California Environmental Protection Agency

AIR RESOURCES BOARD

AIR QUALITY SURVEILLANCE BRANCH

STANDARD OPERATING PROCEDURES

FOR

PICARRO G-1301
METHANE, CARBON DIOXIDE, WATER VAPOR ANALYZER

AQSB SOP 207

First Edition

MONITORING AND LABORATORY DIVISION

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California Environmental Protection Agency

AIR RESOURCES BOARD

Approval of Standard Operating Procedures (SOP)

Title: *PICARRO G-1301 METHANE, CARBON DIOXIDE, WATER VAPOR ANALYZER*

SOP: AQSB SOP 207, First Edition

Section: Operation Support Section

Branch: Air Quality Surveillance Branch (AQSB)

Division: Monitoring and Laboratory Division (MLD)

Prepared by: *PATRICK VACA*

Approval: This SOP has been reviewed and approved by:

__________________________ _____________
Reginald L. Smith, Manager Date
Operation Support Section
Air Quality Surveillance Branch

__________________________ _____________
Kenneth R. Stroud, Chief Date
Air Quality Surveillance Branch

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1.0 GENERAL INFORMATION

1.1 Introduction:

This Standard Operating Procedure (SOP) describes procedures used by the California Air Resources Board (CARB) Air Quality Surveillance Branch (AQSB) to operate the Picarro G-1301 carbon dioxide/methane/water vapor analyzer for measurement in ambient air. The G-1301 operates on a principle known as Cavity Ring-Down Spectroscopy (CRDS). This procedure supplements the G-1301 instrument manual by describing any modifications in operating procedures, if any, implemented by the AQSB and is not intended to be a replacement for the instrument manual.

NOTE: Operators must read the G-1301 instrument manual prior to startup to familiarize themselves with the operation of the instrument

1.2 Principle of Operation:

Cavity Ring-Down Spectroscopy (CRDS) is a form of laser absorption spectroscopy where a laser pulse is trapped in a highly reflective cavity. The Picarro G-1301 CRDS uses two single frequency laser diodes and a cavity with three highly reflective mirrors which support a continuous traveling light wave. A fast photo detector senses the small amount of light leaking through one of the mirrors to produce a signal which is proportional to the absorption inside the cavity. CRDS involves a process in which the cavity is first filled with laser light to a certain threshold. The laser is then abruptly turned off and the light decays to zero in an exponential fashion. This decay or “ring-down” time is measured and is proportional to the concentration of the target species. The laser is tuned to different wavelengths that correspond to the different spectral absorption lines of the target analytes.

1.3 Safety Precautions:

DO NOT operate in an explosive atmosphere. DO NOT operate in the presence of flammable gases or vapors.

The G-1301 analyzer contains no user serviceable components other than the vacuum pump. Do not attempt repairs other than the replacement of the vacuum pump.

The G-1301 analyzer is classified as a Class 1 Embedded Laser Product. CAUTION: Class 3B invisible laser radiation when open. Avoid exposure to the beam. Do not open any enclosures within the instrument. Failure to do so could result in exposure to Class 3B laser radiation, which can permanently damage eyes and skin.

The inlet bulkhead connector can be extremely hot when the instrument is operating, or after it has been shut down. Take care when connecting gas lines or working at the rear of the instrument to wear protective gloves or avoid contact with these surfaces.

1.4 Interferences/Limitations:

The G-1301 analyzer should be operated within an ambient temperature range of 10 to 35 °C.

Under normal operating conditions, the precision check gas cylinder output should be set to **NO MORE THAN** five (5) psi output pressure. Failure to do so may cause irreparable damage to the instrument.

2.0 INSTALLATION PROCEDURE

2.1 List of Tools/Supplies

1) Tools that include open end wrenches, screwdriver set, and wire cutters/strippers.
2) Three-conductor cable (min. AWG 20 gauge)
3) Rack mountable shelf to hold instrument (19” wide by 23” deep).
4) ¼” I.D. Teflon tubing.
5) Small bypass pump (optional).

2.2 Physical Inspection:

The G-1301 analyzer is shipped with the following standard equipment:

- 1 – 19” DAS module - includes all of the data acquisition, control, and communications hardware and firmware to perform all gas handling, spectral collection and reporting to the Control-PC.
- 1 – 19” PVU module - contains power supply and vacuum pump units that provide all DC power to the DAS, and the vacuum required for sample gas sequencing into and out of the DAS.
- 1 – Flexible tubing – with 3/8” Swagelok fitting on each end to connect the vacuum pump in the PVU to the DAS
- 1 – USB Cable – connects the DAS with the Control-PC
- 1 – A/C power cables (North America only)
- 1 – 37-pin analog output connector and cable
- 1 - Software CD
- 1 – Certificate of compliance
- 1 – User Manual

If any of these items are missing contact Picarro for a replacement.
Check items carefully and report any damage to AQSB management and Picarro.

2.3 Power Vacuum Unit (PVU) to Data Acquisition System (DAS) Connections:

All connections are made to the rear of the instrument. Connect the provided USB cable from the PVU module to the DAS module. Ensure that the white arrow on the DAS end of the USB cable is pointing up. Connect the supplied 3/8” Teflon vacuum line from the PVU to the DAS and tighten with wrench. Connect the computer monitor, keyboard, and mouse. (Refer to “Picarro G-1301 Analyzer Users Guide, Getting Started”.)

The G-1301 starts automatically as soon as the power cable is connected to line voltage so ensure that all connections are made **PRIOR** to initial startup.

