Rapid Analyzer Validation Using a Traceable Surrogate Gas Approach

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Preface

The following document is relevant to a select number of Picarro instruments which allow users to employ a surrogate gas validation (SGV) procedure in place of a direct calibration on the primary gas species. This document is applicable to the following analyzers:

- G2103 - Ammonia (NH_3)
- G2108 - Hydrogen Chloride (HCl)
- G2114 - Hydrogen Peroxide (H_2O_2)
- G2205 - Hydrogen Fluoride (HF)
- G2307 - Formaldehyde (H_2CO, HCHO, or CH_2O)

An accompanying document titled “Picarro Surrogate Gas Validation Workbook”, which assists the user in the SGV process, can be found by contacting Picarro support at support@picarro.com. The use of this document is described in this guide.

NOTE: *While equivalent G1xxx analyzers exist for some of the aforementioned analyzers, surrogate gas validation is *not* supported on G1xxx platforms. In addition, the surrogate validation approach could be viable with other G2000 analyzer models as well, but due to design and spectroscopic differences they are not currently supported by Picarro.*

Introduction

What is and isn't Surrogate Gas Validation?

The instruments covered by this document measure gases which are frequently hazardous to the user, whose standards are challenging to produce and blend accurately and safely, and which are often unstable due to reactivity, adsorptivity, or corrosivity.

These qualities often lead users to seek out a safer alternative to assessing the accuracy of their instruments. Toward this end, Picarro developed the surrogate gas validation method. It leverages fundamental spectroscopic principles to assess whether a primary gas is being measured correctly by confirming certain performance metrics on a second safer gas, which is easier and safer to produce and source. With Picarro's Cavity Ring Down Spectroscopy (CRDS), the extinction coefficient of an instrument's laser absorption can be said to be linearly related to the concentration of a gas species in the cavity. Because this is true for each species an instrument's laser measures, deviations in the linearity of the calibration due to laser performance affect species similarly. Of course, for this relationship to hold, the two species must be measured by the same laser and must each have resolvable spectral features within that laser's scanning range.

It is important to note here for clarity that the validation procedure **does not** directly recalibrate either the primary or surrogate gas—it leverages the excellent stability of the Picarro analyzer and the primary/surrogate gas relationship to verify that the analyzer is still performing within factory specifications. Though Picarro's analyzers do offer the ability to change the calibration of the primary gas species directly if the user wishes to do so, this document is not intended to guide users in this task.

Briefly, and broadly, the validation procedure requires that the user provide a scrubbed zero gas to the analyzer to check that both the primary and surrogate gases register to within some acceptable specification near zero (typically a few parts per billion). The procedure then requires that the user confirm that the analyzer's linearity hasn't drifted by checking whether the surrogate gas concentration is accurately captured at three additional span points. If the zero has not drifted beyond spec, and the span is within an acceptable fit accuracy, the instrument is determined to be performing accurately.

What is that acceptable span accuracy? Typically, due to the high uncertainty of primary standards on hazardous, corrosive, and reactive gases, the accuracy of the span is assessed at the level of 5% or 10%. It is important to note that the Picarro instruments are capable of measuring gases at substantially higher accuracy that this, but gas standard producers are typically unable to produce even gravimetrically-prepared tanks that exceed the 5% mark.

How often should I validate my instrument?

Because the drift of Picarro's analyzers is constrained by the instrument's wavelength monitor, which tracks one or more known reference lines (e.g. water vapor), the instrument will not drift monotonically like a conventional non-dispersive infrared analyzer (NDIR), whose measurements depend on the intensity of the light emitted from the source bulb. We recommend that users validate their instruments roughly weekly to monthly depending on their needs and ability to access the instrument.

For users for whom an extremely accurate zero value is important (e.g. users in the air quality formaldehyde community), a more frequent assessment of the zero drift relative to a known scrubbed gas may be appropriate. For brevity, this document does not address this procedure.

Can the instrument handle dry zero air indefinitely?

Picarro analyzers utilize a patented wavelength monitor (WLM) to observe and track one or more well-defined spectral reference lines, chiefly water. Operating in a nearly water-free environment *and* without the presence of small amounts of the primary or validation gas can lead to the WLM scanning away from the correct frequencies for the primary gas, at which point the instrument will read inaccurately. The requisite frequency axis species can be found in the table below. If the user anticipates that the instrument will be used in such an environment, Picarro recommends that the user install a three-way solenoid valve, controlled through the Picarro valve sequencer, and that they switch approximately daily to ambient air, a bubbled zero air stream, or a calibration gas for a few minutes. Users wishing to set up such a configuration should contact support@picarro.com for assistance.

Model	Primary Gas	Frequency Axis Reference Gas Species and Concentrations
G2103	NH_3	H_2O > 400 ppm **OR** NH_3 > 17.5 ppb
G2108	HCl	H_2O> 400 ppm **OR** CH_4 > 2 ppm **OR** HCl > 4 ppb
G2114	H_2O_2	H_2O > 44 ppm **OR** CH_4 > 12 ppm **OR** H_2O_2 > 114 ppb
G2205	HF	H_2O > 0.4% (4000 ppm) **OR** O_2 > 0.75%
G2307	H_2CO	H_2O> 140 ppm **OR** CH_4 > 1.4 ppm **OR** H_2CO > 300 ppb

Table 1: "Frequency axis" gas species—the gas(es) that must be present in the sample air or in a frequently checked reference gas in order for the instrument not to drift with time.

The golden analyzer approach

Each instrument shipped from the factory has a calibration and validation that can be traced back to the original calibration effort on a golden analyzer. We go into full detail on this process in the white papers for each platform, which can be found in our Document Library at https://www.picarro.com/support/documents, but simply, we:

1. Carefully calibrate a "golden" instrument unit for each instrument model, one with exceptionally low drift.
2. Use this golden instrument as a transfer standard to cross-calibrate each instrument built at the factory.
3. Re-check the calibration of the golden instrument over time by checking the calibration of this instrument with a non-reactive proxy gas.

Validation Gas Species, Required Concentrations

Picarro chose the surrogate gas method rather than a direct calibration method keeping in mind that that the method could be performed without additional hardware (change to cavity, lasers, etc.), and that the surrogate gas was a) available as a NIST-traceable standard, b) non-hazardous at the relevant concentrations, c) indefinitely stable, d) not "sticky" on internal surfaces, and e) gaseous across the operational range of the instrument. For many instruments, methane (CH_4) met these criteria. For others, carbon dioxide (CO_2) or oxygen (O_2) did.

Analyzers and their surrogate gas species are noted below. Because the absorption line of the surrogate gas must be within the scanning range of the laser card, which is chosen on the basis of the primary gas spectral line, the spectral features of the surrogate gas are sometimes weaker than they would be elsewhere in the electromagnetic spectrum. As a result, the concentrations of the surrogate gas are often higher than their natural abundances to assess the instrument's absorption range. For example, the methane feature near the G2114's H_2O_2 peak is about 70-fold weaker than that of H_2O_2. To evaluate analyzer linearity and sensitivity of H_2O_2 for this purpose, Picarro recommends purchasing cylinders with concentrations on order 0-100 ppm CH_4 in order to characterize H_2O_2 on order 0-1400 ppb (100 ppm/70 = ~1.4 ppm or ~1400 ppb).

