

Calibration Guide for Picarro Analyzers

(Revision 1, August 2017)



PICARRO

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1. Introduction

This document serves as a general guide on how to approach and successfully calibrate a Picarro cavity ring-down spectrometer (CRDS). The steps described herein can be used on isotopic and/or concentration analyzers that measure CO₂, CO, CH₄, H₂O, C₂H₂, C₂H₄, C₂H₆, CH₂O, O₂ and N₂O. Additional analyzers may require special or extra steps to calibrate properly. If you are unsure if this document applies to your analyzer, please consult with Picarro support (support@picarro.com), your Picarro sales representative and Application Scientist.

2. Basic principles of CRDS

Picarro analyzers measure gas molecules and/or isotopologues based on the principle of laser light absorption. This light, tuned to a wavelength that corresponds to the vibrational mode and frequency of the target molecule and/or isotopologue, enters an empty cavity where it reflects between three high-reflectivity mirrors (Figure 1). When the cavity is brought into resonance, the intensity of the light increases due to constructive interference. Once a threshold in light intensity is reached, the laser source is turned off and since the mirrors are only 99.999% reflective, light slowly bleeds out of the cavity and into the photodetector where its intensity is measured. The exponential decay time of the intensity of the light is expressed as the ring-down time. When sample gas is introduced into the cavity, the light intensity drops more rapidly due to the absorption of light by the target molecule and/or isotopologue – an additional loss mechanism which leads to a faster decay time. The software then converts measurements of absorption at several wavelengths into an optical spectrum. A non-linear curve-fitting algorithm of this optical spectrum is used to quantify the strength of the key absorption peaks, which are then used to calculate species concentration and isotopic abundance.

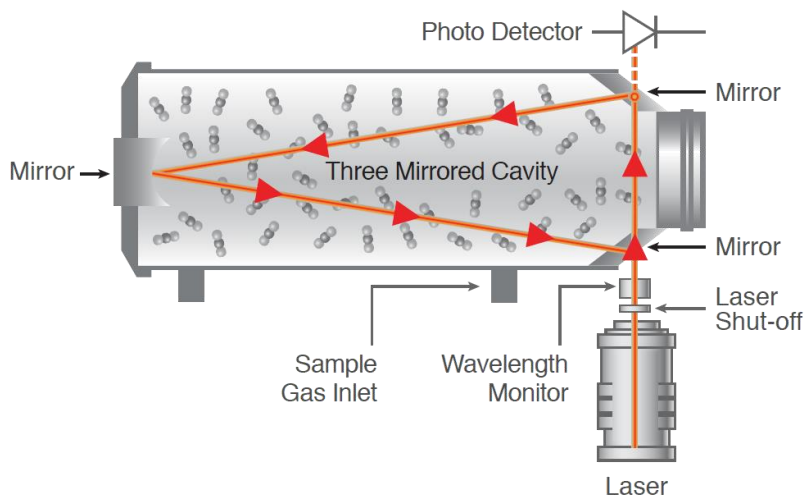


Figure 1 – Schematic drawing of a Picarro cavity and key optical components. The unique cavity design leads to an effective optical path length of over 20 km.
2.1 Calculation of an Isotopic Ratio

2.1 Calculation of an isotopic ratio

Excerpt from the G2201i - an isotopic CO₂/CH₄ analyzer.

The quantities ¹²CO₂_dry (dry mole fraction of ¹²CO₂, corrected for water vapor) and Delta_Raw are the primary analytical quantities reported by the instrument. They are also the quantities that are suitable for practical user calibration. For instance, traceable primary standards of δ¹³C are maintained by national standards laboratories, whereas there are no primary standards for ¹³C¹⁶O₂ mole fraction. We recommend that the users of the G2201-i consider only ¹²C¹⁶O₂ mole fraction and δ¹³C as primary, calibrated quantities.

Other quantities, such as ¹³C¹⁶O₂ mole fraction and the abundance ratio of ¹³C to ¹²C should be regarded as derived quantities, computed from the ¹²C¹⁶O₂ mole fraction, δ¹³C, and the relation

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

where R_{sample} and $R_{\text{reference}}$ refer to the isotopic ¹³C/¹²C ratios of the sample and reference, respectively. If the delta scale is calibrated according to the VPDB scale, then $R_{\text{sample}} = R_{\text{reference}} = 0.0111802$ (see, for instance, Werner and Brand, "Referencing strategies and techniques in stable isotope ratio analysis," Rapid Commun. Mass Spectrom. 2001; 15: 501–519). Entries in the data log for ¹³C¹⁶O₂ mole fraction ¹³C to ¹²C ratio are approximate values only and should not be used in place of Eq. (1).