2.4 Data Logger Connection :

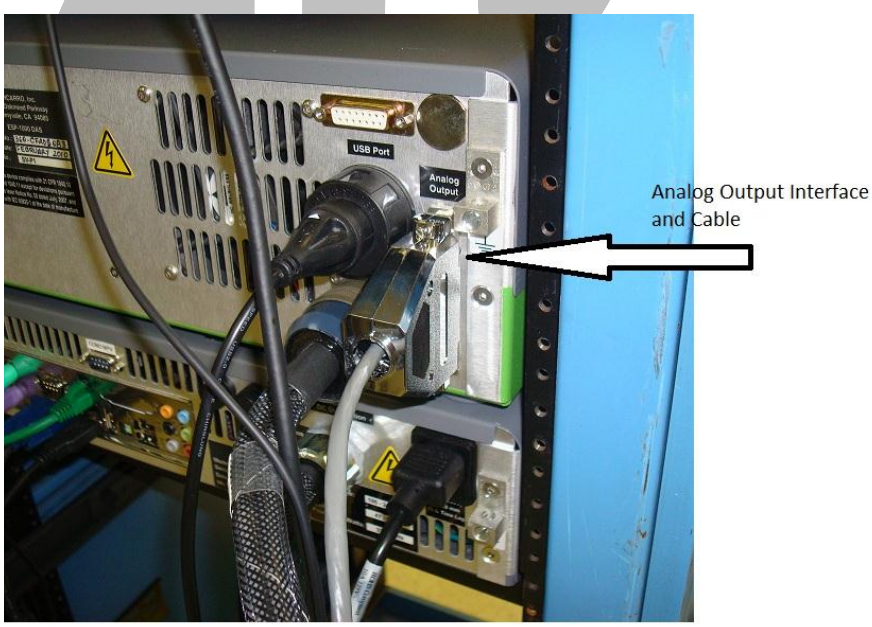
The G-1301 includes an electrical interface located on the rear right hand side of the instrument as shown in figure 1. The electrical interface includes analog outputs for CO_2, CO_2 (corrected), CH_4, and H_2O in a 37-pin connector with a cable attached. The connector wires for the analog outputs are color coded and labeled. G-1301 analog output and data logger assignments are shown in Table 1.

Table 1. Analog Outputs from Picarro Analyzer.

Description	Picarro Ch. Label	Data Logger Channel	Wire Color
CO2 (corrected)	A02	8	Red
CH4	A03	7	Orange
Ground	n/a	n/a	Blue

The G-1301 analog outputs share a common ground which should be connected to both negative data logger channel inputs via a jumper.

Figure 1. Picarro Electrical Interface and Connector.



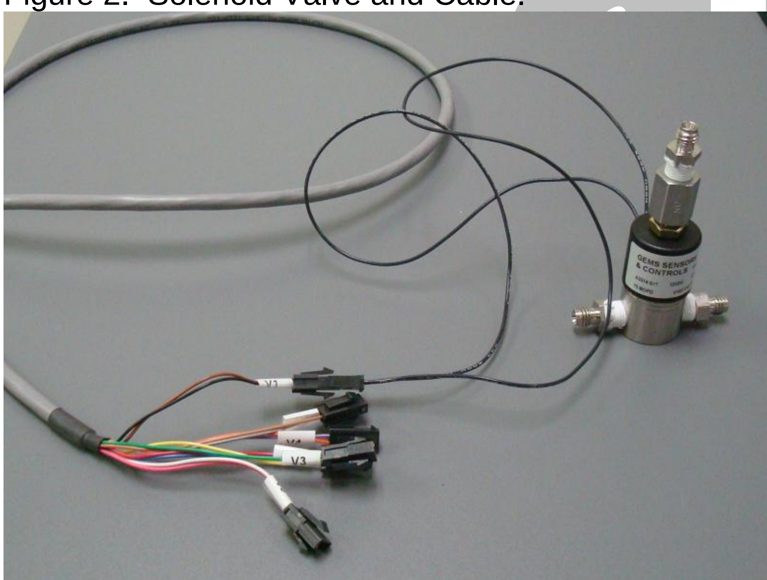
2.5 Strip Chart Connection:

A length of three-conductor cable of suitable length should be prepared. This cable should connect from the data logger to strip chart channels 7 and 8 for methane and carbon dioxide respectively . The common ground wire should be connected to both negative terminals of the strip chart recorder via a jumper.

2.6 Solenoid Valve Connection:

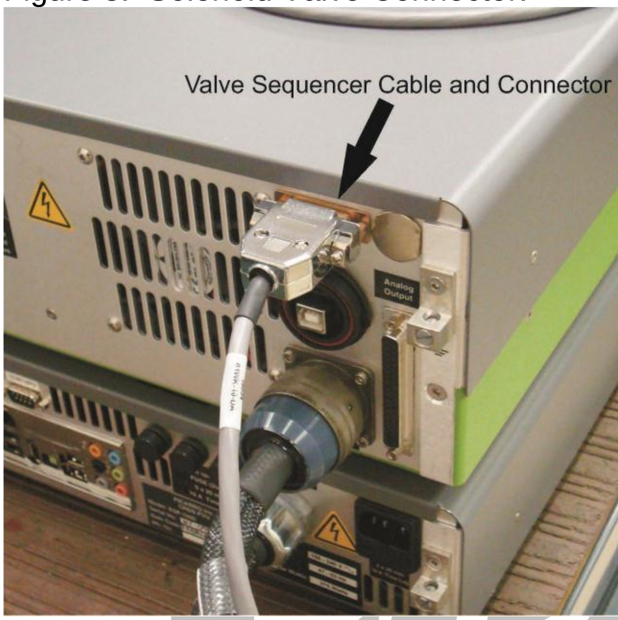
The Picarro G-1301 analyzer includes a cable for connecting up to six external 12 VDC solenoid valves for the analysis of span/precision gases. The standard AQSB configuration includes connecting one solenoid valve to the connector labeled V1 which controls the flow of precision check gas directly from a cylinder.

Figure 2. Solenoid Valve and Cable.



The solenoid valve connects to the instrument via a 15-pin connector located on the back of the instrument as shown in Figure 3.

Figure 3. Solenoid Valve Connector.



2.7 Precision Check Cylinder Connection:

A precision check cylinder will be provided with each instrument by the Operation Support Section. This cylinder should contain methane (~1.9 ppm) and carbon dioxide (~400 ppm). Connect a gas regulator to the normally closed (NC) port of the solenoid valve using 1/8” stainless steel tubing. Connect the normally open (NO) port on the solenoid valve to the sample inlet on the left rear of the Picarro analyzer. Connect the remaining (middle) port on the solenoid valve to the sample manifold as shown in Figures 4-5.