Model	Primary Gas	Surrogate Gas	Surrogate Gas Concentrations
G2103	NH_3	CO_2	0, 200, 1000, 10000 ppm
G2108	HCl	CH_4	0, 7, 50, 100 ppm
G2114	H_2O_2	CH_4	0, 7, 50, 100 ppm
G2205	HF	O_2	0, 20.94% (ambient)
G2307	H_2CO	CH_4	0, 7, 50, 100 ppm

Table 2: Surrogate gases and their recommended concentrations. Picarro recommends that customers purchase surrogate gases from a vendor like Air Liquide/Air Gas which prepares gases with strong accuracy specs

It should be noted that not all surrogate gas validation procedures are identical. While we encourage users of most systems to use three validation gases and a zero, in the case of the G2205 HF analyzer, we encourage users to use just two points—a good ultra-high purity N2, and ambient air, whose O_2 concentration is known to typically three significant figures (20.9%) unless large sources or sinks of O_2 are present in the room (e.g. O_2 tanks, or a furnace/engine). Notably, dry scrubbed zero air cannot be trusted to have exactly ~20.95% O_2 due to blending tolerances, so ambient air is more appropriate.

Choosing the Matrix of your Surrogate Gas

IMPORTANT: "Matrix" in this context refers to the "balance" gas—or gases—used to carry a calibration standard. A 500 ppm standard of CO_2, for example, must have 999,500 ppm of balance gas to achieve the 500/1,000,000 molar mixing ratio it is meant to represent. Typical choices are either ultra high purity nitrogen (N_2), or UHP zero air (ZA), which contains N_2, O_2, and potentially trace amounts of other gases like Ar and CO at ppm or ppb levels. "Zero air" contains virtually **no** CO_2 or H_2O however, differentiating it from ambient air. **Currently, Picarro delivers its surrogate gas validation instruments with spectroscopy relevant to a zero air balance (matrix). If the user's ultimate application will require that the instrument measure the primary gas in a N_2 matrix, the user should discuss this with their sales representative or application scientist before the instrument is tested and shipped, and purchase relevant standards in N_2.**

Currently, Picarro does not support other gas matrices like pure argon. **Helium is known to be incompatible with Picarro analyzers, and can destroy the pressure sensor on the cavity, requiring cavity repair if used routinely as a carrier gas**. An H_2 matrix is likely also incompatible, though this has not yet been tested.

Surrogate Gas Validation Preparation

Procedure Overview

This validation procedure is based on sequentially introducing zero air and three surrogate (proxy) gas standards to the instrument. The zero air allows the user to assess whether the instrument's zero has drifted out of spec on the primary and surrogate gases. The surrogate gas concentrations in three additional cylinders are measured, and a linear regression is calculated to demonstrate the linearity and zero accuracy of the analyzer.

The G2205 HF analyzer requires a different set of materials—UHP N_2 to assess the zero value, and ambient air to assess the span. Users wishing to purchase multiple O_2 standards may of course do so to further confirm linearity of response.

Because instrument performance issues that could affect the accuracy of the primary gas span will likewise affect the surrogate gas span, this procedure provides a means of rapidly validating system performance without requiring direct primary gas measurements. To facilitate data analysis and visualization, Picarro provides an Excel template "Picarro Surrogate Gas Validation Worksheet", which can be obtained by contacting Picarro Technical Support at support@picarro.com or (+1) 408-962-3991.

Procedure Duration

~60 minutes for data acquisition

5-15 minutes for data analysis

Required Supplies

- A separate computer with Microsoft Excel.[1]
- Cylinder of ultra high purity zero air (dry synthetic CO_2-free and hydrocarbon-free air.) for all analyzers but G2205. For G2205, a cylinder of UHP N2.
- (For all but the G2205 HF analyzer) Three surrogate gas standard cylinders, containing different concentrations of the surrogate gas certified at +/- 5 or 10% composition accuracy, depending on manufacturer.
- One or more two-stage regulators, e.g. the Q1-14B-590 regulator by Air Liquide for North American customers.[2] The second stage should have a delivery range of 0-10 psi (0-0.7 bar) and be capable of accurately delivering the recommended 2-3 psi (0.1-0.2 bar) of line pressure.[3] For G2205, a Q1-14B-580 will be required for N_2.
- Sufficient tubing to connect the regulator(s) to the instrument. We strongly recommend using exclusively Teflon or PFA tubing.[4]
- Suitable fixed wrenches for making gas line connections—typically 9/16", 7/16", 1/2", 3/8"—and a 1 1/8" cylinder wrench for North American customers.
- *(Optional)* A0311 16-Port Manifold for easy switching between cylinders and back to the sample stream[5]
- *(Recommended)* ¼" or 1/8" Legris Push-In Union[6] to facilitate rapid sequential connection of multiple gas lines to the instrument. If used, attach ~1 m of tubing to the instrument's gas inlet port, and one side of the union to the other end of the tubing. Thereafter, the union can be used to rapidly attach or detach an input gas line without need for tools.

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[1] It is possible to install and use Excel on the instrument computer, but we broadly recommend avoiding running Excel at the same time as the instrument, as the two will compete for CPU power.

[2] It is adequate to obtain one regulator, and to move it between cylinders during the procedure, however it may be preferable to install one regulator per cylinder for convenience, and switch between cylinders using a quick connect fitting. In either case, the regulator must be flushed three times before use to avoid memory effects. For instructions, See Appendix 3: Flushing Regulators below for instructions on how to go about this process. Doing so will save the user time that would otherwise likely be spent waiting for the gas to equilibrate on the instrument.

[3] Users with a regulator whose delivery side pressure is higher should set up a bleed tee to bleed off excess pressure upstream of the instrument inlet.

[4] e.g. McMaster-Carr 8547K23 ¼" PTFE tubing 1/8" ID or equivalent.

[5] This approach is only viable for instruments measuring non-sticky gases, so is a poor choice for Ammonia and also unsuitable for hydrogen peroxide. Thought the A0311-S manifold with passivated internals can be used for multiple-port sampling, it is currently not a complete solution for calibration/validation because the -S pulls gas from all non-selected positions all the time, wasting calibrant gas.