3. Calibration

3.1 Selecting Standards

Picarro analyzers and systems are most often calibrated by standards from compressed gas cylinders. However, certain peripherals and front-ends require standards in liquid and/or solid form. Section 5 of this guide illustrates how to use gas, liquid and solid standards to perform a successful calibration. Regardless of the standard, the approach to calibration is the same.

Picarro analyzers are calibrated by measuring a standard and comparing its measured values to an accepted value. The quality/accuracy of your final analyzer calibration is a reflection of (1) the number of standards you use, (2) the compositional range of your standards, (3) the method of standard measurement and (4) the accuracy and precision of the standard itself.

1. The minimum number of different standards to calibrate the slope and offset of the analyzer is two, and because CRDS instruments are highly linear, this is often sufficient. However, we do recommend at least three or more standards, to ensure both the linearity of the instrument and the quality of the standards.
2. The range of your standards generally should encompass or exceed the expected range of your dataset. This is important for both concentration and isotopic calibrations.
3. Since standards can be introduced to the Picarro directly or using a variety of peripherals. The sample preparation and the method will control the accuracy of you standard and sample measurement. See section 5 for more details.
4. It is commonly accepted that primary standards, when compared to secondary or even tertiary standards, report accepted values with higher levels of accuracy. Having confidence in the value of your standards leads to a higher degree of confidence in your instrument calibration. We advise the user to assess whether the accuracy and precision of their standards is sufficient for their research needs. The user should be mindful of fractionation within old or used standards that have not been stored properly.

CAUTION: Pressure and flow - When the analyzer is connected directly to a pressurized gas tank or a sample container, the user needs to be mindful of sample flow and pressure (1-3 psi range). If the pressure and flow are too high or too low, damage to valves and the cavity may occur. In either case, the data collected by the analyzer may also be affected. Please refer to the respective analyzer manual or datasheet for a listing of the recommended inlet flowrate.

3.2 Primary vs. Secondary Standards

Primary standards, such as VSMOW2 (Vienna Standard Mean Ocean Water 2), are reference points whose values have been agreed upon by the international community. Such standards are usually produced in small quantities, are available for purchase in a limited capacity and tend to be expensive.

Secondary, or working standards are reference materials that have been measured and compared to primary standards. Therefore, it is generally accepted that secondary standards are not as accurate as

primary standards, yet in many applications this minor loss in accuracy is not significant. Secondary standards are more readily available, can be purchased in larger quantities, are less expensive and may even be produced by the user.

Example: To generate a secondary isotopic CO₂ standard, the user would buy a set of primary standards to perform an initial calibration of the Picarro analyzer. Once the analyzer is calibrated, they can measure the isotopic value of a tank of compressed, uncharacterized CO₂. That tank then becomes a secondary isotopic standard that may be used as a working standard for more frequent calibrations and as an isotopic check during long analytical sessions. These steps can be repeated for any additional number of gas tanks.

3.3 Basic Analyzer Calibration

To illustrate an example of standard selection and calibration, we can look at an isotopic study of soil gases from a geothermal area. CO₂ from soil gas in a geothermal area will originate from biogenic ($\delta^{13}\text{C}$: -21 to -25 ‰), atmospheric (-8 to -10 ‰) and hydrothermal sources (-3 to -8 ‰). The complete range of $\delta^{13}\text{C}$ values from our expected samples will therefore be between -3 to -25 ‰. Since the expected concentration of CO₂ from soil samples (1-100% CO₂) exceeds the operational range of the analyzer, samples are diluted to within 1,000 ppm CO₂ using zero air. To cover the complete isotopic range, three standards are selected (-3 ‰, -15 ‰ and -35‰). Since most sample measurements will occur at 1,000 ppm CO₂, all three isotopic standards are also prepared to be near 1,000 ppm CO₂ (see section 5.1 on standard dilution). A memory test is performed (see section 5.2) and three replicates of each standard are selected and analyzed for a period of 10 minutes each (Figure 2). An average value for this 10-minute period is obtained and all three averages are combined into a single value for a given standard.

