SMALL SAMPLE ISOTOPE MODULE

USER'S MANUAL

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INTRODUCTION

The Small Sample Isotope Module (SSIM) is an accessory designed to work with the Picarro G2101-*i,* G2121-*i*, and G2131-*i* Isotopic CO_2 analyzers, G2132-*i* isotopic CH_4 analyzers, and the G2201-*i* CO_2 & CH_4 analyzers. When sample volumes are too small to be measured in a traditional "continuous flow" mode by the Picarro analyzer (generally requiring >150ml), the SSIM is an essential analyzer sample management peripheral, enabling such small-sample analysis. Combined, the analyzer and SSIM are capable of measuring very small (~20ml) gas samples and performing δ13C-CO2 / δ13C-CH4 measurements. The SSIM automatically prepares and introduces the gas sample(s) to the Picarro analyzer and reports the results, performing the requested number of replicate analyses of each sample.

The SSIM can optionally be paired with the Picarro 16-Port Distribution Manifold to enable it to automatically measure multiple samples (up to eight, not including the gas standard).

The SSIM2 is designed for isotopic ratio measurements, not for concentration measurements. There is some dilution within the SSIM2 as valve 3 switches the input to the analyzer from the zero air tank to the SSIM Sample Volume. The dilution is a few percent (~5% is typical) so concentration change is well within the dynamic range of the analyzer. The $\delta^{13}C$ measurements do not change over this small change in concentration. This dilution does depend somewhat on the pressure of the zero air tank. Lower zero air pressure does result in somewhat less dilution, but it does not completely eliminate the dilution.

Safety note: The SSIM2 is not intended for use in explosive atmosphere environments. Nor is the SSIM2 intended to be used for analyzing explosive levels of gases. This includes methane at explosive concentrations.

Software Updates: Software updates for the SSIM2 may be available on the Picarro Community, http://www.picarro.com/community/picarro_community. To get access to the community, please contact support@picarro.com.

PRINCIPLES OF OPERATION

Internally, the SSIM contains various valves and a sample chamber. Prior to a measurement, the gas system is flushed with purge gas (CO_2 and CH_4 free "zero air") to remove traces of prior samples or atmospheric gas that would contaminate the measurement. Next, the purge gas is pumped out by an external vacuum pump bringing the tubing within the SSIM to a vacuum. At this point, user is prompted to manually open the sample container attached to the SSIM. Because the tubing in the SSIM is under vacuum, the sample expands (using ~20ml of sample) into sample chamber. Meanwhile, zero air is flowing through a 3-way valve to the analyzer, which is at the correct cavity pressure. The valve then switches gas flow from the zero air tank to the SSIM sample volume. The analyzer draws gas from the sample volume which is open only to the analyzer. As the pressure in the sample volume decreases, the outlet valve of the analyzer slowly closes to maintain the correct pressure of the analyzer, with the benefit that the pressure stays at the target pressure. With a chamber pressure sensor, it is possible to monitor the sample chamber pressure equilibrate with the cavity pressure as the analyzer takes in the sample.

16-Port Distribution Manifold: If the 16-Port Distribution Manifold is utilized, then the system performs the requested replicate measurements on each sample and then advances to the next sample inlet port on the 16-Port Distribution Manifold, continuing in this manner until all analyses are completed for each sample present. The SSIM can skip or repeat standard measurements in addition to sample measurements.

SSIM2 Preparation Coordinator routine: The new SSIM prep coordinator routine will run the calibration/standard gas and monitor the analyzer's cavity temperature, cavity pressure, and the wavelength monitor performance until they are stable. This is especially important upon startup or after long periods of idle time. Why? Because the analyzer is constantly making corrections to the wavelength calibration of the lasers using the spectroscopic lines that are being measured. The wavelength monitor provides a very good relative measure of the wavelength of light from the lasers. If the laser is commanded to change its output wavelength by 1 wavenumber, for instance, it will do that very precisely. But the wavelength monitor does not provide information about the absolute wavelength of the laser. We get that information from the spectroscopic lines that we measure. We get this information during the normal course of measuring the lines. After a spectrum is recorded for a given line, the spectrum is analyzed to see how well the laser was centered on the line. Some finite correction is then sent back to the wavelength monitor to provide an ongoing absolute calibration. Normally, the centering is very good and the corrections are very small compared to the width of the line. This is one of the ways that the instrument measurements remain stable as the environment changes temperature or pressure.

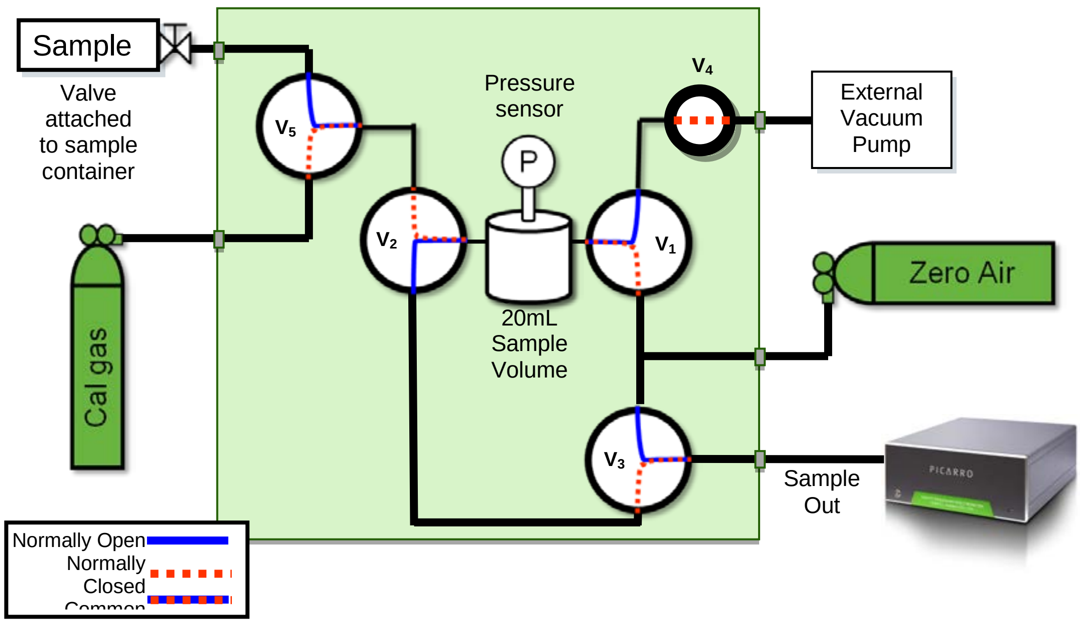
However, if there is not CO_2 or CH_4 going through the cavity, this wavelength correction cannot be calculated because there is no absorption line to measure. The analyzer will make no wavelength correction if the concentration is too low. If the analyzer is running zero air for an extended time (overnight), the laser wavelength calibration will slowly drift off target. When the first sample is run, the wavelength monitor correction will start again, but the first few measurements may be compromised.

The SSIM preparation coordinator was written to make sure the analyzer is ready for samples. It will run the standard gas and monitor the wavelength correction to the wavelength monitor until the correction stabilizes, at which point it will stop and release the analyzer back to the user. In this process it will also make sure the cavity pressure and temperature are stable.

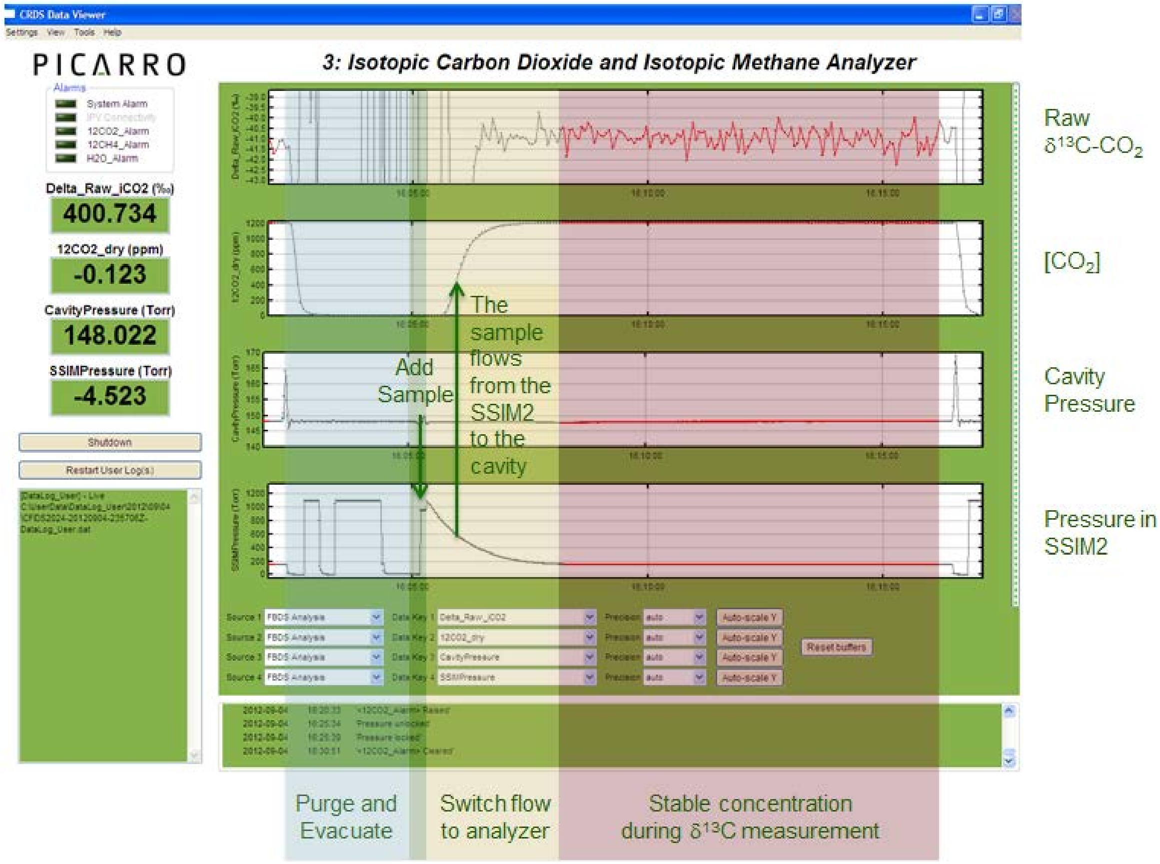
Sample dilution: We have developed a dilution mode to be used in conjuction with syringe injection. In this mode, the SSIM sample volume is filled with zero air after the sample has been injected. This brings the sample volume up to the pressure of the zero air tank. For instance, if 5mL of sample is introduced to the sample volume, the pressure will be 5/20 * 760 Torr ~ 190Torr. If the zero air tank is regulated to 3psi (18psia), the final pressure will be ~900Torr, for a 4.7X dilution. As long as the concentration is within the dynamic range of the analyzer, this will allow one to measure $\delta^{13}C$ with samples smaller than 20mL. This is quite useful in cases where the sample is concentrated. We ran 20uL of pure CH_4 by syringe to get concentrations of just less than 1000ppm after dilution, just within the iCH_4 analyzer's dynamic range. For less concentrated samples, there is a trade-off with precision, which degrades with lower precision. Nonetheless, this may be an option to consider for small samples.

Valve Sequencer: The SSIM2 can be operated with our External Valve Sequencer software. This is described in the G2201-i manual in one of the appendices. The schematic of the valves is needed to understand how to control the SSIM2. This schematic is in the presentation below. If you find the sequencer too limiting, you might be interested in the valve sequencer. Unfortunately, it does not produce a *.csv file with the results averaged.

Internal volumes: The internal sample volume is ~20ml. Inside the SSIM2, the line leading to the sample volume is a 6cm line of 1/8 inch stainless steel. The inner diameter of the 1/8 inch line is 1.6mm with a cross sectional area of 0.02cm^2. So the approximate volume of this line is ~0.12ml. The line leading from the sample volume to the "Sample Out" port is 16cm long with a volume of ~0.32ml.



