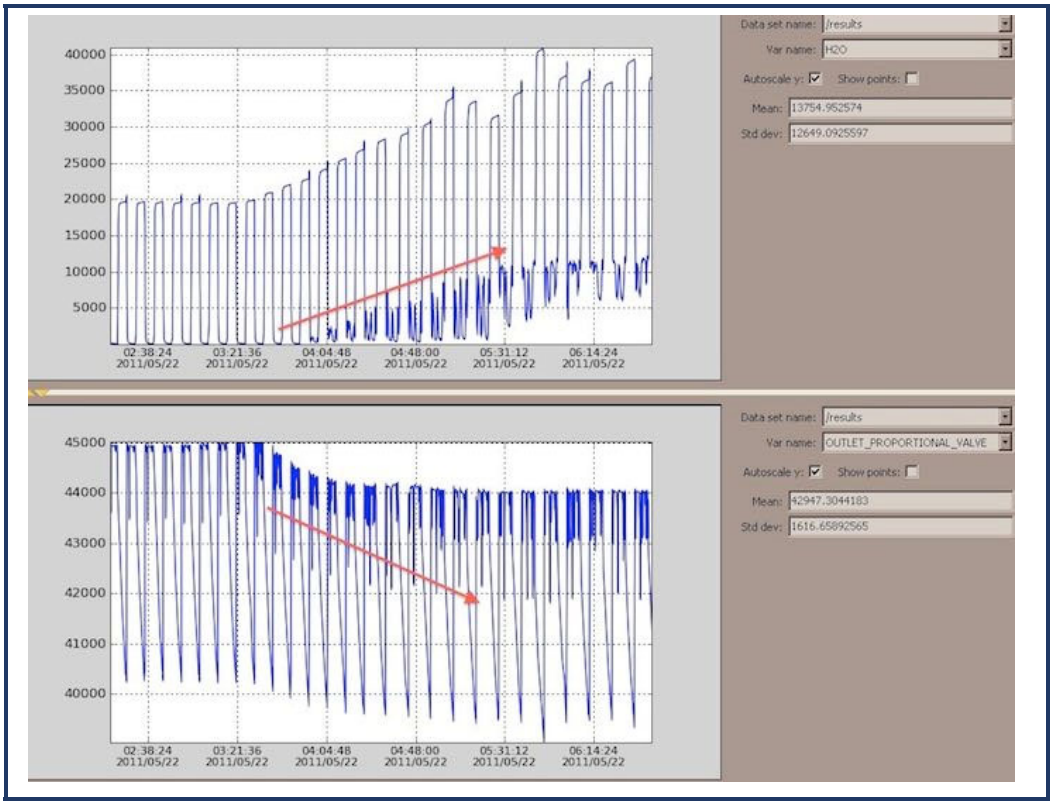


Figure 53: Baseline of Water Concentration and Outlet Valve Change

Problem: Water Pulses Split Into Multiple Peaks

The final example shows what happens if the analyzer's solenoid valve sequencer is running at the same time the coordinator is. The solenoid valve sequencer should be disabled by default for Picarro water isotope analyzers. It the sequencer runs at the same time as the coordinator, the two components send conflicting signals to the valves that control the vaporizer. In this example, the sequencer is turned off following the third pulse, and the final pulse returns to normal.

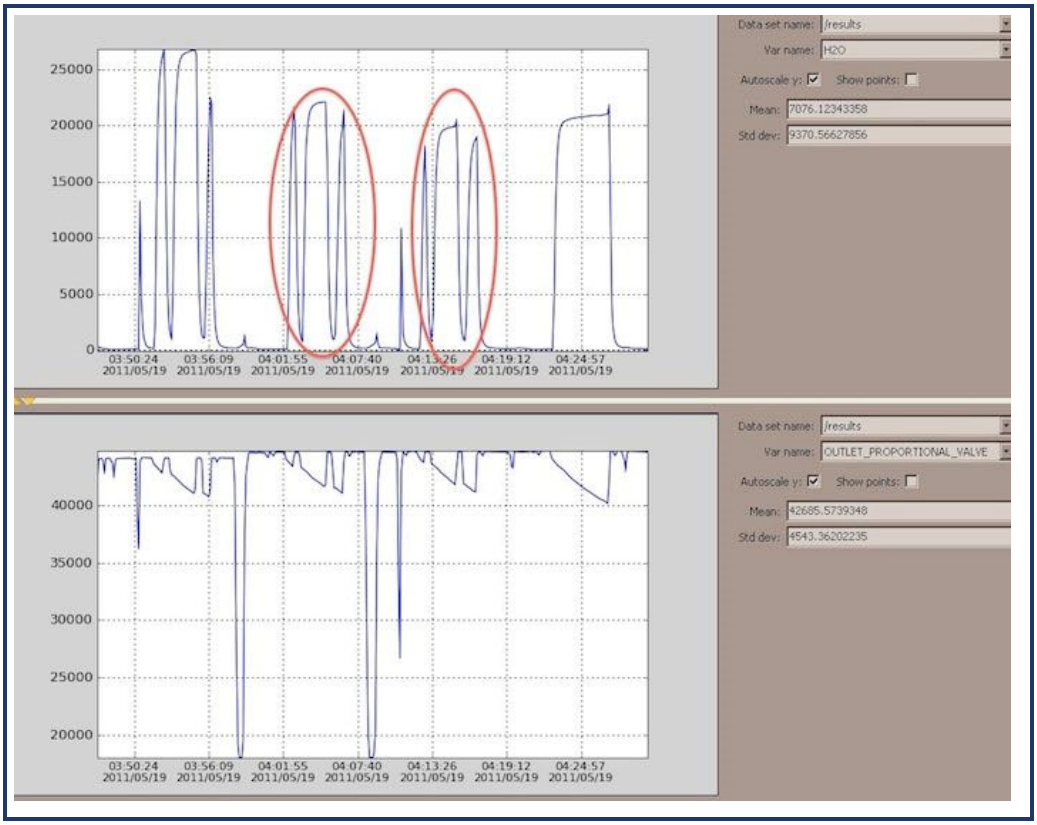


Figure 54: Water Pulses Split Into Multiple Peaks

13. CALIBRATION

Calibrating your Picarro water isotope analyzer involves three steps:

- Measuring the isotopic composition of known standards
- Determining the relationship between the measured value and the known value
- Adjusting the settings on the analyzer to account for any difference between the measured and known values, so that the on-screen readings are accurate.

Picarro recommends calibrating your Picarro L21x0-*i* analyzer using liquid water samples. All water isotope standards should have accepted values for $\delta^{18}O$ and $\delta^{2}H$. If applicable, the standards should also be calibrated for ^{17}O-excess. Picarro recommends referencing all isotope data back to the internationally-recognized VSMOW-SLAP scale.

Upon manufacturing, Picarro guarantees the performance of your analyzer with respect to precision. The system is also calibrated using isotope standards, however Picarro does not certify the analyzer for accuracy. It is the responsibility of the instrument user to verify the factory-calibration and to calibrate the instrument for accuracy.

13.1 Primary and Secondary Standards

The isotopic composition of a water sample is typically determined relative to the known value in a standard using delta notation:

$$\delta^{18}O = \left(\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{standard}} - 1\right) * 1000$$

$$\delta\ ^{2}H = \left(\frac{(\ ^{2}H/\ ^{1}H)_{sample}}{(\ ^{2}H/\ ^{1}H)_{standard}} - 1\right) * 1000$$

$$\delta^{17}O = \left(\frac{(^{17}O/^{16}O)_{sample}}{(^{17}O/^{16}O)_{standard}} - 1\right) * 1000$$

These delta values can be used to construct secondary parameters:

Deuterium-excess (*d*-excess): *d*-excess = $\delta D - (8 * \delta^{18}O)$

^{17}O-excess: $^{17}O\text{-excess} = \ln(\delta^{17}O+1) - (0.528 * \ln(\delta^{18}O+1))$

There are three international “primary” standards:

- **VSMOW2 – Vienna Standard Mean Ocean Water 2**
- **SLAP2 – Standard Light Antarctic Precipitation 2**
- **GISP – Greenland Ice Sheet Precipitation**

The table below shows the isotopic compositions of each standard:

	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	^{17}O-excess (‰)	$\delta^{17}O$ (‰)
VSMOW2	0 ± 0.02	0 ± 0.3	0	0
SLAP2	-55.50 ± 0.02	-427.5 ± 0.3	0	-29.6968
GISP	-24.76 ± 0.09	-189.5 ± 1.2	0.022 ± 0.011	-13.16 ± 0.05

The $\delta^{18}O$ and $\delta^{2}H$ values are defined based on publications by the International Atomic Energy Agency (IAEA):

VSMOW2:
https://nucleus.iaea.org/sites/ReferenceMaterials/Pages/VSMOW2.aspx

SLAP2:
https://nucleus.iaea.org/sites/ReferenceMaterials/Pages/SLAP2.aspx

GISP:
http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Stable_Isotopes/2H18O-water-samples/GISP.htm

By definition, ^{17}O-excess and $\delta^{17}O$ for VSMOW2 is 0. Recommendations have also been made in the literature for the values of ^{17}O-excess for SLAP2 and GISP (Schoenemann et al., 2013). Using those recommendations, $\delta^{17}O$ of SLAP2 and GISP is calculated.

Schoenemann, S.W., Schauer, A.J., and Steig, E.J. (2013) “Measurement of SLAP2 and GISP $\delta^{17}O$ and proposed VSMOW-SLAP normalization for $\delta^{17}O$ and ^{17}O-excess”, Rapid Communications in Mass Spectrometry, doi: 10.1002/rcm.6486

Since these standards are expensive and sample limited, each lab should develop their own secondary, or working, standards. Example sources for secondary standards include:

- **Local precipitation (variable isotopic composition)**
- **Local tap water (variable, related to local precipitation)**
- **Kona Deep, Destiny Deep Sea Water (~ 0 ‰)**
- **Snow or ice from your favorite alpine region (depleted)**
- **Tap water from your colleagues across the globe (*variable*)**

The isotopic composition of a secondary standard should first be measured against a primary standard. Once calibrated with respect to the VSMOW-SLAP isotope scale, it can be used for routine, daily calibration. About 1.2 L of a secondary standard would be enough for a year's supply. This assumes each standard is measured 2x per day using a standard 2 mL autosampler vial, and that the analyzer is operated 300 days per year (2 mL / vial x 2 standard vials / day x 300 days = 1.2 L).

13.2 Tools, Equipment and Samples Required

1. Waters with known isotope signatures, i.e., a verified $\delta^{18}O$, $\delta^{2}H$ and ^{17}O-excess (if applicable) value.
   - **Picarro recommends all labs purchase one supply of primary isotope standards from IAEA or USGS. These primary standards should not be used on a daily basis. Instead, they can be used to calibrate secondary or in-house standards.**
   - **Secondary or in-house standards that bracket the isotope space of your sample set. A set of three working water isotope standards is also available from Picarro (part number C0350). These standards have been calibrated for $\delta^{18}O$ and $\delta^{2}H$ against the VSMOW-SLAP scale.**
2. 2 mL sample vials with caps. Picarro sells water isotope kits for 500 or 1,000 samples (part number C0328 and C0329, respectively). These kits include 10 µL syringes, 2 mL glass vials with caps and injection port septa. Quantities vary based on the kit selected; visit the Picarro Store for more information: https://picarroinc.force.com/picarrosupport

3. Pipette for transferring water from primary storage (e.g., pressurized stainless steel barrels) to secondary storage (e.g., sealed amber vials) and eventually into sample vials (2 mL sample vials with caps and septa).
4. Permanent marker or label maker for labeling sample vials.
5. Refrigerator (or freezer) for storing water standards. If storing waters in the freezer, ensure the water is either stored in an expandable container or that the container has ample room for water expansion upon freezing. Also ensure the water is completely defrosted before conducting any analysis or sub-sampling from the water. For additional information on storing water isotope standards, please see section **Sample and Standard Handling**.

13.3 Calibration methodology

You should calibrate your samples using water standards that are introduced to the analyzer using an identical (or as close to identical) methodology as the samples.

- **For clean liquid water samples, analyze your standards using the same method, i.e., with the High Precision Vaporizer and Autosampler.**
- **When using the Micro Combustion Module (MCM) to analyze plant waters and other contaminated waters, also analyze your standards using the MCM.**
- **For ambient atmospheric monitoring, calibrate your system using liquid water standards of known isotopic composition using a Standards Delivery Module or dual mode kit. You can also design your own lab-built nebulizer or bubbler. For ambient atmospheric studies, calibrate for both accuracy in delta space and the dependence of delta value on water vapor concentration.**
- **For matrix bound water analyzed using the Induction Module (IM), measure your liquid water standards using the sample introduction methodology and heating recipe.**
- **For the Continuous Water Sampler, produce large volumes of tertiary water standards that can be analyzed on the CWS. Calibrate these standards using the High Precision Vaporizer and Autosampler.**

Picarro isotopic water analyzers are not calibrated for water vapor concentration. If high accuracy water vapor concentration is desired, calibrate your system with a dew point generator that can introduce vapor streams of known concentration.

13.4 Performing Calibration Measurements

Since the Picarro analyzer is extremely linear, it is only necessary to use three calibration standards to calibrate each 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 they span a representative 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.

Each calibration standard should be introduced into the analyzer for an interval long enough for the analyzer to yield a stable measurement of that sample. In the case of water isotopes, it is important to ensure sample-to-sample isotopic memory is overcome prior to using injection pulses for calibration. For example, if there is a large difference in the isotopic composition of two adjacent standards, it is important to increase the number of injections per vial for the purpose of calibration. For example, if the system is calibrated directly with VSMOW and SLAP, which represent the largest natural variability in oxygen and hydrogen isotopes, Picarro recommends at least 10 injections are made per vial prior to averaging 3-5 injections for the purpose of calibration. Such a high number of injections is not required for samples that are more closely spaced in isotopic composition.