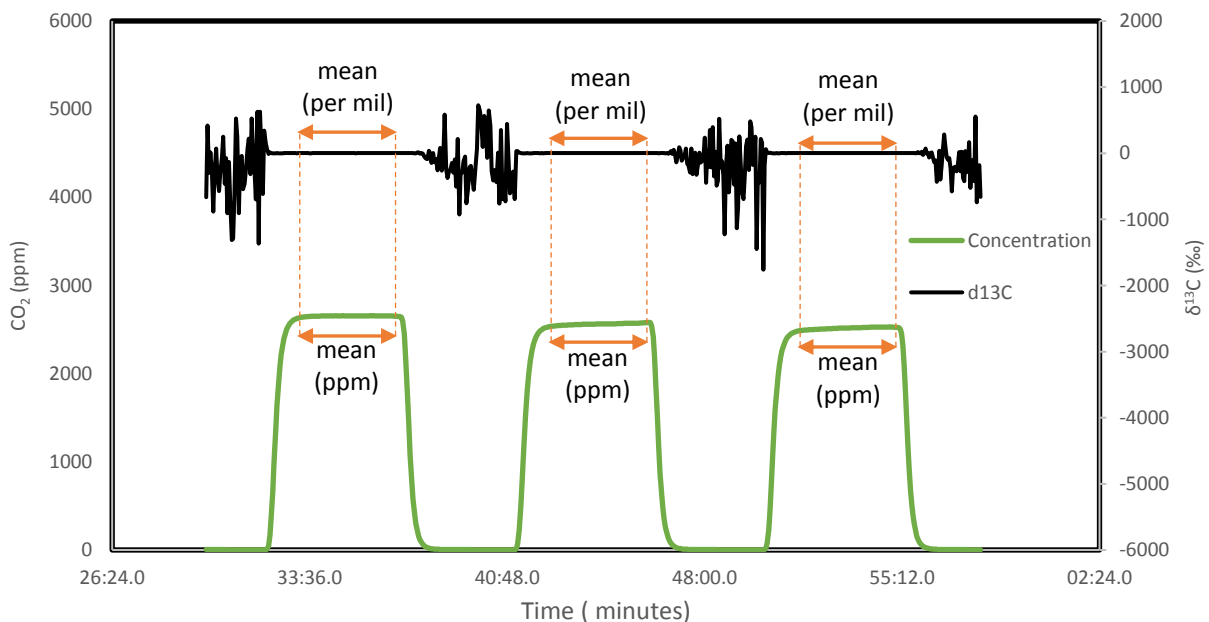


Figure 2 – Measurements of three replicates of the same isotopic standard. Concentration data (green) shows three stable plateaus when the standard is connected. Measurements are separated by measurements of pure zero-air as a background (not required). Isotopic measurements are very noisy when zero-air is measured, since both ¹²C and ¹³C are below the detection limit, but once CO₂ is introduced the isotopic measurements become very stable. In this example, the precision of our isotopic standard over three replicates is ± 0.1 per mil.

On each Picarro analyzer, the user has access to *Data Recal* – a software tool designed to aid in the calibration of the analyzer (Figure 4). In it, the “reported” (and averaged) standard values are compared to their “certified” values and plotted on a linear correlation plot (Figure 3). The following plot serves as a visual representation of the linear calibration and the selected range of isotopic compositions from the geothermal example.

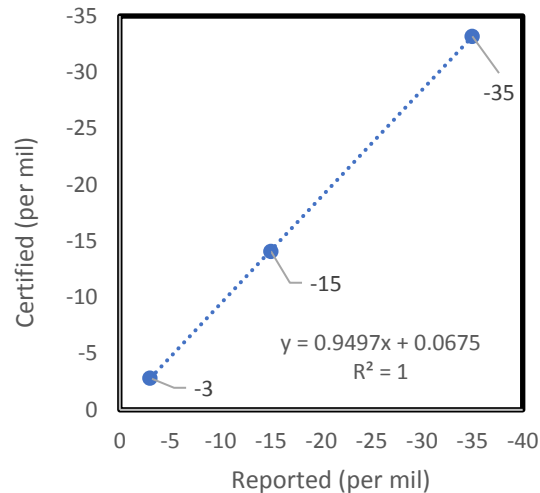


Figure 3 – A linear calibration plot with standard separation that covers the complete range of samples from -3 to -25 ‰. Each blue dot represents an average value our isotopic standards selected to cover this range.