Schematic for the SSIM

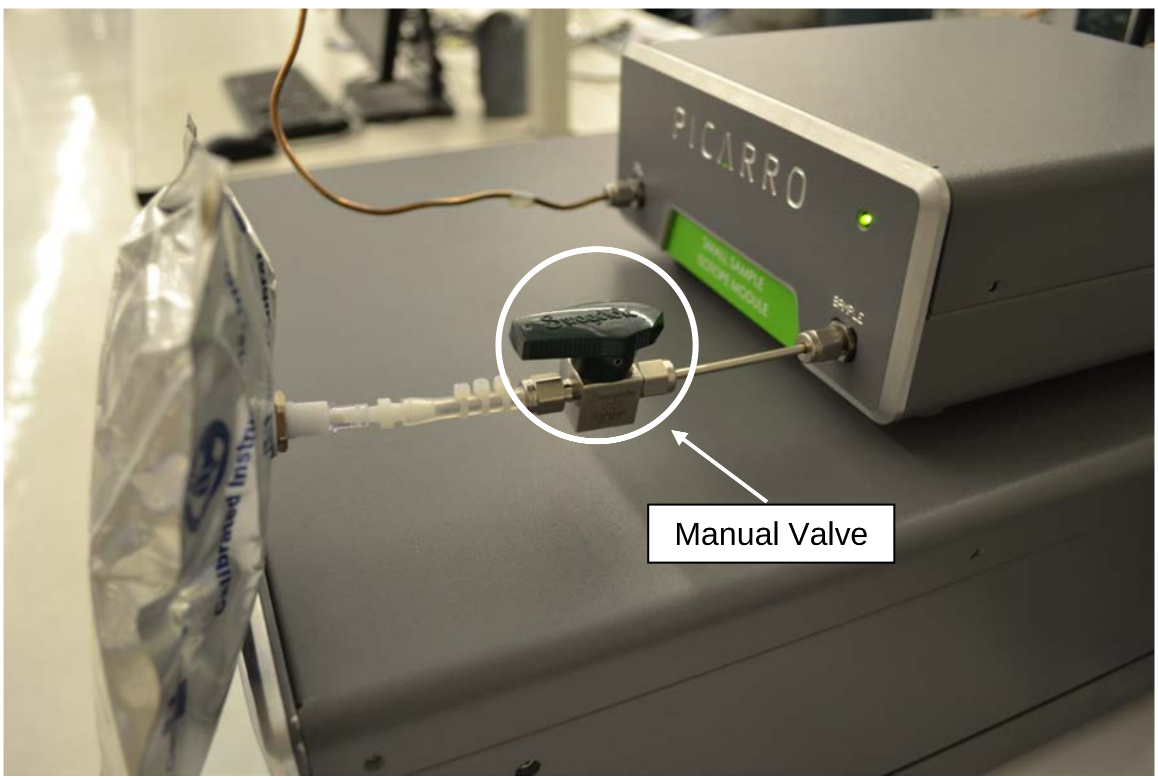


GUI output for a sample run on the SSIM2.

PRE-INSTALLATION REQUIREMENTS

Prior to setting up the SSIM, the user will need to complete the following steps:

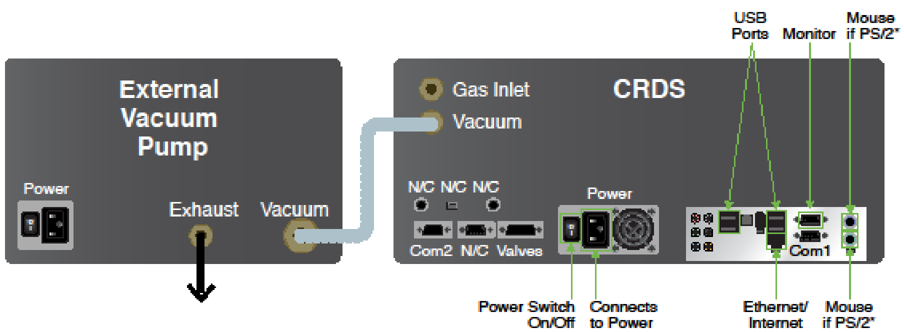
1. A pressurized cylinder of dry, CO_2 and CH_4 free “zero air” complete with a pressure regulator so that gas can be supplied at ≥1 psi (0.07 bar) and <8 psi (~0.5 bar). It should have <1 ppm CO_2 and <5 ppb CH_4 and <10 ppm H_2O. This is generally what “zero air” is specified to contain, for example.
2. Various lengths of 1/8” tubing (stainless steel recommended) with 1/8” Swagelok connections on each end.
3. A pressurized cylinder of calibrated CO_2/CH_4 gas having a known concentration and known $\delta^{13}C$ value, complete with a pressure regulator so that gas can be supplied at ≥1 psi (0.07 bar) and <8 psi (~0.5 bar). Picarro typically uses a pressure of 3 psi.
4. Sample container(s) (Mylar bags or fixed containers for example) which can be attached to the system via 1/8” Swagelok and which have manual valves so that they can be isolated from the system during purging. It is also possible to use an injection port if using a syringe.



Example of a sample bag connected to the SSIM input via a manual valve

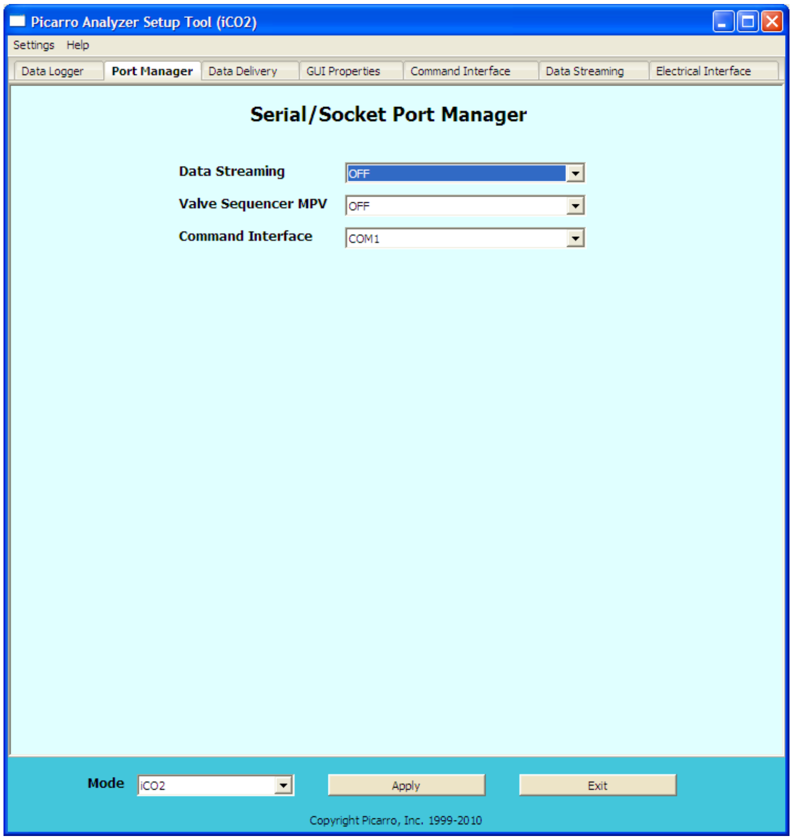
	Note: these manual valves on the sample bags/containers are a requirement.

5. Appropriate wrenches (7/16, 1/2, 9/16, and 11/16 inches) for attachment of gas connections.
6. The basic gas analyzer setup (CRDS Analyzer & External Vacuum Pump) should be completed. The information can be found in the manual of the CRDS analyzer.



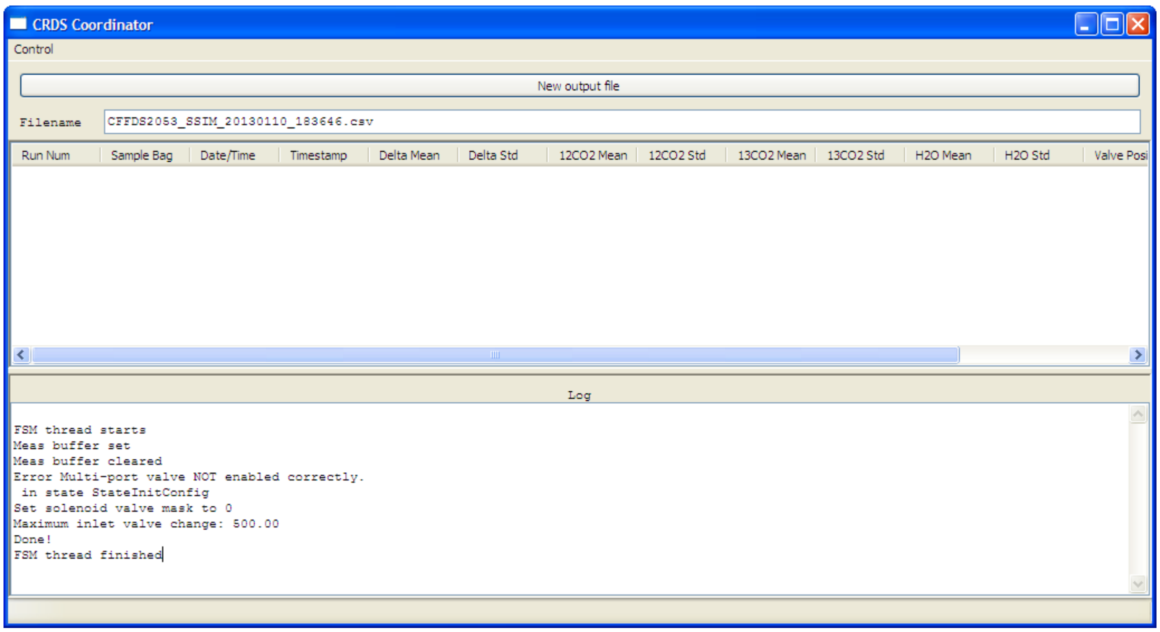
Basic Carbon Analyzer Setup

7. If using the 16-Port Distribution Manifold, find its manual to refer to while following the rest of the manual. The 16-Port Distribution Manifold is a great tool when the analysis of multiple samples is desired. It will be convenient to place the 16-Port Distribution Manifold directly on top of the CRDS when preparing to set up the CRDS with the 16-Port Distribution Manifold.
8. Prior to operation and especially if the SSIM is to be used on an analyzer that is also used with other valves for different applications (such as the 16-Port Distribution Manifold), the Valve Sequencer in the Picarro GUI needs to disabled (and then re-enabled after use of the SSIM is finished if necessary). The user can do this through the “Setup Tool” in the “Utilities” folder in the desktop. Set the “Valve Sequencer MPV” to “OFF.” Disabling and re-enabling the Valve Sequencer must occur while the software is stopped. Changes will be accepted upon restarting the software.



Setup Tool Port Manager

Note: If the Valve Sequencer is not properly disabled the following error will appear in the coordinator window. This is the same message the occurs if the 16-Port Distribution Manifold is not turned on or improperly connected.



