

SI2104: Traceable calibration of Hydrogen Sulfide (H₂S)

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Abstract

In this white paper, we discuss the calibration of Hydrogen Sulfide in Picarro’s Cavity Ring Down Spectrometers.

History

Version	Release Date	Author	Notes
0.1	2017 0624	C. Rella	Initial Draft
0.2	2017 0625	C. Rella	Modified water vapor description
0.3	2017 0626	C. Rella	Additional HITRAN reference

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Spectroscopy

Hydrogen Sulfide (H_2S) is measured in the near infrared region of the spectrum. Figure 1 shows the spectral region that the instrument uses to quantify H_2S , H_2O , and CO_2 . The CRDS instrument rapidly (in about 2-5 seconds) scans this spectral region using a narrowly tunable Distributed Feed Back (DFB) fiber-coupled laser. The resulting spectrograms are analyzed using a non-linear least squares optimization algorithm, using pre-calculated model functions for each of the spectral features in this region. The concentrations of H_2S and CO_2 are reported by the instrument on the user interfaces and the data logs. The water vapor spectrum is associated with a rare isotopologue of water in which one of the two hydrogen atoms is replaced with a deuterium ($^1H^2H^{16}O$). The concentration of this rare species of water does not provide an accurate measurement of total water vapor in the sample gas, and is therefore not reported on the user interfaces.

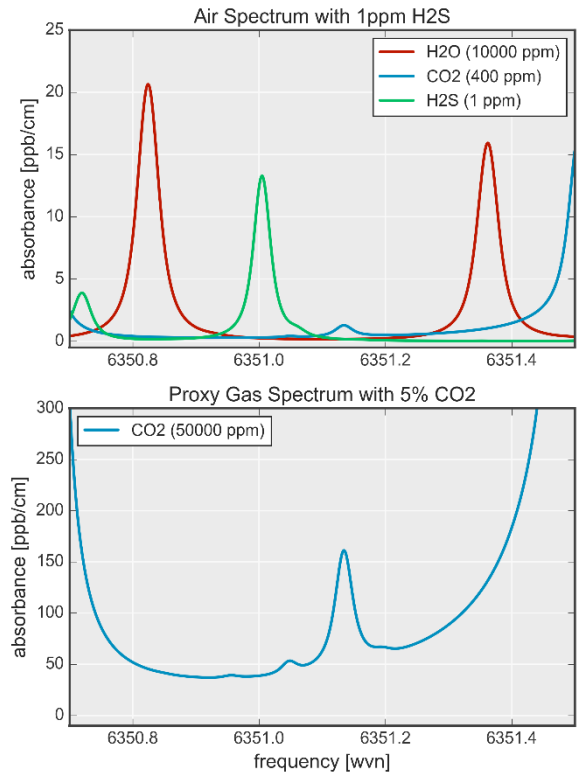


Figure 1: H_2S spectral region, showing major features for H_2O and CO_2 . CO_2 can be used as a 'proxy' for the calibration and proper operation of the instrument.

Original Calibration of H_2S at Picarro

In 2008, Picarro measured the calibration factor of an early H_2S instrument, using a single gravimetrically prepared gas bottle. This calibration factor of 79.575 ppb H_2S per ppb/cm has not been changed until the release of the SI2104 instrument.

Gravimetric calibration of H_2S for the SI2104

For the calibration of the new instrument, we have obtained three gravimetrically prepared standards of H_2S in specially coated cylinders from AirGas, Inc. These standards were prepared with concentrations of about 1 ppm, 5 ppm, and 10 ppm H_2S in air. In addition, a cylinder of pure zero air containing nominally zero H_2S was also used in the calibration process. Using a Silconert-coated regulator and PFA tubing, the gas from each of these cylinders were directed sequentially into the inlet of the H_2S analyzer. The reported H_2S concentration was allowed to stabilize for several minutes before recording the result. The 1 ppm and 10 ppm bottles were measured twice at different times in the calibration process to verify the repeatability of the measurements. The figure below shows one representative time series from this experiment, showing the evolution of the H_2S concentration as reported by the analyzer during the measurement of the 5 ppm bottle.