In certain applications it might be difficult to obtain isotopic standards that cover the complete compositional range of your expected dataset. In such cases, it is important that a good linear calibration with 3 or more standards is performed. The performance of the analyzer past the last reference point (e.g. point -35 ‰ in figure 3) is linear, but be mindful of a possible degradation in accuracy. Exactly how much will depend on your R^2 regression.

NOTE: Carrier gas – Picarro analyzers can measure isotopic samples in a matrix of air and/or pure nitrogen. Most analyzers by default will measure in a matrix of air, but this can be expanded to a matrix of pure N_2 if an additional mode is installed. Because a change in the N_2 - O_2 ratio can affect spectral broadening it is important that sample measurements and system calibrations are performed in the same mode. If the N_2 - O_2 ratio changes post-calibration, the isotopic measurements will be affected (by ~5 to 10 per mil, between zero-air and N_2). With custom standards, samples with custom N_2 - O_2 gas matrix compositions may be measured.

3.3.1 Concentration dependence of isotope analyzers

An important factor to consider in any isotope analyzer based upon an optical absorption measurement is the concentration dependence of the measurement of delta. The isotope ratio reported by the instrument is based upon the measurement of two distinct absorption lines (one for each isotopologue). Each of these measurements have their own slope and offset, each of which can drift a small amount over time. Once the ratio of these measurements is computed to derive the isotope ratio, the drift can exhibit

a nonlinear dependence on concentration. The concentration dependence exhibited by the G2132-*i* is described in detail in Rella et al. (2015); this treatment can be generally applied to other isotope analyzers.

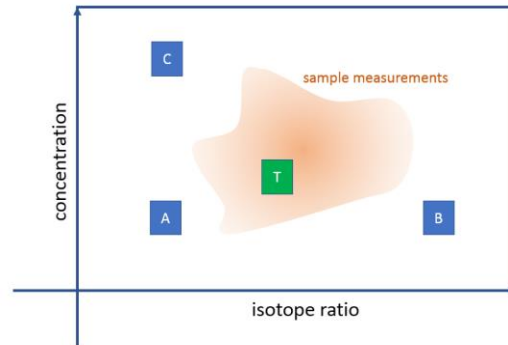
The slope and offset calibration method for isotopes, described above, applies when the concentration of the standards and the sample are the same. If the concentrations differ between the measurements of the standards and the sample, then a calibration error can be introduced if the effect of concentration on the calibration is ignored. Any error in the slopes of the individual isotopologue measurements appears as drift in the slope and offset of the delta calibration, above. A drift in the offsets, however, appears as a concentration dependence in the reported isotope ratio that is, to lowest order, of the form $\frac{c_0}{c}$, where c is the concentration of the gas in the sample or standard, and c_0 is a small coefficient that can vary from instrument-to-instrument, and over time. It is often the case, in practical situations, that the drift in c_0 causes errors in isotope ratio that is equal to or larger than the drift in the isotope ratio slope and offset parameters from Fig. 3. It is therefore important to include at least two concentrations at the same (or similar) isotope ratio in the calibration regime of almost all isotope analyzers, so that c_0 can be quantified over time. The two concentrations should span the full range of concentrations that will need to be calibrated in the final measurement, including the variability in the sample and the variability in the standards themselves.

The table below lists typical ranges of values for c_0 , for different instrument types. In other words, any given instrument can be expected to explore the range of values of c_0 listed in the table. These values should be used to guide the calibration strategy, but should not be viewed as specifications.

Instrument	Measurement	c_0
G2201i, G2131i, G2121i, G2101i	$\delta^{13}\text{CO}_2$	$\sim \pm 0.5$ ppm CO ₂
G2201i, G2132i, G2210i	$\delta^{13}\text{CH}_4$	$\sim \pm 5$ ppb CH ₄
L2120i, L2130i, L2140i	$\delta^{18}\text{O-H}_2\text{O}$	$\sim \pm 1$ ppm H ₂ O
L2120i, L2130i, L2140i	$\delta\text{D-H}_2\text{O}$	$\sim \pm 5$ ppm H ₂ O
G5101i, G5130i, G5131i	$\delta^{15}\text{N-N}_2\text{O}$	$\sim \pm 1$ ppb N ₂ O

Example: A drift of 1 per mil at 400 ppm CO₂ means that $c_0 \sim 0.001 * 400 = 0.4$ ppm. (0.001 is the fractional expression of 1 per mil).