Coordinator Error Message

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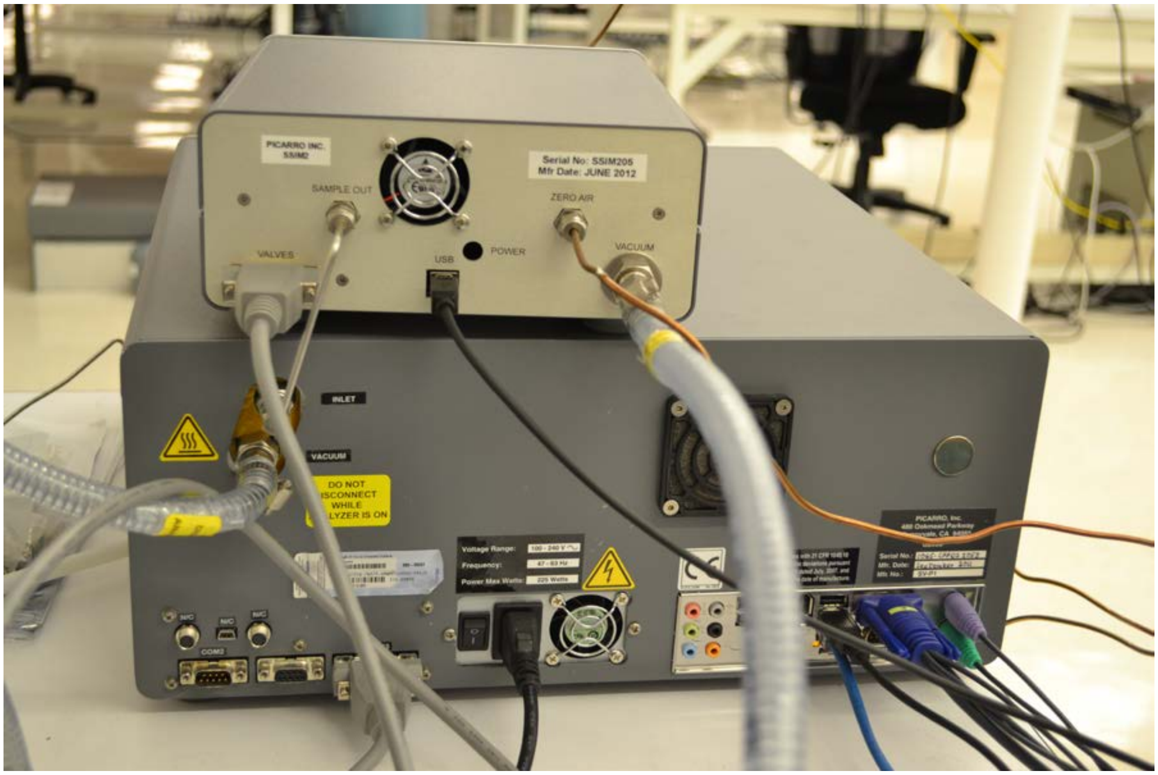
SSIM HARDWARE SETUP & INSTALLATION

Follow the steps described in this section to make the proper gas and electrical connections. All gas connections should be made with 1/8” Swagelok. There are two possible configurations – one with and one without the 16-Port Distribution Manifold. This section includes installation information for both of the configurations.

Based on one’s configuration, either follow Section 1 (SSIM - Picarro Analyzer Setup) or Section 2 (SSIM - Picarro Analyzer - 16 Port Distribution Manifold Setup)

	Note: It is imperative that all gas connections be free of leaks in order to achieve proper measurement of sample and ensure performance of the system. For more details on ensuring leak-free connections, see Troubleshooting section at the end of this document. All gas connections should be made with 1/8” Swagelok (stainless steel tubing recommended).

SECTION 1: SSIM – CRDS ANALYZER SETUP



Properly Set Up SSIM with a G2101-i CRDS Instrument

Note: This module enables very precise measurements of isotopic ratios of small samples. For the best precision measurements, the analyzer should be allowed to run for at least 2 hrs prior to making the final connection to the analyzer (the analyzer must be stabilized).

If the SSIM is used alone with the analyzer, the required hardware setup steps are:

1. Before starting, make sure all the "Pre-installation Requirements" have been met.
2. Position SSIM near the analyzer's inlet connection to minimize the dead space of gas line connecting the SSIM **"Sample outlet"** (located on SSIM's rear side) and the analyzer gas **"Inlet."** Prepare tubing to connect (but **DO NOT yet connect SSIM to analyzer**) these connections. A short length of 1/8" stainless tubing having 1/8" Swagelok connections on both ends should be used. Picarro

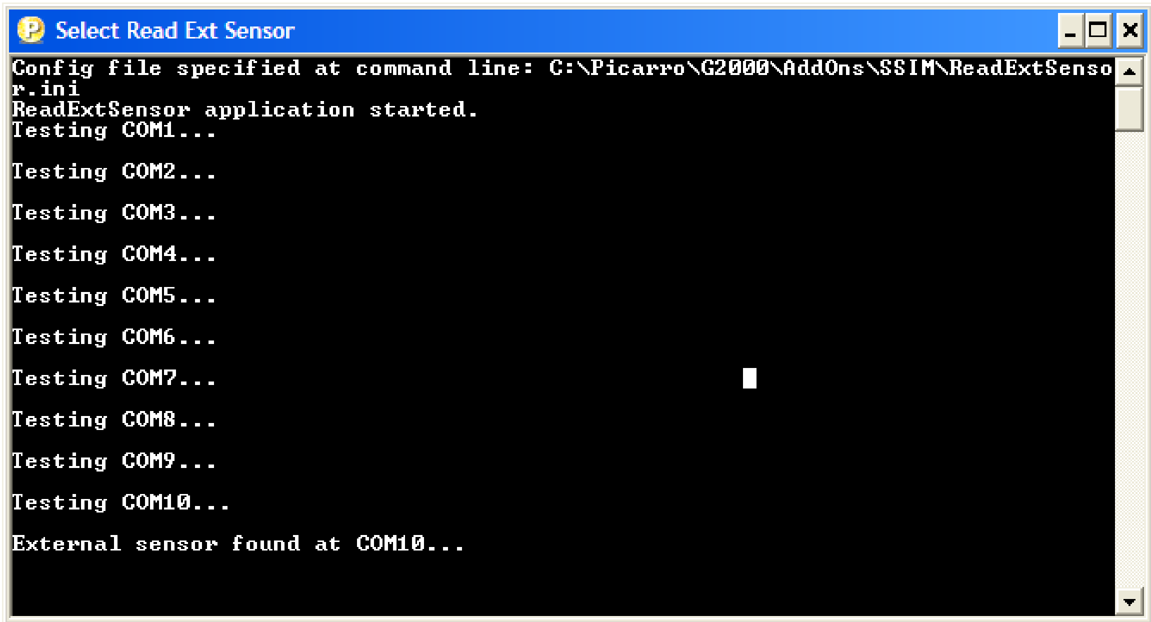
supplies the tubing that attaches from the Sample outlet of SSIM to the analyzer's gas inlet.

	Note: it is not necessary to shut down the analyzer during the installation of the SSIM, but it is imperative that gas pressures from the high-pressure cylinders be regulated to ≥1 psi (0.07 bar) and <8 psi (~0.5 bar) prior to connecting the SSIM and the analyzer (typically 3 psi).

3. Connect the external vacuum pump to the **"Vacuum" port** on the SSIM with the supplied vacuum line. Connect the pump to line power.
4. Attach the purge gas supply (zero air as mentioned on Step 1 of Pre-Installation Requirements) to the back **"Zero Air"** connection of the SSIM and supply gas at optimally ≥1 psi (0.07 bar) and <8 psi (~0.5 bar) (typically 3 psi).
5. Attach the sample bag or container to the **"Sample" port** on the front of the SSIM using a very small length of 1/8" tubing.

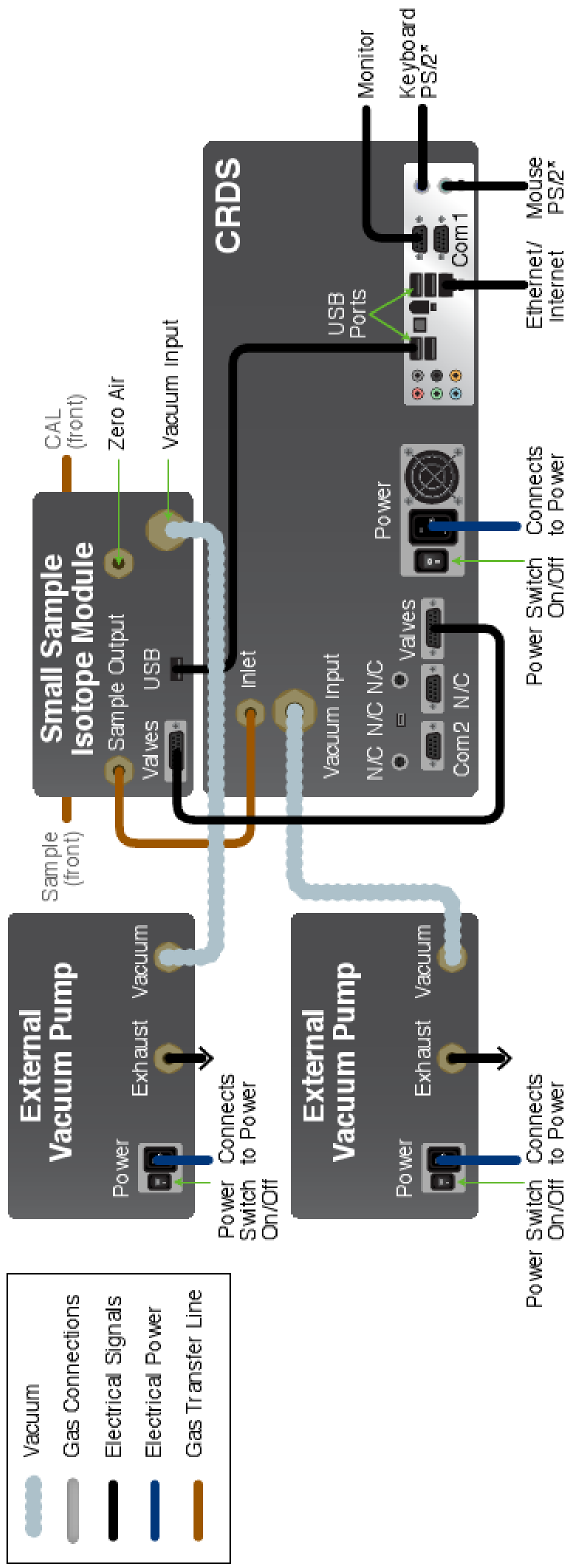
	Note: it is required that the sample containers have manual valves to isolate it during the purging of the SSIM.

6. Connect the SSIM to the analyzer as described in step 2.
7. Make the cable connections between the SSIM and the analyzer: "**Valves"** (back of the SSIM) – "**Valves"** (back of the CRDS). **USB** (back of the SSIM) - **USB** (back of the CRDS).
8. Turn on the external vacuum pump.
9. Locate the "Read Ext Sensor" program on the Desktop and double click it. A window will appear which will find the SSIM chamber pressure sensor at a port. Once the Read Ext Sensor program is on, SSIM Pressure can be monitored on the main GUI by selecting SSIM Pressure on the pull-down menu, allowing it to be logged in the UserData.dat files. It is acceptable to minimize the Select Read Ext Sensor window, but not closed. If at any time the software is restarted, the "Read Ext Sensor" program needs to be closed and restarted.
10. It may be necessary to point the Read Ext Sensor to the Arduino driver. This can be accomplished via the path: C:\Instrument Install Software\arduino-0022\drivers



Read External Sensor (SSIM Pressure)

11. Upon installation of the Read Ext Sensor program, it may be necessary to point to the arduino drivers via the path C;\Instrument Install Software\arduino-0022\drivers\FTDI USB Drivers



SSIM - CRDS ANALYZER SETUP

SECTION 2: SSIM-16 PORT DISTRIBUTION MANIFOLD- CRDS ANALYZER SETUP

	Note: This module enables very precise measurements of isotopic ratios of small samples. For the best precision measurements, the analyzer should be allowed to run for at least 2 hrs prior to making the final connection to the analyzer (the analyzer must be stabilized).

If the SSIM is used with the 16-Port Distribution Manifold and the analyzer, the required hardware setup steps are the following.

