

SI2205 and SI2306: Traceable calibration of Hydrogen Fluoride (HF)

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Abstract

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

History

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Spectroscopy

Hydrogen Fluoride (HF) is measured in the near infrared region of the spectrum. Figure 1 shows the spectral region that the instrument uses to quantify HF, H₂O, and O₂. 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 HF, H₂O, and O₂ are reported by the instrument on the user interfaces and the data logs.

Original Calibration of HF at Picarro

In 2008, Picarro measured the calibration factor of an early HF instrument (Model G1205) operating at a cavity pressure of 70 Torr, using a permeation oven and a certified permeation tube. Because Picarro instruments include careful measurements of the temperature and pressure of the gas, and because ringdown is an absolute measurement of the total loss in the optical cavity, the instrument-to-instrument repeatability is typically about 1%. For this reason, and because reactive gases are extremely hard to calibrate to better than 5-10% accuracy, we have elected to retain this calibration factor. In 2016, Picarro elected to increase the cavity pressure to 140 Torr, which allowed us to increase the flow (and thus the response time) dramatically. The original 70 Torr calibration factor was rescaled by taking into account the change in the number density in the cavity (i.e., a factor of 2 from the ideal gas law) as well as changes in the line shape when going from 70 to 140 Torr. The line shape was computed from a normalized Galatry profile in which the pressure-normalized γ - and z - were used to compute the line shape changes at the two pressures. The observed change in the modeled line shapes at the two pressures were then applied as a ratio to the original 70 Torr calibration factor. As a result, we arrive at a final calibration factor of 0.2041 ppb HF per ppb/cm absorbance.

Validation of the HF Calibration

HITRAN Spectral Database

We have validated the absolute HF calibration using two methods. In the first method, we have used the HITRAN database (Rothman et al. 2012¹) to directly calculate the absorption of the HF spectral line employed in the Picarro HF instrumentation. Using the intensity value, ground state energy, and partition function from HITRAN, and our measured line shape parameters to relate integrated

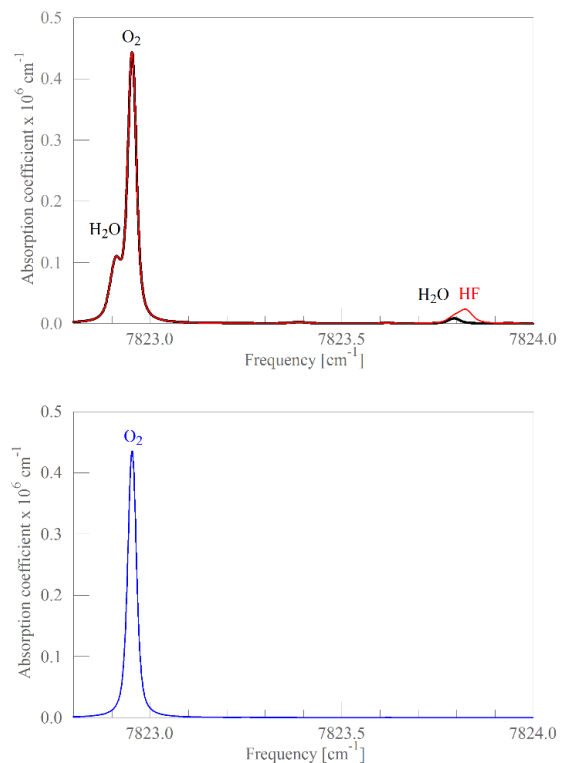


Figure 1: HF spectral region, showing major features for H₂O and O₂. The instrument reports all three species. O₂ can be used as a 'proxy' for the calibration and proper operation of the instrument.

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

absorption to peak absorption, we arrive at a calibration factor 0.1950, which is 4.5% smaller than the 0.2041 calibration based on the permeation tube measurements.

Gravimetrically prepared cylinders

In the second method of validation, we have obtained gravimetrically prepared standards of HF in specially coated cylinders from AirGas, Inc. These standards are prepared in the concentration range of 3-5 ppm. The instrument cannot measure these concentrations directly because the absorption loss is too high (leading to a ring down time that is too fast to measure properly). Thus, to use these cylinders to validate the calibration, we performed two dilution experiments. The setup for dilution experiment #1 is shown in the figure below. All the experiments in this section were performed on a single instrument (S/N: MADS2070), which we have designated as our 'Golden' HF analyzer. We will describe how this Golden analyzer is used in more detail in later sections.