For routine daily calibration, secondary standards can be interspersed with samples during a given run. The order in which you run the standards can provide information about parameters, such as drift and sample-to-sample isotopic memory, that are helpful in assessing data quality. Picarro recommends the following daily calibration procedure:

- **Measure three standards that bracket the expected composition of samples at the beginning of the autosampler run.**
- **Measure one of those standards again in the middle of the autosampler run.**

- **Measure the three same standards again at the end of the autosampler run.**

At the completion of the autosampler sequence, the standards can be used to construct a bracketed calibration. Plot the measured values of the standards on the x-axis, and the known values (versus VSMOW-SLAP) of those standards on the y-axis. A linear regression can then be used to correct your sample data to the VSMOW-SLAP scale. If necessary the standard that was run at the beginning, middle and end of the autosampler sequence can be used to correct drift. Finally, remember that standard operating procedure is to discard the first three injections for any sample vial and then average the remaining injections to get the value of that water. The total number of injections made, and the number discarded can be optimized based on performance requirements and the sample-to-sample jumps in isotope space. It is possible to correct sample data to the VSMOW-SLAP scale by post-processing the Coordinator output data. Alternatively, Coordinator data can be analyzed using ChemCorrect™. Finally, if there is a desire to update the on-screen readings, the Picarro software can be updated by following the instructions given in the next section.

13.5 Updating the Instrument Calibration for Accurate On-Screen Readings

Once you have measured your standards, you can use either of the methods described below to calibrate the analyzer. **Method 1** requires you to make a graph (known standards versus measured standards) to calibrate the analyzer. **Method 2** does not require you to make a graph; however, the effect of this calibration is harder to reverse than Method 1.

Method 1: Using the CRDS Data Viewer to Update the On-Screen Readings

For isotope standard measurements, plot the analyzer's reported isotope value on the horizontal (x) axis and the standards' known isotopic composition on the vertical (y) axis. This graph will help you to determine the linear relationship between the known calibration values and the analyzer's reported values.

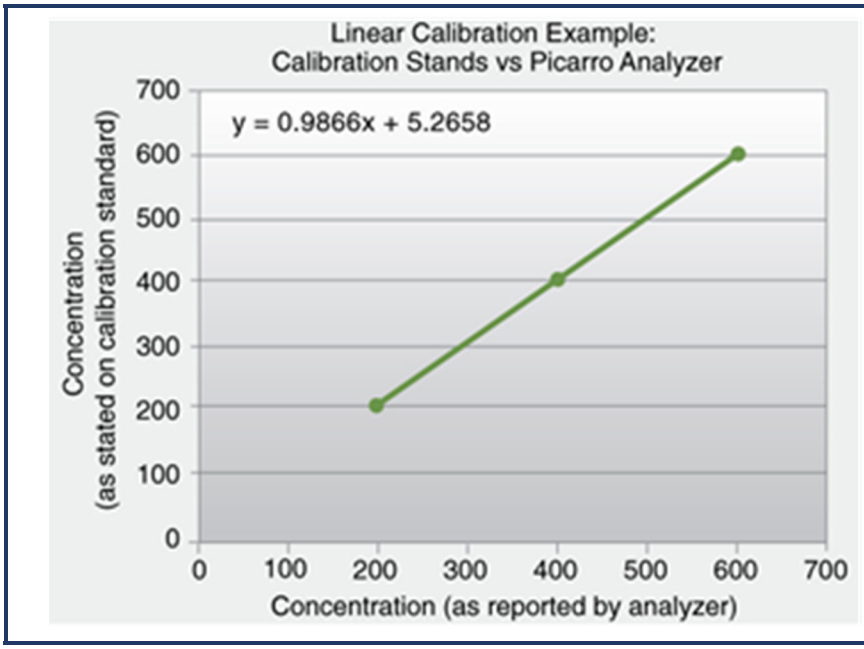
Calculate a linear best-fit equation from the data. The slope and intercept of the best-fit line through these points are the two values that are used to calibrate the analyzer. Determining the linear relationship between the

known values and the analyzer's reported values enables the calculation of a calibration offset (slope and intercept). This adds a correction term to the analyzer's factory or previous calibration.

The analyzer's calibration is intended to be altered infrequently. Instead of recalibrating frequently to increase the accuracy of the data, users often verify the calibration by measuring three or more water standards and using the same regression procedure described here to calculate an offset by which to correct their data offline (see previous section). In the calibration example data below, fitting the three standards yields the linear equation y = 0.9866x + 5.2658 with the slope m = 0.9866 and the intercept b = 5.2658. This equation would be used with x = raw data measured by the analyzer (labelled "CRDS Reported") to give y = corrected data (labelled "Certified" value).

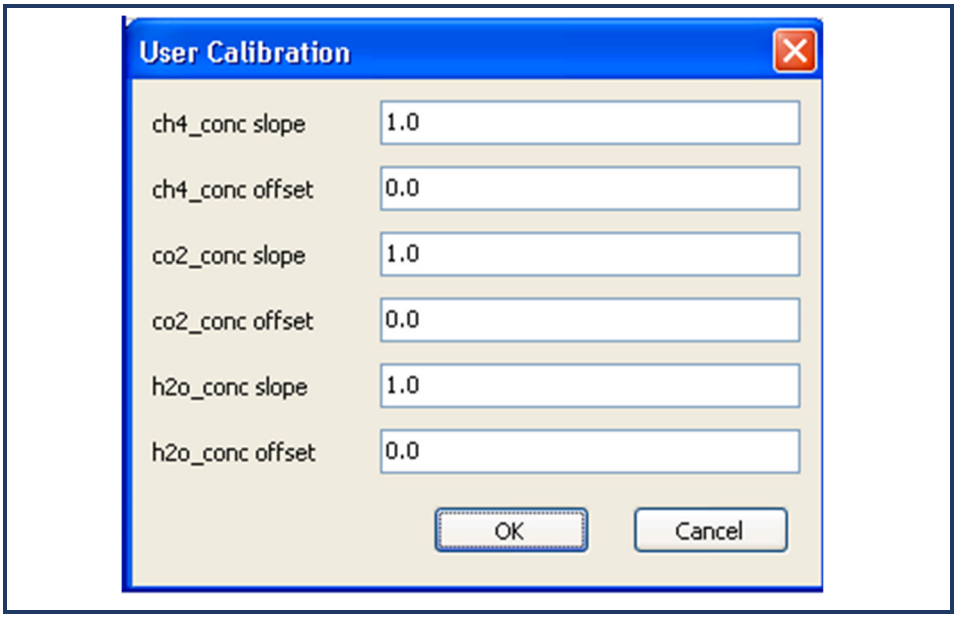
	CRDS Reported Value	Certified Value
Calibration Point #1	200.1	202.7
Calibration Point #2	600.3	597.6
Calibration Point #3	400.0	400.0

Figure 55: Linear Calibration Example



Enter these calibration values into the software by selecting the "User Calibration" from the Tools menu on the CRDS Data Viewer. Enter the slope and intercept for each species. This is a password-protected function, with the default password "picarro."

Figure 56: User Cal Dialog



After the calibration is entered, it will take effect immediately after clicking "OK."

To return to the factory calibration, simply set the slope to "1" and the intercept to "0" for each species.

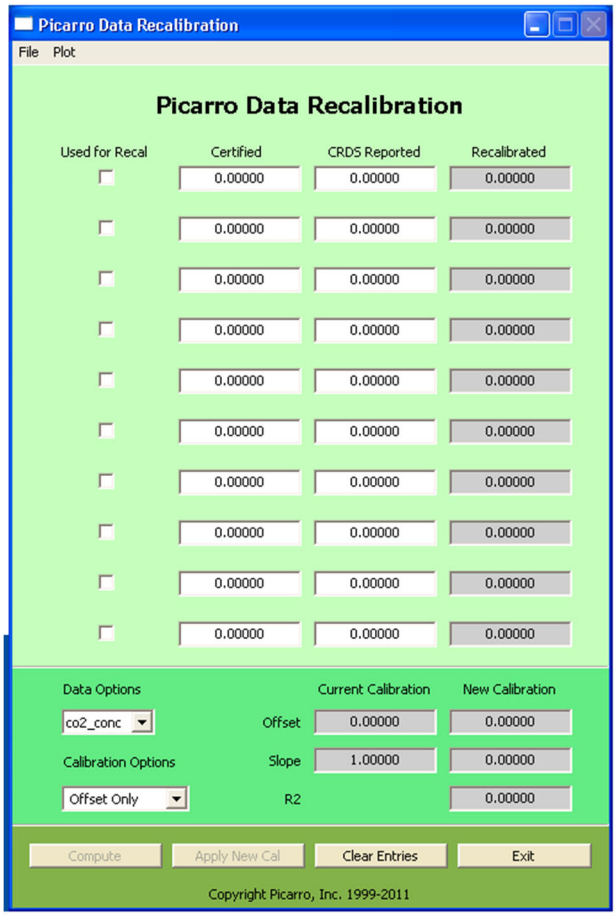
This calibration approach and functionality is available across all Picarro analyzers. In the example data given above the species measured were CO_2, CH_4 and H_2O concentration. The same method applies for isotope data, including $\delta^{18}O$, $\delta^{17}O$, $\delta^{2}H$.

Method 2: Using the "Picarro Data Recalibration Tool" to Calibrate the Analyzer

This tool can be used after you have performed the calibration measurements of standards with your Picarro analyzer.

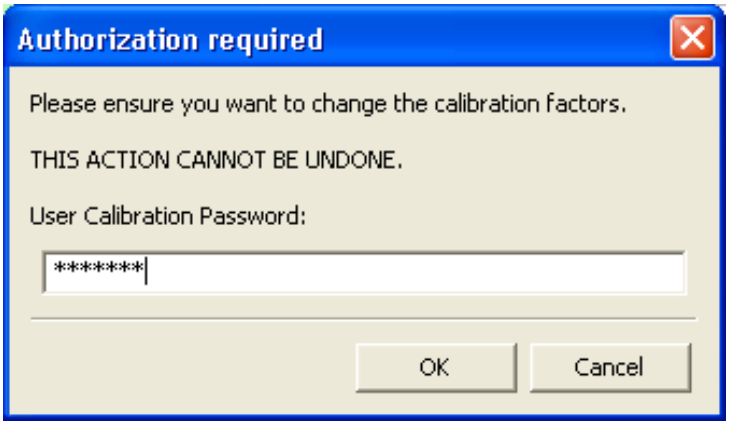
The Picarro Data Recalibration ("Data Recal" icon) software can be found in the "Picarro Utilities" folder in the desktop, and it can be used to recalibrate the data analyzed by Picarro analyzers.

Figure 57: Data Recalibration Tool



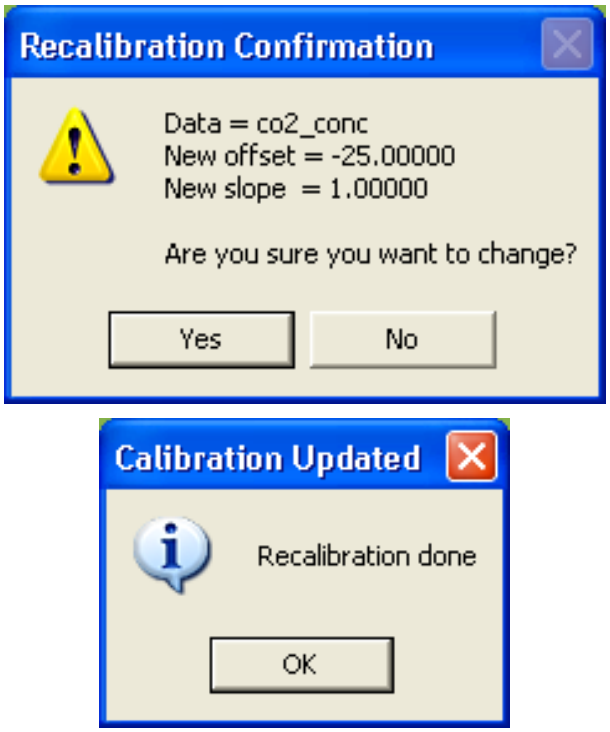
1. Double-click the “Data Recal” icon to pull up the window to the left.
2. Click on “Clear Entries” to reset the values in the “Picarro Data Recalibration” window.
3. Enter data values into the “Certified” (expected delta values).
4. Enter data values into the “CRDS Reported” (delta reported by Picarro analyzer) columns.
5. Check the boxes in the “Used for Recal” column that you want the software to base the calibration on.
6. Click the “Compute” button. The recalibrated values will appear in the rightmost column called “Recalibrated.”
7. Click “Apply New Cal” if you want to apply the calibration to your future measurements.
8. The default User Calibration Password is “picarro.” Click “OK” to continue. NOTE: This action cannot be undone from the “Picarro Data Recalibration Window,” but it CAN be undone in Method 1 in the “User Calibration” window.