An example of a calibration scheme is shown in the figure below. Three standards (A, B, and C) are used to calibrate the instrument by bracketing the range of values expected from the experiment, and a separate calibrated target T is used to confirm that the calibration system and the instrument are operating properly.



3.4 Slope and Offset of Calibration

Every Picarro analyzer ships with a default user calibration value of 1 for slope and 0 for offset. While new user calibrations will likely result in changes to both, we recommend that only offset changes are applied during more frequent calibrations.

If a new slope calibration is to be applied, the user must be mindful of their experimental uncertainty. For example, a change in the slope calibration from 1 to 0.95 may not represent a change in the system's linearity, but may simply reflect the experimental uncertainty. If during your slope calibration, a new value of 0.9 or 0.85 is suggested by the Data Recal tool (Figure 4), please repeat the measurements of your standards. In most cases, such large changes in slope are a result of uncertainty and do not indicate a bad non-linearity of the analyzer. If your analyzer continues to suggest a large change in slope, please consult with Picarro Support before applying a new calibration.

NOTE: If you are uncertain about the state of your current slope and offset values, they can be reset back to their user default values of 1 and 0, respectively. In your Picarro GUI, navigate to "Tools -> User Calibration -> (password: picarro) ->" Then change the slope and offset values of your parameter of interest to 1 and 0, respectively.

1. Select parameter you want to calibrate (e.g. CO₂, δ¹³C, H₂O, ...)

2. Enter values for “Certified” and “CRDS reported” values of the standard you measured. **ENABLE** them by selecting the “Used for Recal” box.

3. Select if you want to calibrate “Offset only” or “Slope and Offset”.

4. Your current and new calibration values will be displayed here once you click “Compute”. 0 and 1 represent factory default values for Offset and Slope, respectively.

Used for Recal	Certified	CRDS Reported	Recalibrated
<input type="checkbox"/>	0.00000	0.00000	0.00000
<input type="checkbox"/>	0.00000	0.00000	0.00000
<input type="checkbox"/>	0.00000	0.00000	0.00000
<input type="checkbox"/>	0.00000	0.00000	0.00000
<input type="checkbox"/>	0.00000	0.00000	0.00000
<input type="checkbox"/>	0.00000	0.00000	0.00000
<input type="checkbox"/>	0.00000	0.00000	0.00000
<input type="checkbox"/>	0.00000	0.00000	0.00000
<input type="checkbox"/>	0.00000	0.00000	0.00000
<input type="checkbox"/>	0.00000	0.00000	0.00000
<input type="checkbox"/>	0.00000	0.00000	0.00000

Data Options: H₂O

Calibration Options: Offset Only

	Current Calibration	New Calibration
Offset	0.00000	0.00000
Slope	1.00000	0.00000
R2		0.00000

Buttons: Compute, Apply New Cal, Clear Entries, Exit

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Figure 4 – Screenshot of the Picarro Data Recalibration tool (DataRecal) installed on every Picarro analyzer. A more detailed guide is included in the analyzer manual.

3.5 Offline Correction

If the user is not comfortable with changing the calibration of the analyzer, an offline correction of the dataset is recommended. Measuring standards along with samples is good practice regardless and it enables the user to correct their data for slope and/or offset offline. Be mindful that in order to correct for slope, at least 2-3 standards must be included between your samples, whereas for offset corrections, only 1-2 is sufficient. One place where a similar correction occurs is the ChemCorrect software package available on Picarro water isotopic analyzers (e.g. L2130i).

4. Frequency of Calibration

There is no golden rule that determines how often a Picarro analyzer needs to be calibrated. Every spectroscopic instrument suffers from a small amount of drift. The user must assess if the amount of instrumental drift affects their sample measurements and ultimately, the resolution of their final dataset. A powerful tool that aides in the characterization of precision and drift is the Allan Variance plot. Each Picarro analyzer ships with a Certificate of Compliance (CoC) that reports which tests have been performed to guarantee the drift and precision. Data from these CoC tests is used to create an Allan Variance plot specific to that instrument. The following example illustrates how an Allan variance plot is constructed for the G2131i isotopic CO₂ analyzer and how it may be used to determine the precision and frequency of calibration.