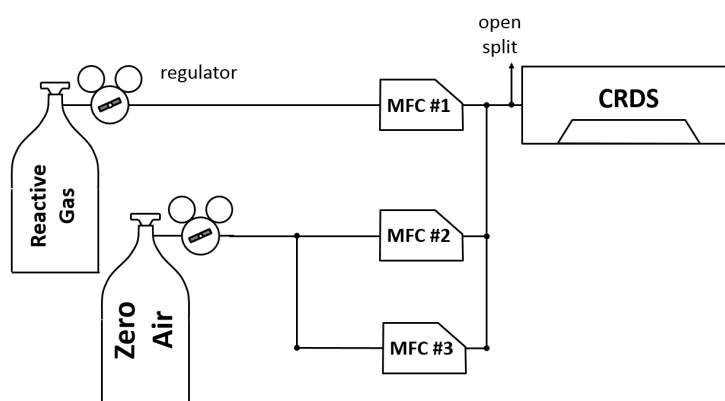


Figure 2: Schematic for performing Dilution Experiment #1. PFA tubing was used throughout, and the regulator on the reactive gas cylinder was Silconert-coated for improved performance.

Calibrated mass flow controllers (MFCs)² were used to prepare the gas mixtures. The total flow from the dilution system always exceeded the ~2 slm flow through the instrument, with the excess gas directed to ambient via the open split. The reactive gas concentration as prepared by the dilution system is given by the following expression:

$$c_{\text{reactive}} = \frac{f_1}{f_2 + f_3} c_{\text{cylinder}}$$

First we ran the dilution system with $f_1 = 32$ sccm; $f_2 = 500$ sccm, and $f_3 = 2, 3, 4, 5,$ and 6 slm, with steps 400 seconds long. The rated cylinder value is 5.16 ppm^3 . We ensured that the concentration delivered by the system was stable prior to beginning the measurements. The time series measured using these settings is shown in Figure 3.

² MFCs (MCS-50SCCM-D, MC-500SCCM-D, MC-10SLPM-D; Alicat, Inc, Tucson, AZ). The accuracy of the MFCs used in this experiment is $\pm 0.8\%$ of reading $+0.2\%$ of full scale.

³ HF in balance air (Cyl #: C482326, AirGas, Radnor, PA), 5.16 ppm , accuracy $\pm 10\%$.

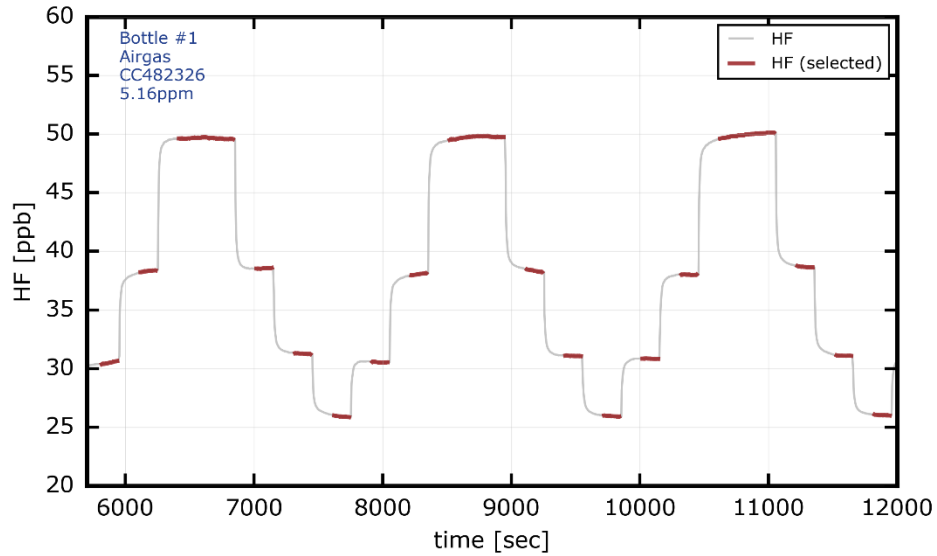


Figure 3: time series from three-MFC dilution system, with f_1 set to 32 sccm.

We performed a second experiment with f_1 set to 50 sccm. This time series is shown below.

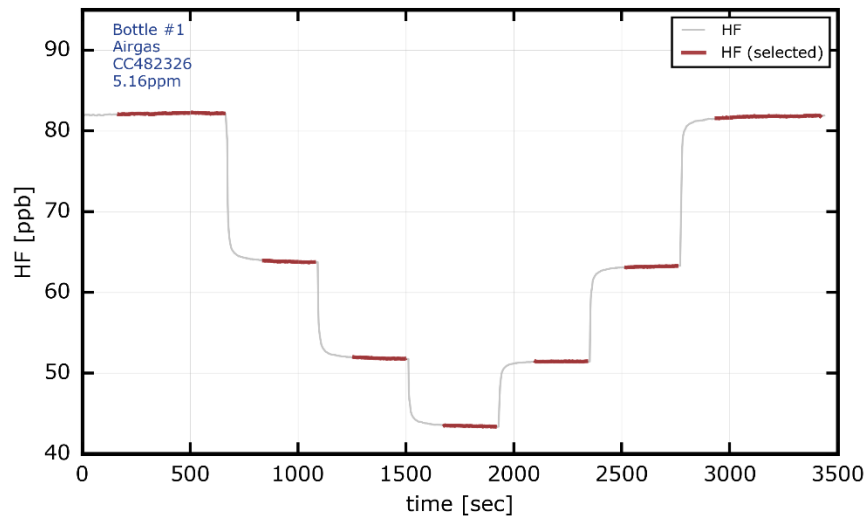


Figure 4: time series with f_1 set to 50 sccm.