Figure 58: Password Window



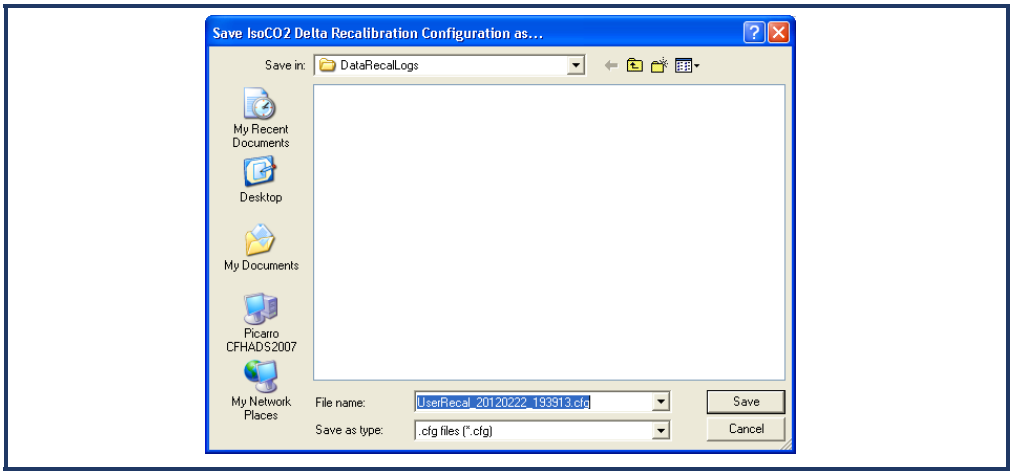
9. Review the values in the window, and click "YES" to confirm, then OK to continue.

Figure 59: Confirmation Windows



10. You now have the option to save your calibration settings. Click "Cancel" if you don't want to save your new calibration setting.

Figure 60: Save Calibration Dialog



11. You have now calibrated your analyzer. The next time you do any sample measurements, the on-screen measurement readings will be based on the new calibration setting.

13.6 Literature and Other Useful Resources

There are many useful resources regarding calibrating systems for accurate water isotope measurements. A non-exhaustive list is below:

- **International Atomic Energy Agency (1993) "Reference and intercomparison materials for stable isotopes of light element", IAEA Technical Document 825.**
- **Schoenemann, S.W., Schauer, A.J., and Steig, E.J. (2013) "Measurement of SLAP2 and GISP $\delta^{17}O$ and proposed VSMOW-SLAP normalization for $\delta^{17}O$ and ^{17}O-excess", Rapid Communications in Mass Spectrometry, doi: 10.1002/rcm.6486**
- **Van Geldern, R. and Barth, J.A.C. (2012) "Optimization of instrument setup and post-run corrections for oxygen and hydrogen stable isotopes measurements of water by isotope ratio infrared spectroscopy (IRIS)", Limnology and Oceanography: Methods, doi: 10.4319/lom.2012.10.1024**
- **Wassenaar, L.I., Coplen, T.B., and Aggarwall, P.K. (2014) "Approaches for Achieving Long-Term Accuracy and Precision of $\delta^{18}O$ and $\delta^{2}H$ for Waters Analyzed using Laser Absorption Spectrometers", Environmental Science and Technology, doi: 10.1021/es403354n**

14. BEST PRACTICES AND OPERATIONAL TIPS

14.1 Pulse Customization

Pulse Analysis

There is a delay of a few seconds at both the beginning of the pulse and the end of a pulse where the pulse analysis ignores incoming data. Therefore, only the most stable center portion of the pulse is included in the pulse analysis. Although the default settings should be adequate for most uses, one can adjust the delays by editing the appropriate Coordinator .ini script. Please be sure to keep a copy of the original file in case of any mistake. The example below is for the High Precision Mode Coordinator on a L2130-*i* with a Picarro Autosampler.

- Edit the `validTimeAfterTrigger` or `validTimeBeforeEnd` fields in the following file:

  C:\Picarro\G2000\AppConfig\Config\Coordinator\CoordinatorLIMS_G2000_A0325.ini

  The default settings are: `validTimeAfterTrigger = 100, validTimeBeforeEnd = 15`

- One can similarly adjust the level that triggers a pulse analysis event by changing the 6500 value in the upslope or downslope trigger in the following file:

  C:\Picarro\G2000\AppConfig\Config\Coordinator\CoordinatorLIMS_G2000_A0325.ini

  The default settings are: `thres1Pair = [6500, 30000]` and `thres2Pair = [5500, 30000] #this is the downslope trigger`

14.2 Adjusting Injection Volume

For best results, liquid sample injections should be provided to the instrument at a concentration of **20,000 ± 1,000 ppmv (parts per million by volume).** Each liquid injection will be labelled as “good” in the coordinator if this concentration is between **17,000 - 23,000 ppmv**. If the concentration is significantly above or below this range (i.e., < 16,500 ppmv or > 25,000 ppmv) or if the dry background is > 500ppmv, the pulse will not be analyzed and the data will not appear in the coordinator.

To achieve the appropriate injection concentration:

1. Dry nitrogen or zero air (< 50ppmv water concentration) should be supplied to the instrument at **2.5 ± 0.2psi** (17.2 ± 1.4kPa), with a flow of approximately **200 sccm (Standard Cubic Centimeters per Minute)**. If Drierite (or similar) is used for the dry air (rather than a nitrogen or zero air tank) supply, a measured background level of **~ 100-200ppmv** will produce satisfactory data. Remember to select the Measurement Mode appropriate to your background gas matrix (see section **Switching Between Measurement Modes**.)
2. Sample injection volume (controlled by Autosampler) should be set at **~ 2µL**.

If the resulting concentration peak after the 2nd or 3rd liquid injection is substantially different from 20,000 ppmv:

1. **The injection volume may need to be scaled appropriately:** for example, if the resulting concentration peak of an initial 'test' injection is 16,000 ppmv, then the injection volume needs to be adjusted by the factor 20,000/16,000 = 1.25. To accomplish this, multiply the current injection volume in the Autosampler method by 1.25.
2. **The injection quality may need improvement**. Bad Injections can cause incorrect injection concentrations. Bad injections can be from a clogged needle, damaged vaporizer septum, or incorrect dry gas pressure/flow restriction. For rapid optimization of injection volume use the high throughput coordinator.

<u>Five failed injections will lead to a Time Out:</u> Every time there is a liquid injection into a vaporizer by the Autosampler, a pulse of water vapor should enter the cavity and be analyzed. If something goes wrong (e.g., syringe breaks), and the pulse analysis fails, the software will try injecting five times in a row. After 5 failed injection pulses, the coordinator will time out. You will need to restart the coordinator to continue the experiment. This is a built-in safety mechanism that helps prevent un-intended sample contamination following multiple pierces of the vial septum.

14.3 Syringe Lifetime

A common failure in liquid water analysis is syringe breakage. These consumable parts, although replaceable, can be expensive. We recommend the following best practices for enhancing syringe lifetime.

Summary:

- **Recommended syringe size: 10 µL**
- **Manually clean syringe between each autosampler run:**
- **With deionized water**
- **Make sure plunger moves smoothly in the barrel**
- **Use a lubricant, like N-Methyl-2-pyrrolidone (NMP), if necessary**
- **Use the Autosampler Training program (rather than the Autosampler Controller program) to change the syringe**
- **Check syringe injection and fill speed, and the injection depth**

Details

Picarro analyzers ship with 10 µL syringes from SGE Analytical Science (10 µL syringe part # 002982, 10R-C/T-5/0.47C). The thicker plunger on these syringes makes them more robust than 5 µL syringes. They also tend to last longer, even without the use of lubricant.

Even though the precision of the injection volume with a 10 µL syringe is slightly worse than from a 5 µL syringe, the improved concentration dependence of our most recent isotopic water analyzers (in particular the L2130-*i* and the L2140-*i*) means there is no degradation in the precision of isotopic measurements.

Syringe Injection, Fill Speed And Injection Depth:

If syringes frequently break after 20 or 30 injections, double check the Autosampler training. Here are some parameters to check:

- **The syringe fill and inject speed. On the Picarro Autosampler, we recommend 0.5 µL/sec.**
- **The depth to which the needle penetrates into each vial when drawing up a new sample. If this "sample depth" is too deep, the syringe's needle can hit the bottom of the vial, eventually causing breakage of the needle.**

Syringe lubricant:

Although recommended prior to 2012, Picarro no longer uses a syringe lubricant, such as NMP (N-Methyl-2-Pyrrolidinone), to lubricate a syringe during a run. Dependent on your sample type, manually cleaning a syringe with NMP *between* runs can still be desirable.

To clean the syringe between runs:

1. When using the Picarro Autosampler (part number A0325), close the Autosampler Control at the end of the run.
2. Open the Autosampler Training tool by double-clicking the icon on the desktop. Select configuration from the menu on the left, and then click on the text “Syringe Volume.”
3. Select syringe size in the pop-up window. This is useful when exchanging the syringe or changing from a 5 to 10 µL syringe.
4. Click on “Syringe Exchange.” The Autosampler will now move to the pre-programmed syringe exchange position.
5. Remove the syringe and manually rinse the syringe using NMP until the plunger moves easily in the barrel. Spin the plunger while rinsing it with NMP, so that all sides of the plunger move smoothly through the barrel. Be careful not to pull out the plunger aggressively and then force it back into the syringe. This can cause the plunger to crumple.
6. Once the syringe is moving freely, rinse it manually 3 or 4 times using deionized water.
7. Re-insert the same syringe back into the Autosampler, click “Next” on the screen, and manually depress the metal block holding the plunger, as per instructions on the screen. This is important as it sets the dead volume of the syringe.
8. Close the Autosampler Training tool using the Exit button. Then re-open the Autosampler Controller to create the next run's sequence. This manual cleaning takes less than 5 minutes, and it is a worthwhile addition to standard protocols performed between runs.

Picarro does not recommend using NMP with the Micro Combustion Module (MCM). The MCM acts to destroy interfering organics, such as ethanol and methanol, using an oxidative catalytic technology. If a small amount of NMP enters the vaporizer, it may volatilize and be oxidized in the MCM. This will introduce exogenous water vapor, and potentially skew the isotopic signature data.

Samples with Precipitates

The High Precision Vaporizer can operate with liquid waters containing as much as approximately 200 g/kg total dissolved solids (TDS). In principle, water samples can be analyzed without filtration, especially if the precipitate has settled and the syringe is collecting water from near the top of the vial. However, running samples with high TDS will decrease syringe life, require more vaporizer maintenance, and possibly decrease the lifetime of the vaporizer valves (which must be replaced in the factory).

Therefore, samples should be filtered or centrifuged when possible. The "purer" the liquid being injected into the vaporizer, the longer the syringe, septa, and vaporizer can go without replacement or maintenance.

Dissolving the precipitate by lowering the pH of the fluid is not recommended for these reasons: (i) the sample will likely fractionate, and (ii) introducing acid to the vaporizer, stainless steel tubing, and potentially the cavity, may result in corrosion that requires repair.

14.4 Analyzing Samples with High Total Dissolved Solids

Picarro's High Precision Vaporizer can be used to measure saline samples. However, these samples present two unique challenges to instrument performance and lifetime:

1. Salty samples generate residue in the syringe, which decreases syringe lifetime. See the **Syringe Lifetime** section in this manual for more information on increasing syringe lifetime when running salty samples.
2. Upon vaporization, dissolved solids create a residue in the vaporizer, which can increase the memory effect and influence data quality.

Memory refers to the effect of the previous sample on the current measurement due to carryover of trace amounts of the previous sample. Water is especially subject to this effect because it adheres to surfaces even at temperatures well above the boiling point. It is a common problem encountered by all methods of isotopic analysis.

In Picarro analyzers, the memory is a function of the entire assembly (vaporizer, connection to the analyzer, and the analyzer itself). It is commonly accounted for by performing multiple injections of the same sample.

The simplest way to correct for memory is to ignore the first 2 or 3 injections of a sample and only use the later injections. For waters with closely clustered isotopic values, this usually means running 6 injections per sample and ignoring the results of the first two injections. In more extreme cases, running 8 injections and ignoring the first 3 or 4 will yield better results.

The effect of memory is stable over time. This means that the same percentage of the previous sample is carried over to the new sample each time.

However, memory should be characterized every one to two months, particularly if samples with high levels of insoluble material or high dissolved solids are frequently analyzed. These materials build up in the vaporizer and can increase the retention of old sample.

This effect can be quantified using the following procedure:

1. Inject a sample of water at least 20 times (40-50 times is preferable).
2. Switch to a new sample with significantly different (> 100‰ for δ^2H) isotopic value and inject the new sample the same number of times as the previous sample.
3. Switch back to the original sample and again measure that multiple times.
4. Calculate the 'true' value of each sample by averaging the last 5 to 10 injections of that sample.
5. Then subtract an individual injection from the 'true' value of the previous sample and divide this by the difference in isotope space between the 'true' value of the current sample and the previous sample. This will yield a memory coefficient (in percent) for each injection, *x*, where, for example 99% means that 99% of the true isotope difference between two samples of water has been attained after *x* injections. The first injection of sample will be in the range of 94% to 97%. By the 4^{th} injection, it will be approximately 98% for δ^2H and 99% for $\delta^{18}O$. Typically, the memory effect is larger for δ^2H than for $\delta^{18}O$.

If you are running salty samples and you see a decrease in the memory coefficient, Picarro recommends cleaning the vaporizer. The vaporizer might need cleaning approximately every 200 mg of salt injected, and the cleaning will take about 12 hours of downtime. Contact Picarro to receive instructions on cleaning the vaporizer, or to the order the Vaporizer Cleaning Kit (part number C0211).

Although vaporizer cleaning will improve the performance of your High Precision Vaporizer, salt build up can decrease the lifetime vaporizer valves and eventually lead to valve failure. This is particularly true if salts get into the valves themselves, preventing good seals at the valves. Vaporizer valves can only be replaced in the Picarro factory.

14.5 Sample and Standard Handling

Sample Storage

Whenever possible samples should be stored in sealed vial in a refrigerator or freezer. If samples are frozen prior to analysis it is essential to have sufficient headspace in the vial to prevent breakage during phase change, and to ensure the entire sample is returned to liquid form prior to isotope analysis. Parafilming the cap of the storage container is also recommended. If samples are stored in 2 mL autosampler containers, the cap with septa should be replaced once pierced.