[6] www.legris.com part 3106 56 00 for ¼" or 3105 53 00 for 1/8"

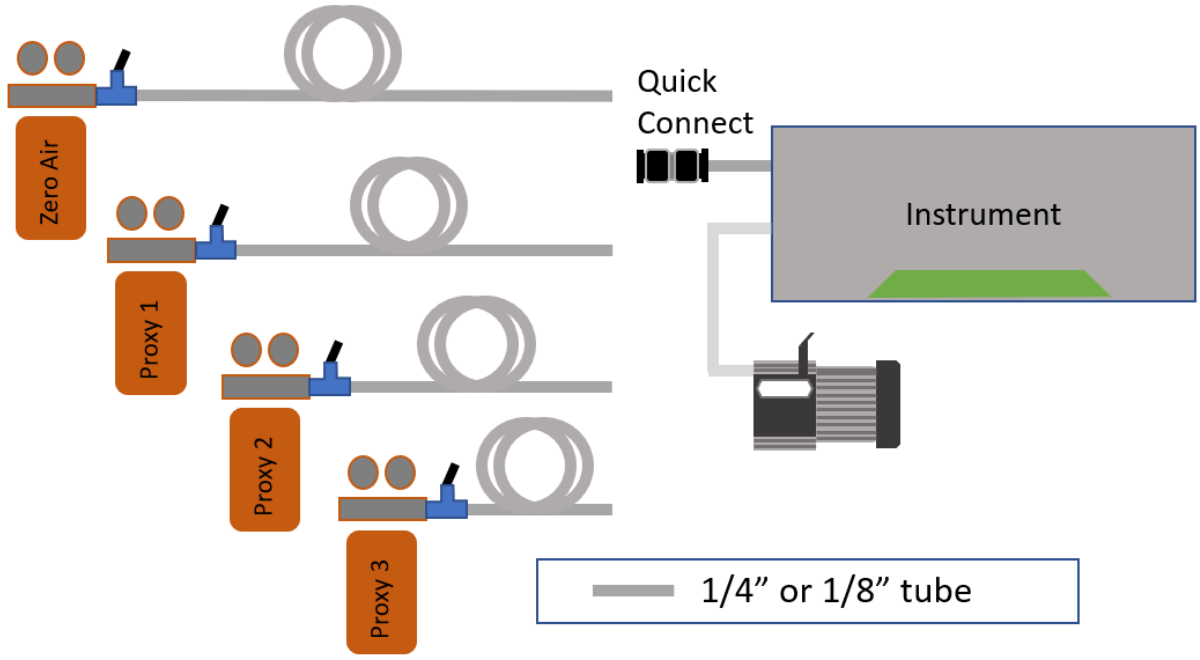


Figure 1: A simplified diagram of zero and proxy gases being connected to the instrument using a quick connect fitting and manual switching between tanks. If the user has only one regulator to move between tanks, the user should be especially sure to flush the regulator three times between each cylinder to avoid memory effects.

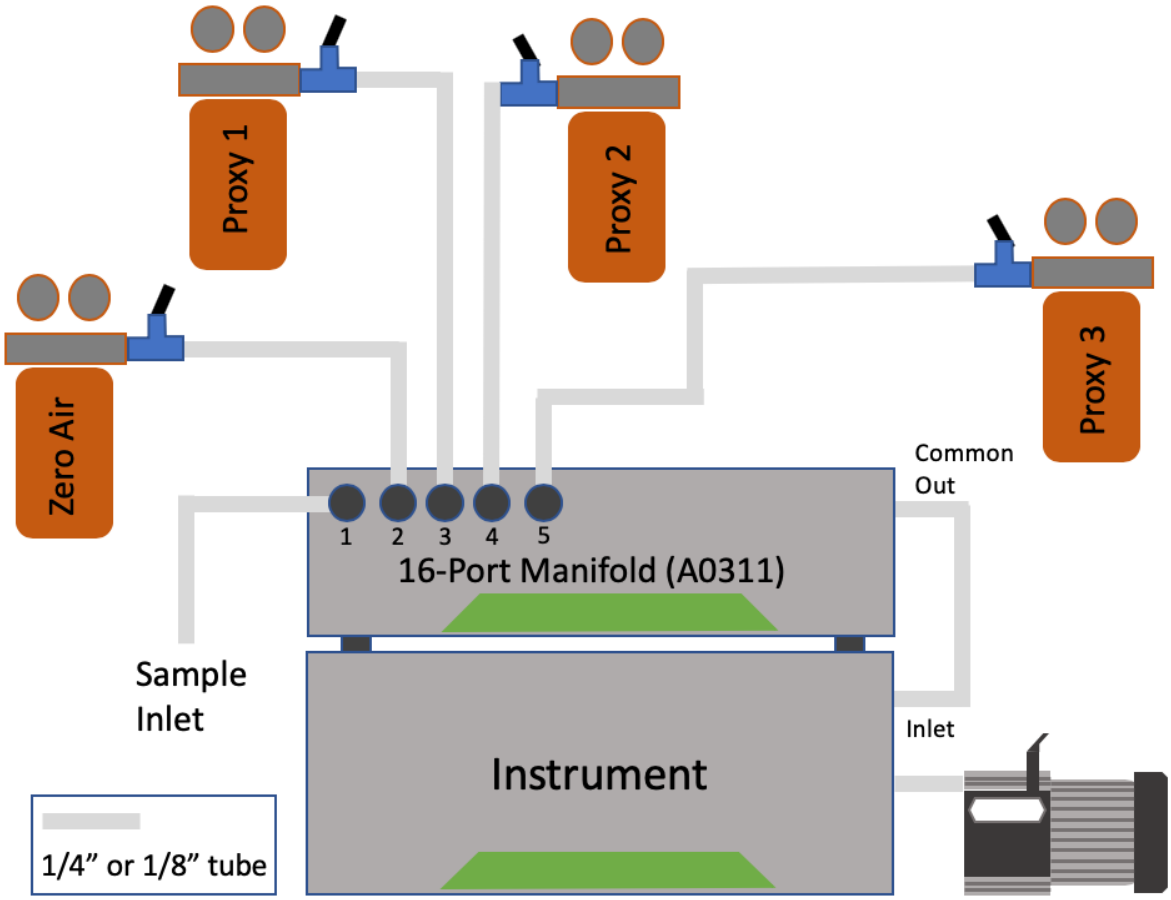


Figure 2: Flow diagram for validation for users with the 16-Port Manifold, Part A0311. Note that position 1 is dedicated for the sample line. For simplicity, we depict positions 2-5 as the appropriate choices for surrogate gas validation technique, but users who switch operationally between multiple sample lines may wish to dedicate the zero and proxy gases to higher positions on the manifold. For users with A0311, the purging step can be skipped as long as the validation steps are done frequently, e.g. daily.

Surrogate Gas Validation Procedure

1. With the instrument running and the graphic user interface (GUI, below) displaying measurements, ensure that both the primary and surrogate (proxy) gas are showing in the plots, like in the example below highlighted in **red**. If the proxy gas isn't showing, select it from the dropdown Data Keys highlighted in **light blue**.