We can then plot the measured concentration vs. the expected concentration from this dilution system (given the assigned value of the cylinder and the set flow rates through the MFCs). Figure 5 shows these data, along with a 1:1 line for reference.

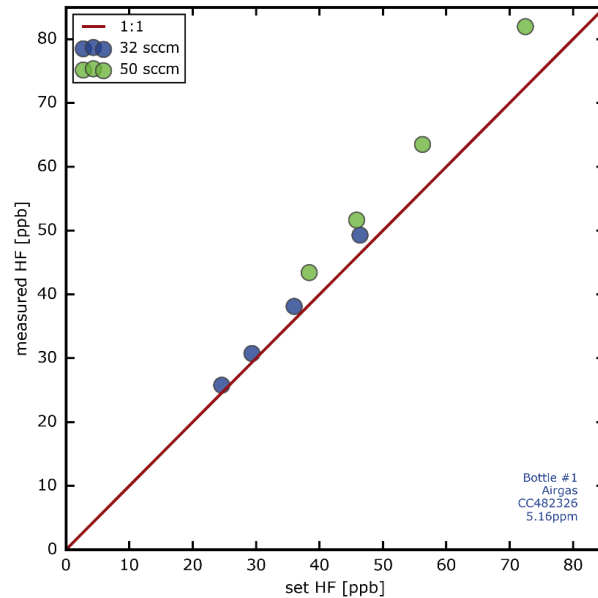


Figure 5: Measured HF signal as a function of the expected value, for two different values of f_1 .

It appears from this figure that the slope of the calibration curve depends upon the flow through MFC #1. This can be seen more clearly when plotting the ratio of the measured signal to the expected signal for the two data sets, as is shown in Fig. 6.

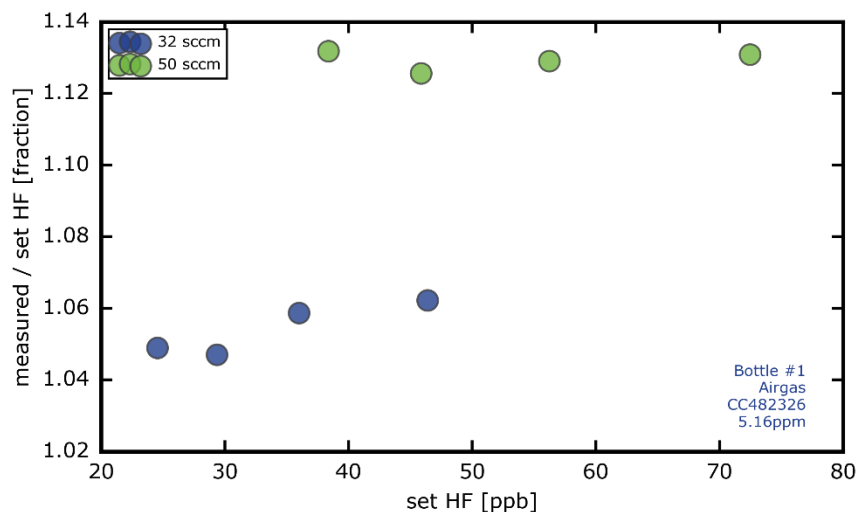


Figure 6: ratio of the measured HF signal to the setpoint, for two flows through the reactive gas MFC.

Looking at Fig. 6, we note that for a given flow through MFC #1, the ratio of the measurement to the setpoint is relatively constant, indicating that the instrument responds linearly to the measurement. This is especially clear in the 35 – 50 ppb range, where the set values overlap between the two data sets, indicating that instrument linearity is not the cause of the error. We may also reject the hypothesis of a flow error in the reactive gas MFC; we tested the dilution with a non-reactive gas (methane) and found that the dilution system works as expected given the specifications of the MFCs. We therefore conclude

that some of the HF is being lost due to reactivity in the dilution system, and that at lower flows, some of the HF is lost due to reactivity of the wetted surfaces of the delivery system. MFC #1 itself is a likely candidate, because the wetted surfaces have not been passivated with Silconert.

Unfortunately, the maximum flow through MFC #1 is 50 sccm, so we could not test the system at higher flows. We can however test the calibration with an even simpler dilution system. The system schematic is shown in Fig. 7. In this simple experiment, we treat the instrument as a constant flow device⁴. A constant and sizeable flow of reactive gas is prepared by setting the regulator to a few p.s.i.g.; the orifice in the figure is sized such that the flow is about 500 sccm. Most of this flow goes through the open split. When the MFC flow is greater than the flow through the instrument, the excess zero air flow exits through the open split, and the instrument will not see any HF. When the MFC flow is less than the flow through the instrument, HF will make up the flow deficit, leading to measurable HF in the instrument.

