

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.



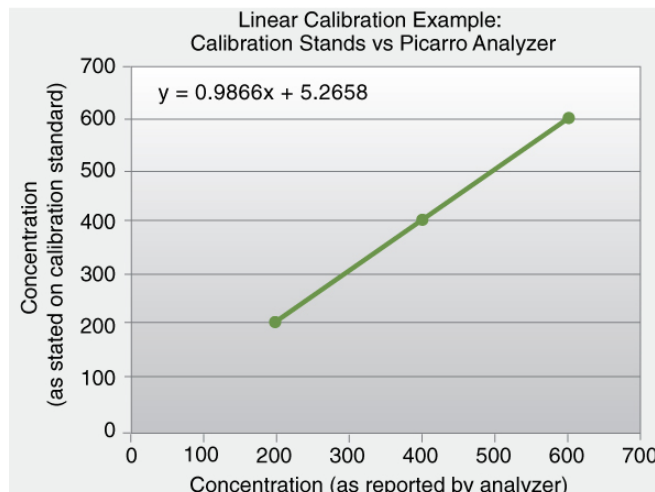
Summary and Relevance:

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 the 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 analyzer's reported concentration values in this way, a calibration offset (slope and intercept) can be calculated so as to add a correction term to the analyzer's 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: $Data_{corrected} = 0.9866 \cdot Data_{raw} + 5.268$.

	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.

A note on calibrating isotope analyzers: The concentration and isotope calibrations are separately specified in the calibration file of isotope analyzers and they are not linked, therefore, the calibration for concentration must be done separately from that for isotope ratio. Isotope calibrations are accomplished in the same manner described above, but with gas standards differing in isotopic content, ideally measured at the same concentration.

A note on calibrating ammonia, water vapor and hydrogen fluoride: Since these gases are extremely sticky, it is therefore difficult to easily create a known calibration sample of such gases. The best means of doing so for hydrogen fluoride and ammonia gas, for example, is by using a calibrated permeation tube (available from companies such as Kin-Tek: www.kin-tek.com/permeat.html). Such tubes produce a known amount of gas depending on the temperature of the oven in which the tube is enclosed. The amount of gas can be further reduced by diluting it with dry gas and introducing that mixture into the analyzer. For water vapor, a dew point generator can be used. Typically, a zero (or very low level) of gas and some “span” or higher level will be sufficient to calibrate the analyzer, though interspersed values can be used as in the method described above to further constrain the “best fit” calibration line. When calibrating these gases, care must be taken to minimize sample lines and to wait an adequate amount of time after introducing the gas into tubing and connections so that it uniformly coats all surfaces and so that all adsorption sites within the plumbing are filled and not causing anomalous drops in concentration as it continues to stick to internal surfaces. Once the analyzer is reading a stable value for the concentration only then should the data be considered stable and of a quality to be used in calibration. Depending on flow rates and gas concentration levels, this can take from minutes to hours (if, for example, a high amount of hydrogen fluoride or ammonia is introduced into long sample lines and subsequently, zero-air is then introduced).