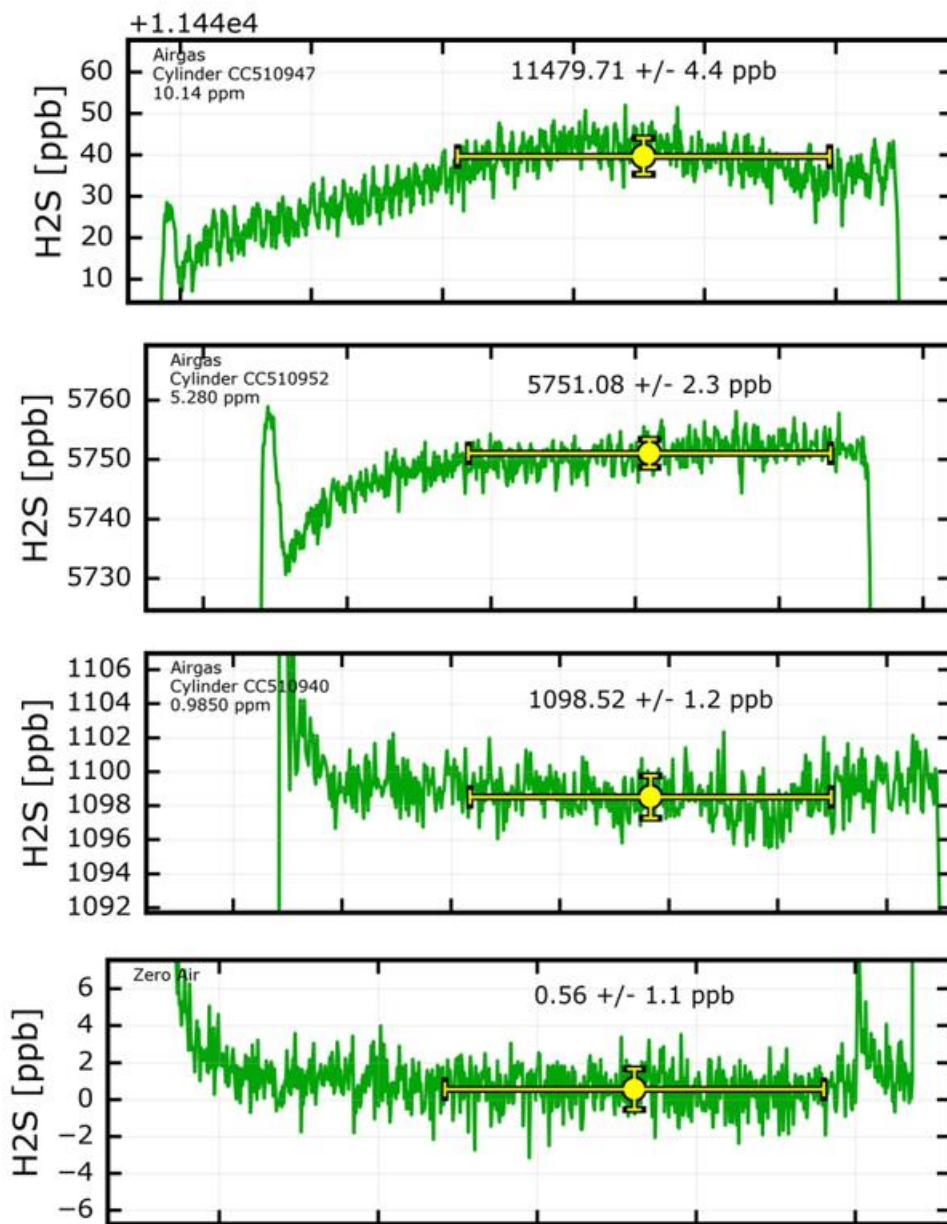


Figure 2: Cylinder measurements of H₂S in air, for 10 ppm, 5 ppm, 1 ppm, and zero air. The green curve indicates the raw time series reported by the analyzer; the yellow point indicates the mean value of the measurements reported over the time represented by the yellow horizontal error bar; the vertical error bar indicates the standard deviation of the measurement over this time period. The values associated with the mean and standard deviation are shown above the yellow point. The analytical value as reported by the manufacturer for each cylinder is listed in the upper left of each panel.