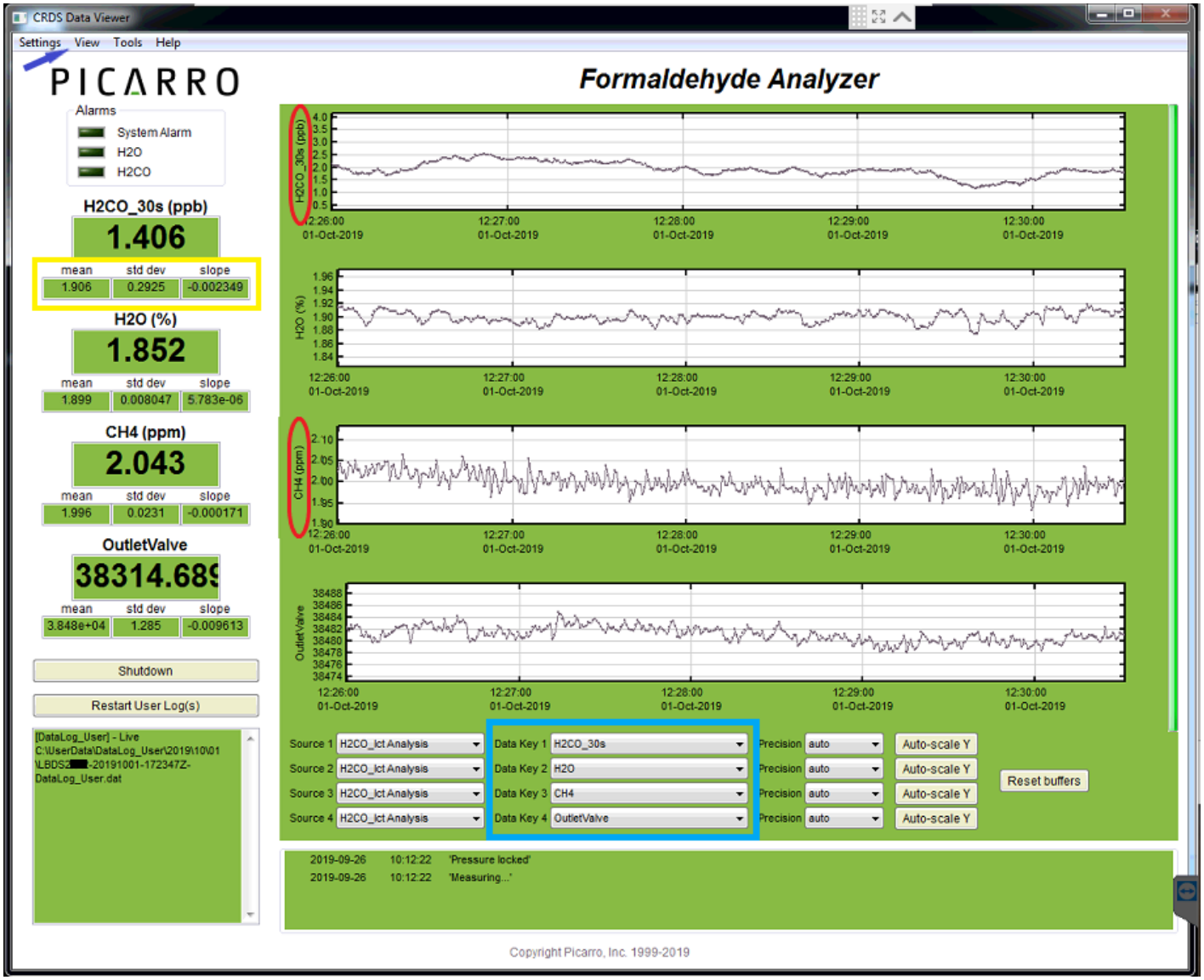


Figure 3: Graphic User Interface (GUI) showing primary gas (here, formaldehyde) and proxy gas (here, methane).

2. From the top View menu (**dark blue** arrow) select "Lock Time Axis When Zoomed". and "Show Statistics", which will bring up the boxes highlighted in **yellow** above.

3. Users who wish to, or who are required to, record and store the data for their validations should at this point click “Restart User Logs” and write down the name of the validation file on their worksheet—they may use the worksheet from Appendix 4: Validation Worksheet Log or adapt their own.

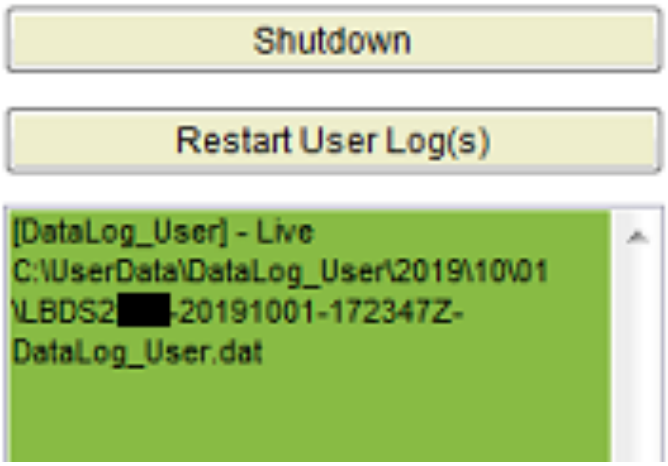


Figure 4: An example of the file name/location for users need to retain raw data from the validation procedure.

4. At this point, the user may choose between the manual switching method, or the automated method associated with the A0311 16-port Manifold.

Method 1: Manual Switching

5. **Determine the zero value.**
    a. Attach a regulator to the zero air (N_2 for G2205) cylinder if not already installed, with the output pressure set to zero. Flush the regulator three times using the technique discussed in Appendix 3: Flushing Regulators, and then adjust the output line pressure upwards to 2-3 psi (0.1-0.2 bar).
    b. Attach the zero air line to the instrument using the setup seen in Figure 1.
    c. Allow a few minutes for the cavity pressure to stabilize. The system may indicate erroneous concentration measurements or may pause update of displayed concentration values until the pressure is stable.
    d. Once the proxy and primary gas have stabilized, wait five minutes.
    e. On the primary gas (or any) plot, hold the left mouse button and drag to select the last five minutes of data. When a single plot is zoomed in, the remaining plots should be, also. (If not, select “Lock Time Axis When Zoomed” from the “View” menu.) Confirm that the primary and proxy gas are stable over this period of time when zoomed in, and if so, write down the values recorded under “Mean” for each gas species as “Primary Gas Zero” and “Proxy Gas Zero” on a copy of the worksheet from Appendix 4: Validation Worksheet Log. ***(Important: do***

not copy from the larger window above the "Mean" value, as this will continue to update while the mean stays constant.) We recommend that the user also take a screen capture ("Prt Scr") at this point for their records. If the user is unable to get a zero value within the spec of the instrument zero drift, the user's zero gas may have trace amounts of the primary gas. If this is the case, the user should follow the instructions in "Choosing Appropriate Scrubbing Materials" to remove these trace concentrations in line between the zero gas and analyzer.

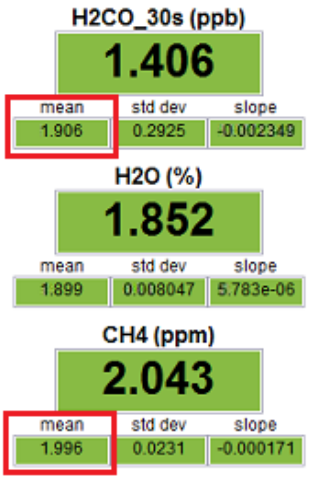


Figure 5: Mean values for the primary and proxy gases.