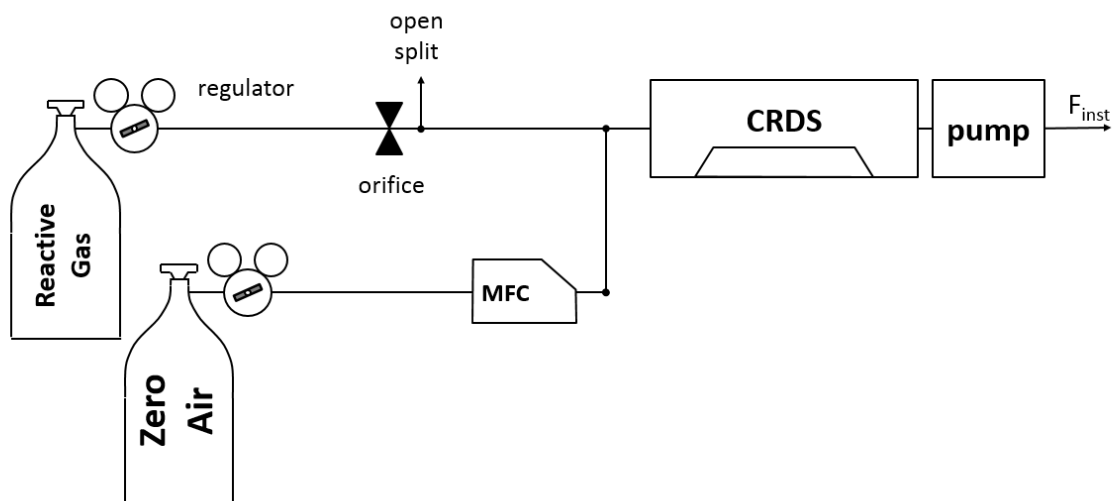


Figure 7: Single MFC dilution method

The concentration at the instrument is given by the following expression:

$$c_{inst} = \frac{f_{inst} - f_{mfc}}{f_{inst}} c_{cyl} \text{ for } f_{inst} > f_{mfc}$$

⁴ This is an excellent approximation, since the flow through the instrument is set by a sapphire orifice upstream of the cavity (not shown), which is held at constant pressure, and the open split ensures that the pressure upstream of the orifice is at ambient atmospheric pressure.

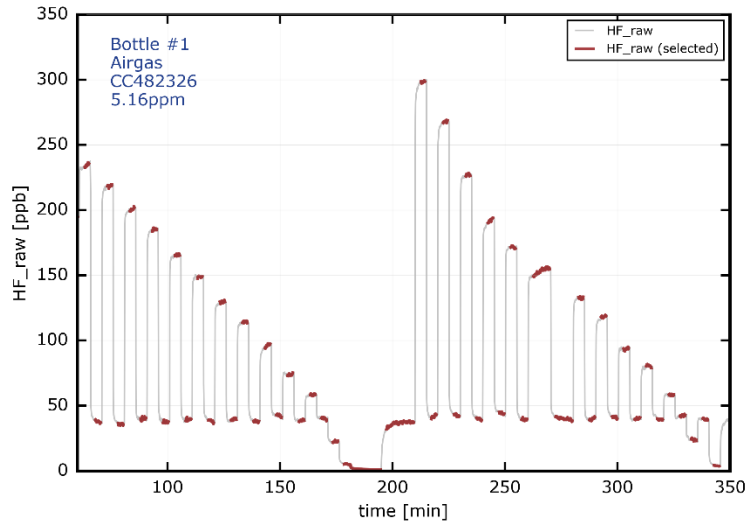


Figure 8: Time series for the single MFC dilution system. After each step, the flow is set to a nominal value to test for drift in the system (either in concentration or the flow of the analyzer). The stability of these steps (at about 40 ppb) indicates the stability of the dilution system.

Figure 8 shows the time series for the same cylinder used in the three-MFC dilution system. After most steps, the flow returns to the same value (producing about 40 ppb on the plot); the stability of these steps is indicative of the stability of the flow through the instrument and the HF source. Using the equation above, we can then calculate the expected concentration for each step. These data are shown in Fig. 9. These data are well fit by a line with a slope of 1.175.