1. Position the SSIM near the analyzer's inlet connection to minimize the volume of the gas line connecting the SSIM **"Sample" outlet** (located on SSIM's rear side) and the **"Inlet" port** back of the CRDS analyzer. Prepare tubing to connect (but **DO NOT yet connect SSIM to analyzer**) these connections. It should be a short length of 1/8" stainless tubing having 1/8" Swagelok connections on both ends.

	Note: it is not necessary to shut down the analyzer during installation of the SSIM, but it is imperative that gas pressures from the high-pressure cylinders be regulated to ≥1 psi (0.07 bar) and <8 psi (~0.5 bar) prior to connecting the SSIM and analyzer (typically 3 psi).

The easiest way to make all connections requires that the 16-port distribution module be placed on top of CRDS analyzer first. Position the SSIM to the right side of the 16 port manifold, and make sure it faces the front of the CRDS analyzer. This will allow use of the supplied sample delivery tubing provided by Picarro.

2. Connect the external vacuum pump to the **"Vacuum" port** on the SSIM with the supplied vacuum line. Connect the pump to line power but do not switch on until just before sample analysis begins.
3. Connect line power, the hand pad, and the **"COM MPV"** connection on the Distribution Manifold to the CRDS Analyzer's **"COM 2"** port with the supplied cables.

Note: for full details about the 16-Port Distribution Manifold, see the User's Guide for this accessory.

4. Connect the **"Sample" output** from the rear of the Distribution Manifold to the **"Sample"** input located the front of the SSIM (Tubing provided).
5. Attach the zero air supply to the back **"Zero Air"** connection of the SSIM and supply gas at optimally **≥1 psi (0.07 bar) and <8 psi (~0.5 bar) (typically 3 psi).**
6. Attach the calibration gas standard supply to the **"Cal"** input of the SSIM (front side of the SSIM). Supply gas at optimally **≥1 psi (0.07 bar) and <8 psi (~0.5 bar) (typically 3 psi).**
7. Attach sample containers to only **EVEN-NUMBERED** "Sample" ports on the front of the Distribution Manifold using as minimal as possible length of 1/8" tubing

Note: all ODD-NUMBERED ports on the Distribution Manifold must be capped with 1/8" Swagelok caps. (These odd-numbered ports are used in the purge operation). IF SAMPLES ARE CONNECTED TO ODD-NUMBERED PORTS, THEY WILL BE EXHAUSTED THROUGH THE VACUUM PUMP AND WILL BE LOST!!! It is required that the sample containers have manual valves to isolate them during the SSIM's purge operation.

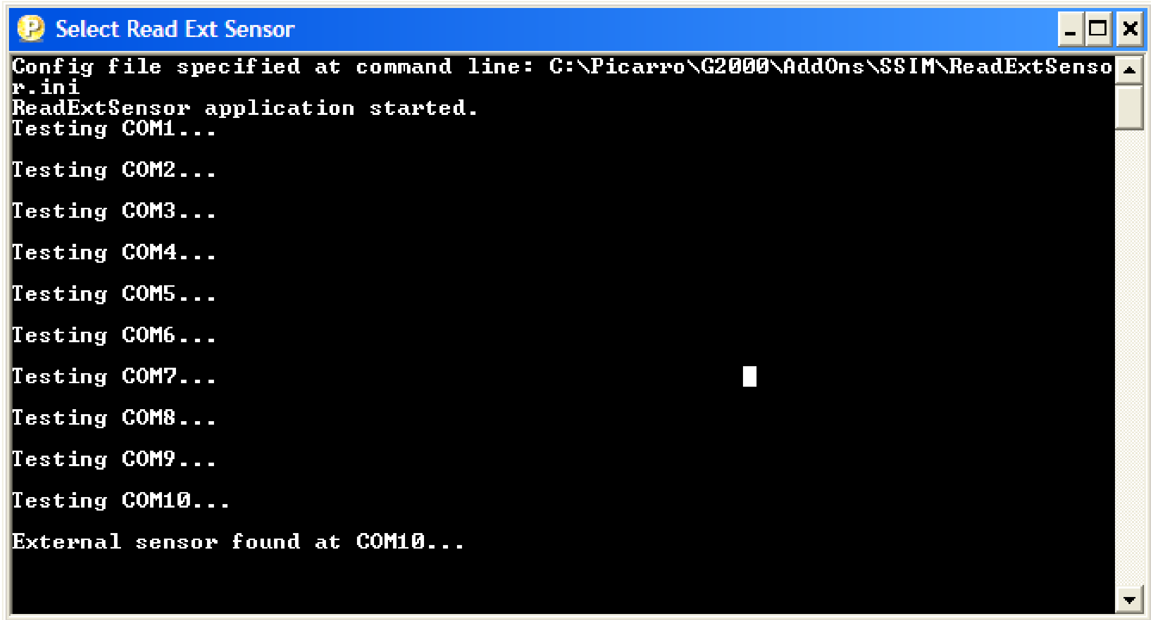
Note: Remember to tighten the caps already present on the odd-numbered ports.

8. Connect the SSIM to the analyzer as described in step 1. (Tubing supplied)
9. Make the cable connections between the SSIM and the analyzer: **Valves** (back of the SSIM) - **Valves** (back of the CRDS). **USB** (back of the SSIM) - **USB** (back of the CRDS).
10. Turn on the external vacuum pump.
11. Turn on the 16-Port Distribution Manifold.

Note: if the valve in the Distribution Manifold is not recognized by the software, it may be necessary to re-start both the analyzer "GUI" software as well as the SSIM Coordinator program.

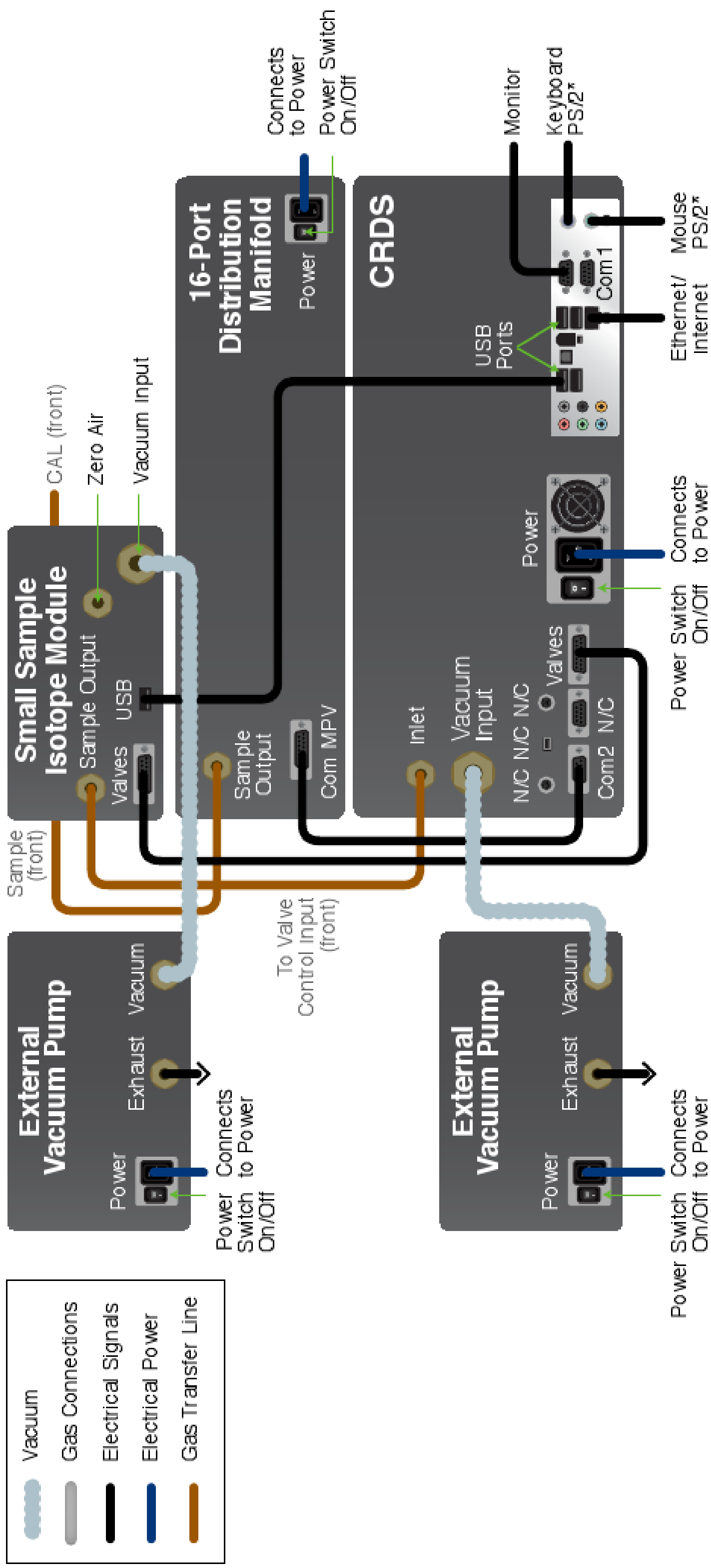
12. Locate the "Read Ext Sensor" program on the Desktop and double click it. A window will appear which will find the SSIM chamber pressure sensor at a port. Once the Read Ext Sensor program is on, SSIM Pressure can be monitored on the main GUI by selecting SSIM Pressure on the pull-down menu, allowing it to be logged in the UserData.dat files. It is acceptable to minimize the Select Read

Ext Sensor window, but not closed. If at any time the software is restarted, the "Read Ext Sensor" program needs to be closed and restarted.



Read External Sensor (SSIM Pressure)

13. Upon installation of the Read Ext Sensor program, it may be necessary to point to the arduino drivers via the path C;\Instrument Install Software\arduino-0022\drivers\FTDI USB Drivers

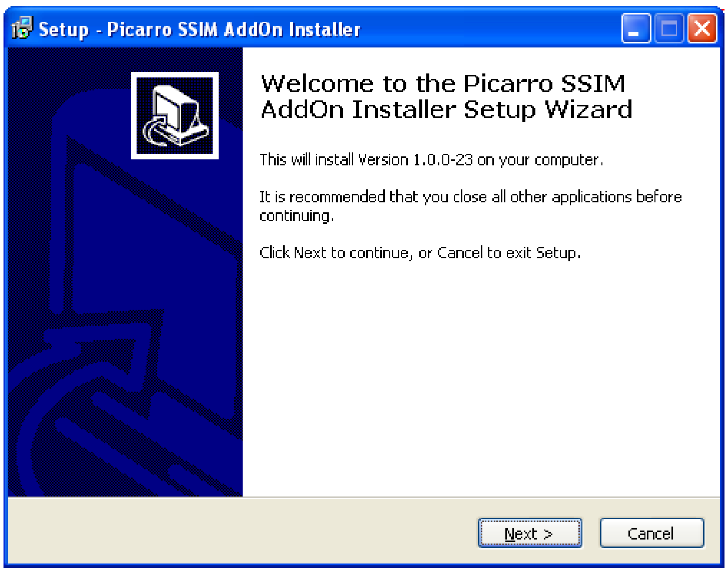


SSIM - CRDS ANALYZER – 16 PORT DISTRIBUTION MANIFOLD SETUP

OPERATION AND SOFTWARE – TAKING A MEASUREMENT

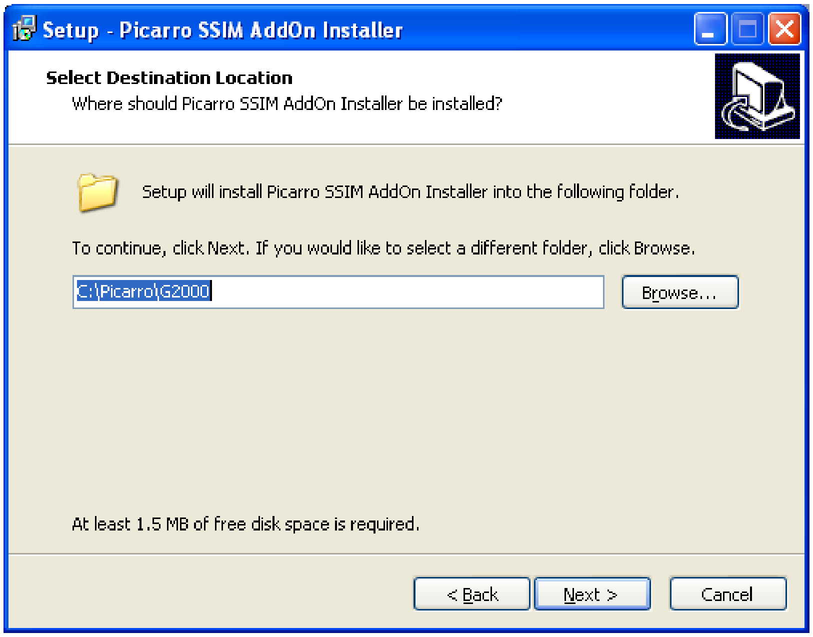
Once all connections have been made, and samples have been attached to the system, it is appropriate to begin (if this has not been completed already) by installing the Coordinator program according to the steps below. The Installer is available on the provided USB Flash drive or it can be requested from the Picarro Support staff.