Two types of autosampler vial are recommended for use with your Picarro Autosampler:

- **2 mL glass vial with cap and septa (Picarro part number C0322, or as part of a consumables kit, C0328 or C0329)**
- **If samples or standards are limited, it is also possible to use 2 mL vials with 250 µL inserts. These vials act to limit headspace for small samples. Picarro recommends the use of fixed inserts to avoid water vapor passing between the insert and the wall of the larger 2 mL vial. For example, Agilent LS Screw Vial (Agilent part number 5188-6591, available from Fisher Scientific).**

Standard Storage

Selecting the proper containers for long term storage is critical to avoid any change of isotope composition with time due to evaporation or exchange. The following is a list of storage methods for isotope standards.

Glass ampoules: The most reliable containers are glass ampoules that are sealed with a gas torch, such as those provided from the International Atomic Energy Agency with VSMOW2 and SLAP2. After filling and sealing, ampoules can be sterilized by heating the ampoules to about 105°C

overnight. This will eliminate the possibility of the growth of algae or other biological activities. Leaking ampoules should be discarded.

Stainless steel barrels: Internal laboratory standards can be stored in stainless steel barrels (25 to 50 liters). These barrels can be obtained from suppliers for the juice, wine and beer processing industries. When using this method, water standards should be kept under a slight overpressure of argon or nitrogen gas. The dispensing system ideally consists of a valve with a tube down to the bottom of the barrel to extract the water and a second valve with a manometer and tube connector to keep a headspace overpressure of inert gas in the barrel. Due to the overpressure in the barrel, water can be dispensed by opening the first valve. The laboratory standard has no contact with the atmosphere and therefore no risk exists of any evaporation during storage.

Amber vials and glass bottles*:* For routine work, a 250 mL glass bottle can be filled from the appropriate internal laboratory standard barrel. 2 mL aliquots of these standards can then be moved to a standard autosampler vial with septa cap for routine, daily calibration. Glass bottles should be filled from their source on a regular basis (every few weeks), without discarding the remaining portion of the standards. This handling method minimizes isotope fractionation during evaporation and exposure to air while the bottle is open.

It is recommended that once an autosampler vial is pierced by a needle, that the vial be discarded and not used repeatedly. For example, if a multi-day autosampler run is set up, the first standard water should not be used again for the last standard water in the sequence. Exceptions can occur if the cap with septa is replaced between the first and last analysis. Once a septa is pierced the sample is susceptible to isotopic fractionation due to evaporation and loss of the water through the cap.

Recommended Reading:

Tanweer, A., Groening, M., van Duren, M., Jaklitsch, M., Poltenstein, L. (2009) “Technical Procedure Note No. 43 Stable Isotope Internal Laboratory Water Standards: Preparation, Calibration and Storage.” Isotope Hydrology Laboratory, International Atomic Energy Agency, Vienna, Austria.

15. SERVICE AND MAINTENANCE

15.1 Particulate Filter for Analyzer

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** chapter of this manual or contact Picarro.

Particulate filters can become clogged after years of use in dirty environments. The symptoms of a clogged filter include the analyzer reporting “pressure low” or there being no flow into the instrument, causing unusual measurements.

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 the water evaporates. If this occurs, it is important to NOT turn off the analyzer or replace the filter until the filter 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.

There are two in-line, sub-micron particulate filters before the measurement cavity:

- **The first filter is user-replaceable and is found immediately following the inlet at the back of the analyzer. Replacement filters can be purchased from Picarro to be installed by the user.**
- **The second filter, which is directly attached to the cavity, is NOT user-replaceable. NEVER remove this filter, as it is directly attached to the cavity.**

Tools Required

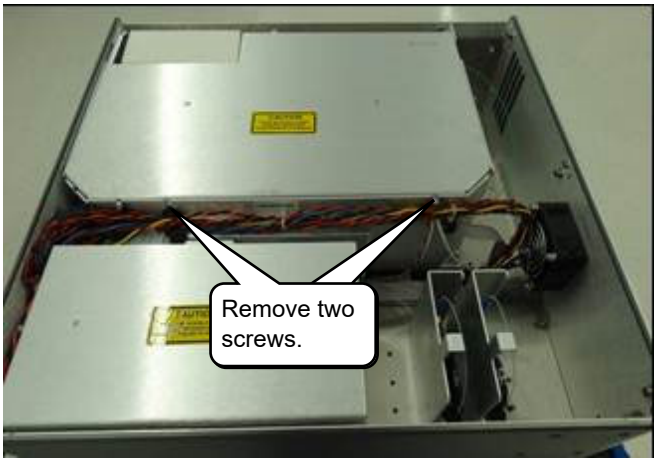
- **2 mm hex driver**
- **9/16” open end wrench**
- **5/8” open end wrench**
- **11/16” open end wrench**

Removing the Old Particulate Filter

The following procedure is **ONLY** for the **user-serviceable particulate filter** (first filter).

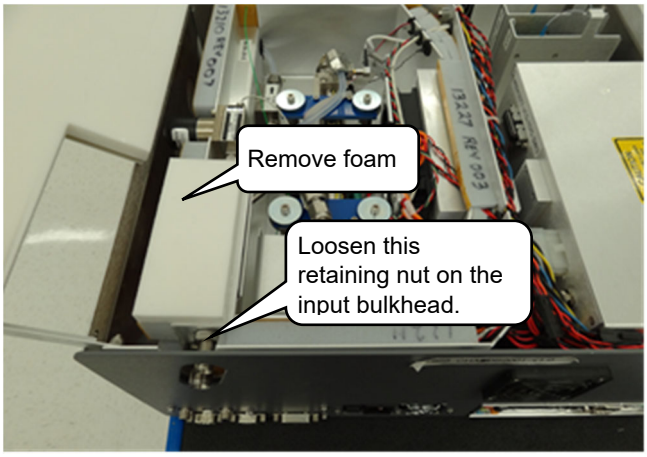
1. Move the analyzer to a clean work environment. Verify that the AC power cord is NOT attached to the instrument. Removing the cover while power is applied to the analyzer could result in exposure to Class 3B laser radiation.
2. Using a 2 mm hex driver, remove the top lid of the analyzer by removing six M3 x 6 mm socket flathead screws.
3. Loosen the two screws on the inner long side of the bigger box. Open the lid.

Figure 61: Loosen Inner Cover Screws



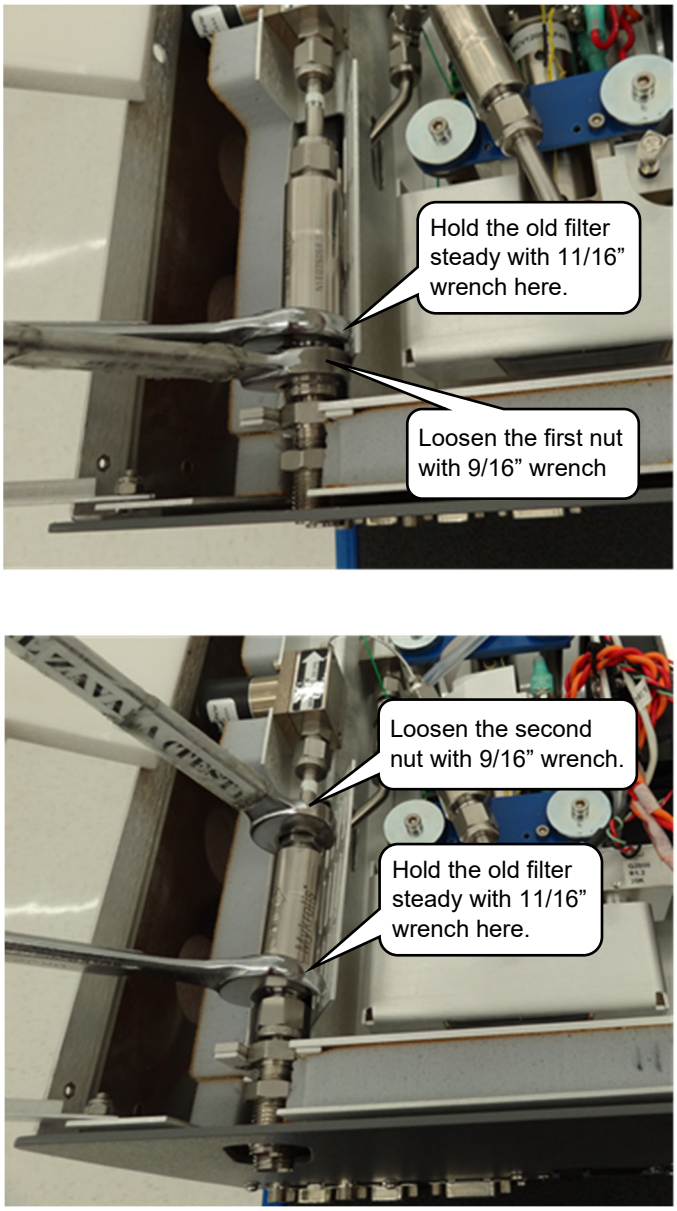
4. Using a 5/8” wrench, loosen the retaining nut on the input bulkhead (about 1 full turn should be enough).
5. Slide the foam towards left side of the analyzer (from the back of the analyzer) to remove it.

Figure 62: Foam Removal and Retaining Nut Loosening



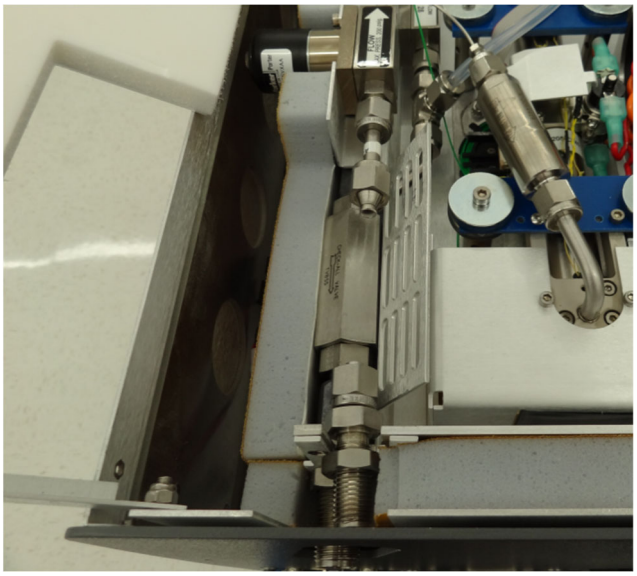
6. Using the 9/16” and 11/16” wrenches, loosen the two nuts that are securing the filter to the analyzer.

Figure 63: Loosening Filter Nuts



7. Slide the filter slightly towards the back of the analyzer and lift it out.

Figure 64: Filter Removed

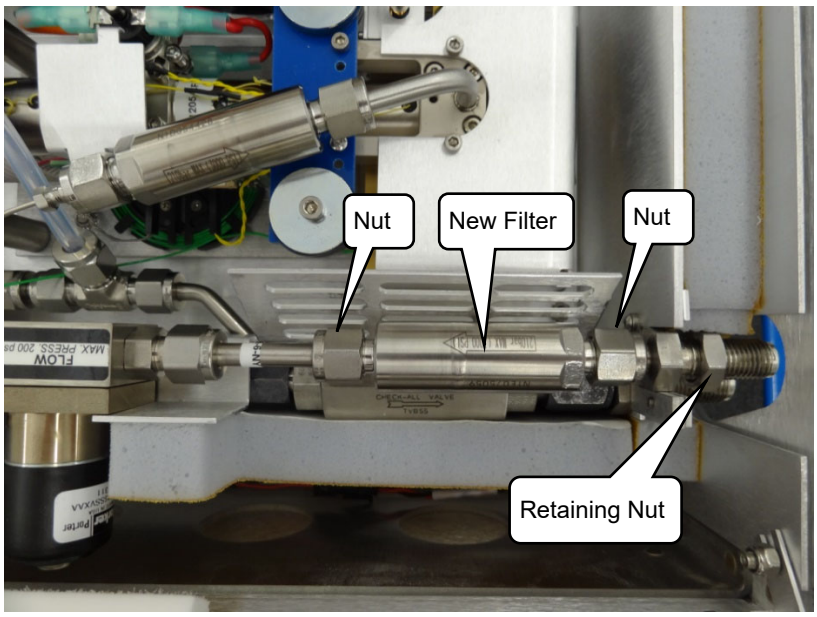


Installing the New Particulate Filter

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.

Figure 65: Installing New Filter



3. Reposition the filter foam cover, then using a 5/8” wrench, tighten the retaining nut on the bulkhead fitting. The metal edge of the filter cover should be under the foam.
4. Close the inner cover and secure with the two screws.
5. With a 2mm hex driver, reattach the analyzer’s top with six screws.

15.2 Vaporizer Injection Port Septum

The injector port septum should be replaced every 200-300 injections. The more closely grouped the needle piercings are on the septum, the earlier the septum will need to be replaced. If the septum is not changed, it will be difficult to maintain the vacuum inside the vaporizer, which will degrade the quality of the data.