The results from the measurements of the cylinders are plotted against the assigned value associated with the analytical measurement as reported by the manufacturer of the gas cylinder. This calibration plot is shown in Fig. 3. The slope from the linear fit is 1.117, indicating that the instrument, using the calibration factor of 79.575 ppb per ppb/cm, reports *higher* than the actual amount by about 12%. In other words, the proper correction factor determined from this four-bottle experiment is 71.233 ppb H₂S per ppb/cm.

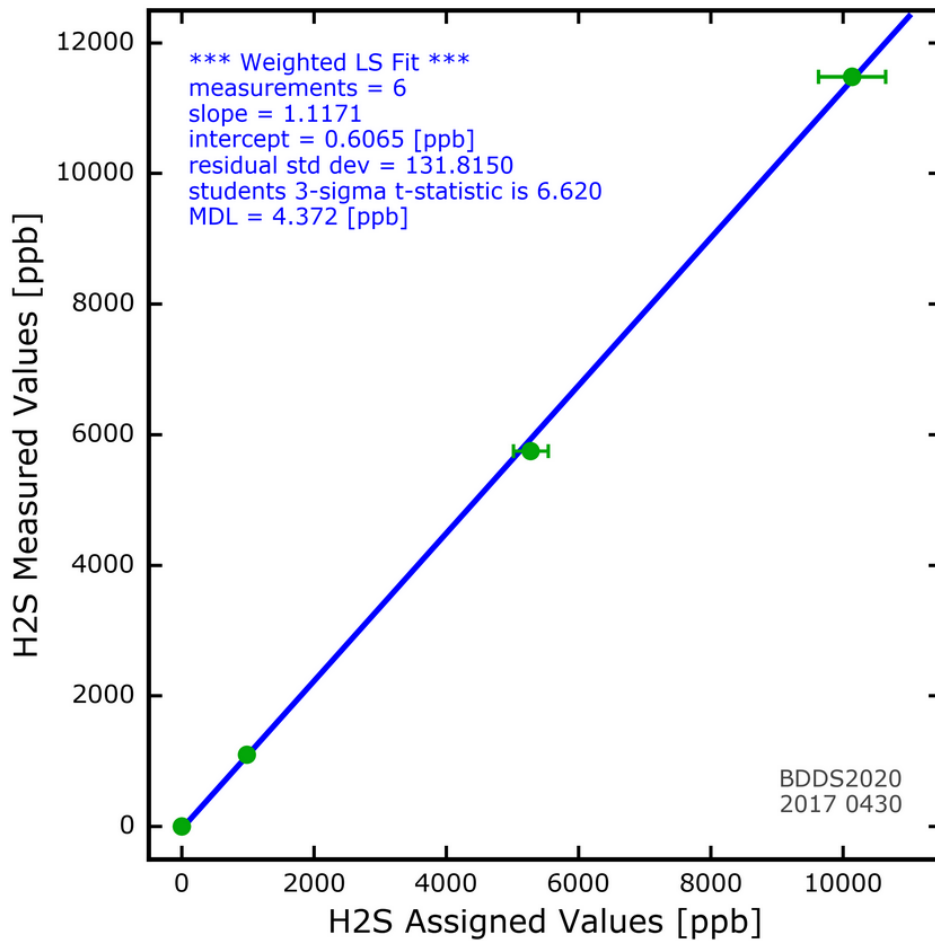


Figure 3: measured cylinder values plotted against the assigned values for each cylinder (green symbols). The horizontal error bars indicate the analytical accuracy as determined by the manufacturer. The vertical error bars are given by the standard deviation of the individual measurements (as determined in Fig. 2); they are smaller than the size of the symbol. The slope of 1.117 ppb / ppb and the offset of 0.61 ppb is the result of a weighted least squares fit to a line (indicated by the blue line).