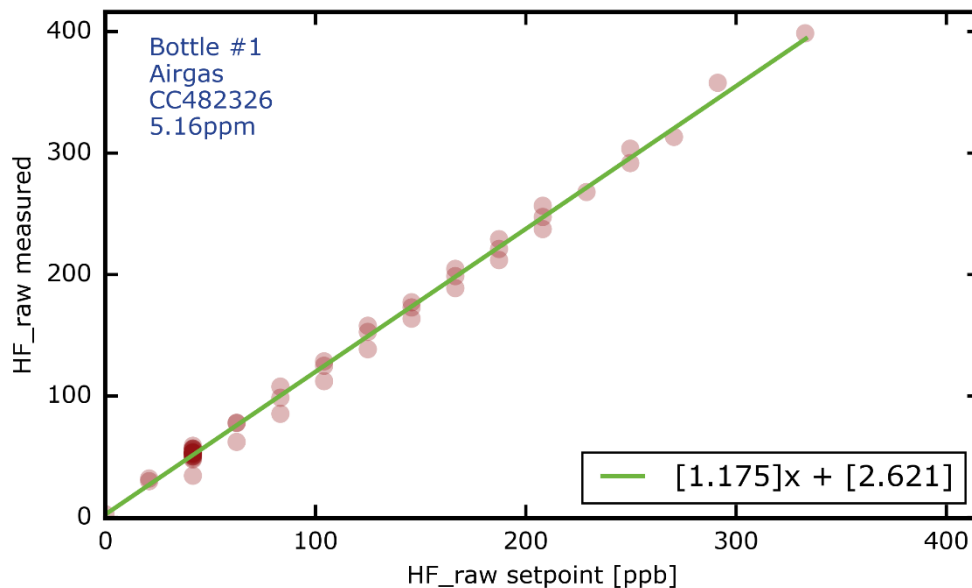


Figure 9: Measured HF vs. set point for the single MFC experiment.

We also measured the slope of the calibration curve as a function of time throughout this experiment, using groups of 5 measurements. The time series of the calibration slope is shown in Fig. 10.

The concentration at the instrument is given by the following expression

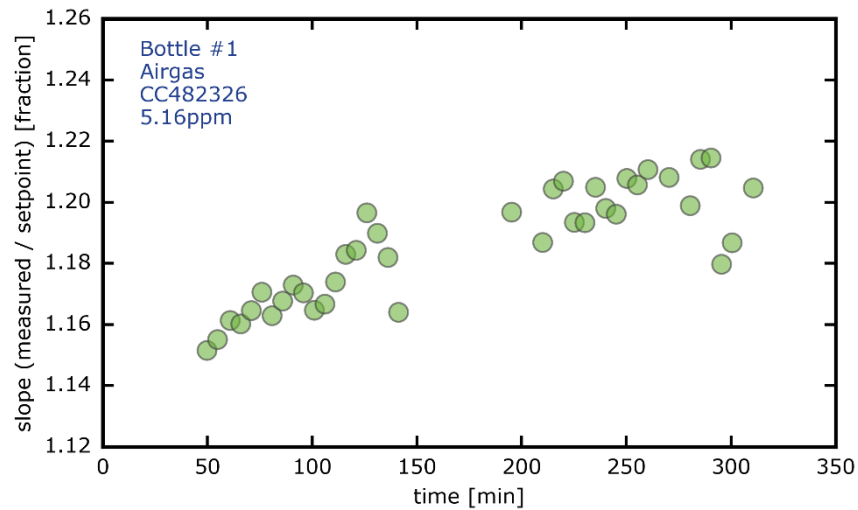


Figure 10: measured slope as a function of time during the experiment.

The data appear to be drifting upward slowly, appearing to saturate at a value of about 1.21. We attribute this to residual pickling of the regulator and tubing.

We summarize these two experiments in the following table, for CC482326:

Experiment	Calibration Slope
3-MFC dilution: $f_1 = 32$ sccm	1.06
3-MFC dilution: $f_1 = 50$ sccm	1.13
1-MFC dilution: reactive flow ~ 500 sccm	1.21

As a further point of validation, we performed an experiment using the single MFC system and a second cylinder⁵, prepared by the same vendor using the same gravimetric process. Interestingly, using the same analyzer and the same MFC and orifice and regulator, measured within 24 hours of Bottle #1, the calibration slope is substantially different, 0.90 vs. 1.21. We attribute this difference to the preparation

⁵ HF in balance air (Cyl #: C482443, AirGas, Radnor, PA), 5.13 ppm, accuracy $\pm 10\%$.

of the bottles and or the storage of the reactive gas in the cylinder, rather than to the dilution system or the instrument.

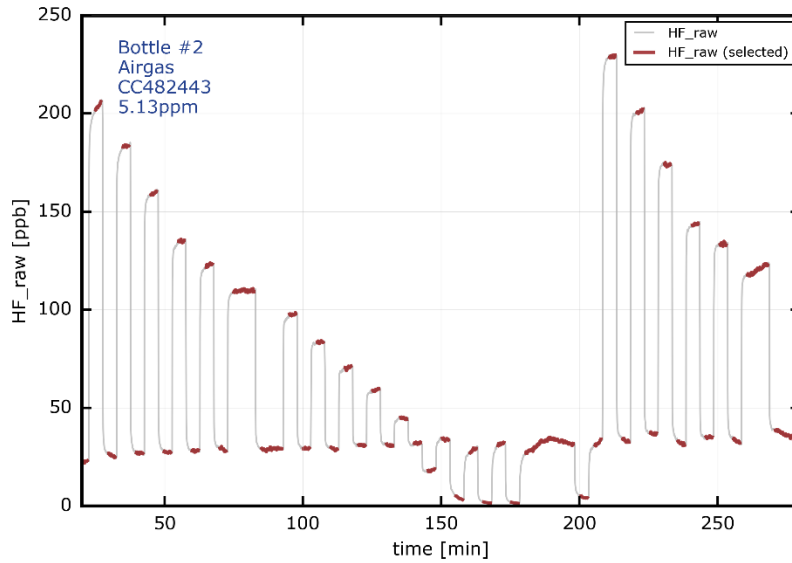


Figure 11: Time series for Bottle #2, using the 1-MFC dilution system.