6. **Determine the span values.**
    a. Remove the zero gas line from the quick connect, allowing the instrument to run briefly on room air. Flush the regulator on the first surrogate gas cylinder, and attach its gas line to the quick connect, again at 2-3 psi (0.1-0.2 bar), starting with the lowest concentration.
    b. Allow the new tank to stabilize, and once it has, wait five minutes.
    c. As with the zero, zoom in on the five minutes of stable measurements, and record the mean value of the proxy tank. Take a screen capture for your records.
    d. Repeat steps 4.a.-c. for the remaining span tanks.
7. At the end of this process, the user should have noted down a single zero value for the primary gas, and 4 values (a zero and 3 spans) for the proxy. Note: *G2205 users will have just a zero value for N_2 and an ambient span value for an O_2 proxy gas or ambient air.*
8. Users who wish to, or who are required to, retain the raw data from the validation procedure should at this point note the name of the file in the lower left corner of the screen (if not noted before) and hit "restart user log(s)". This will bookend the validation procedure so that it doesn't contain additional irrelevant data at the end. Users should then copy over the validation file to a central folder or another computer for their records.
9. Detach the gas line from the instrument and close any open cylinders.

Method 2: 16-port Manifold

5. For users with the 16-port manifold, configure the manifold with the gases in the positions as called out in Figure 2, and purge each regulator three times to the room before beginning this procedure.
6. Select “Show/Hide Valve Sequencer GUI”. If the valve sequencer doesn’t show up immediately, hit “alt-tab” to bring it to the foreground.

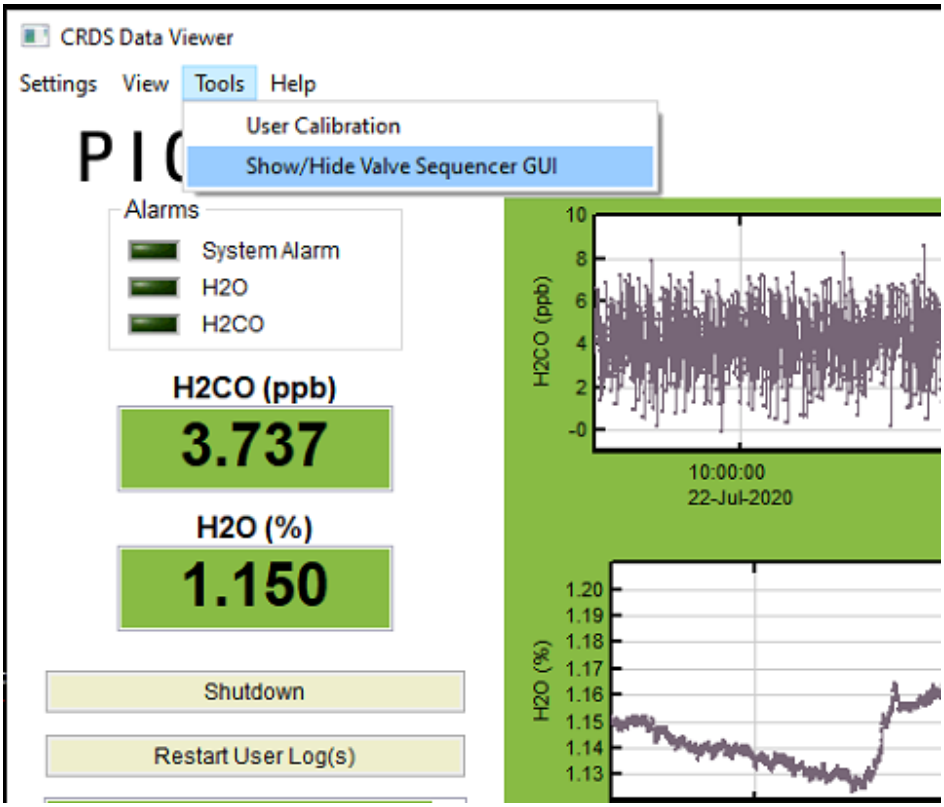


Figure 6: Showing Valve Sequencer Window.

7. In Valve Sequencer, set the manifold to run the validation procedure itself with 10-minute periods for each cylinder.
    a. Under Step #1, for “Rot. Valve Code” enter 2, and for Duration enter “10”.
    b. Under Step #2, for “Rot. Valve Code” enter 3, and for Duration enter “10”.
    c. Under Step #3, for “Rot. Valve Code” enter 4, and for Duration enter “10”.
    d. Under Step #4, for “Rot. Valve Code” enter 5, and for Duration enter “10”.
    e. Under Step #5, for “Rot. Valve Code” enter 1, and for duration enter “999” (users who wish to assess the validation process offline on a routine basis should enter “1400” for daily validation, or “10040” for weekly validation).
8. Under the “Action” menu, select “Start Sequencer”, and confirm that the valve audibly switches to position 2, and that the “Remaining Time (min)” entry begins counting down

from 10 minutes. If the sequencer does not start, consult the troubleshooting section of the A0311 manual, especially regarding com ports.