Validation of the H₂S Calibration

Cylinder Value Reassignment

The instrument can be used as a transfer standard to adjust the bottle assignments such that they lie on the best fit calibration line in Fig. 3 with a slope of 1.1171. The new assigned values for each cylinder are shown in the table below.

Cylinder #	assigned value (from manufacturer)	Measurement	Adjusted Assigned Value	% difference
CC510947	10.14 ppm	11.482 ppm	10.2784 ppm	+1.36%
CC510952	5.28 ppm	5.751 ppm	5.1482 ppm	- 2.50%
CC510940	0.985 ppm	1.0985 ppm	0.9834 ppm	- 0.16%

Each cylinder assigned value is shifted by < 3% in all cases, which is less than the 5% stated analytical accuracy of the cylinder assignments from the manufacturer. We therefore conclude that the calibration determined from this experiment is consistent with the reported accuracy of each of the cylinders.

HITRAN Spectral Database

We have used the HITRAN database (Rothman et al. 2012¹, Kochanov et al. 2016²) to directly calculate the absorption of the H₂S spectral line employed in the Picarro H₂S instrumentation. Using the intensity value, ground state energy, and partition function from HITRAN, and our measured line shape parameters to relate integrated absorption to peak absorption, we arrive at a calibration 75.30 ppb H₂S per ppb / cm, which is 5.7% greater than the 71.233 value based on the measurement based upon the four gravimetrically prepared cylinders. We note that the HITRAN database provides an uncertainty for this line of 5-10 %, which is consistent with the observed discrepancy between the HITRAN calculation and the gravimetric calibration.

Calibration Summary

We summarize the calibration results in the table below:

Method	Calibration Slope	Relative Slope
2008 Direct Cylinder Calibration	79.575	1.117
2017 Four Cylinder Calibration	71.233	1.000
Hitran 2012 Result	75.300	1.057

Final Conclusion: Picarro will apply the four cylinder calibration factor to all SI2104 instruments.

Method for Calibration of Individual Instruments

Because H₂S is a reactive gas that can adhere to surfaces, it is difficult to prepare and deliver a constant and known concentration of H₂S, a fact which complicates individual instrument calibration. The desire to have all instruments measuring the same value further complicates the situation. We have therefore selected the following calibration approach:

1. Carefully calibrate a “Golden” instrument. We have described this process in detail in the preceding sections.
2. Use this Golden instrument as a transfer standard to cross-calibrate each instrument built at the factory. Using the Golden instrument as the calibration reference, rather than the gas preparation system, means that the stability and repeatability requirements for sample preparation can be relaxed dramatically.

¹ Rothman, Laurence S., et al. "The HITRAN2012 molecular spectroscopic database." Journal of Quantitative Spectroscopy and Radiative Transfer 130 (2013): 4-50.

² R.V. Kochanov, I.E. Gordon, L.S. Rothman, P. Wcislo, C. Hill, J.S. Wilzewski, HITRAN Application Programming Interface (HAPI): A comprehensive approach to working with spectroscopic data, J. Quant. Spectrosc. Radiat. Transfer 177, 15-30 (2016).

3. Ensure the calibration of the Golden instrument over time by checking the calibration of this instrument with a non-reactive proxy gas. In the case of H₂S, this proxy gas is CO₂.

The apparatus used for performing the cross-calibration experiment is shown below. The flows through the MFCs are set to produce a set of concentration challenges to both instruments simultaneously. Because the two instruments share a single gas preparation system, losses of H₂S in this system do not affect the ultimate calibration of the Device Under Test (DUT).