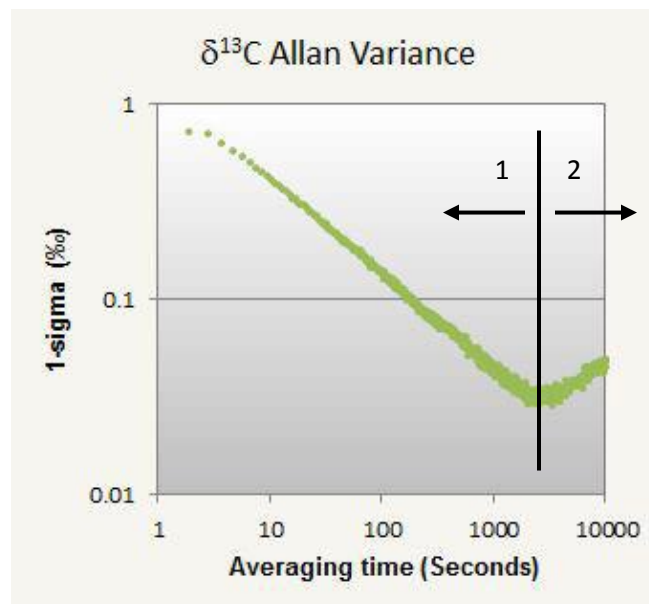


Figure 5 – The following Allan Variance plot was constructed by connecting the G2131i analyzer directly to a tank of 380 ppm CO₂ for 24 hours. At short averaging times, the Allan deviation is large due to instrument noise. As averaging times increase, the Allan deviation improves (zone 1). However, after a certain period of averaging time, the drift of in the instrument begins to increase and dominate, leading to an increase in the Allan deviation (zone 2).

The Allan variance plot in Figure 5 tells the user that to achieve 0.1 ‰ precision on a single measurement, an averaging time of ~300 seconds must be used. In other words, a single sample needs to be measured for at least 5 minutes. At about 2000-3000 seconds, the instrumental drift begins to dictate the precision and the error on a single measurement begins to increase. Over 24 hours and 1-hour averaging intervals the drift of a G2131i is characterized as 0.5 ‰ (listed in CoC). Using the CoC and the Allan Variance plot the user must decide if re-calibration or offline post-correction is the most appropriate method to correct for instrumental drift.

NOTE: All Picarro analyzers ship with a data viewing program called *DatViewer*. Newer versions of this software enable the user to create an Allan variance plot.

As a general guideline for both isotopic and concentration analyzers, we recommend a three-point standard check at the beginning of a longer analytical session. If adjustments to slope and offset are required, this is the best time to apply them.

Analytical Session	Frequency and Calibration type
Short	For datasets collected within 24 hours we recommend you use secondary standards between your sample runs and correct for drift (i.e. offset) in an offline fashion.
Intermediate	For analytical sessions lasting for a week, a periodic check and re-calibration of the offset is recommended. Offline correction remains an option.
Long	A recalibration of both the slope and offset is usually required over a month or longer. For more on slope and offset see Section 3.4. Offline correction remains an option.
All times	Regardless of your calibration frequency, we recommend you use secondary standards as period checks of the instrument drift and performance. It is good analytical practice and it gives the user the ability to post-correct the data without losing valuable sample measurements.

NOTE: For more information on application specific calibrations see Section 5.

5. Application Specific Examples of Calibration

Picarro analyzers are compatible with a variety of front ends, peripherals and modes of sample delivery. It is important to consider when to calibrate the analyzer only, versus the system as a whole. Our recommendation is that if your analyzer will be used primarily with a front-end, that you calibrate the system as a whole (see section 5.2). If you plan to use your analyzer as a standalone instrument, with only occasional use of front-ends, we suggest you calibrate the analyzer only (see section 5.1 and 5.3) and post-correct the effects of peripherals using secondary standards.

Here we present three examples of calibration, from three different applications and using three different analyzer setups. Picarro analyzers are compatible with many other front-end than the ones listed here, so if you are unsure which practice applies to your system, consult with Picarro Support (support@picarro.com) or a Picarro application scientist.