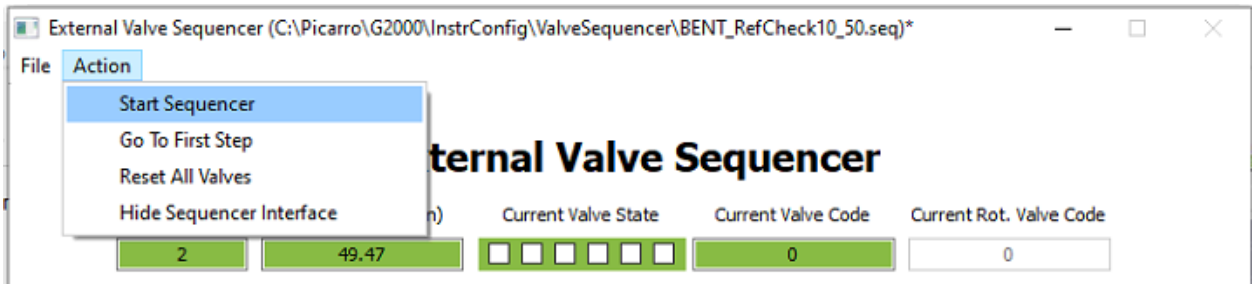
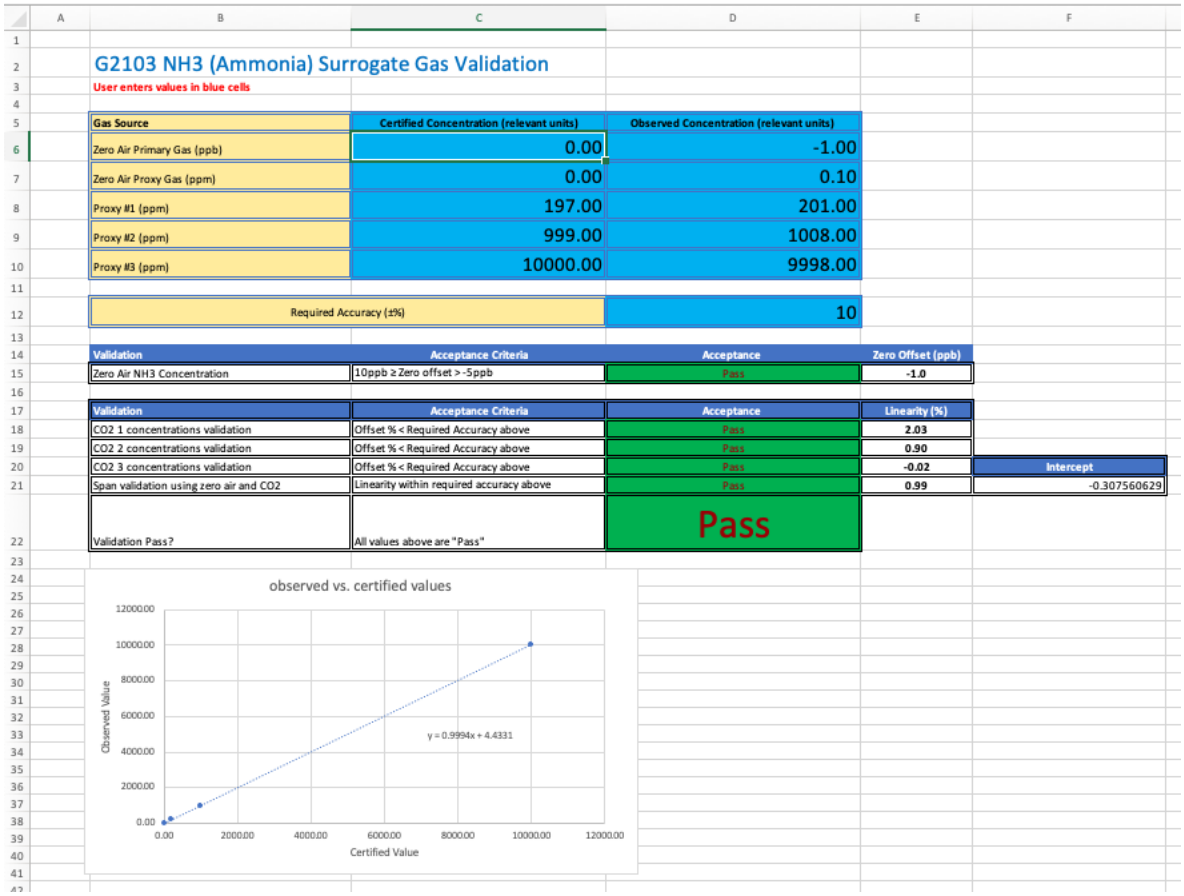


Figure 7: Starting the valve sequencer from the Action menu.

9. **Set a 40 minute alarm** to return to the instrument after the sequence has completed and returned to sample air on position 1. Waiting for too long may make it impossible to zoom in on the GUI, requiring the user to sort through the data file.
10. Choosing the latter 5 minutes of each plateau of the run, zoom in and note the mean value for the proxy gas, remembering to note the zero value for the primary gas. If plateaus are not stable with 10 minute windows, reconfigure the valve sequence with 15-minute windows and repeat.
11. At the end of this process, the user should have noted down a single zero value for the primary gas, and four values (a zero and three spans) for the proxy gases.
12. Users who wish to, or are required to, retain the raw data from the validation procedure should at this point note the name of the file in the lower left corner of the screen (if not noted before) and hit “restart user log(s)”. This will bookend the validation procedure so that it doesn’t contain additional irrelevant data at the end. Users should then copy over the validation file to a central folder or another computer for their records.
13. Users who perform this validation in person will want to close the cylinder and toggle valves at this point. Users who wish to perform the validation offline as part of a routine scheduled procedure may leave the valves open.
14. In Valve Sequencer, confirm that the valve has returned to position 1 (or the appropriate sample position for the user’s setup) and from the “Action” menu, select “Stop Sequencer” to ensure the system stays in this position until the user wishes to validate the instrument again. Users who have set their system to validate daily or weekly may leave the sequencer running, and do not need to purge their regulators with each new validation.

Data Processing and Calibration Assessment

An Excel template with these calculations is available through the Picarro document library at https://www.picarro.com/support/documents with the name "Surrogate Gas Validation Worksheet". It will perform the calculations automatically once the necessary values have been entered into the template.



G2103 NH3 (Ammonia) Surrogate Gas Validation

User enters values in blue cells

Gas Source	Certified Concentration (relevant units)	Observed Concentration (relevant units)
Zero Air Primary Gas (ppb)	0.00	-1.00
Zero Air Proxy Gas (ppm)	0.00	0.10
Proxy #1 (ppm)	197.00	201.00
Proxy #2 (ppm)	999.00	1008.00
Proxy #3 (ppm)	10000.00	9998.00

Required Accuracy (±%)	10

Validation	Acceptance Criteria	Acceptance	Zero Offset (ppb)
Zero Air NH3 Concentration	10ppb ≥ Zero offset > -5ppb	Pass	-1.0

Validation	Acceptance Criteria	Acceptance	Linearity (%)	
CO2 1 concentrations validation	Offset % < Required Accuracy above	Pass	2.03	
CO2 2 concentrations validation	Offset % < Required Accuracy above	Pass	0.90	
CO2 3 concentrations validation	Offset % < Required Accuracy above	Pass	-0.02	Intercept
Span validation using zero air and CO2	Linearity within required accuracy above	Pass	0.99	-0.307560629
Validation Pass?	All values above are "Pass"	Pass		

Figure 8: An example of the Excel template for the G2103 NH3 analyzer.

Because our instruments do not ship with Excel (to encourage users to dedicate system memory to the instrument), the user will have to check the validation on a separate computer, or install Excel themselves for brief use during validation. When you open the spreadsheet, save the document as a new spreadsheet with the name in form "G2###_Validation_YYYYMMDD". Choose the tab from the bottom right that corresponds to your instrument/gas species, and perform the following steps:

1. In cells C6-7, enter zero if not already entered, and in C8-10 specify the certified concentrations for the surrogate gas from the cylinder or associated documentation.

(Please note that the certified composition often varies slightly from the requested concentration, e.g. a 2 ppm cylinder may actually be 2.1 ppm.) [7]

2. In cells D6-10, specify the observed mean values noted in the section above.
3. In Cell D12 specify the accuracy requirements for the system. This is typically 5 or 10%. This number should match the accuracy of your standards.
4. As the data are copied in, the analysis spreadsheet will update various cells and columns. When all the data has been copied over, inspect the results in cells E18-21. If the observed surrogate gas values are within the specified accuracy range, the typical acceptance criteria are met, and the cells D18 to D21 will become green and indicated "pass".
5. If cell D22 is green and indicates "Pass" for all results in D18-21, the analyzer was successfully validated.
6. If the procedure returns a "Fail" result, rerun the validation, ensuring that the regulators are flushed, that the zero value is produced with a scrubbed zero gas, and checking that the plateaus have stabilized before noting the mean value. If this does not return a "Pass" result, contact Picarro technical support at support@picarro.com.