NOTE: If the G-1301 analyzer is being operated in conjunction with other ambient gas analyzers that are calibrated daily then a separate inlet/manifold should be used.

Figure 4. Solenoid Valve Connections.

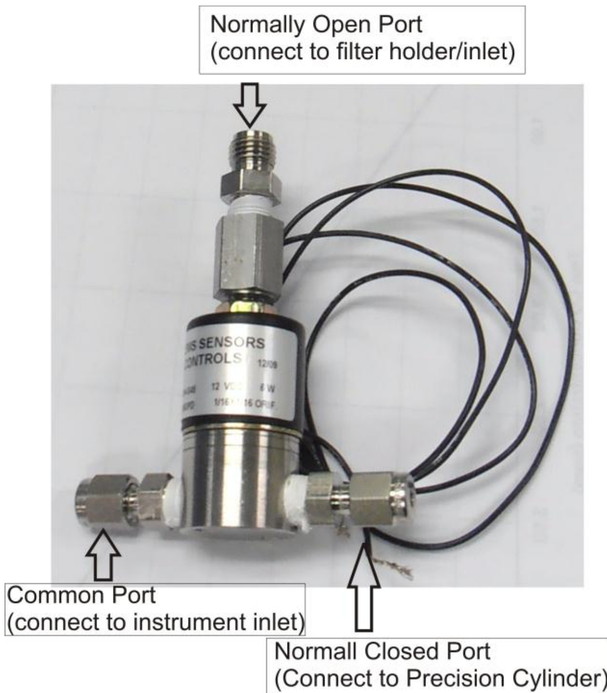
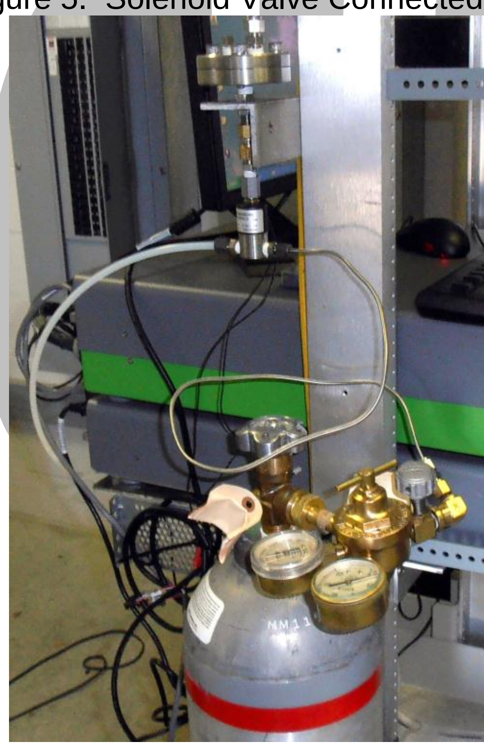


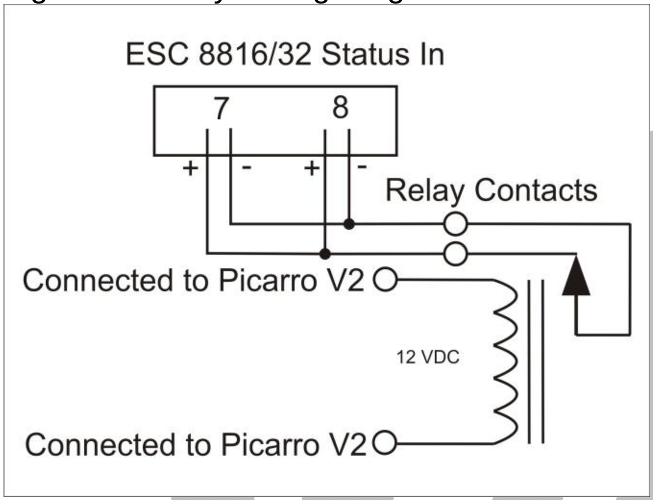
Figure 5. Solenoid Valve Connected to Cylinder.



2.8 Relay Connection:

A 12 VDC Single Pole Single Throw (SPST) relay is connected to the solenoid valve cable connector V2. This relay is used to control the flagging of precision checks on the ESC 8816/32 data logger. Figure 5 shows the wiring diagram for the relay.

Figure 5. Relay Wiring Diagram.



2.9 Start Up and Shut Down Procedures:

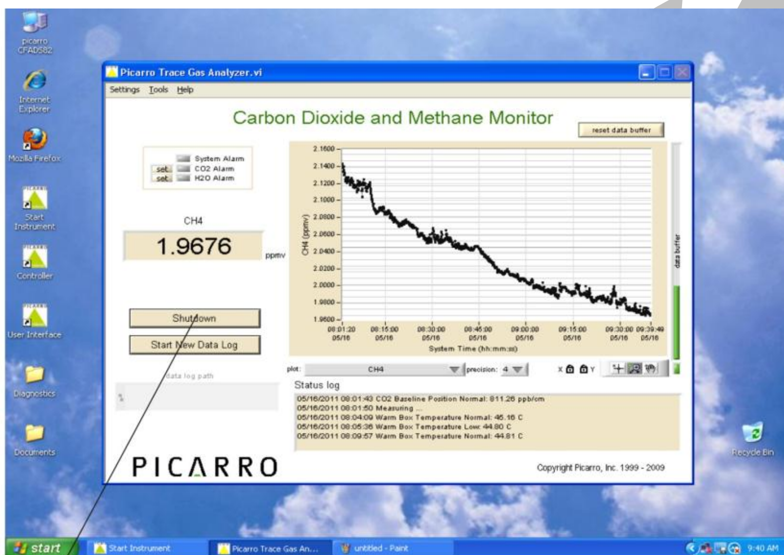
Start-Up – When the analyzer is initially set up the unit starts automatically when the power cord is plugged in. If the analyzer is plugged in and the power is off then it can be started by depressing the round power switch located on the lower Front of the instrument as shown in Figure 6.