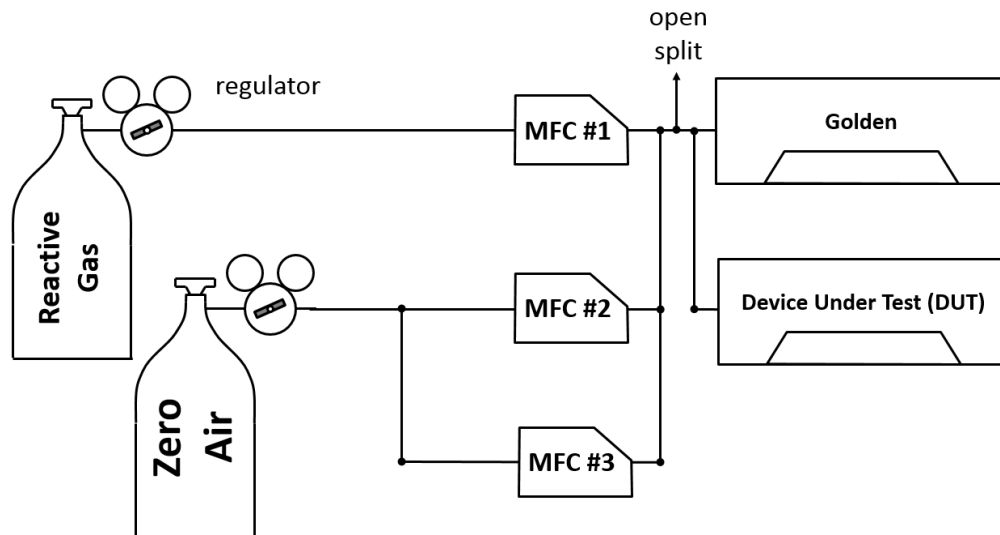


Figure 4: Cross-calibration setup used to transfer the calibration of the Golden instrument onto the DUT.

For a typical dilution profile, we keep MFC #2 and MFC #3 at a constant flow of 500 sccm and 2 slm, respectively, and step MFC #1 from 1 to about 20 sccm and back down, over a period of several hours. This pattern is generally repeated twice. A typical time series is shown below.

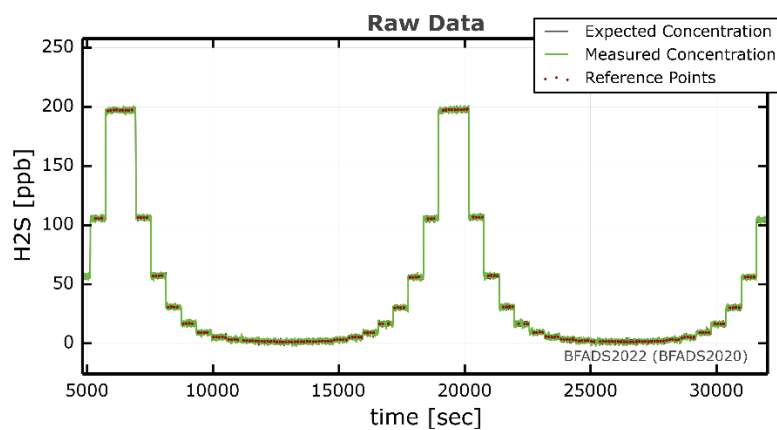


Figure 5: Time series for the Golden Instrument (BFADS2022, in gray) and the DUT (BFADS2022, in green). The reference points (shown in red) are selected from both time series to meet minimum criteria for stability. These points are used in further analysis.

Note that it is not necessary to assume that the concentration delivered by the dilution system is determined by the concentrations in the bottles and the flows through the MFCs – the Golden instrument provides traceability to the DUT. From these data we can determine the calibration of the instrument, by plotting the DUT measurements as a function of the Golden instrument values. These calibration data are shown in Fig. 8. To create this figure, we determine the slope (1.0003 ppb / ppb) and offset (-0.70 ppb) from the first cycle of data, and then we apply that slope and offset to the second cycle of data. This second cycle of data are plotted in Fig. 6.