1. Double click on the file "setup_SSIM.exe" in order to begin the installation process. The Picarro SSIM AddOn Installer window will appear. Click "**Next**."



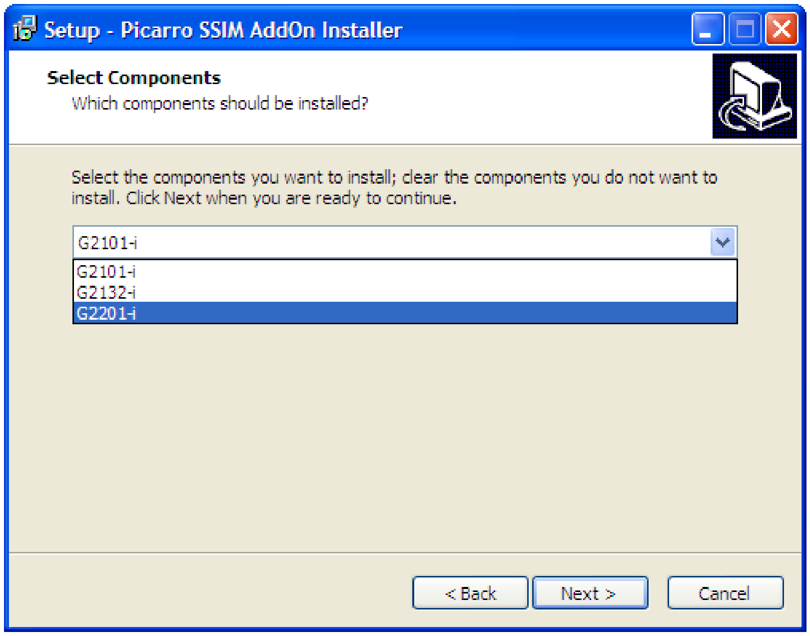
Picarro SSIM AddOn Installer

2. Upon clicking "**Next**," you will be prompted to select a destination for the installed files. It is recommended that the user maintains the default entries. Click "**Next**."



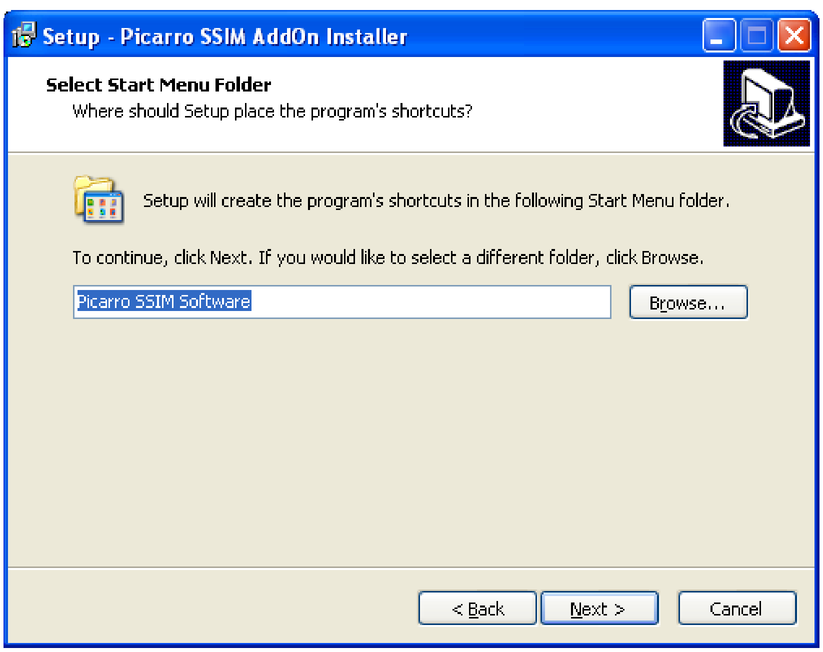
Picarro SSIM AddOn Installer

3. Upon clicking "**Next**," you will be prompted to select the type of CRDS analyzer. The drop down menu includes several options:
   - **G2101-i**: Measures isotopic CO2
   - **G2132-i**: Measures isotopic CH4
   - **G2201-i**: Measures isotopic CO2 and CH4



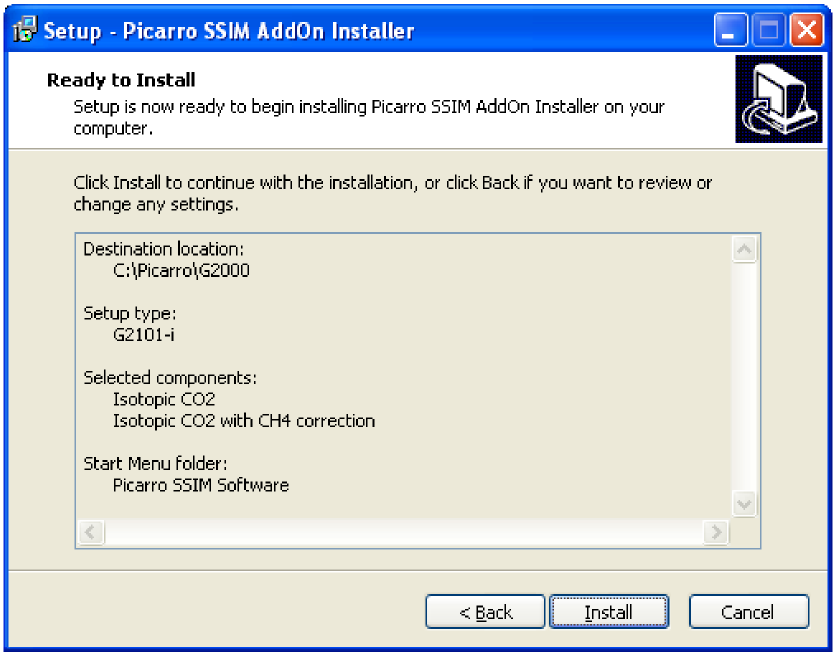
Picarro SSIM AddOn Installer

4. After selecting the correct instrument model and clicking "**Next**," a window will appear asking for a folder in which to place the program's shortcuts. It is recommended that the user maintains the default entries.



Picarro SSIM AddOn Installer

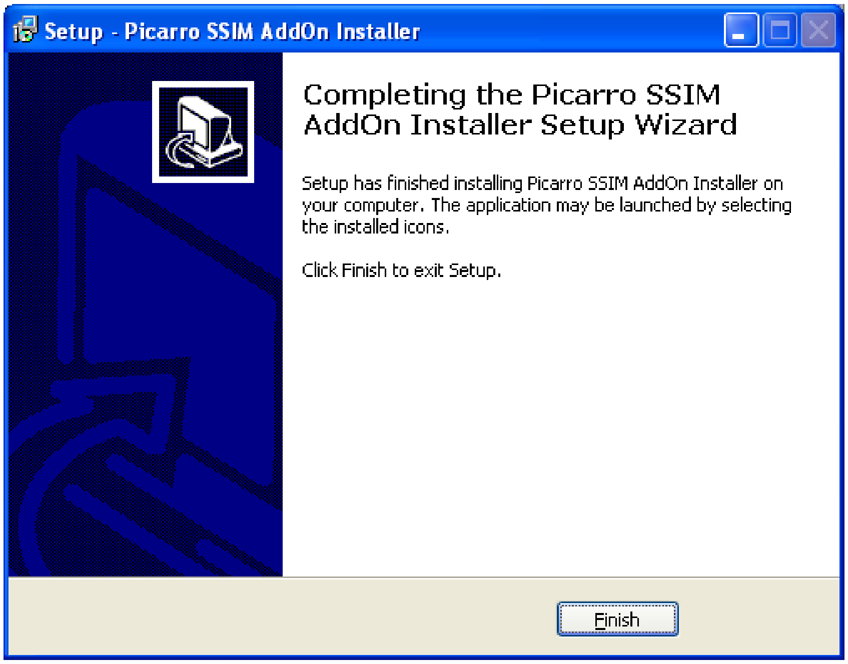
5. Upon clicking “**Next**,” a window will appear that outlines the details of all previous selections that had been made during the installation process. Click “**Install**” after reviewing your choices, or click “**Back**” to make any changes.



Picarro SSIM AddOn Installer

(This window describes the installation of a G2101-i instrument. The text may vary depending on the CRDS instrument chosen.)

6. When the installation is complete, the following window will appear. Click “**Finish**” to end. Several icons will appear on the desktop following the completion of the installation.



Picarro SSIM AddOn Installer

It is recommended that the first step upon launching the Coordinator program be to perform the Ready Test by following the steps below. The Ready Test program will use a reference gas (CAL) to ensure the instrument is ready to make measurements.

1. Locate the "Coordinator Launcher" program on the desktop and double click it. A screen will appear, allowing the user to choose from various programs, including "Ready Test." Choose the Ready Test mode, then click "**Launch**" to continue.

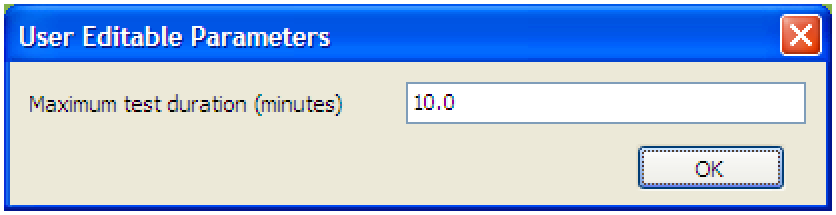
Picarro Coordinator Launcher

(This image was taken from a G2101-I analyzer – depending on the CRDS

![PICARRO logo]

instrument being used, the drop down menu may vary)

2. Upon clicking "**Launch,**" the "User Editable Parameters" screen will appear. The time indicated is the time after which the program will shut down if the appropriate instrumental conditions have not been met. It is not recommended to change the default time. Click "**OK**."



Maximum Ready Test Time

3. Upon clicking "**OK**," the coordinator window will appear. At any time during analysis, a new comma-delimited (CSV) file can be created and is saved to **C:\Isotopedata.** A file is automatically started each time the Coordinator is started. Various messages about the state of the system are displayed in the bottom window and prompts to the user are also noted there in capital letters. The upper portion of the coordinator window shows the various parameters measured during analysis, and is identical to the data that is saved in the CSV file.

Note: If the user ever desires to close the Coordinator, the red "X" can be used to simply close the window which will terminate the program. Allow the program to terminate itself (it could take nearly one minute depending on the state of the SSIM and analyzer). The Coordinator, if allowed to close itself properly, will return the SSIM and analyzer to a safe state.)