Figure 6. Location of Power Switch.

Upon start up the instrument will load and start the Graphical User Interface (GUI) and show the operating conditions. Under normal start up from a cold environment the instrument may take up to several hours to reach the nominal conditions for sampling to begin. After conditions have reached the proper state, the sample pump will activate and data points will begin to appear on the GUI.

Shut-Down – **Method A** (recommended): Place the computer mouse onto the bar labeled “Shutdown” on the G-1301 trace gas analyzer window (see figure 7.) and left click the mouse.

Figure 7. Shutdown Procedure.



Left click mouse here to shut down

A small window will appear which states “would you like to prepare the instrument for shipping?”. Left mouse click on the box labeled “shut down in current state” unless the instrument is being shipped or transported between locations which are at different elevations. If this is the case then select the option “prepare for shipment”. Following this selection the message “are you sure?” will appear. Click yes to continue with shutdown. The final step in the shutdown process is to shut down Windows XP as you would normally.

Method B: If the instrument fails to shut down properly using method A then press the power switch on the front of the instrument and hold for five seconds. The instrument should proceed with automatic shutdown.

Method C: This method should only be used in the case where the G-1301 is locked up completely and the mouse no longer functions. Unplug the power cord from the receptacle. Wait for approximately two minutes. Replace the power cord in the receptacle and the instrument should restart automatically.

Upon start up the instrument will load and start the Graphical User Interface (GUI) and show the operating conditions. Under normal start up from a cold environment the instrument may take up to several hours to reach the nominal conditions for sampling to begin. After conditions have reached the proper state, the sample pump will activate and data points will begin to appear on the GUI.

3.0 CONFIGURATION

3.1 Picarro G-1301 Configuration:

All instrument operating parameters are pre-set at the factory and should not be changed by field personnel.

The analog output interface is configured by making changes to the [Analog] section of the configuration file Picarrocrds.ini. Table 2 shows the standard configuration for the AQSB greenhouse gas monitoring network.

Table 2. Picarro Analog Interface Configuration.

Description	Channel	Units	Slope	Zero	V_Max	V_Zero
CO2 (Corrected)	A02	ppmv	700	0	1	0
CH4	A03	ppmv	12	0	1	0

The analog voltage offset and slope for each channel are determined at the factory and should not be changed. An example of the Picarrocrds.ini file is shown in Appendix D.

3.2 Data Logger Configuration:

Picarro G-1301 analog outputs are all configured to a voltage range of 0-1 Vdc. The data logger channels should be assigned and configured as shown in Table 3.

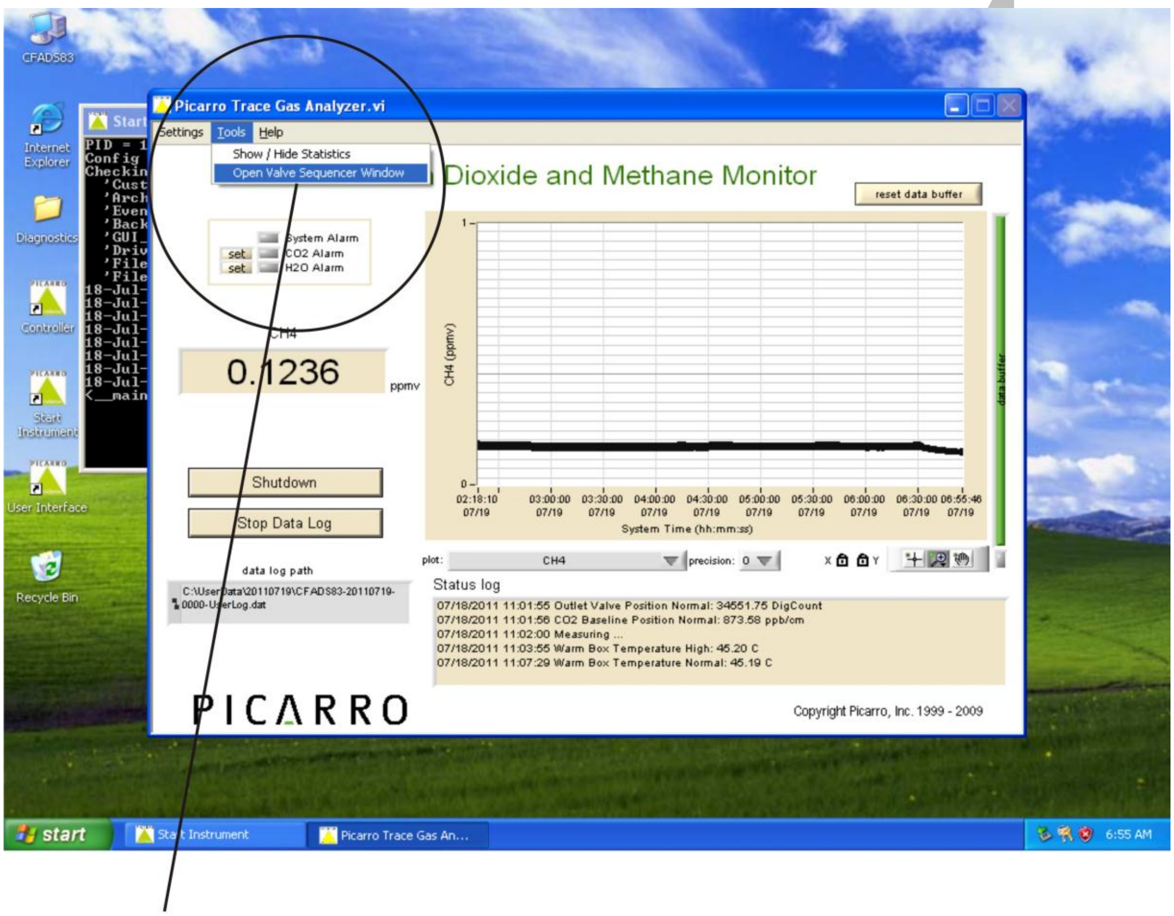
Table 3. ESC 8816/8832 Data Logger Configuration.