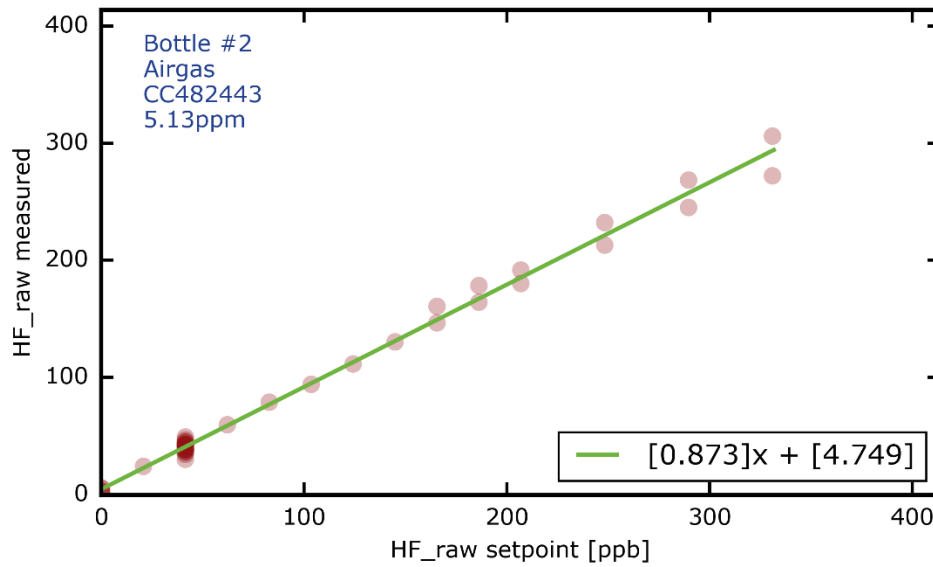


Figure 12: Measured HF vs. set point for the single MFC experiment, for Bottle #2.

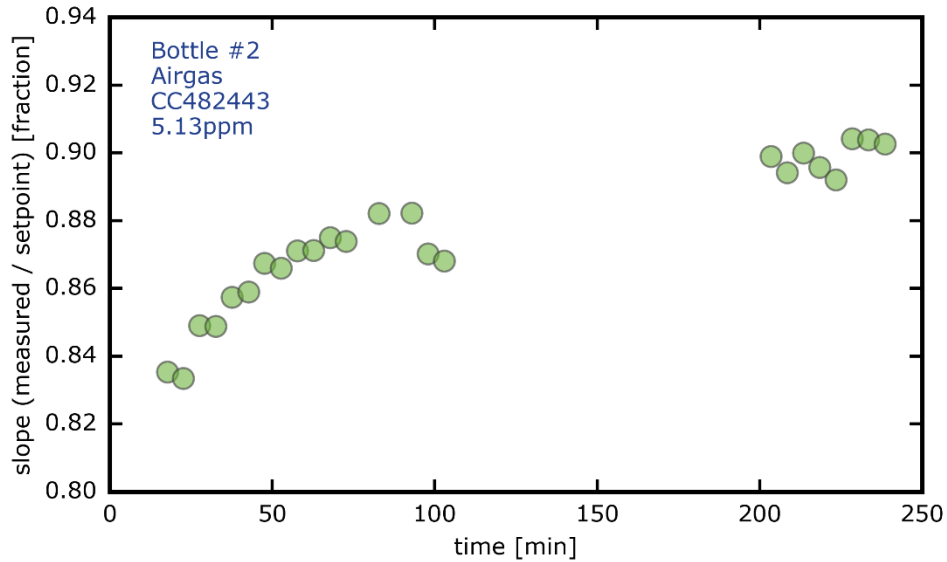


Figure 13: measured slope as a function of time during the experiment, Bottle #2.

From these validation experiments using gravimetrically prepared standards, we draw the following conclusions:

1. For HF, the choice of wetted materials and flows can affect the overall delivery of the reactive gas to the instrument.
2. The calibration slope *increases* with *increasing* flow through the reactive gas delivery system, from which we infer that one or more materials in the system is reacting with the HF and reducing the total amount of HF delivered to the instrument.
3. For the current state of the art, the actual concentration present in gravimetrically prepared cylinders can differ substantially.

We summarize the HF calibration slope measurement of the ‘Golden’ HF instrument below:

Method	Relative Slope
2008 Permeation Tube Calibration	1.0
2012 HITRAN	0.955
Bottle #1 dilution	1.21
Bottle #2 dilution	0.90

Final Conclusion: Given the reasonable agreement with the HITRAN 2012 value for HF, and because the recent gravimetrically prepared standards bracket our nominal calibration constant, we have decided to retain the calibration constant as defined by the 2008 permeation tube experiment; i.e., a calibration constant of 0.2041 ppb HF per ppb/cm of absorbance. This calibration factor will be applied to all SI2205 and SI2306 instruments.