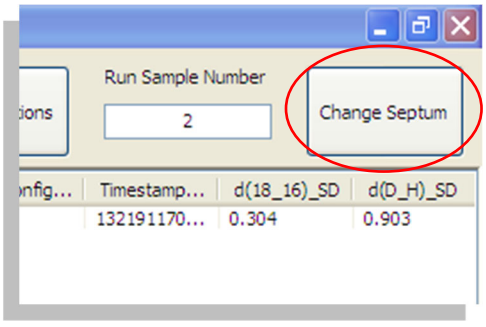
Tools Required

- **Tweezers**
- **New Septum**

Replacing the Septum

1. Is your autosampler running (i.e., actively injecting samples)?
   - **If yes, click the Change Septum button in the Coordinator window. This button is used to pause the autosampler and the vaporizer in the middle of an analysis to physically change the septum on the vaporizer.**

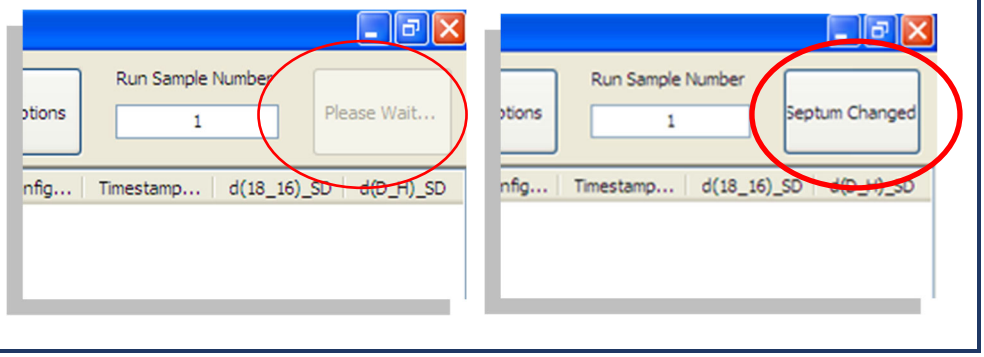
Figure 66: Change Septum Button



   - **If no, proceed directly to step 3. If you happen to click on the Change Septum button in the Coordinator window anyway, the software will wait indefinitely. To resolve this:**
   - **Start a job on the autosampler, or**
   - **Manually end the Coordinator window**

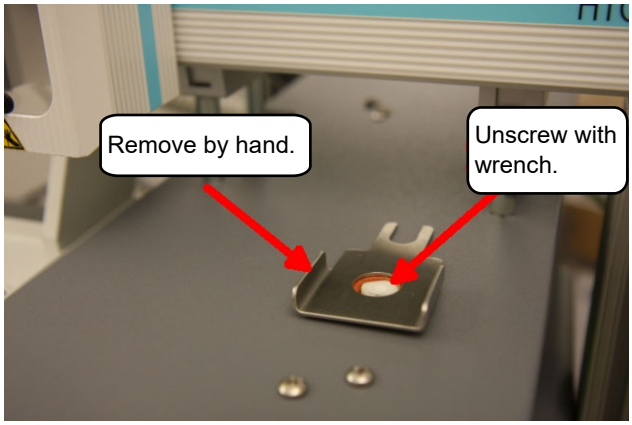
2. Wait for the Change Septum button to change to Septum Changed (see below). This will happen when the current injection analysis is complete.

Figure 67: Septum Change Sequence



3. Remove the protective metal cover around the injection port (ensure that the insulation foam stays attached to the cover).

Figure 68: Septum Removal



4. Unscrew the cap of the port.

CAUTION

BURN HAZARD: The bottom of the cap is very hot.

5. The old septum will usually stick to the port, but if it is in the cap, use tweezers to remove the old septum.
6. Insert a new septum into the cap and screw the cap back onto the port by hand until it comes to a hard stop. This should be finger-tightened only.

CAUTION

EQUIPMENT DAMAGE: Do not over-tighten or use a wrench, as the injector port will be damaged.

7. Replace the metal cover around the injection port.

8. If you had not used the Change Septum Button in the Coordinator window to change the septum, you are finished. Otherwise, click the Septum Changed button. The analyzer will restart the vaporizer purge cycle and then wait for the next sample injection.

15.3 Cleaning

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

16. TROUBLESHOOTING

16.1 Analyzer 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 Technical Support. More troubleshooting information is available on the Community section of our website. Choose from the following symptoms:

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.

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

User Interface Program Does Not Start

Context: The computer is typically configured to automatically start the instrument and its associated user interface program after booting up. If it does not start automatically, the program may be launched by double-clicking the “Start Instrument” icon on the desktop. Communication problems with the analyzer may occur if the analyzer fails to initialize correctly on power up.

- **Shut down the computer using the following procedure only:**

1. Click on the computer’s “Start” menu in the lower left hand corner.

Do not simply restart Windows by selecting “Restart” in the drop-down box on Step 3, since this does not cycle the power to the analyzer.

2. Select the red “Shut Down” button.

3. Select “Shut down” in the drop-down box.
4. Wait for the computer and analyzer to turn off completely and the shutdown to complete normally.
5. After a few seconds, restart the computer by momentarily depressing the front panel power button.

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.

- **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.**
- **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.**

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.

If the computer responds to the mouse, a normal Windows shutdown may be carried out:

1. Click on the computer’s “Start” menu in the lower left hand corner.
2. Select the red “Shut Down” button.
3. Select “Shut down” in the drop-down box.
4. Wait for the computer and analyzer to turn off completely and the shutdown to complete normally.

5. After a few seconds, restart the computer by momentarily depressing the power button.

If the computer does not respond to the mouse:

6. Hold down the power switch on the front panel for a few seconds until the computer and the instrument power off.
7. After another few seconds, restart the analyzer by momentarily depressing the power button.

16.2 ChemCorrect Troubleshooting

This section lists solutions to a common problem that may be encountered while using the ChemCorrect software.

ChemCorrect Processing Software Hung Up (froze).

Recommendation: Check that you ran a coordinator compatible with ChemCorrect. Coordinators for the ^{17}O-excess mode are not compatible with ChemCorrect. Coordinator output csv files should contain columns with baseline_shift for L2130-i and L2140-*i*.

If the above checked out, the other usual cause is syntax error and/or missing/empty row(s) in the coordinator output file. The three files listed below are user-editable:

Instruction Set: C:\Picarro\ChemCorrectExe\chemcorrect_inst xx.csv

Standard Library: C:\Picarro\ChemCorrectExe\standards file.csv

Coordinator Output csv file or source file: HBDSxx _CC_IsoWater_xx.csv

The instruction set is usually not edited unless you're an avid user. The standards file syntax is not too complicated to follow. The most common errors occur in the coordinator output file. These are the items to check:

The number of injections that you set ChemCorrect Analysis to ignore has to be less than the total injections/sample.

There can't be any empty row or blank value (as a result of broken/bent needle, or sample ran out of liquid). This is not an issue if you have ChemCorrect version 1.2.0 or later.

"Line" column has to be sequential and start at 1

"Time Code" column has to be chronological.

Port number should correspond with the correct sample number.

If you have to edit this source file, use Excel (an exception to all previous warnings to use Notepad++ because it's a lot easier – but be careful). When done editing, close the file, when asked "Do you want to save changes...?", click "**yes**", when asked to keep the format, click "**yes**".

Sometimes above syntax errors will crash ChemCorrect and you won't be able to run the software, instead an error message pops up with a path to the error log file. If this happens, please report this bug to help us improve our software. The temporary work around is to delete this file "chemcorrect.clt" in the ChemCorrectExe root directory.

17. TRANSPORTATION and STORAGE

If the instrument will be transported or stored, the following procedure can be used to prepare the instrument and repack it into the original carton. All original packing materials the analyzer was shipped with should have been retained.

1. Ensure clean dry gas is still attached to the instrument prior to shutting down. This prevents condensation inside the system during storage or shipment.
2. Click the “Shutdown” button on the GUI (see **Shut Down** section of this manual for details).
3. Disconnect all tubing and electrical connections from the analyzer.
4. To prevent contamination and possible damage to the connector threads, place caps on all gas connections.
5. Place the analyzer in a plastic bag with a packet of desiccant. Seal the bags with tape.
6. 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

Equipment Damage: 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.

18. LIMITED WARRANTY

Picarro, Inc. warrants its Products to be free from defects in material and workmanship and to perform in the manner and under the conditions specified in the Product specifications for twelve (12) months from shipment.

This warranty is the only warranty made by Picarro with respect to its Products and no person is authorized to bind Picarro for any obligations or liabilities beyond this warranty in connection with its Products. This warranty is made to the original Purchaser only, is non-transferable and may only be modified or amended by a written instrument signed by a duly authorized officer of Picarro. Sub-systems manufactured by other firms, but integrated into Picarro Products, are covered by the original manufacturer's warranty and Picarro makes no warranty, express or implied, regarding such sub-systems. Products or parts thereof which are replaced or repaired under this warranty are warranted only for the remaining, un-expired portion of the original warranty period applicable to the specific Product replaced or repaired.

DISCLAIMER

THE FOREGOING WARRANTY IS EXCLUSIVE AND IN LIEU OF ALL OTHER WARRANTIES WHETHER WRITTEN, ORAL OR IMPLIED, AND SHALL BE THE PURCHASER'S SOLE REMEDY AND PICARRO'S SOLE LIABILITY IN CONTRACT OR OTHERWISE FOR THE PRODUCT. PICARRO EXPRESSLY DISCLAIMS ANY WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE.

The Purchaser's exclusive remedy with respect to any defective Product shall be to have Picarro repair or replace such defective Product or credit the Purchaser's account, whichever Picarro may elect in its sole discretion. If it is found that any Product has been returned which is not defective, the Purchaser will be notified and such Product returned at the Purchaser's expense. In addition, a charge for testing and examination may, at Picarro's sole discretion, be made on any Product so returned.

These remedies are available only if: i) Picarro is notified in writing by the Purchaser promptly upon discovery of a Product defect, and in any event within the warranty period; ii) Picarro's examination of such Product discloses to Picarro's satisfaction that such defects actually exist and the Product has not been repaired, worked on, altered by persons not authorized by Picarro, subject to misuse, negligence or accident, or connected, installed, used or adjusted otherwise than in accordance with the instructions furnished by Picarro.

The following warranty conditions shall apply to all Picarro, Inc. products unless amended by a written instrument signed by a duly authorized officer of Picarro:

ADJUSTMENT – No electrical, mechanical or optical adjustments to the product(s) are permitted.

PARTS AND LABOR - New or factory-built replacements for defective parts will be supplied for twelve (12) months from date of shipment of the product. Replacement parts are warranted for the remaining portion of the original warranty period. There will be no charge for repair of products under warranty where the repair work is done by Picarro, Inc.

NOT COVERED BY THE WARRANTY – Damage to any optical surface from improper handling or cleaning procedures. This applies specifically to those items subjected to excess laser radiation, contaminated environments, extreme temperature or abrasive cleaning. Damage due to ESD, abuse, misuse, improper installation or application, alteration, accident, negligence in use, improper storage, transportation or handling. No warranty shall apply where the original equipment identifications have been removed, defaced, altered or where there is any evidence of alterations, adjustments, removal of protective outer enclosure, any attempt to repair the product by unauthorized personnel or with parts other than those provided by Picarro, Inc.

DAMAGE IN SHIPMENT - Your analyzer should be inspected and tested as soon as it is received. The product is packaged for safe delivery. If the product is damaged in any way, you should immediately file a claim with the carrier or, if insured separately, with the insurance company. Picarro, Inc. will not be responsible for damage sustained in shipment. All Picarro products are F.O.B. origin, shipped from the Picarro factory or Picarro distributor. The price of all Products, unless otherwise specifically stated, is Ex- Works, Sunnyvale, CA as defined by Incoterms, 2001. The cost of normal packaging for shipment is included in the invoiced price. Where Buyer specifies special packaging, a charge will be made to cover any extra expense.

CLAIMS ASSISTANCE - Call Picarro, Inc. Customer Service or your local distributor for assistance. Give our representative the full details of the problem. Helpful information or shipping instructions will be provided. If requested, estimates of the charges for non-warranty or other service work will be supplied before work begins.

RETURN PROCEDURE - Customers must obtain a Return Merchandise Authorization Number from Picarro, Inc. prior to returning units. Products being returned for repair must be shipped in their original shipping cartons to avoid damage.

APPENDIX A – REMOTE DATA ACCESS

A.1 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.

A.2 Remote Data Access

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

- Send data from the instrument to a list of e-mail accounts.
- Measure the offset of the host computer system clock from a set of Internet time servers and (optionally) to resynchronize the clock based on 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 set up 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 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 time servers.

The initialization file is:

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

and 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 64K bytes in length, it is backed up, appending a numeric extension to the file name, and a new file is opened. A total of ten backup log files are kept.

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 time 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.

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. 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 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 email 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 email 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.

Dial-up

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 connection name 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.

Examples 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

APPENDIX B – THE DATA FILE VIEWER

B.1 Introduction

The Picarro Data File Viewer software is located in the Picarro Utilities folder on the desktop. The software allows the user to graph and to conduct statistical analysis of the raw data. Additional functions include Allan Variance plot and quadratic or polynomial fittings.