Example Results

In the example below, we collected data using four methane cylinders of nominally 0, 2.058, 10.0, and 100.2 ppm. Approximately five minutes of data were averaged for each concentration.

Below, the data are plotted as pairs of certified ("nominal") and observed methane concentration values. By fitting a linear regression, we obtain:

$$CH4_{observed}\ (ppm) = 0.99998 \times CH4_{nominal}\ (ppm) - 0.00165$$

The discrepancy in the slope of the fit is therefore less than 0.00187%, and the zero error is 1.65 ppb (comparable to 0.0236 ppb of H_2O_2.) This data clearly validates the proper functioning of the instrument and demonstrates the system's linearity.

Note: Scaling for the relative sensitivity difference between methane and H_2O_2 (methane produces spectra 70-fold weaker) these standards are comparable to 0, 30, 145.7, and 1427 ppb of hydrogen peroxide in terms of their utility in evaluating the fundamental performance characteristics of the instrument.

[7] Note that cell values specified here and below will differ slightly for a two-point validation on the G2205 HF instrument.

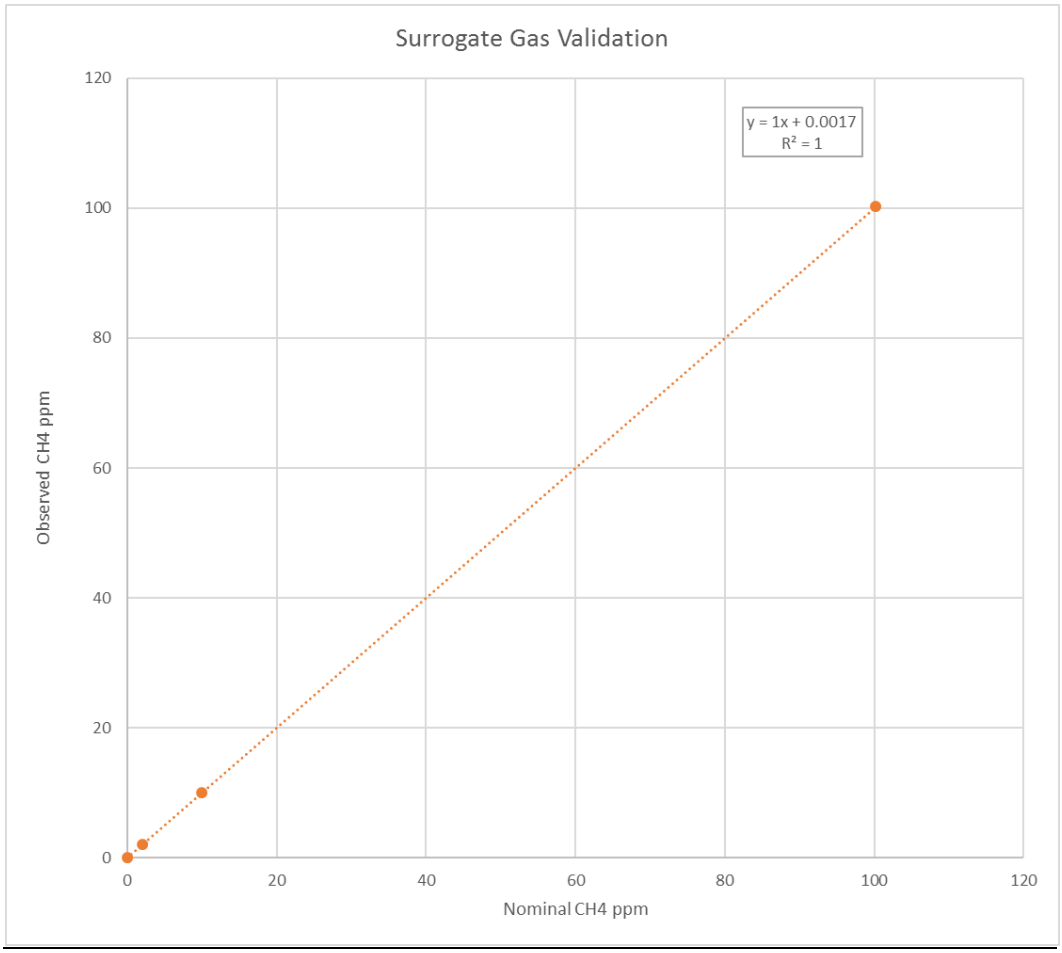


Figure 9: Surrogate gas validation results using zero air and three methane concentration standards.

Choosing Appropriate Scrubbing Materials

It should be noted that even ultra high purity (UHP) zero air may occasionally have a small (ppb to ppt) amount of many of the gases covered in this document. If individuals who wish to generate a very clean zero for the surrogate gas validation process, we recommend using a species-specific scrubber from the list below. We recommend users assemble a scrubbing canister if they do not already have one on hand. The following materials are broadly suitable for all scrubbing systems.

Item description	Qty	OEM p/n	Price (2020 USD)	Link to web site
Vessel, Peptide Plain, 500 mL	**1**	Ace Glass, 6408-10	**$155**	https://us.vwr.com/store/product?keyword=89054-248
Adapter, PTFE, Ace thread to 1/8" NPT with O-ring	**2**	Ace Glass, 5838-75	**$80**	https://us.vwr.com/store/product?keyword=89052-590
Swagelok PFA fittings (1/8" NPT to 1/4" OD tube)	**2**	PFA-420-1-2	**$20**	https://www.swagelok.com/en/catalog/Product/Detail?part=PFA-420-1-4

Table 3: Recommended supplies for zeroing the Picarro analyzer

The following scrubbing agents are appropriate for their respective primary gases.

Primary Gas	Item description	Qty	OEM p/n	Price (2020 USD)	Link to web site
NH_3	Phosphoric Acid Impregnated Activated Charcoal (PAIAC)	25 kg	Carbon Activated, HPO-A60 (8x20)	$450	https://activatedcarbon.com/
HCl, HF	Activated Charcoal, Coconut Shell				https://activatedcarbon.com/
H_2O_2	Manganese Greensand	Nom 0.5 ft^3	n/a	Nom. $150	Various
H_2CO	DrieRite*	1 kit	CO360	$199.50	http://store.picarro.com/For-Analyzer/Calibration/Desiccant-Drier-Kit.html

*Table 4: Scrubbing material to generate a clean zero, by gas species. *The listed DrieRite kit doesn't require assembling a vessel, as one is provided.*