Description	Channel	Units	High EU	Low EU	Slope	Intercept
CH4	7	ppm	12	0	12	0
CO2	8	ppm	700	0	700	0

3.3 Valve Sequencer Configuration:

An external valve sequencer is used to control a 12 VDC solenoid valve on a prescribed schedule. A second solenoid valve connector is used to power a 12 VDC relay in place of the valve which provides a contact closure to the data logger for the purpose of flagging precision check data as calibration. Figure 8 shows the procedure for opening the external valve sequencer.

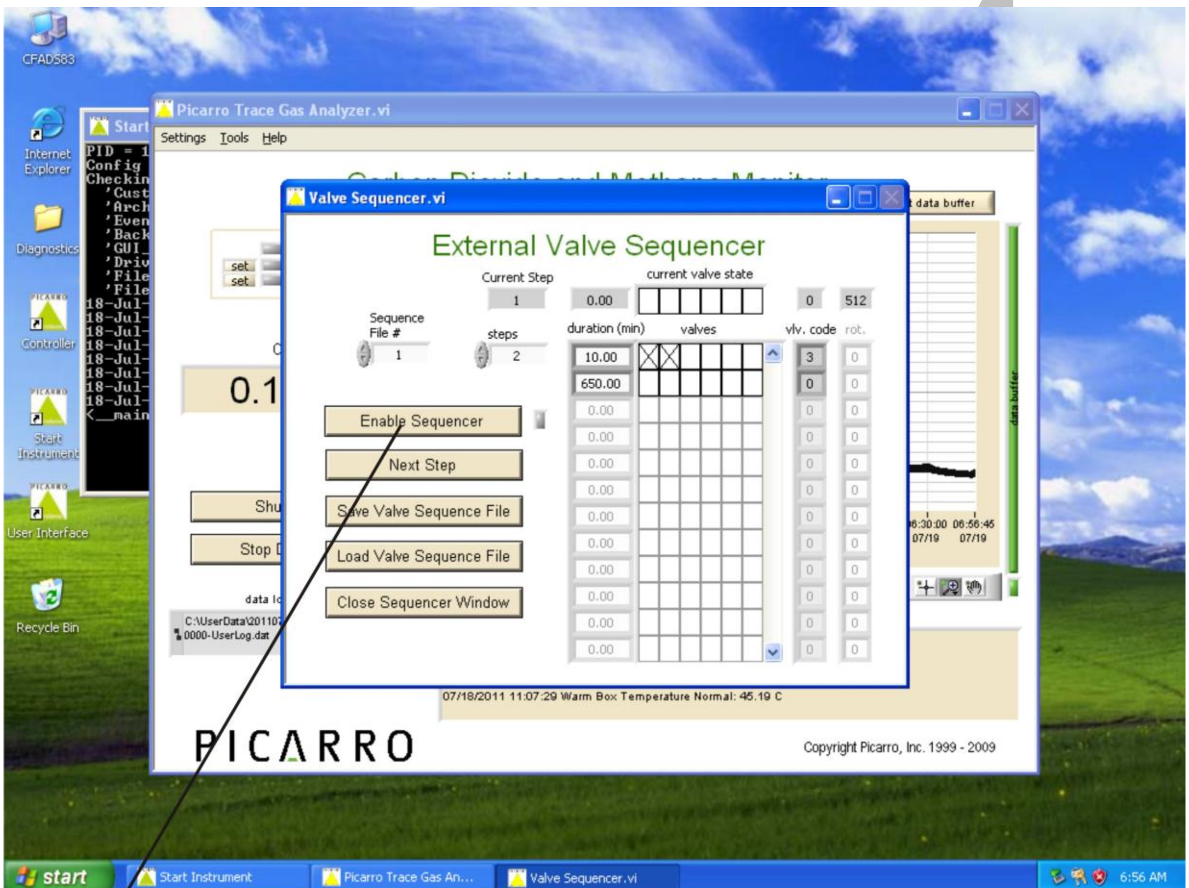
Figure 8. Opening Valve Sequencer.



To open valve sequencer window choose “tools” and then “Open Valve Sequencer Window”

The valve sequencer window will appear and can be modified as necessary. Under normal operating conditions, the valve sequencer window should be loaded and running and does not require any user input. Occasionally when the instrument re-starts after a power outage the valve sequencer does not load properly and must be manually reloaded and started. Figure 9 shows the valve sequence exactly as it should appear. If the valve sequence is re-loaded or re-programmed, then it needs to be started manually by left mouse clicking the bar labeled “Enable Sequencer” on the left hand side of the sequencer window as shown in Figure 9. The sequence is programmed to contain two steps for a total of 660 minutes (11 hours). Step one should be for duration of 10 minutes with valves one and two enabled (indicated by a X in the first two squares). Step two should be for duration 650 minutes with valves one and two disabled (indicated by empty boxes) exactly as shown in Figure 9.

Figure 9. Valve Sequencer Window and Example Sequence.



Click here to start or disable sequence

4.0 CALIBRATION INFORMATION

4.1 Calibration Introduction:

A calibration is a procedure for checking the accuracy of an instrument to a known “true” standard. The G-1301 shows excellent linearity over the entire operating range. Calibrations are performed by direct injection of high accuracy gas standards (NOAA/NIST).

4.2 Calibration Overview:

The analyzer is calibrated at the factory by comparison to a reference instrument which has been challenged with standard gas of several known concentrations which fall within the range of typical ambient results. The results of this comparison are then used to calculate a slope and intercept which are saved to the instrument configuration.

5.0 CALIBRATION PROCEDURE

5.1 Calibration Transfer Standards and Equipment:

Two National Oceanographic and Atmospheric Administration (NOAA) or National Institute of Standards and Technology (NIST) certified gas standards.

High purity stainless steel gas regulator.

1/8" stainless steel tubing for connection to analyzer inlet.