The Picarro Data File Viewer includes two main menus: **File** and **New.**

Figure 69: File Menu

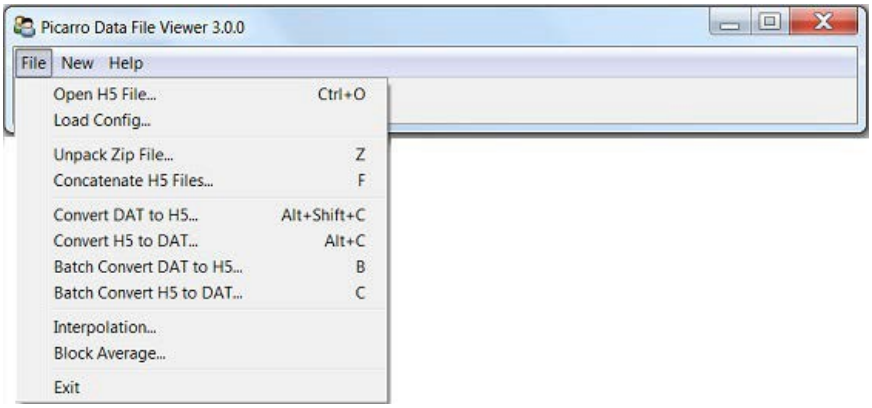
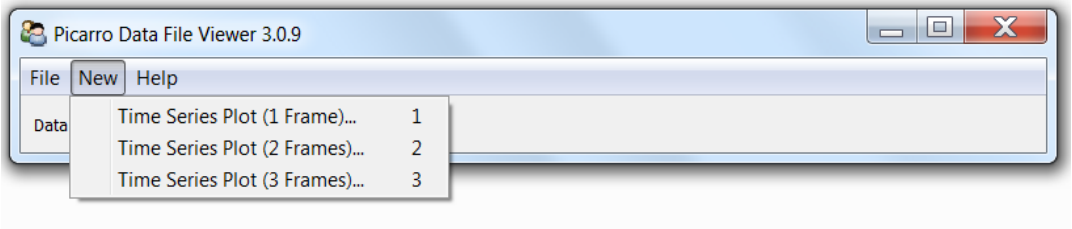


Figure 70: New Menu



B.2 The File Menu

This section describes the functions available from the Data File Viewer File menu.

Open H5

File > Open H5 opens a Picarro data file (HDF5 format) for data analysis and visualization. After opening the data file, you can create a new time series plot. Refer to *New Time Series Plot* for more information.

Load Config

File > Load Config loads a configuration file (ini format) to restore parameters of a workplace. Refer to *Save Configuration* for more information.

Unpack Zip File

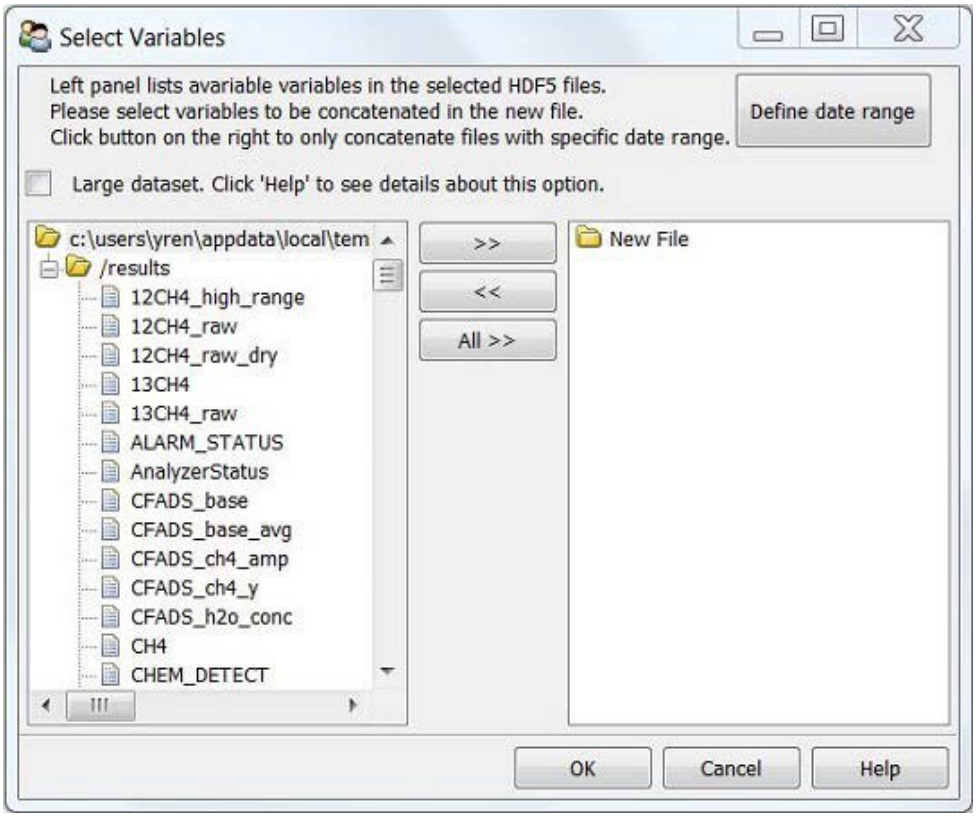
Use File > Unpack Zip File to concatenate all H5 files inside the zip file into a single H5 file. Refer to Concatenate H5 Files for details.

Concatenate H5 Files

Use **File > Concatenate H5 files** to concatenate multiple files and zip archives of H5 files into a single H5 file. Navigate to the desired folder or use the **Define date range** button to specify a date range of files to concatenate. (See next section.)

After selecting the path of the data files, Data File Viewer will automatically search an H5 file in the specified zip/folder and look for all available variables in the H5 file. The variables are then listed in the left panel, and users can use "**>>**" button to move variables to the right panel for concatenation.

Figure 71: Select Variables Form



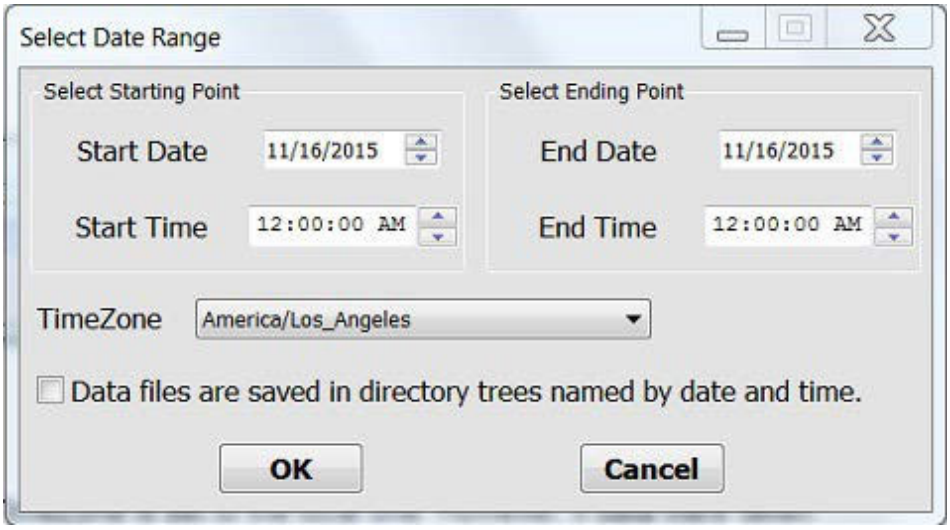
Define Date Range

Data File Viewer can search data files within the desired date range and then concatenate such files into an H5 file.

By default, TimeZone is set to your local time zone. However, if data were taken elsewhere, select the time zone where data were taken.

Select File > Concatenate H5 files, then click Define date range to specify the desired date range.

Figure 72: Defining Date Range



Data files are saved in directory trees named by date and time option.

Picarro software saves data in a directory tree that is named by the creation year, month, and day. (See example directory tree in the following image.) Select this option if the target folder has this file structure. This way, Data File Viewer will only search folders within the desired date range, which can substantially reduce processing time.

Figure 73: File Structure of Data File Viewer

NOTE

To save processing time, Data File Viewer does not open data files, but only determines data acquisition time based on the file name.

CAUTION

Do not define a time range for data files whose names have been changed.

NOTE

Data File Viewer does not concatenate data files exactly within the defined time range. This is because the time extracted from file name is different from the data acquisition time. To not miss data points, Data File Viewer expands the specified time range, so the resulting dataset normally has a wider time range than the user specification.

Convert DAT to H5

Select **File > Convert DAT to H5** to convert a file in DAT format to HDF5 format. These formats are described below:

- DAT format: DAT files accepted by DatViewer store tabular data (numbers and text) in plain text.
- Each line of the file is a data record. Each record consists of one or more fields separated by whitespaces.
- The first line of data file indicates column names.
- There must be a field “EPOCH_TIME” to store the acquisition epoch time (expressed as seconds since Jan 1, 1970) of the data. Otherwise, the first and second fields must be “DATE” and “TIME”. The “DATE” field must have the format “mm/dd/yyyy” or “yyyy-mm-dd”, and the “TIME” field must have the format “HH:MM: SS(.sss)” where (.sss) is an optional fraction of seconds.
- HDF5 format: HDF5 is a data model, library, and file format for storing and managing data. (See the HDF5 Home Page on the HDF Group Web site for more information.) When converting DAT to HDF5 format, Data File Viewer creates a table named “results” to the contained data.

Convert H5 to DAT

Select **File > Convert H5 to DAT** to convert a file in a HDF5 format to DAT. These formats are described in *Convert DAT to H5*.

NOTE

Data File Viewer does not concatenate data files exactly within the defined time range. This is because the time extracted from file name is different from the data acquisition time. To not miss data points, Data File Viewer expands the specified time, column name "fineLaser-Current_1_controlOn" will be replaced with "fineLaserCurr_1_ctrlOn".

Interpolation

Interpolation describes the method for constructing data points with a range of a discrete set of known data points. Select **File > Interpolation** to perform interpolation on a time grid with a constant interval.

Block Average

Select **File > Block Average** to divide a dataset into small blocks based on a user-defined block size. The average is calculated for data in each block, and the results are saved in a new H5 file.

NOTE

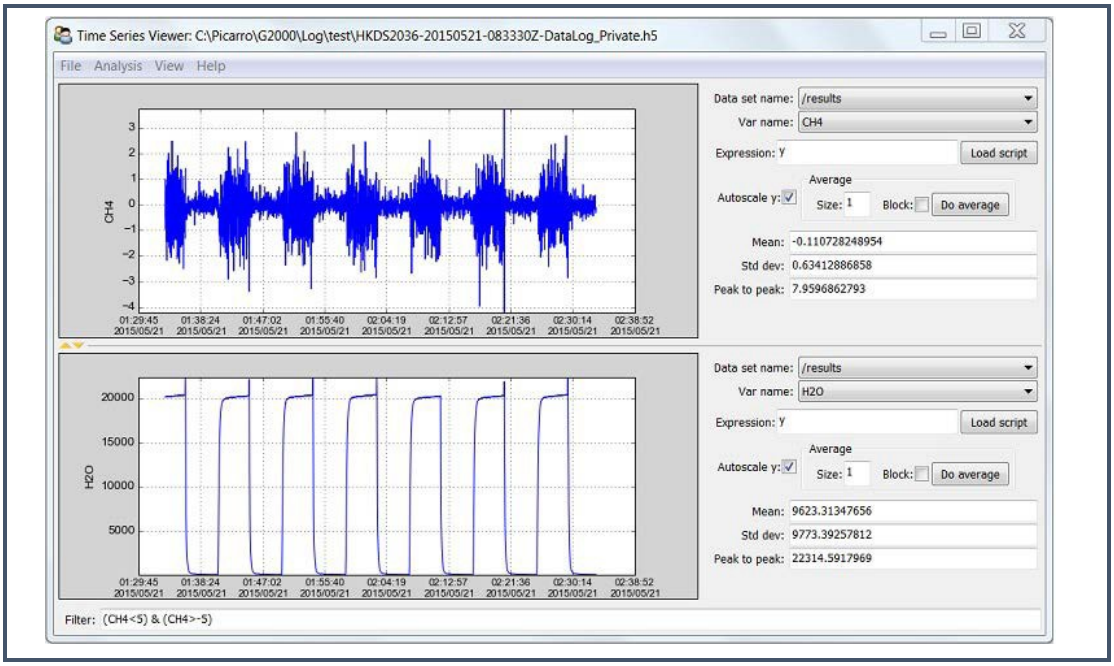
The specified block size must be greater than the average data interval.

Because the data interval is normally not a constant (unless interpolation is performed), fluctuations in the data interval will affect block averaging if the block size is comparable to the average data interval.

B.3 New – Time Series Plot

You can specify to include create time-series plots with one, two, or three frames. New plots display in the Time Series Viewer.

Figure 74: Time Series Viewer

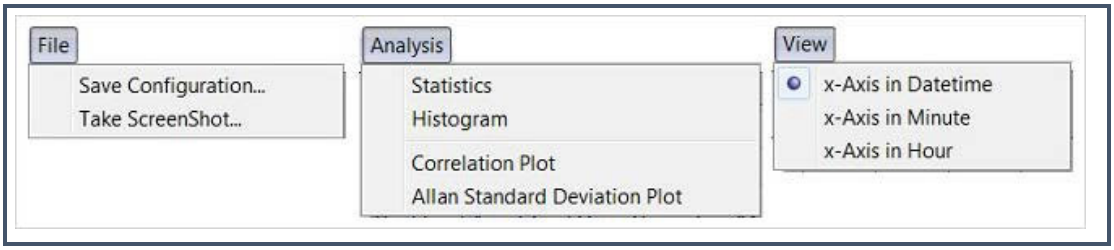


The next section describes the options available on the Time Series Viewer menu bar. Refer to *Time Series Viewer Canvas* on page 163 for information the Time Series Viewer UI features and options.

B.4 Time Series Viewer Menus

The Time Series Viewer form includes the following menus:

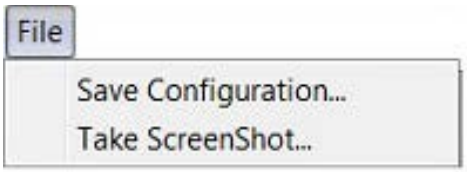
Figure 75: Time Series Viewer Menus



Time Series Viewer File Menu

Use the File menu to save a configuration or take a screenshot.