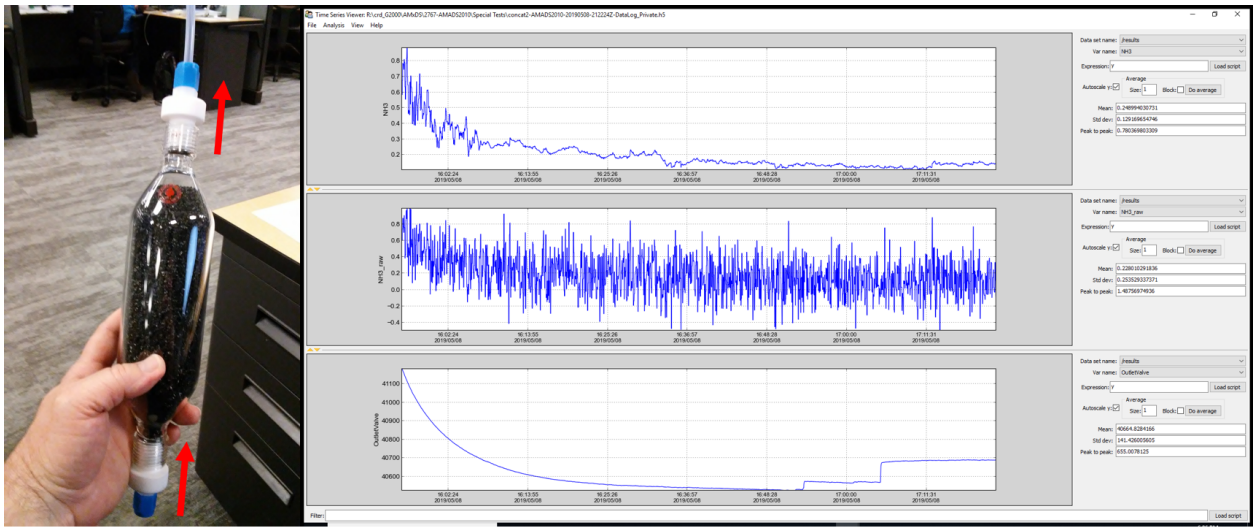


Figure 10: Left: Phosphoric Acid Impregnated Activated Charcoal scrubber, assembled; Right: The result of applying a PAIAC scrubber to a UHP Nitrogen zero in lab at Picarro HQ.

When these components are assembled, the resulting canister should look like the image above, with the possible exception of the scrubbing agent. *Ensure that the scrubber cartridge is held upright, and that air enters from below and exits above so that particulate matter isn't entrained into the analyzer.*

Use this canister when assessing the zero value of the primary and surrogate gases as part of the surrogate gas validation or zero offset assessment procedures outlined earlier in this document.

Picarro Support

To obtain a copy of the surrogate gas template, or if you have any questions about using this procedure, please contact Picarro at support@picarro.com or (+1) 408-962-3991.

Sourcing Calibration Standards

Americas, Airgas for Air Liquide:

Griffith Brown handles Picarro inquiries and is the best point of contact on procuring gases for Picarro analyzers. griffith.brown@airgas.com Tel: +1 (408) 396-3494

For general inquiries, contact info@airgas.com or +1 (855) 625-5285

Europe, Air Liquide:

Germany, Austria & Switzerland, Oliver Schlegel, oliver.schlegel@airliquide.com, Tel: +43 6246 721 81 620

Spain & Portugal, Adelino Fernandes, adelino.fernandes@airliquide.com, Tel: +351 21 416 49 83

France: Christophe Guichard, christophe.guichard@airliquide.com, Tel: +33 1 58 07 84 33

Italy: Guiseppe Magon, giuseppe.magon@airliquide.com, Tel: +39 0544 274036

Nordics & Benelux, Jack de Jong, jack.dejong@airliquide.com, Tel: +31 20 794 6996, or Erik Den Otter (erik.denotter@airliquide.com).

UK: John Pritchard, john.pritchard@airliquide.com, Tel: +44 7970 234332

Asia Pacific, Air Liquide

Australia: Hassan Mustapha, hassan.mustapha@airliquide.com, Tel: +61 3 9290 1152

Japan, Shigeru Ideriha, shigeru.ideriha@airliquide.com, Tel: +81 3 6414 6701

China, Iris Shi, iris.shi@airliquide.com, Tel: +86 21 6090 3604

Appendix 1: White paper references

Picarro has developed a series of white papers explaining the spectroscopy, calibration, and validation of individual instruments, which can be found at the Picarro Document Library, under the “Whitepaper” tab:

https://www.picarro.com/support/documents

Appendix 2: Materials compatibility and cautions

Tubing and Fittings

As rule of thumb, reactive and hazardous gas systems fare best with tubing, fittings, and regulators that are passivated. 1/4” PTFE and PFA tubing and fittings are broadly compatible with all species noted in this document.

At the 1/8” tubing size, Picarro has historically recommended silicon-passivated stainless steel products like SilcoTek’s Silconert™, which uses a vapor-deposited passivation process for coating tubing surfaces. Throughout Picarro’s line, only one system can be considered incompatible with Silconert—the G2205 hydrogen fluoride system—because HF destroys silicates. This is, however, only a matter of concern if the concentration of the HF gas provided to the tubing exceeds 25 ppm.

Appendix 3: Flushing Regulators

Regulators that have not been used in days or weeks, and regulators that were most recently used with another cylinder, will tend to show memory effects if they are not flushed before use. This phenomenon may result from residual air in the regulator stages themselves, or even from the re-equilibration of seals within the regulator. Especially with Picarro analyzers with low flow rates, such memory effects can take minutes or even hours to stabilize. Flushing regulators is an efficient and effective way to cut down on this delay.[8] Follow these steps:

1) Attach regulator to cylinder, tightening the thread with a cylinder wrench (typically 1 1/8”), and leaving the line that exits the regulator free to vent to ambient.
2) Ensure the (typically black) delivery pressure control knob is spun all the way out (showing thread), and if present, ensure that the black toggle valve is open (sticking straight up).
3) Crack open the main cylinder valve **and immediately close it**. You should see the pressure on the first stage rise rapidly, while the pressure on the second stage remains at 0 psig.
4) Dial in the black regulator knob all the way. The second stage pressure should slowly rise until its maximum output pressure (not necessarily the maximum value on the gauge), and the pressure on the first stage gauge should slowly drop. When the first stage nears zero, the second stage gauge will rapidly drop to zero.
5) When both gauges have dropped to zero, dial the delivery pressure control knob all the way back out.
6) **Repeat steps 3-5 two more times for three total flushes.**
7) After the third flushing, open the cylinder valve fully, retreating ¼ turn from full open to prevent sticking. If the regulator has a toggle valve on it, close the toggle valve and dial in the black regulator knob until you reach 2-3 psig. At this point, you’re ready to run gas to the analyzer, and need only open the toggle valve at the appropriate time. If you have no toggle valve, simply wait to dial in the black knob to 2 psig until you’re ready to connect up the relevant tubing.

[8] A video tutorial on this process may be found by searching on the Picarro website for “Flushing Regulators” or by going to: https://mktg.picarro.com/acton/media/39674/videos

Appendix 4: Validation Worksheet Log

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Date:	
User:	
Instrument:	
Serial Number:	
File Name:	
Primary Gas Sp:	
Secondary Gas Sp:	

Gas Source	**Certified Concentration**	**Measured Concentration**
Primary Gas Zero		
Proxy Gas Zero		
Proxy #1		
Proxy #2		
Proxy #3		

Zero Offset (Primary Gas)	
Linearity	
Pass/Fail? Reason for Fail, if fail:	