CAUTION: Pressure and flow - When the analyzer is connected directly to a pressurized gas tank or a sample container, the user needs to be mindful of sample flow and pressure (1-3 psi range). If the pressure and flow are too high or too low, damage to valves and the cavity may occur. In either case, the data collected by the analyzer may also be affected. Please refer to the respective analyzer manual or datasheet for a listing of the recommended inlet flowrate.

5.1 Analyzer only

Primary standard example: NOAA (<http://www.esrl.noaa.gov/gmd/ccl/services.html>)

Secondary standard example: Air Liquid (<https://industry.airliquide.us/scott-gas-mixtures>, enquire about Picarro's Air Liquid datasheets)

When calibrating a concentration analyzer, such as the G2508, the user has the option to connect the standard to the analyzer directly from a tank or using a Tedlar bag. Direct connections to a tank are preferred as they minimize the chance of leaks and eliminate any dilution of the standard from remnant gas in the bag. Tedlar bags are an acceptable option but they may lead to a lower degree of confidence in calibration. It is up to the user to determine how accurate they are in their preparation of Tedlar bags and in turn how confident they are about their final calibration (see section 3.1). For applications where 1-10 ppm levels of accuracy are required, a direct connection to a tank is recommended, or the use of precise mass flow controllers (MFC).

The same steps can be applied to the calibration of an isotopic analyzer such as the G2201i. Because the concentration dependence of our isotopic analyzers is very low, Tedlar bags become a much more attractive option. The user may purchase a high concentration isotopic standard in a tank, which he or she can then dilute with an appropriate carrier gas to produce isotopic standards in Tedlar bags at desired concentrations. Example - Higher concentration standards may be transported in the field in portable culture tubes, and zero-air can easily be generated using a portable pump and Ascarite (sodium hydroxide). This example demonstrates how the user may prepare and analyze isotopic standards in the field.

Companies that provide gas standards can often create custom mixtures of gases at desired concentrations. Concentration analyzers that measure multiple species can thus be calibrated using a single standard tank and a tank of zero-air. Using MFCs, the user can then dilute the standard down to three or more concentration reference points. Isotopic analyzers that measure multiple species may also combine them in a single tank (e.g. CO₂ and CH₄), but the user will require different tanks for different isotopic compositions. It is difficult to mix your own standards with custom isotopic ratios.

5.2 Analyzer and front-end (L2130i)

Primary standard example: IAEA (<https://nucleus.iaea.org/rpst/referenceproducts/referencematerials/>)

Secondary standard example: Picarro (Secondary Water Isotopes Standards Kit)

The L2130i isotopic water analyzer is typically paired with a vaporizer and an autosampler. Since the L2130i is regularly used with a vaporizer and autosampler, we typically calibrate the system as a whole, not the analyzer directly. Therefore, the analyzer is calibrated using water standards loaded onto the autosampler where they are collected, vaporized and introduced to the analyzer as water vapor.

NOTE: Certain analyzers, such as the L2130i have a special mode that supports the measurement of liquid and gas samples using only liquid standards for calibration. Unless your analyzer has a special mode that supports such cross-compatibility, please calibrate the system as a whole and not the analyzer only.

Analyzers that measure “sticky” molecules, such as H₂O and NH₃, are more prone to memory effects. When performing calibration and sample measurements of these molecules it is important that the strength of this memory effect is characterized (Figure 6). The calibration procedure is an excellent opportunity to do so, including the L2130i. The strength of the memory effects is a function of the relative difference in isotopic composition between your standards or samples and tends to be stronger for δD. While the general approach to calibration as outlined in sections 3 can be taken, an additional test is often useful to define the number of replicates required for accurate measurements of “sticky” molecules. The following example illustrates how memory might affect the number of replicates you need to measure.