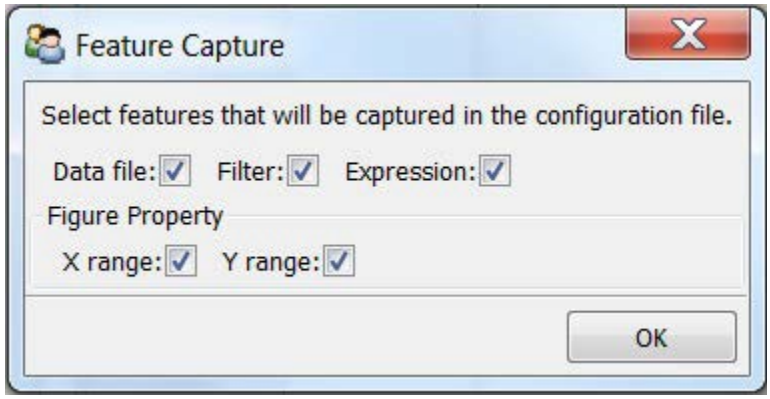
Figure 76: Time Series Viewer – File Menu



Save Configuration

Click **File > Save Configuration** to open the Feature Capture form. With this form, you can save figure properties, expressions, filters, and other settings to a configuration file so that it can be easily loaded in the future.

Figure 77: Time Series Viewer – Feature Capture



CAUTION

If a feature is not captured, it will be omitted when the configuration file is loaded.

Depending on the features captured, loading a configuration file can have different effects. For example:

- If all features are captured, a saved workplace is reproduced.
- If Data file is not captured, saved parameters will be applied to the data file in memory.
- If Expression is not captured, plots will not be transformed.
- If X (Y) range is not captured, figures will be auto-scaled on the x (y) axis.

Take Screenshot

Use **File > Take ScreenShot** to take a screenshot of the Time Series Viewer and save it as a .png to a specified file.

Time Series Viewer Analysis Menu

Use the Analysis menu to calculate statistics, generate a histogram, and to plot correlations and Allan Standard deviations.

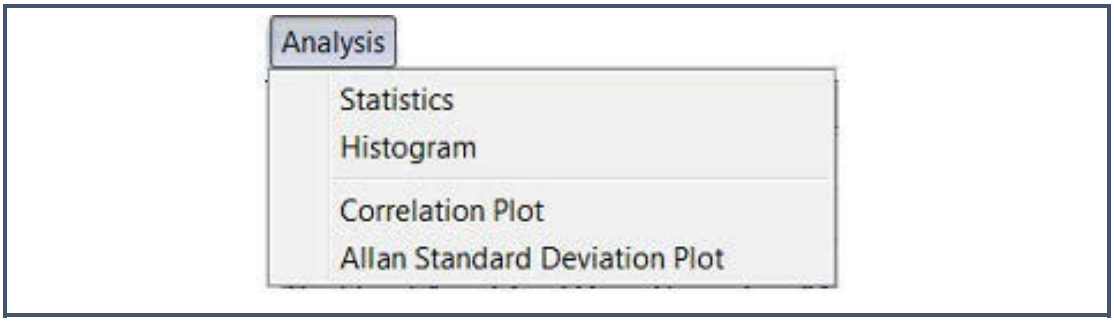


Figure 78: Time Series Viewer – Analysis Menu

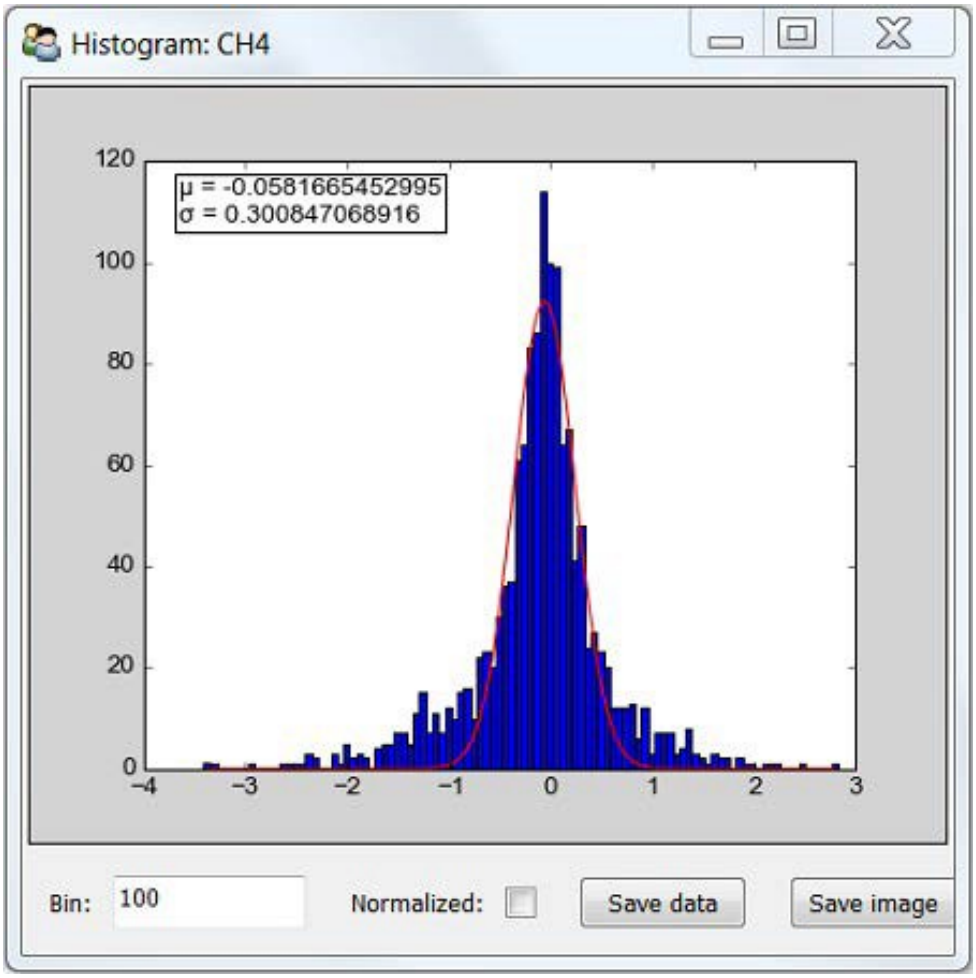
Statistics

Use **Analysis > Statistics** to calculate mean, standard deviation and peak to peak for all plots in the current window.

Histogram

Use **Analysis > Histogram** to generate a histogram of data as shown below.

Figure 79: Histogram Window



- **Red Line**: A Gaussian function fitted to the histogram. Fitting results of μ and σ are shown in the top-left corner of the plot.
- **Bin**: Specifies the number of intervals that the range of values is divided into.
- **Normalized**: When selected, the sum of the histograms is normalized to 1.
- **Save data**: Saves histogram data to a CSV file.
- **Save image**: Saves the histogram image as a JPEG/PNG/PDF file.

Correlation Plot

Use Analysis > Correlation Plot to plot Y-axis data in one frame versus that in the other. This can be used when two or more frames exist in the current Time Series Plot window. See Correlation/XY Plot on Page 166 for details.

Allan Standard Deviation Plot

Use **Analysis > Allan Standard Deviation Plot** to create an Allan Standard Deviation plot (versus a standard deviation plot) for data in the current window. See Allan Variance for more information.

Time Series Viewer View Menu

Use the View menu to view X-axis information in date-time, minute, or hour format.

Figure 80: Time Series Viewer – View Menu

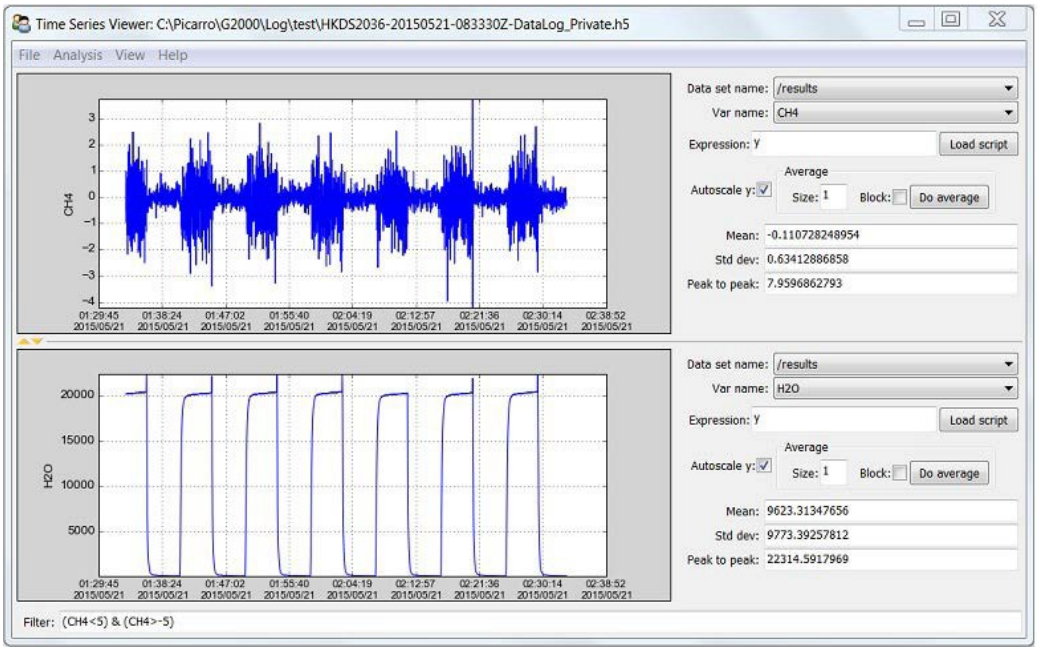
NOTE

When switching from DateTime to Minute or Hour, the X-axis data is subtracted from the earliest point shown in the panel and then converted to the desired unit.

The Time Series Viewer Canvas

The Time Series Viewer canvas is comprised of interactive graphs and a variety of configuration options.

Figure 81: Time Series Viewer Canvas



Mouse Options and Graph Transform

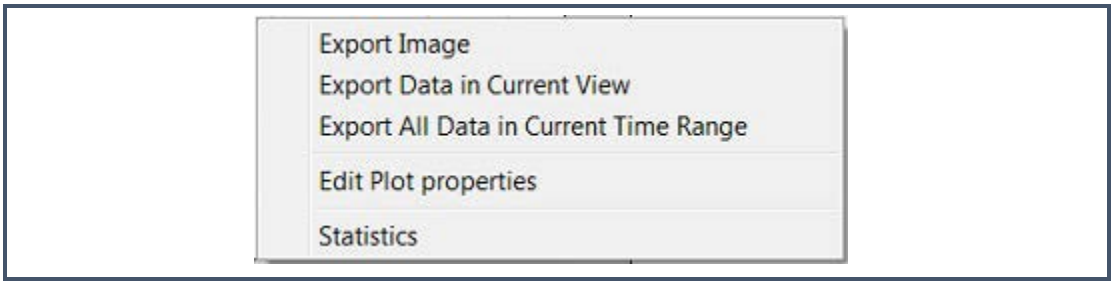
The following mouse actions can be used in the canvas graphs:

- Left click and drag: Zooms into the selected area of the plot.
- Left click and drag with the SHIFT key down: Pans the plot.
- Left click and drag with CTRL key down: Zooms out from the plot.
- Left click and drag with ALT key down: Stretches the plot.
- Right-click: Opens an additional menu. Refer to the next section.

Right-click Menu

Right-clicking on the canvas provides opens a pop-up menu.

Figure 82: Canvas Right-click Menu



Export Image: Exports the current plot as a jpeg, png, or pdf file.

Export Data in Current View: Exports only date/time and the selected variable in the current view to an HDF5 or CSV file.

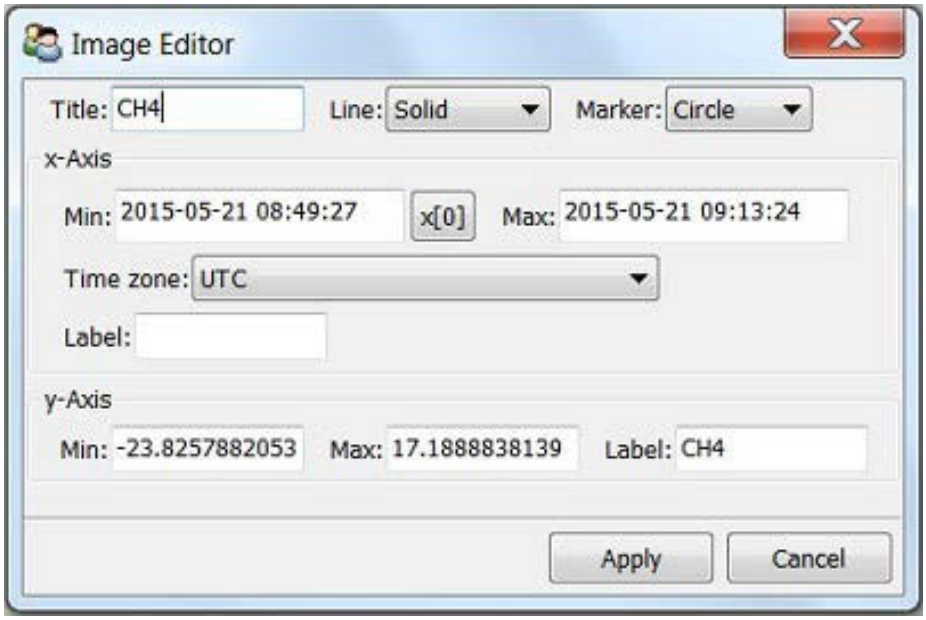
Export All Data in Current Time Range: Exports all variable columns of the selected dataset in the current time range to an HDF5 file. Refer to *Concatenate H5 Files* on page 155 for more information.