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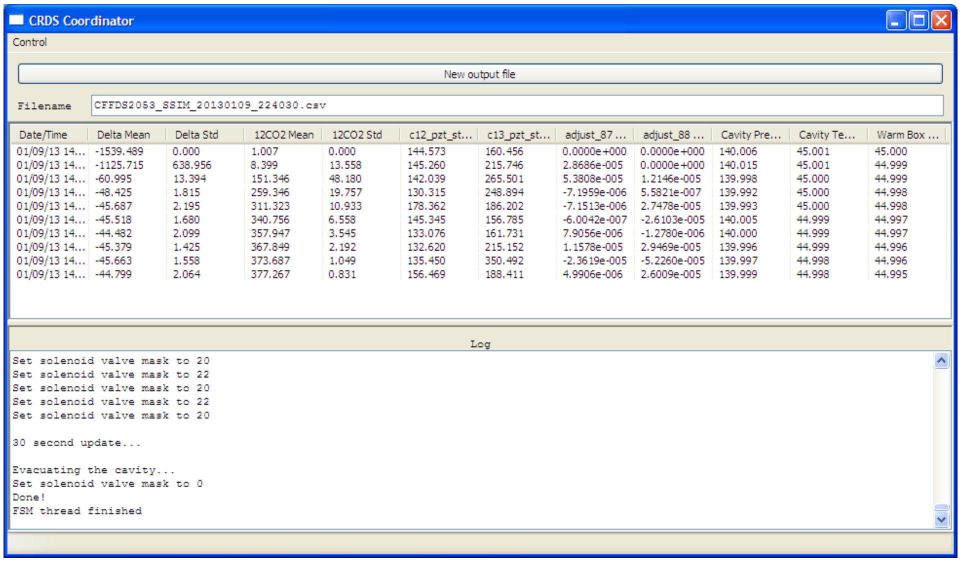


Coordinator Window

4. The Ready Test program will run until the analyzer has met the necessary conditions that determine stability or it will shut down after ten minutes. Every thirty seconds that it is running, an update will be printed.

Following the installation of the Coordinator program and running the Ready Test, it is time to begin analysis by launching the Coordinator program. Based on one's configuration, either see section 1 (SSIM - CRDS Analyzer Setup) or section 2 (SSIM - 16 port distribution manifold Setup - CRDS Analyzer).

SECTION 1: SSIM - CRDS ANALYZER SETUP

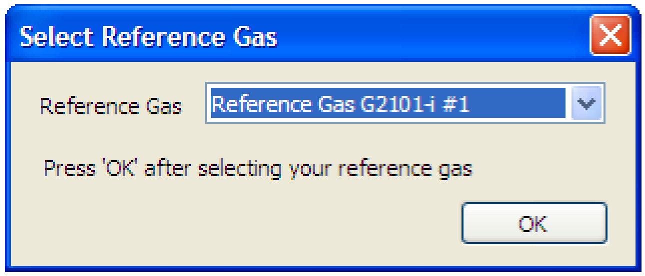
If using the SSIM alone with the analyzer, follow the steps below:

1. Locate the “Coordinator Launcher” program on the desktop and double click it. A screen will appear, allowing the user to choose “**SSIM G2101-i,**” “**SSIM G2101-i w/ HP CH4,**” or “**Ready Test.**” The available drop-down options depend on which instrument is being used. Choose the appropriate coordinator mode, and then click “Launch” to continue. In the “User Editable Parameters” window (next step) there will be an option to proclaim if the user is using the 16-Port Distribution Manifold (MPV) or not.
    - **SSIM G2101-i:** To make discrete iCO2 measurements.
    - **SSIM G2101-i w/ HP CH4:** To make discrete iCO2 measurements and (if the G2101-i is in the proper mode) high precision measurements of CH4.
    - **Ready Test:** To make a direct measurement of the reference gas while checking the stability of the analyzer.

Picarro Coordinator Launcher

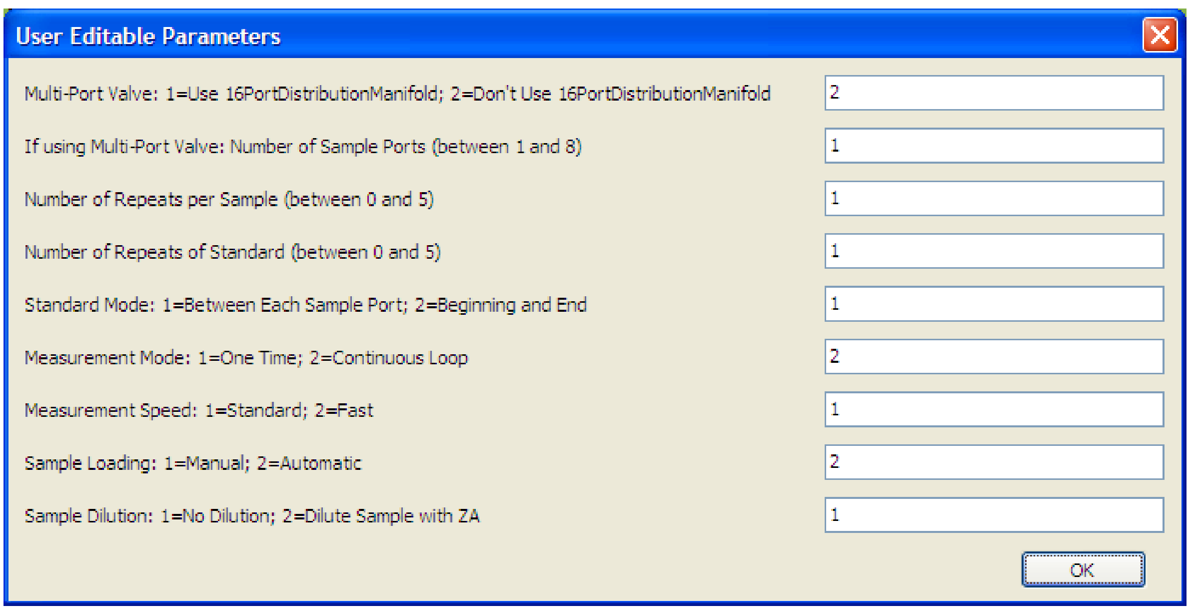
(This image was taken from a G2101-i analyzer – depending on the CRDS instrument being used, the drop down menu may vary)

2. Upon clicking “**Launch,**” the “Select Reference Gas” screen will appear. Select the appropriate reference gas being used. Reference gasses can be added, removed, or changed by editing the ReferenceGases.ini file in C:\Picarro\G2000\AddOns\SSIM.



Reference Gas Selection

3. After clicking **"OK,"** the "User Editable Parameters" screen will appear. Enter the appropriate values based on the description below. Once finished click "**OK**" to continue.



User Editable Parameters Window

- **Multi-Port Value:** Specify whether using the 16 Port Distribution Manifold. Enter 2 if "Don't Use 16-Port Distribution Manifold", or 1 if"Use 16-Port Distribution Manifold". Enter 2.
- **If using Multi-Port Value: Number of Sample Ports:** Specify the number of sample ports of the 16 Distribution Manifolds the user will be measuring from. The number of samples can range from 1 to 8. When not using the 16 Port Distribution Manifold, enter "1".
- **Number of Repeats per Sample:** Specify the number of times the user wants to measure each sample. The number can be as little as 0 and as great as 5.

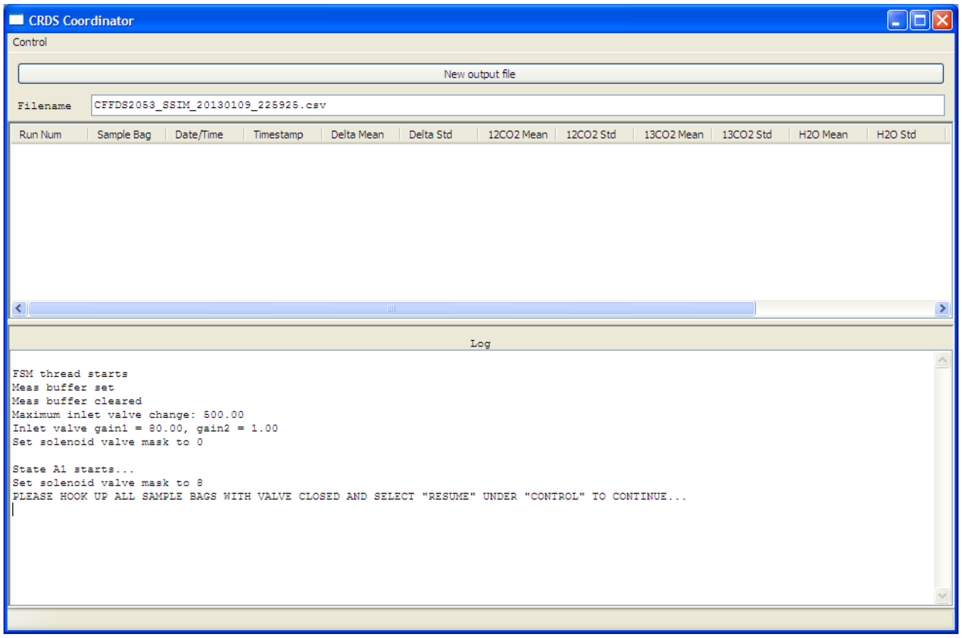
- **Number of Repeats of Standard:** Specify the number of times the user wants to measure each standard. The number can be as little as 0 and as great as 5.
- **Standard Mode:** Enter 1 if wanting to measure standard between the measurement of each sample port, or 2 if wanting to measure the standard just in the beginning and at the end.
- **Measurement Mode:** Enter 1 if samples will be measured one time, or 2 if they will be measured in a loop (CRDS will continue to measure until the user ends the program).
- **Measurement Duration:** Enter 1 if wanting standard measurement (12 minutes per measurement), or 2 if wanting fast measurement (8 minutes per measurement)**.** The times do not include the 3 minute purge and pump cycle to clean the SSIM and analyzer between measurements.
- **Sample Loading:** Enter 1 if loading each sample manually, or 2 if loading sample automatically. Manual mode should be used if the user plans to manually change sample bags while running the instrument. Automatic mode should be used if the user plans to walk away from the instrument while in use.
- **Sample Dilution:** Enter 1 if no dilution is to be used, or 2 if the injected sample is to be diluted with zero air.

4. The Coordinator window will appear. At any time during analysis, a new comma-delimited (CSV) file can be created and is saved to **C:\Isotopedata.** A file is automatically started each time the Coordinator is started. Various messages about the state of the system are displayed in the bottom window and prompts to the user are also noted there in capital letters. The upper portion of the coordinator window shows the various parameters measured during analysis, and is identical to the data that is saved in the CSV file.

Note: If the user ever desires to close the Coordinator, the red "X" can be used to simply close the window which will terminate the program. Allow the program to terminate itself (it could take nearly one minute depending on the state of the SSIM and analyzer). The Coordinator, if allowed to close itself properly, will return the SSIM and analyzer to a safe state.)

5. After the SSIM has completed the purge and pump steps, it will prompt the user to attach a sample container with manual valve closed.

Important: make sure the manual valve (connected to the sample bag) is closed or the sample will be lost! The system pumps out the gas lines all the way up to the manual valve.