5.2 Calibration Procedures:

Detailed instructions on calibrating the G-1301 are shown in Appendix C., Picarro Application Note AN015 "Calibrating the Picarro Analyzer". In summary, two NOAA certified standards which bracket the ambient range of concentration for methane and carbon dioxide, nominally 1.800 and 2.500 ppm for methane and 380 and 450 for carbon dioxide are analyzed for ten minutes each. The instrument is allowed to stabilize for five minutes and the results from the following five minutes are averaged for each of the standards. These results are then plotted with the true concentration on the vertical axis and the instrument response on the horizontal axis. A linear best-fit equation is then calculated from the results and this slope and intercept is entered into the configuration file "picarrorcds.ini" as "User Slope" and "User Intercept" as detailed in Appendix C.

A verification of the calibration should be conducted periodically (nominally once per year) and compared to the previous laboratory comparison and factory calibration. The results of this verification should be collected and submitted to AQSB management for review. Under normal operating conditions, the calibration factors on the instrument should not be changed by field personnel.

6.0 ROUTINE SERVICE CHECKS

6.1 General Information:

The following routine service checks should be performed in accordance with the maintenance schedule (Table 3). Perform the routine service checks at the prescribed intervals at a minimum. The AQSB Monthly Quality Control Check Sheet (Appendix A) should be completed weekly and submitted monthly to the station operators supervisor. The station operator should keep a copy of the Quality Control Check Sheet in the air monitoring station.

Table 4. Maintenance Schedule.

Task Performed	Daily	Weekly	Monthly	Annually	As Needed
Review Hourly Average Data	X				
Check Instrument Display for Errors	X				
Check Instrument Time		X			
Check Strip Chart Traces		X			
Check for agreement with Data Logger		X			
Record Pump Hours on Check Sheet		X			
Download Data Files to Thumb Drive		X			
Copy Data Files to MLD Server		X			
Complete and Submit Monthly Maintenance Check sheet			X		
Perform Calibration Verification with Certified Standards				X	
Replace Pump or Diaphragms					X

6.2 Daily Checks:

If remote access is available review hourly average data and check instrument status display for any error messages.
Review hourly average results (if applicable)

6.3 Weekly Checks:

Visually check the instrument display for proper operation. Check the instrument time and adjust if not within +/- 2 minutes. Check strip chart traces for alignment and agreement with instrument and DAS. Record the accumulated pump hours from the pump hour meter on the rear of the instrument. Download data files to the thumb drive. Copy data files to MLD server (X: drive).

6.4 Monthly Checks:

Complete and submit monthly maintenance check sheet to supervisor.

6.5 Annual Checks:

Perform a verification of the instrument calibration with certified standards.

6.7 As Needed Checks:

Replace pump or pump diaphragms about every 10,000 hours.

7.0 MAINTENANCE PROCEDURES

7.1 <u>General Information</u>:

The Picarro G-1301 methane, carbon dioxide, and water vapor analyzer is designed to operate unattended for long periods of time and other than the routine checks outlined in section 6 of this SOP, the G-1301 requires little maintenance.

7.2 <u>Dusting and Fan Filter</u>:

The outside surfaces of the instrument should be dusted periodically using a damp cloth or paper towel. The fan filter on the front of the instrument should be cleaned or replaced when a noticeable amount of dust has accumulated. The location of the fan filter is shown in figure 10.

Figure 10. G-1301 Fan Filter Location.

8.0 TROUBLESHOOTING

In the case of a power failure, the Picarro G-1301 analyzer is designed to re-start when power is restored. Occasionally this causes the instrument computer to lock up when re-booting. Should this condition occur, the G-1301 should be unplugged briefly and then re-started as normally.

If any conditions occur with the G-1301 such as erratic sample concentrations or unusual error messages (i.e. scan timeout error) etc. Picarro technical support should be consulted.

APPENDIX A. PICARRO G-1301 MONTHLY MAINTENANCE CHECK SHEET.

MONTHLY QUALITY MAINTENANCE CHECK SHEET
PICARRO G-1301 METHANE, CARBON DIOXIDE, AND WATER VAPOR ANALYZER

Location: ______________________ Month/Year: ________________
Station Number: ______________________ Technician: ________________
Property Number: ____________ **S/N:** ______ Agency: ________________

OPERATOR INSTRUCTIONS:

1. Daily Checks: Check instrument status display. Record any errors in comments section.
2. Weekly Checks: Check computer time and adjust if necessary.
   Check chart traces for proper operation.
   Visual check of instrument readings: results should fall within the following ranges: **CO_2 - >375 ppm and <600 ppm**
   CH_4 - >1.7 ppm and <3.0 ppm

Date:					
Pump Hours					
Data Files Downloaded					
Cylinder Pressure					

Change inlet particulate filter (5 micron). Date: ______/______/______/______

3. Weekly Checks: Copy data files from thumb drive to MLD server
4. Monthly Checks: Complete and submit Monthly Maintenance Check sheet.
5. Annually: Perform calibration check with certified standards.
   Date of last calibration check: ___________

Date:	Comments or Maintenance Performed:

Reviewed by:_____________ Date: _____________

APPENDIX B. PICARRO G-1301 CALIBRATION REPORT.

Calibration Report - Picarro G1301

Methane, Carbon Dioxide, Water Vapor Analyzer

ID Information:

Station Name:	**Arvin-Digiorgio**
Site #:	**15-249**
AIRS #:	**60295002**
Serial #:	**CFADS90**
Station Address:	**19405 Buena Vista Ave.**
Agency:	**CARB**
Calibration Date:	**12/13/2011**
Report Date:	**12/27/2011**

Cylinder Information:

Serial #	**CC309300**	**CC309765**
CO2 Conc. (ppm):	**497.13**	**337.7**
CH4 Conc. (ppb):	**2023.1**	**1621.7**
Cylinder Press. (psi):	**1890**	**1860**
Outlet Press. (psi):	**<5**	**<5**
Certification Date:	**11/1/2010**	**10/1/2010**
Expiration Date:	**11/1/2012**	**10/1/2012**

Note: Each cylinder analyzed for 10 minutes, average of last 5 minutes used for calibration.