Edit Plot properties: Opens the Image Editor form, where the following options can be specified:

- **Title**: Edits the title of the plot.
- **Line**: Specifies the line pattern of the plot. If **None** is selected, the data points will be plotted without connecting lines.
- **Marker**: Specifies the marker type to indicate data points. If **None** is selected, data points will not be shown.
- **Min and Max**: Specifies the minimum and maximum of data range for the X-axis and the Y-axis.
- **x[0]**: Sets the earliest time of the dataset as the minimum of the X-axis.

- **Time zone**: Sets the time zone for date/time variables. This defaults to the local time zone.
- **Label**: Specify a label for the X-axis and the Y-axis.

Figure 83: Image Editor Form



- **Statistics**: Calculates the mean, standard deviation, and peak to peak for data in the current view.

Dataset Name and Var Name

An HDF5 file can store one or more tables. Each of these tables is called a Dataset. A table can contain one or more columns. Each column is called a variable (Var).

Use the **Dataset name** drop down to select the dataset that will be used for this time series graph. Use the **Var name** drop down to select the column in the dataset to use in the graph.

Autoscale Y

When the Autoscale Y option is selected, the Time Series Viewer will autoscale on the Y-axis to make sure that all data within the range of the X-axis is displayed.

Average

If **Block** is selected, a block average is calculated when you click the Do average button is clicked. Otherwise, a moving average is calculated.

For a block average, **Size** specifies block size in unit of a minute. For a moving average, **Size** specifies subset size in unit of data points.

REMINDER

Averaging is performed after the Filter and Expression are performed.

Mean, Std Dev, and Peak to Peak

The **Mean**, **Std dev** (Standard deviation) and **Peak to peak** fields provide all the statistical information of data in the current view.

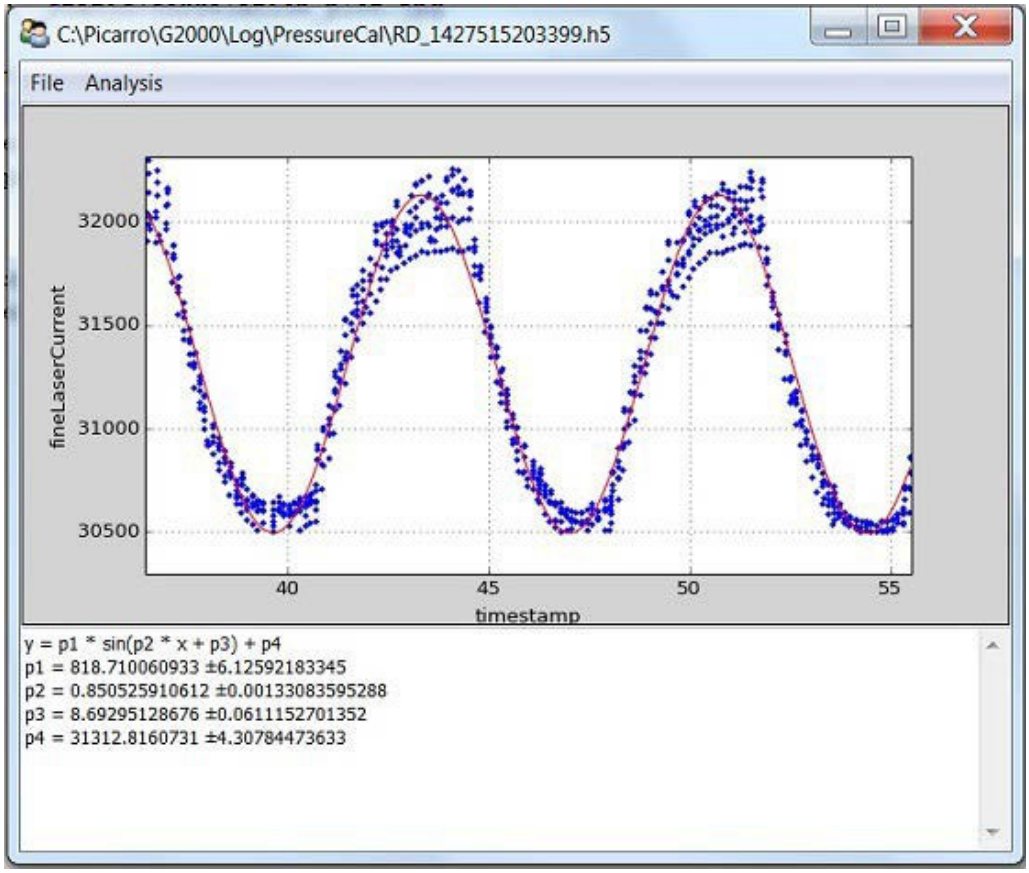
Correlation/XY Plot

The Correlation/XY Plot window includes two menu items: **File** and **Analysis**. For details about the File menu, see *Save Configuration* on page 160.

REMINDER

The canvas in this plot is interactive. For details about the plot canvas, see *The Time Series Viewer Canvas* on Page 163.

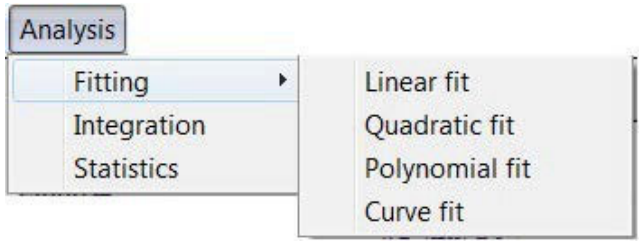
Figure 84: Correlation/XY Plot



Analysis Menu

The Analysis Menu includes three options: Fitting, Integration, and Statistics.

Figure 85: Analysis Menu

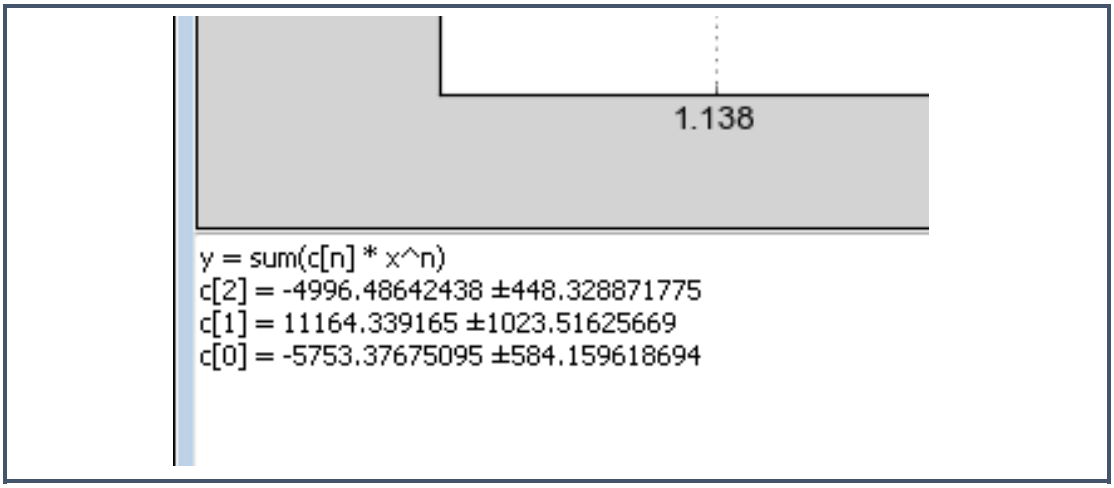


- **Fitting** allows you to specify one of four fitting methods to include in the Correlation/XY plot:
- **Linear fit: Specifies to fit to linear function $y = c_1x + c_0$**
- **Quadratic fit: Specifies to fit to quadratic function $y = c_2x^2 + c_1x + c_0$**

- **Polynomial fit: Specifies to fit polynomial function of degree n: $y = \Sigma c_n x^n$**
- **Curve fit: Specifies to use non-linear least squares to fit an arbitrary function to data.**
- **Integration** calculates area under the curve using the composite trapezoidal rule.
- **Statistics** calculates mean, standard deviation, and peak to peak for data in the current view.

After applying any of the above Analysis options, the results, statistics, or fitting function with coefficients are displayed in the lower portion of the Correlation Plot window.

Figure 86: Results of Quadratic Fitting



APPENDIX C – EXTERNAL VALVE SEQUENCER

C.1 Introduction

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.

C.2 Default Configuration

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

C.3 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.

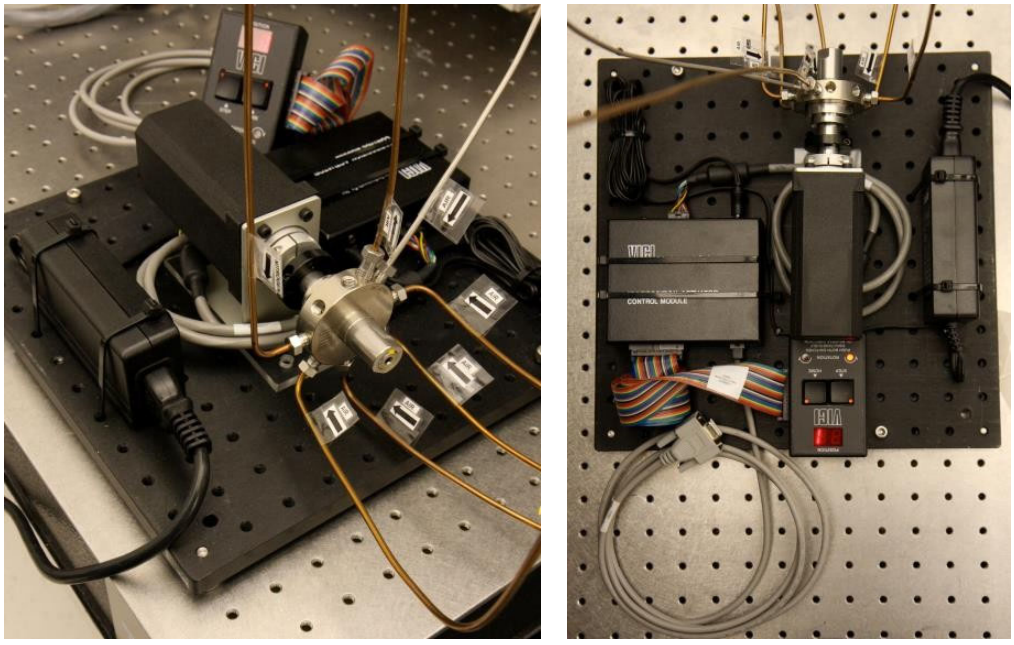
The valve connector cable should be connected to the 15-pin connector at the lower left corner of the analyzer. There are six pairs of wires with connectors labeled V1, V2, … V6 with 2-pin female Molex connectors (Molex#43020-0200) for connection to the solenoid valves. For valves wired with matching Molex connectors, connect V1 to the 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.

C.4 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 micro electric 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 micro electric 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.

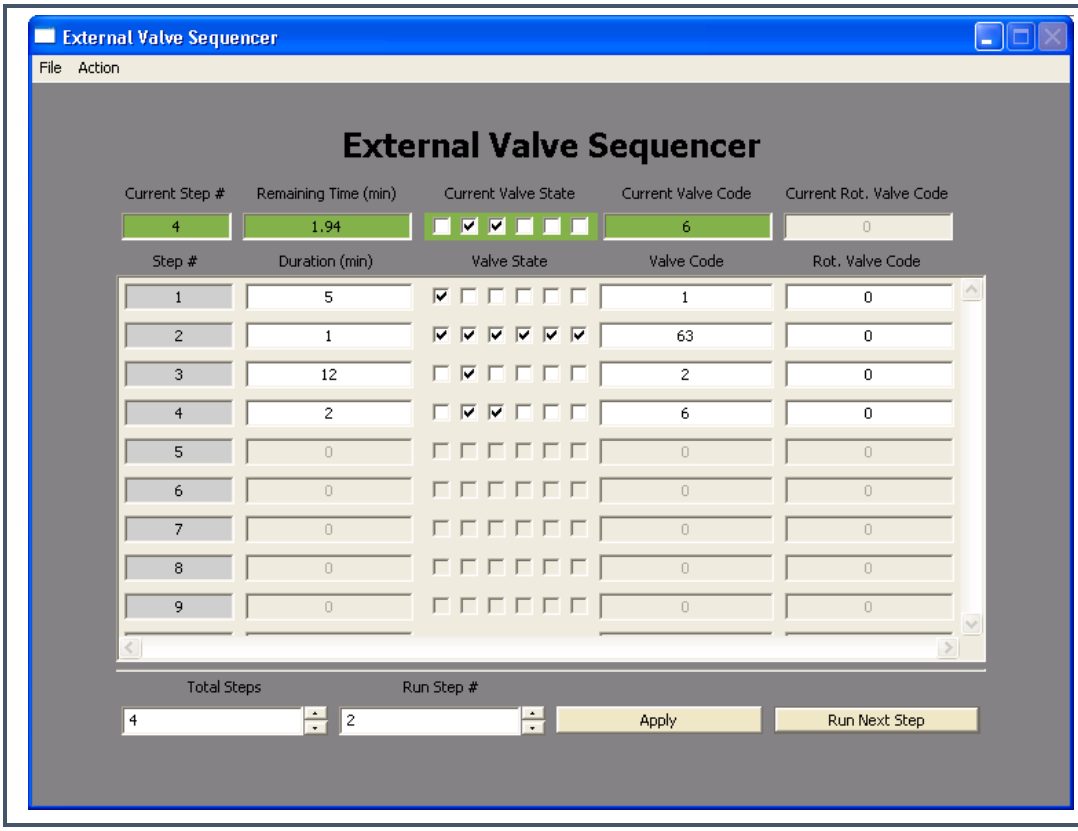
Figure 87: 8-port Valve Setup



C.5 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:

Figure 88: Valve Sequencer GUI



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

C.6 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. 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 checkmark 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 gray box display a value of 512,256 or be grayed-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.

C.7 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