Method for Calibration of Individual Instruments

Because it is difficult to prepare and deliver a constant and known concentration of HF, individual instrument calibration becomes a challenge. 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.
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.
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 HF, this proxy gas is O₂.

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 HF in this system do not affect the ultimate calibration of the Device Under Test (DUT).

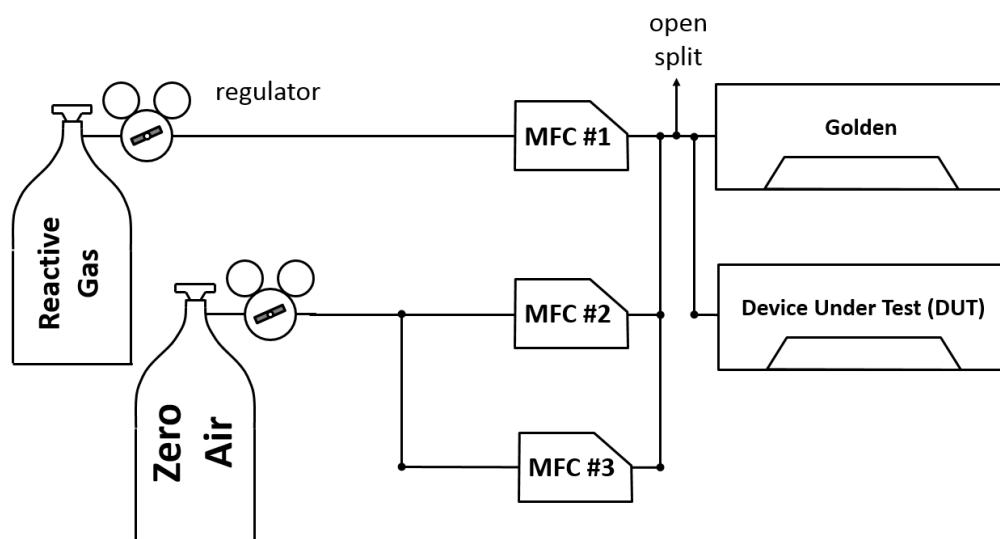


Figure 14: Cross-calibration setup used to transfer the calibration of the Golden instrument onto the DUT.

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.

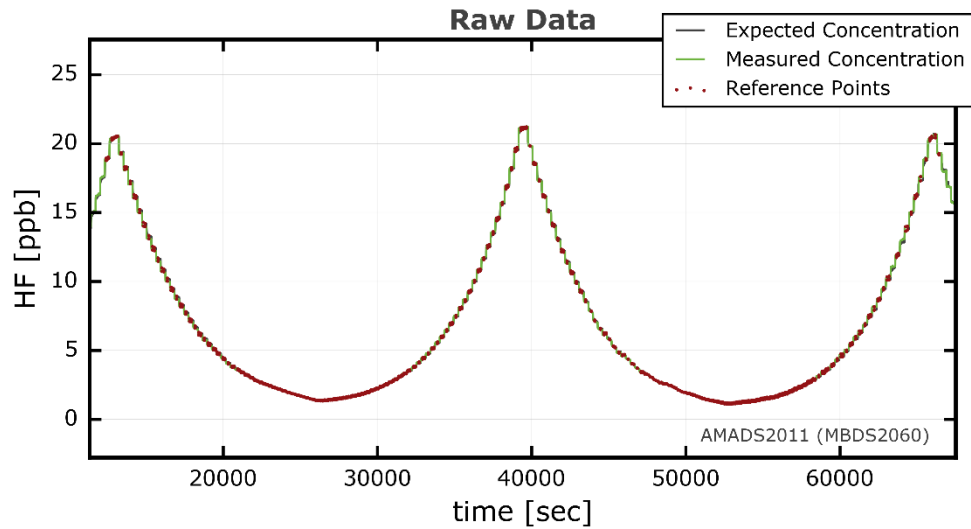
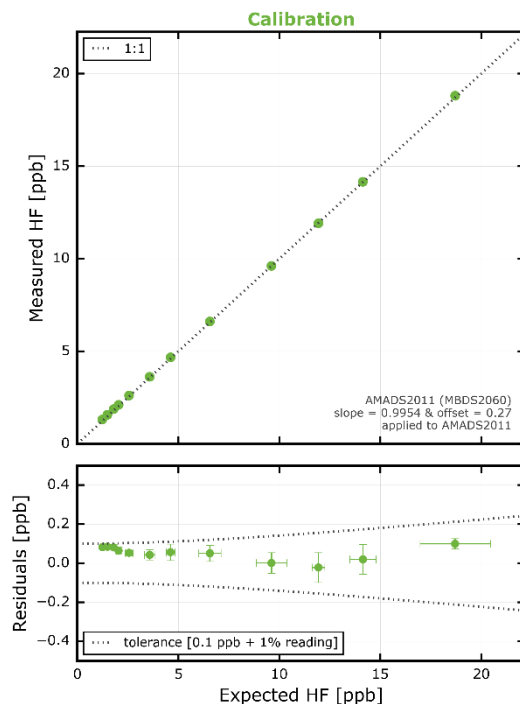


Figure 15: Time series for the Golden Instrument (MBDS2060, in gray) and the DUT (AMADS2011, in green). The reference points (shown in red) are selected from both time series to meet minimum criteria for stability. These points are used in further analysis.