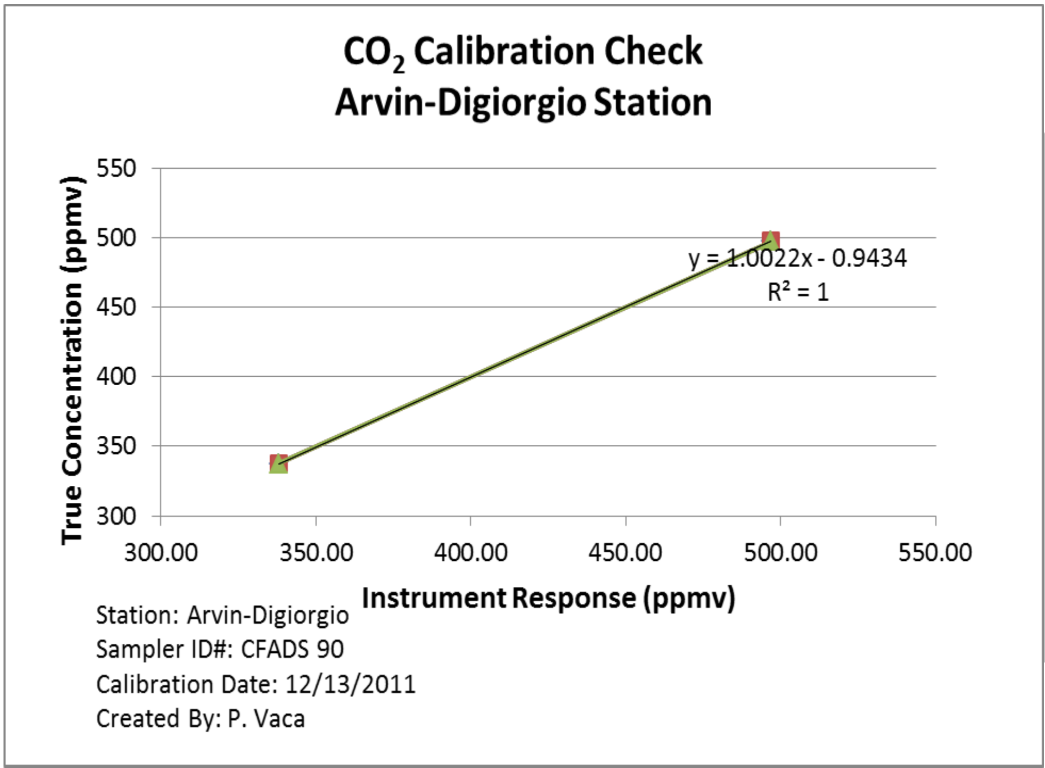
Calibration Results:

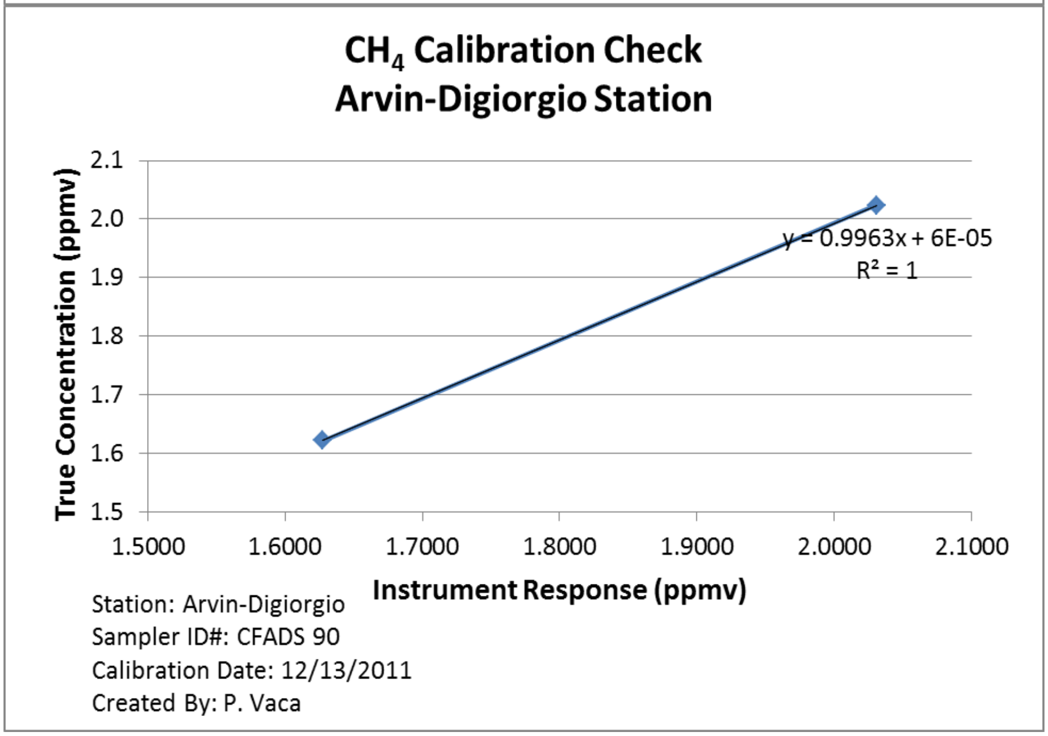
	Concentration (ppm)		
	TRUE	**CFADS90**	**% Difference**
CO2_01	**497.13**	**496.98**	**0.030**
CO2_02	**337.7**	**337.90**	**-0.059**
CH4_01	**2.0231**	**2.0306**	**-0.371**
CH4_02	**1.6217**	**1.6277**	**-0.370**

Regression Analysis:

CO2 Slope	**1.0022**
CO2 Intercept	**0.9434**
CH4 Slope	**0.9963**
CH4 Intercept	**6.00E-05**

Comments:	Cylinders analyzed by direct injection into sample inlet		
Calibrated by:		**Checked by:**	


CO_2 Calibration Check
Arvin-Digiorgio Station
True Concentration (ppmv)
550
500
450
400
350
300
300.00
350.00
400.00
450.00
500.00
550.00
Instrument Response (ppmv)
y = 1.0022x - 0.9434
R^2 = 1
Station: Arvin-Digiorgio
Sampler ID#: CFADS 90
Calibration Date: 12/13/2011
Created By: P. Vaca


CH_4 Calibration Check
Arvin-Digiorgio Station
True Concentration (ppmv)
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.5000
1.6000
1.7000
1.8000
1.9000
2.0000
2.1000
Instrument Response (ppmv)
y = 0.9963x + 6E-05
R^2 = 1
Station: Arvin-Digiorgio
Sampler ID#: CFADS 90
Calibration Date: 12/13/2011
Created By: P. Vaca

APPENDIX C. PICARRO APPLICATION NOTE AN015.