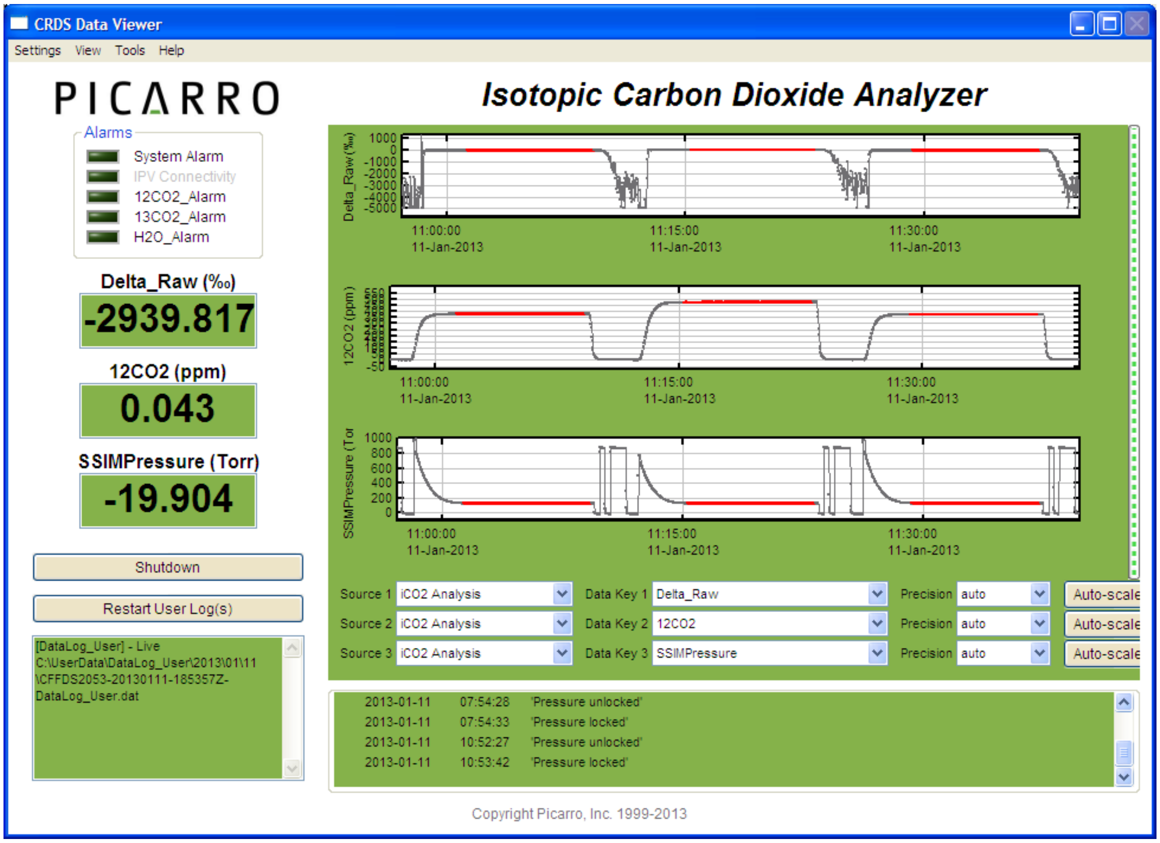
Coordinator Window

6. The SSIM will then initiate another pump and purge cycle. Once complete, coordinator will prompt user to open the sample bag manual valve and then “Resume” under the “Control” menu.

7. If the user is in the manual injection mode and not using the 16 Port Distribution Manifold, the coordinator will prompt the user to attach the sample bag with valves closed and then opened before each sample measurement.

8. The analysis of the sample will begin (duration of measurement is 12/8 minutes depending on the measurement option chosen – standard or fast). The gas concentration and isotope ratio data will look similar to the figure below where a standard was measured, followed by a waiting period (where the analyzer simply measures zero air before the user prompts the software to begin the next measurement), then followed by a sample, and finally another measurement of the standard.

Note: it is normal to have alternating “Pressure High/Pressure Low” warnings in the GUI Status Log since the analyzer is constantly adjusting the pressure during the discontinuous gas flow that occurs as a result of the SSIM’s purging and gas delivery steps. If these warnings persist and are accompanied by a persistent “System Alarm” indicator, this could indicate a problem and it is advisable to contact Picarro.



The GUI above is for a G2101-i analyzer (measures iCO2). Depending on the type of CRDS analyzer being used, the look of the main GUI will vary slightly

9. The Coordinator will continue to prompt the user for samples until the Coordinator program is terminated.

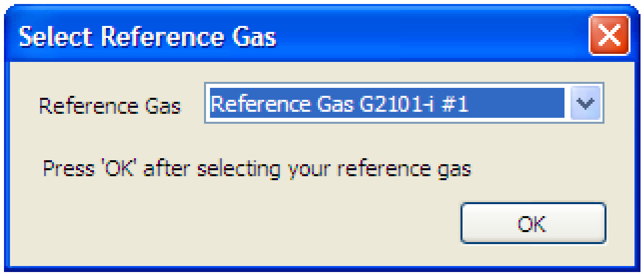
SECTION 2: SSIM–16 PORT DISTRIBUTION MANIFOLD–CRDS ANALYZER SETUP

If the SSIM is used with the 16-Port Distribution Manifold and the analyzer, follow these steps:

1. Locate the “Coordinator Launcher” program on the desktop and double click it. A screen will appear allowing the user to choose “**SSIM G2101-i,**” “**SSIM G2101-i w/ HP CH4,**” or “**Ready Test.**” The available drop-down options depend on which instrument the user is using. Choose the appropriate coordinator mode, and then click “Launch” to continue. In the “User Editable Parameters” window (next step), there will be an option to proclaim if the user is using the 16-Port Distribution Module (MPV) or not.
   - **SSIM G2101-i:** To make discrete iCO2 measurements.
   - **SSIM G2101-i w/ HP CH4:** To make discrete iCO2 measurements and (if the G2101-i is in the proper mode) high precision measurements of CH4.
   - **Ready Test:** To make a direct measurement of the reference gas while checking the stability of the analyzer.

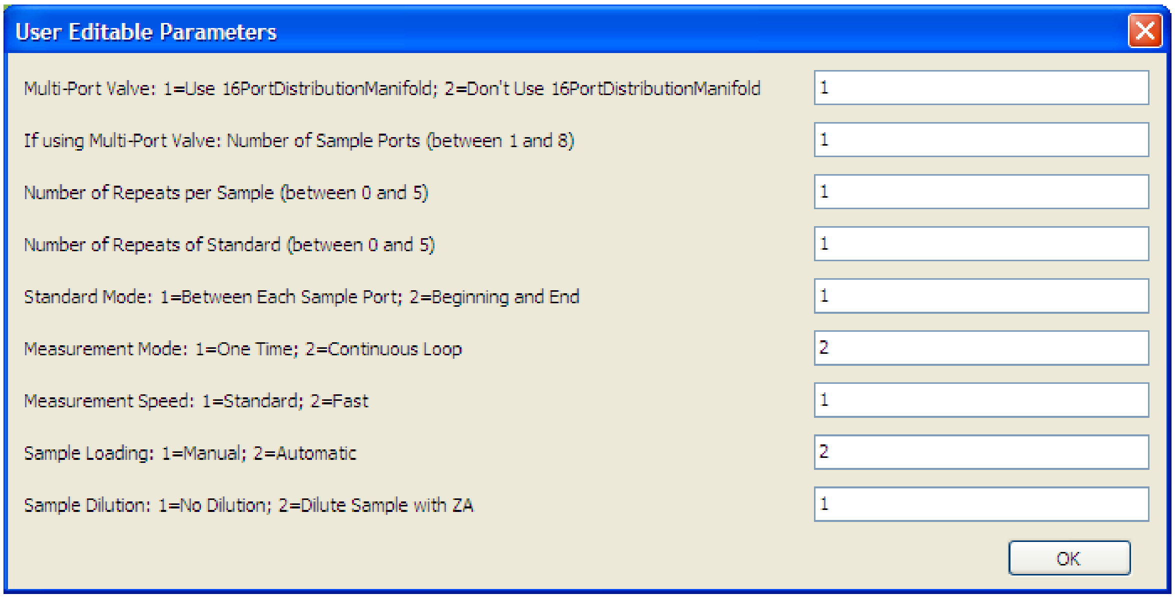
Picarro Coordinator Launcher

2. Upon clicking “**Launch,**” the “Select Reference Gas” screen will appear. Select the appropriate reference gas being used. Reference gasses can be added, removed, or changed by editing the ReferenceGases.ini file upon installation.



Reference Gas Selection

3. Once the user clicks "**OK**," the "User Editable Parameters" screen will appear. Enter the appropriate values to continue.
    - **Multi-Port Value:** Specify whether using the 16 Port Distribution Manifold. Enter 2 if "Don't Use 16-Port Distribution Manifold," 1 if "Use 16-Port Distribution Manifold". Enter 1.
    - **If using Multi-Port Value: Number of Sample Ports:** Specify the number of sample ports of the 16 Distribution Manifolds the user will be measuring from. The number of samples can range from 1 to 8.
    - **Number of Repeats per Sample:** Specify the number of times the user wants to measure each sample. The number can be as little as 0 and as great as 5.
    - **Number of Repeats of Standard:** Specify the number of times the user wants to measure each standard. The number can be as little as 0 and as great as 5.
    - **Standard Mode:** Enter 1 if wanting to measure standard between the measurement of each sample port, or 2 if wanting to measure the standard just in the beginning and at the end.
    - **Measurement Mode:** Enter 1 if samples will be measured one time, or 2 if they will be measured in a loop (CRDS will continue to measure until the user ends the program).
    - **Measurement Duration:** Enter 1 if wanting standard measurement (12 minutes per measurement), or 2 if wanting fast measurement (8 minutes per measurement)**.** The times do not include the 3 minute purge and pump cycle to clean the SSIM and analyzer between measurements.
    - **Sample Loading:** Enter 1 if loading each sample manually, or 2 if loading sample automatically. Manual mode should be used if the user plans to manually change sample bags while running the instrument. Automatic mode should be used if the user plans to walk away from the instrument while in use.
    - **Sample Dilution:** Enter 1 if no dilution is to be used, or 2 if the injected sample is to be diluted with zero air.

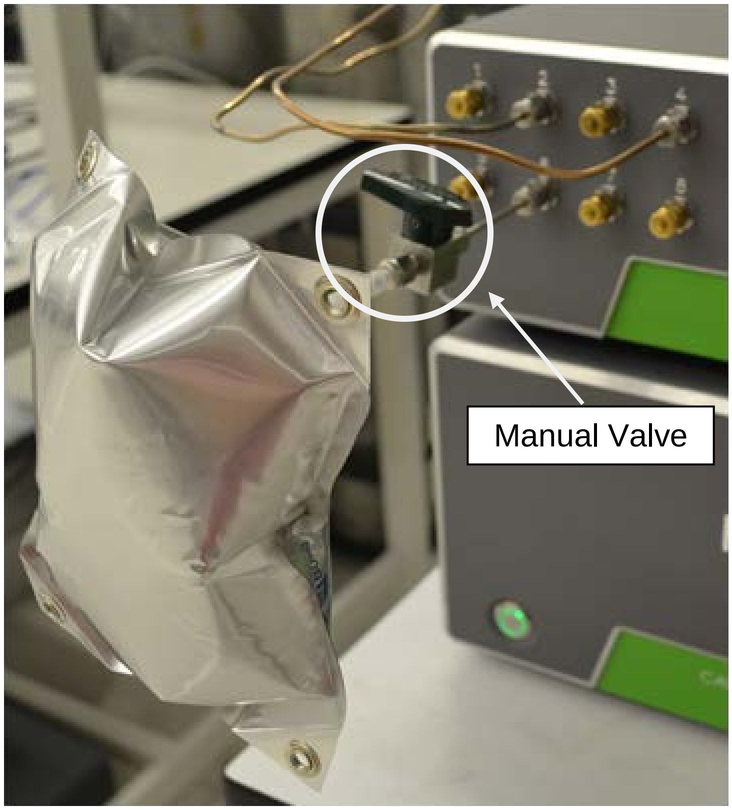


User Editable Parameters Window

4. The Coordinator window will appear. At any time during analysis, a new comma-delimited (CSV) file can be created and saved to C:\Isotopedata. A file is automatically started each time the Coordinator is started. Various messages about the state of the system are displayed in the bottom window and prompts to the user are also noted there in capital letters. The upper portion of the coordinator shows the various parameters measured during analysis, and is identical to the data that is saved in the CSV file.