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. 16. To create this figure, we determine the slope (0.9954 ppb / ppb) and offset (0.27 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. 16.



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 0.2041 ppb per ppb/cm that is applied to all instruments, for the following reasons:

1. The response time of the two instruments is 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. For example, using the data in Figs. 15 and 16 and performing a simple time response correction, we found that the calibration curve slope became 1.0018 ppb / ppb.
2. Because HF is retained on the wetted surfaces of the instruments, sometimes for hours or more, the

Figure 16: Calibration data derived from Fig. 15.

fact that each instrument may have been exposed to differing amounts of HF can also distort the calibration curve.

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 0.2041 ppb 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. 16.

From this second set of data, we also derive the linearity of the instrument⁶, which is defined as the ratio of the maximum excursion of the residual from a linear fit to the

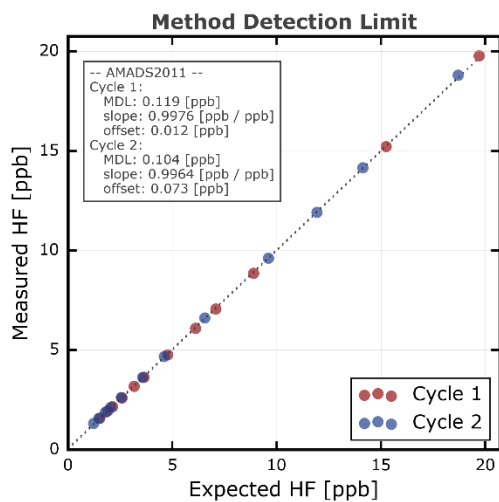


Figure 18: MDL plot

total span of concentration.

Figure 17 shows this linearity plot; the gray dotted lines in the lower figure indicate the requirement of 1% for the linearity.

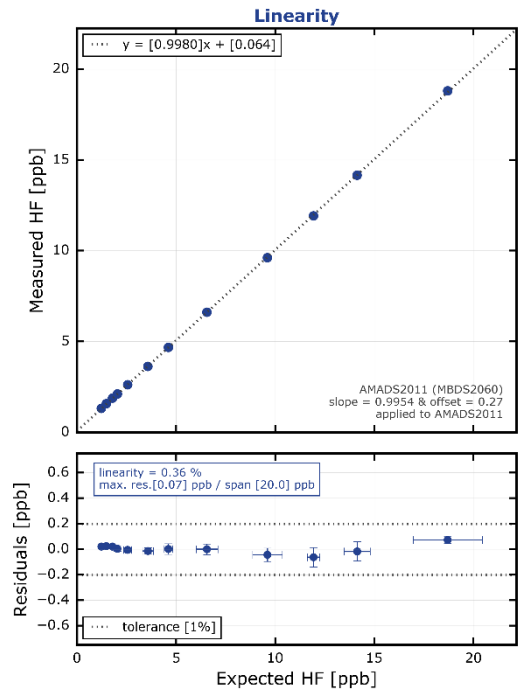


Figure 17: Linearity plot

Finally, from each cycle, we can determine the Method Detection Limit (MDL)⁷. The MDL data are shown in Fig. 18. The MDL must be lower than 0.5 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. It is very difficult to keep HF standards stable for long periods of time. For example, permeation tubes and gravimetrically prepared cylinders of HF generally have a certified life of no more than 6 months. We therefore have little direct evidence of the stability of our HF 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)⁸, 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

⁶ IEC 61207-1

⁷ SEMI C10-1109

⁸ 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.

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 HF⁹, we may then conclude that the HF calibration slope in the SI2205 and the SI2306 should 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 HF, we recommend a yearly calibration validation, using either the reactive gas HF itself, or, more simply, the non-reactive proxy gas O₂. There is no need to perform a true calibration in which the calibration slope is changed according to the results of a direct HF calibration experiment.

Summary

For all Picarro HF instruments (SI2205 and SI2306):

1. The calibration factor relating the optical absorbance in the measurement cell to the concentration of HF is the same value for all instruments: 0.2041 ppb HF per ppb/cm of absorbance.
2. This calibration factor, derived from a permeation tube experiment, has been validated against the 2012 HITRAN spectroscopic database and against two gravimetrically prepared cylinder standards that were diluted using calibrated mass flow controllers.
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 HF and a non-reactive proxy gas, O₂.
4. While in the field, the calibration of the instrument can be verified using a direct HF calibration experiment, or, more simply, by testing with O₂.

⁹ 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.