Calibrating the Picarro Analyzer

Picarro WS-CRDS analyzers are exceptionally stable, minimizing the need for calibration. But when calibration *is* necessary, the analyzers' several decades of linear dynamic range simplify the calibration process.

Summary and Relevance:

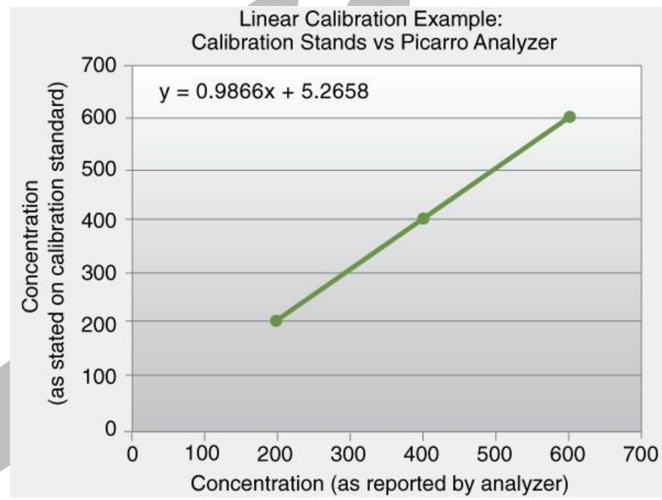
Since the Picarro analyzer is extremely linear, it is only necessary to use three calibration standards to calibrate each gas or isotopic species (two points define the calibration line and a third intermediate point is used for verification). The exact value of each calibration standard is not of particular importance as long as they span a representative range of values over which the analyzer will typically be operated. It is reasonable to use a concentration of zero for the low calibration value, for example. (Although it is not necessary to use more than three standards, additional standards can be used to further constrain the linear calibration coefficients.)

To perform a calibration or verification of calibration, the user simply introduces the first calibration standard into the analyzer for an interval long enough for the analyzer to yield a stable measurement of that sample. The stated concentration of the calibration sample (a permeation tube or calibrated gas bottle, for example) and value the analyzer reads for that sample are recorded for each calibration standard used. These values can then be plotted, as shown below, in a spreadsheet, for example, to determine the linear relationship between the known calibration values and the analyzer's reported values. A linear best-fit equation can be calculated from the data. It is important to plot the analyzer's reported concentration on the horizontal axis and the gas standards' stated concentrations on the vertical axis. The slope and intercept of the best-fit line through these points are the two values that are used to calibrate the analyzer. By determining what the linear relationship is between the known calibration values and the analyzers' reported concentration values in this way, a calibration offset (slope and intercept) can be calculated so as to add a correction term to the analyzers' factory or previous calibration.

Changing the analyzer's calibration is intended to be done infrequently. Instead of recalibrating frequently to increase the accuracy of the data, users often just verify the calibration by measuring three or more gas standards and use the same regression procedure described here to calculate an offset by which to correct their data offline.

Using the equation in the graph below, this would be accomplished point-by-point by calculating the corrected data "y" by using the analyzer's data "x" so that:
$Data_{corrected} = 0.9866*Data_{raw}+5.268.$

	Value given by analyzer	Value of calibration Standard
Calibration Point #1	200.1	202.7
Calibration Point #2	600.3	597.6
Calibration Point #3	400	400



Calibration values are input into the software by modifying the "Picarrocrds.ini" file found in C:\Picarro\CFADSxx\GUI\ directory (where CFADSxx is the instrument's serial number). This is a simple ASCII text file and will automatically open in a default text editor. The calibration section of the file will look like the following example.

[CALIBRATION]
CONCENTRATION_CH4_GAL_INTERCEPT=-0.00329
CONCENTRATION_CH4_GAL_SLOPE=0.9936753
CONCENTRATION_CH4_USER_INTERCEPT=0.000
CONCENTRATION_CH4_USER_SLOPE=1.000

CONCENTRATION_H2O_CONC_INTERCEPT=0.00
CONCENTRATION_H2O_CONC_SLOPE=0.73
CONCENTRATION_H2O_USER_INTERCEPT=0.000
CONCENTRATION_H2O_USER_SLOPE=1.000

CONCENTRATION_CO2_GAL_INTERCEPT=-0.82643
CONCENTRATION_CO2_GAL_SLOPE=0.7110114
CONCENTRATION_CO2_GAL_H2O_RATIO_SLOPE=0.01244
CONCENTRATION_CO2_USER_INTERCEPT=0.000
CONCENTRATION_CO2_USER_CONC_SLOPE=1.000

Note: before changing these values, it is useful to save a copy of the picarrocrds.ini file (under a different file name) in case the user wants to return to the factory calibration.

In this latter example, the two calibration values for each species labeled by “GAL” and “USER” correspond to the factory and user calibrations, respectively. The numbers for the “GAL” or factory, calibration should not be changed. Rather, only the “user” or offset from the factory values (in red) should be changed – the analyzer will automatically add the two intercepts from “GAL” and “USER” and multiply the slopes from “GAL” and “USER.” So, to revert to the factory calibration, the “USER” intercept should be set to 0 and the “USER” slope should be set to 1.0.

After the calibrations are changed in the file, save the file, and re-start the analyzer’s software to enable the new calibration. This is done simply by clicking the “Shutdown” button, and then re-starting the analyzer software by double-clicking the User Interface icon on the desktop.