Note: If the user ever desires to close the Coordinator, the red "X" can be used to simply close the window which will terminate the program. Allow the program to terminate itself (it could take nearly one minute depending on the state of the SSIM and analyzer). The Coordinator, if allowed to close itself properly, will return the SSIM and analyzer to a safe state.

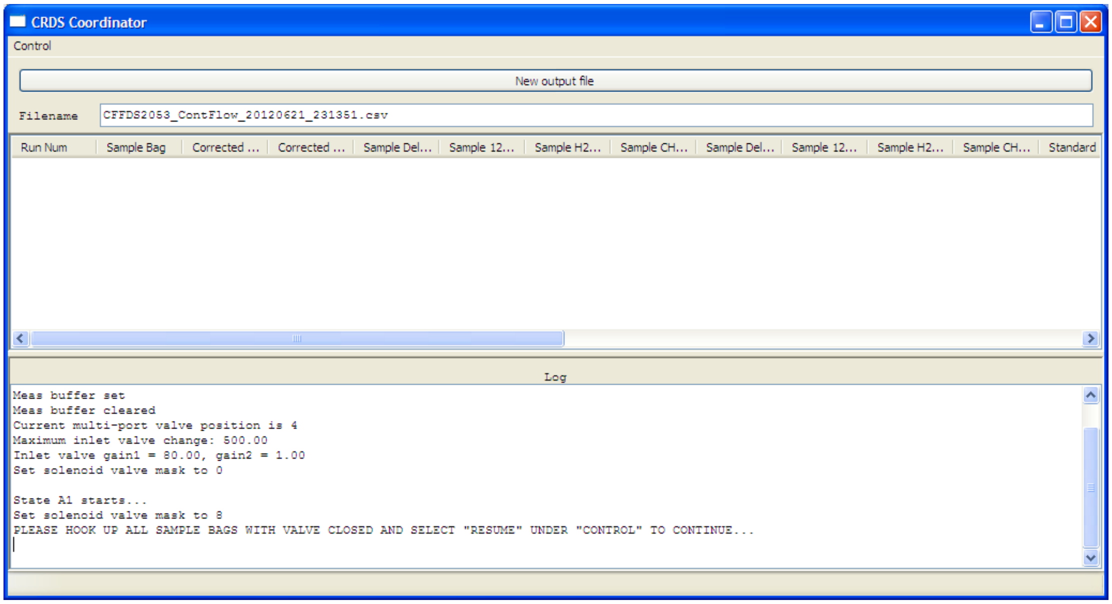
5. After the SSIM has completed the purge and pump steps, it will prompt the user to attach all sample container(s) with the manual valve(s) closed.



Example of a sample bag connected to the 16-port manifold via a manual valve

Important: make sure the manual valves are closed or the samples will be lost! The system pumps out the gas lines all the way up to the manual valve.

6. The SSIM will then initiate another pump and purge cycle for all selected input ports and will prompt the user to open the manual valve(s). Then select “Resume” under the “Control” menu.



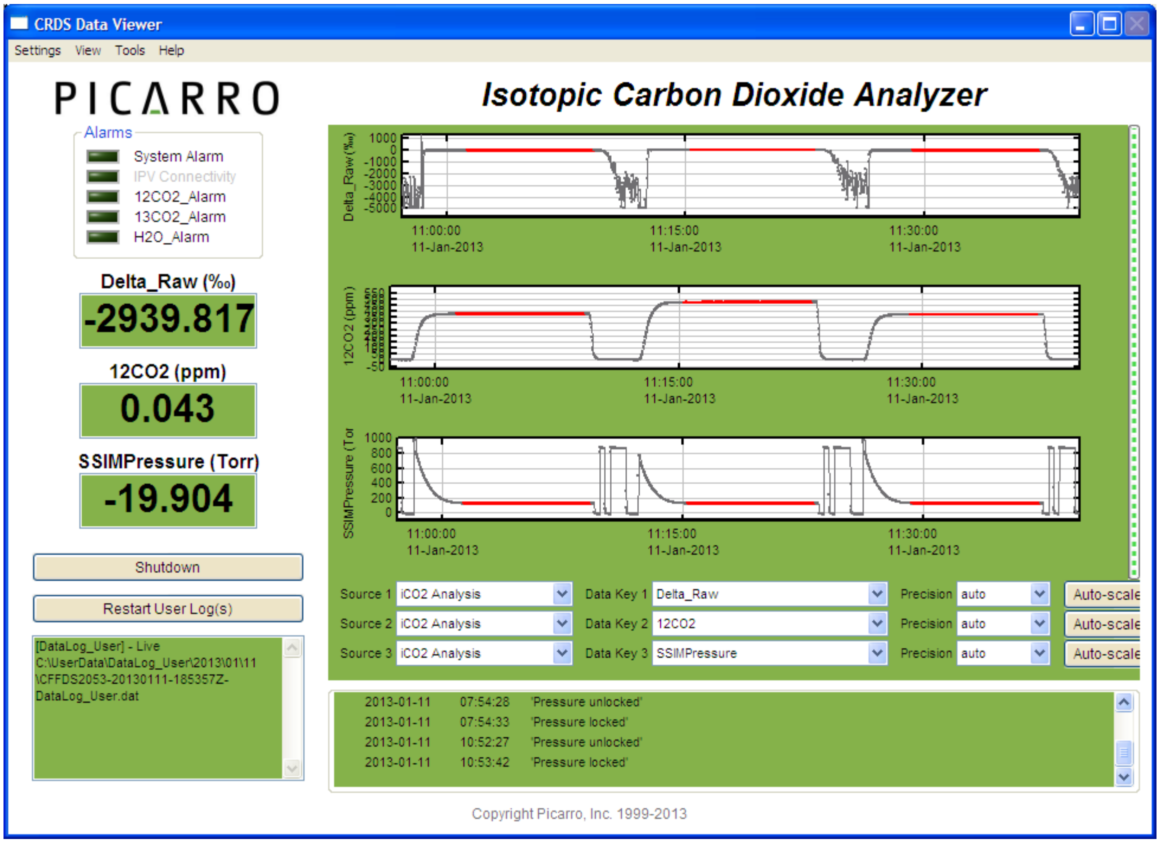
CRDS Coordinator Window

7. The sample from the first sample port will expand into the sample chamber of the SSIM. There the sample will make its way to the analyzer, where measurements will be taken automatically. At this point, no further user input is necessary to analyze sample(s) from sample container(s).

8. The analysis of the samples will begin (duration of measurement is 12/8 minutes depending on the measurement option chosen – standard or fast).

	**Note: it is normal to have alternating "Pressure High/Pressure Low" warnings in the GUI Status Log since the analyzer is constantly adjusting the pressure during the discontinuous gas flow that occurs as a result of the SSIM's purging and gas delivery steps. If these warnings persist and are accompanied by a persistent "System Alarm" indicator, this could indicate a problem and it is advisable to contact Picarro.**

9. The Coordinator will measure samples until it finishes the job (if the user has selected the Measurement Mode to be "One Time") or it will continue to run until the Coordinator program is terminated (if "Continuous Loop" was selected).



The GUI above is for a G2101-i analyzer (measures iCO2). Depending on the type of CRDS analyzer being used, the look of the main GUI will vary slightly

PICARRO

USE-CASE RECOMMENDATIONS AND TROUBLESHOOTING

LEAK TIGHTNESS:

It is critical that there be no leaks in the plumbing connections associated with the SSIM and analyzer. It is possible to use the analyzer itself as a diagnostic to find leaks. The purge (zero air) should be nearly dry, as should the calibration standards. By looking at the analyzer's water vapor concentration measurement during the time that it is not measuring samples (it will be drawing gas from the Zero Air" port of the SSIM) a leak in the plumbing associated with the zero air supply or SSIM-to-analyzer connecting will be evidenced by a high water level (significantly higher than ~50ppm for example). A similar check can be used for the calibration gas – during a calibration measurement, the water should be indicating near zero if there is no leak. For leaks in the sample container connections, this can be more elusive depending on the water content of the sample, but can be diagnosed by filling the sample containers with dry gas.

One way to run dry gas through the SSIM as if the dry gas were a sample is to run "Sample Inject" in "2: Run sample diluted in ZA (Zero Air)." Do not add any sample. The SSIM will be evacuated, and then it will ask for the sample to be connected and the manual valve opened. Connect a sample, but do not open the manual valve. Just select resume when asked to open the manual valve. Then the SSIM will fill the empty sample volume with zero air, and introduce this to the analyzer. High H_2O/CO_2/CH_4 levels in these samples indicate that there is a leak in the connections.

ELECTRICAL CONNECTIONS:

If the valve control cables are not appropriately attached, this may cause unexplained errors in the Coordinator program and the cabling should be checked and the analyzer and/or Coordinator software should be restarted if necessary. If the message appears that the multi-position (rotary) valve is not correctly recognized, consult the user's guide for the Distribution Manifold or contact Picarro. The locking screws on the valve control cables should be used in order to insure a reliable connection between the instrument and the SSIM.

PUMP LIFETIME:

The vacuum pump has a rated lifetime of 10,000 hours and has an hour meter attached to it so this can be checked if necessary. An ageing pump will have the same symptom as a plumbing leak – the Coordinator program may time out. One way to monitor if the pump is functioning well is to track the SSIM Pressure on the GUI to determine if it is able to evacuate the sample chamber. A functional pump, when switched on, should vibrate noticeably.

USE CASE EXAMPLES:

We have had a number of questions about using the SSIM2 in different cases. Here are a few use cases in which you might be interested.

I have 100ml of sample. Should I use SSIM2?

One has two alternatives:

1. Our δ^{13}C analyzers typically draw 25ml/min. So 100ml of sample run directly into the analyzer would produce ~4 minutes of data.
2. In contrast, the SSIM2 could measure five 20ml replicates of the sample for 9 minutes each. This produces 45 minutes of data for the sample. Of course, this takes longer than 4 minutes, but one makes a more precise measurement.

It is often the case that one needs to make multiple measurements on a given sample. One might want to run some of the sample on a GC, for instance. The SSIM 2 will allows one to make a long measurement with a small portion of the sample, which leaves the rest for other measurements.

I have less than 20mL of sample, but the CO_2 and CH_4 concentrations are higher than ambient. Can I use the SSIM2?

There are a number of studies that produce samples that are only a few milliliters in volume but have high concentrations. Underground soil gas samples often have percent level-CO_2 concentrations, but one is only able to get a few ml of sample. The CO_2 and CH_4 levels in the headspace of water samples can be 1000ppm or higher, but the headspace itself may only be 5ml.

There are two considerations in these cases.

1. **Dilution**: The sample must be diluted with zero air. The SSIM2 has a minimum volume of 20ml (23ml through the 16-port manifold), as 20ml is needed to fill the cavity. As long as the concentration after dilution falls within the dynamic range of the analyzer, one can measure δ^{13}C of the sample. For instance, say one has a 5mL sample with 2000ppm of CO_2. After dilution, the sample will be at 500ppm. This is in the dynamic range of our G2131-*i* and G2201-*i* analyzers. While one could dilute a sample in many ways, the SSIM2 can dilute a sample to 20ml after it is injected into the SSIM2.
2. **Precision**: The δ^{13}C precision improves with higher concentration, so it is good to dilute as little as possible.

I have pure CO_2 samples. How much sample do I need in these cases?

Pure samples are common for CO_2 sequestration studies and for natural gas exploration. These samples can be easily run on the SSIM2 with proper dilution. Picarro's $\delta^{13}C$ -CO_2 analyzers have a upper limit of their dynamic range at 2000ppm. This concentration will also provide the best precision. To get 20ml at 2000ppm CO_2, one needs 40ml of pure CO_2. One should dilute this sample with zero air to 20ml for each replicate.

While one could dilute a sample in many ways, the SSIM2 can dilute a sample to 20ml after it is injected into the SSIM2.