It is important to note that this slope and offset are **not** applied to the DUT instrument calibration itself; the DUT retains the default calibration of 71.233 ppb H₂S per ppb/cm that is applied to all instruments, for the following reasons:

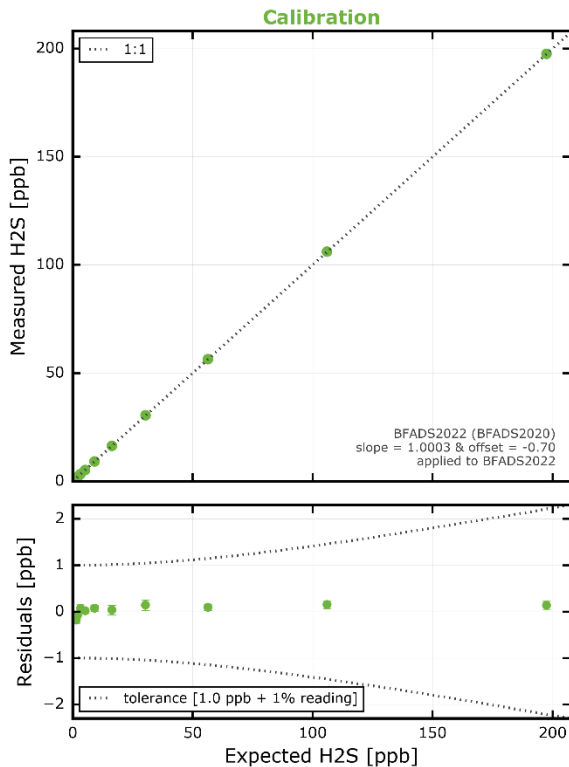


Figure 6: Calibration data derived from Fig. 5.

We do apply a pass / fail check on the calibration curve: the calibration slope must be within 5% of 1.0 (i.e., $0.95 \leq \text{slope} \leq 1.05$). If the test passes this criterion, then the standard calibration constant of 71.233 ppb H₂S per ppb/cm is retained; if the test fails, we investigate the failure and rework the instrument. In addition, the residuals of the calibration curve must lie within the gray dotted lines on the lower panel of Fig. 8.

1. The response times of the two instruments are not identical, which can lead to small but measurable differences in the signals observed on the two instruments as the concentration system, even though they share an inlet and sample preparation system. These differences can distort the calibration curve.
2. Because H₂S is retained on the wetted surfaces of the instruments, sometimes for many minutes or more, the fact that each instrument may have been exposed to differing amounts of H₂S can also distort the calibration curve.

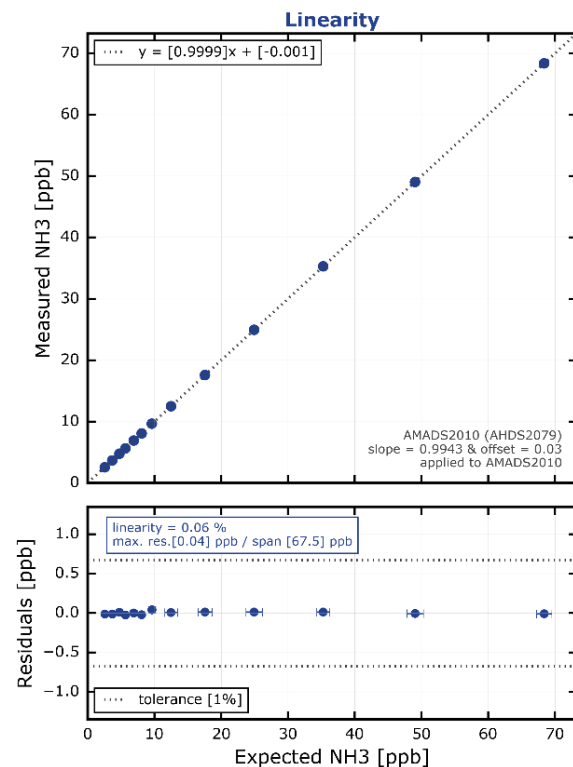


Figure 7: Linearity plot.