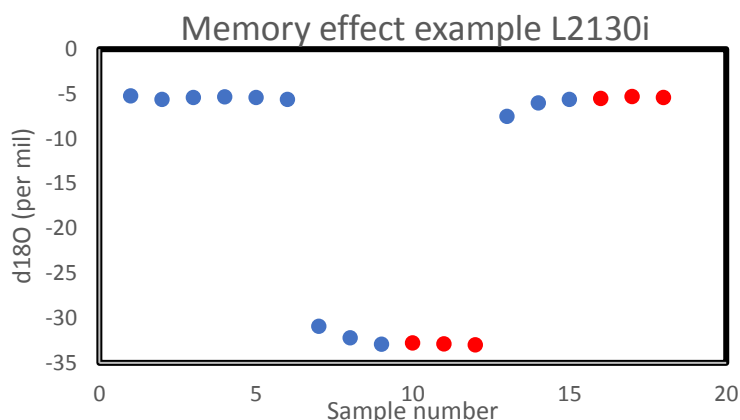


Figure 6 - An example dataset in which two isotopic water standards were measured back-to-back with six replicates each. The last three replicates (in red) are within 99 % of the true value of the standard. Depending on your standard (or sample) isotopic separation, the memory “tail” might be longer or shorter. In other words, you might require more or less replicates to make accurate measurements.

For additional details on how to determine the memory of your water system, please refer to the following guide available on the Picarro Community:

http://www.picarro.com/resources/knowledgebase/water_isotope_analyzers/memory_what_is_it_and_how_do_i_manage_it

5.3 Analyzer and front-end (Combustion Module)

Primary standard example: USGS (<https://isotopes.usgs.gov/lab/referencematerials.html>)

Secondary standard example: Potato starch and corn starch

The Picarro-CM-CRDS is typically paired with an analyzer that can measure the $\delta^{13}\text{C}$ composition of CO_2 . For this example, we are going to consider that the CM is paired with a G2131i analyzer. The user does most of his primary research on atmospheric CO_2 with only periodic experiments with combustion. In such a scenario, we would recommend that the analyzer is calibrated using primary and secondary gas standards, and that primary and secondary combustion standards are only used for offline post-correction of his data.

If the CM becomes a permanent configuration, then we would recommend the analyzer is calibrated by introducing solid or liquid samples into the CM. That way, the system calibration takes into account any effects introduced by the CM or the intermediate peripherals (Liaison or Caddy). The effects of these front-ends, if installed and configured properly, is constant and can thus be part of the system calibration.

The selection of liquid or solid samples would follow the sample selection procedure as outlined in section 3 and the same sample calibration steps as outlined in section 4. Depending on the composition of your samples and the proportion of water in them, an estimation of memory may also be useful. See section 6.2 on how to estimate the memory of your system.

5.4 Isotopic N₂O standards

Secondary, site-specific isotopic standards for N₂O are difficult to obtain and only a few are commercially available from the USGS (<https://isotopes.usgs.gov/lab/referencematerials.html>) and Air Liquide (please refer to their product data sheet).

Currently, the only acceptable primary reference is managed by Prof. Naohira Yoshida (Institute of Technology, Tokyo, <http://nylab.chemenv.titech.ac.jp>).

Secondary isotopic N₂O standard provider: <http://www.airgas.com> (by Air Liquid)

7. Materials and Resources

Primary Calibration Standards

- IAEA (<https://nucleus.iaea.org/rpst/referenceproducts/referencematerials/>)
- NOAA (<https://www.esrl.noaa.gov/gmd/ccl/services.html>)
- USGS (<https://isotopes.usgs.gov/lab/referencematerials.html>)

Secondary Calibration Standards

- Air Liquid (<https://industry.airliquide.us/industries/research-and-analysis>)
- PraxAir (<http://www.praxair.com/>)

Tubing, Connectors and Valves

- Swagelok (<https://www.swagelok.com/>)
- Valco (<https://www.vici.com/>)
- Omega (<http://www.omega.com/prodinfo/flowmeters.html>)
- Alicat (<http://www.alicat.com/products/mass-flow-meters-and-controllers/mass-flow-controllers/>)
- MKS (<https://www.mksinst.com/product/catalog.aspx?CatalogID=3>)
- USA Plastic (<https://www.usplastic.com/catalog/default.aspx?catid=864>)

Sampling Bags and Syringes

- Calibrated instruments (<http://www.calibrated.com/>)
- Restek (<http://www.restek.com/>)
- Sigma Aldrich (<https://www.sigmaaldrich.com/>)
- Fisher Scientific (<https://www.fishersci.com/>)

Picarro Calibration References from Literature

Rella, C.W., et al., “Local- and regional-scale measurements of CH₄, δ¹³CH₄, and C₂H₆ in the Uintah Basin using a mobile stable isotope analyzer,” *Atmos. Meas. Tech.*, 8, 4539–4559, 2015.