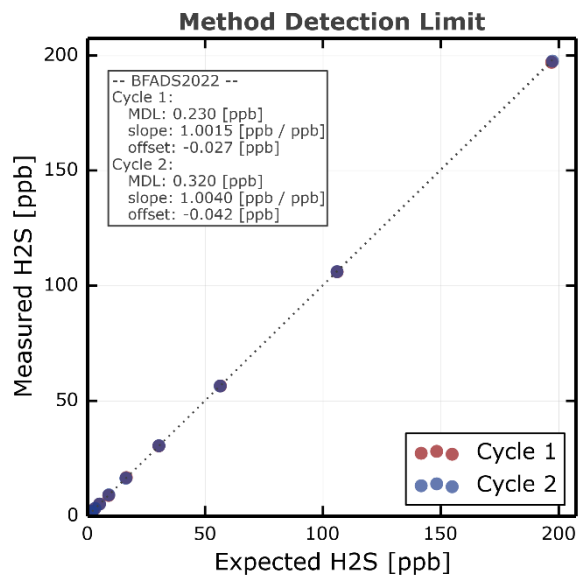


Figure 8: MDL plot

From this second set of data, we also derive the linearity of the instrument³, which is defined as the ratio of the maximum excursion of the residual from a linear fit to the total span of concentration. Figure 7 shows this linearity plot; the gray dotted lines in the lower figure indicate the requirement of 1% for the linearity.

Finally, from each cycle, we can determine the Method Detection Limit (MDL)⁴. The MDL data are shown in Fig. 8. The MDL must be lower than 3.0 ppb on both cycles for the instrument to pass the test.

Stability of the Calibration Over Time

It is important to be assured that the calibration of each individual instrument will be stable between calibration verification events, which may occur as

frequently as once per year, or even more seldom. Due to the reactivity of H₂S on the surface of the gas cylinder, it is very difficult to keep H₂S standards stable for long periods of time. We therefore have little direct confirmation of the stability of our H₂S instruments over time. There exists however ample evidence of the stability of the calibration of CRDS spectrometers over time periods of months and years. In Yver Kwok et al. (2015)⁵, 47 Picarro CRDS instruments that measure CO₂, CH₄, and CO were studied, including 15 CRDS instruments that were calibrated in the field using highly accurate greenhouse gas standards. It was found that the calibration slope drifts typically about 0.1% / year; the largest drift observed overall was 0.3%. Because the CRDS spectrometers in these greenhouse gas instruments are functionally identical to the spectrometers used to quantify H₂S⁶, we may then conclude that the H₂S calibration slope in the SI2108 will exhibit a similar level of stability (<0.5%) over life. Because we expect the instrument stability to exceed our ability to deliver a known concentration of H₂S, we recommend a yearly calibration validation, using either the reactive gas H₂S itself, or, more simply, the non-reactive proxy gas CO₂. There is no need to perform a true calibration in which the calibration slope is changed according to the results of a direct H₂S calibration experiment.

³ IEC 61207-1

⁴ SEMI C10-1109

⁵ Yver Kwok, C., Laurent, O., Guemri, A., Philippon, C., Wastine, B., Rella, C. W., Vuillemin, C., Truong, F., Delmotte, M., Kazan, V., Darding, M., Lebègue, B., Kaiser, C., Xueref-Rémy, I., and Ramonet, M.: Comprehensive laboratory and field testing of cavity ring-down spectroscopy analyzers measuring H₂O, CO₂, CH₄ and CO, Atmos. Meas. Tech., 8, 3867-3892, doi:10.5194/amt-8-3867-2015, 2015.

⁶ The key exception is that the target wavelength as determined by the near-infrared spectra of the molecules is different. However, the pressure and temperature sensing and control systems, the wavelength monitor, the laser technology, the ring down cavity design, the electronics, and the firmware & software are all the same.

Summary

For all Picarro H₂S instruments (SI2104):

1. The calibration factor relating the optical absorbance in the measurement cell to the concentration of H₂S is the same value for all instruments: 71.233 ppb H₂S per ppb/cm of absorbance.
2. This calibration factor, derived from three gravimetrically prepared cylinders and zero air, has been validated against the 2012 HITRAN spectroscopic database, and against a second gravimetrically prepared cylinder.
3. The proper calibration of all instruments is verified at the factory using a Golden instrument. The stability of the Golden instrument will be verified periodically (about once / year), using both reactive H₂S and a non-reactive proxy gas, CO₂.
4. While in the field, the calibration of the instrument can be verified using a direct H₂S calibration experiment, or, more simply, by testing with CO₂.