

# SI2103 and SI2306: Traceable calibration of Ammonia (NH<sub>3</sub>)

Chris W. Rella, Ph. D. Picarro Research Fellow and Director of Research and Development

## Abstract

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

## History

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## Spectroscopy

Ammonia (NH<sub>3</sub>) is measured in the near infrared region of the spectrum. Figure 1 shows the spectral region that the instrument uses to quantify NH<sub>3</sub>, H<sub>2</sub>O, and CO<sub>2</sub>. 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 NH<sub>3</sub>, H<sub>2</sub>O, and CO<sub>2</sub> are reported by the instrument on the user interfaces and the data logs.

### Original Calibration of NH<sub>3</sub> at Picarro

In 2010, Picarro measured the calibration factor of an early NH<sub>3</sub> instrument, using a gravimetrically prepared gas bottle. This calibration factor has not been changed since that time: this calibration factor is 8.75 ppb NH<sub>3</sub> per ppb / cm.

### Validation of the NH<sub>3</sub> Calibration

#### HITRAN Spectral Database

The absolute NH<sub>3</sub> calibration has been validated using three methods. In the first method, we have used the HITRAN database (Rothman et al. 2012<sup>1</sup>) to directly calculate the absorption of the NH<sub>3</sub> spectral line employed in the Picarro NH<sub>3</sub> 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 8.549 ppb NH<sub>3</sub> per ppb / cm, which is 2.3% smaller than the 8.75 value based on the gravimetrically prepared cylinder measurement.

#### Validation by the National Physical Laboratory

In a recent paper (Martin et al. 2016)<sup>2</sup> by a group at NPL, a world-class metrology center in the United Kingdom, the absolute calibration of a G2103 instrument bearing the standard calibration factor of 8.75 ppb NH<sub>3</sub> per ppb / cm was calibrated against primary gravimetric standards carefully prepared by NPL, in the concentration range of 10 – 220 ppb. The calibration of the G2103 over that range agreed to about 1% of the standards, with an expanded uncertainty on the measurements of 2%.

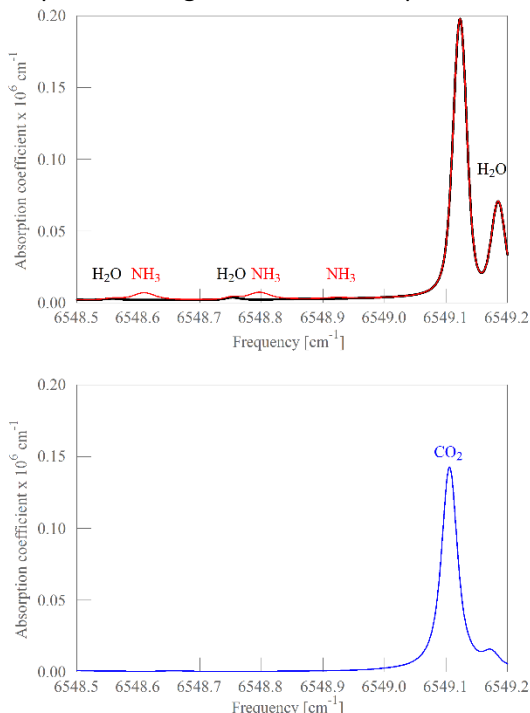


Figure 1: NH<sub>3</sub> spectral region, showing major features for H<sub>2</sub>O and CO<sub>2</sub>. The instrument reports all three species. CO<sub>2</sub> can be used as a 'proxy' for the calibration and proper operation of the instrument.

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

<sup>2</sup> Martin, Nicholas A., et al. "The application of a cavity ring-down spectrometer to measurements of ambient ammonia using traceable primary standard gas mixtures." *Applied Physics B* 122.8 (2016): 1-11.

## Gravimetrically prepared cylinder

In the third method of validation, we have obtained a gravimetrically prepared standard of  $\text{NH}_3$  in a specially coated cylinder from AirGas, Inc. This standard was prepared with a concentration of about 50 ppm. Because the instrument does not operate extremely accurately at these high concentration levels, we performed a dilution experiment to reduce the concentration below 1000 ppb. The setup for this dilution experiment is shown in the figure below. All the experiments in this section were performed on a single instrument (S/N: AEDS2079), which we have designated as our 'Golden'  $\text{NH}_3$  analyzer. We will describe how this Golden analyzer is used in more detail in later sections.

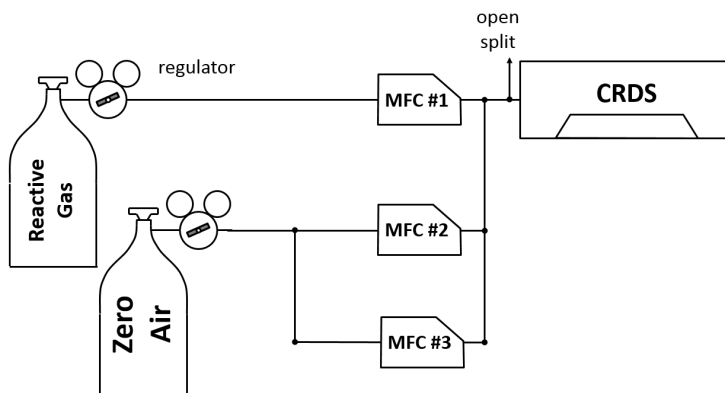


Figure 2: Schematic for performing Dilution Experiment #1. PFA tubing was used throughout, and the regulator on the reactive gas cylinder was Silconert-coated for improved performance.

Calibrated mass flow controllers (MFCs)<sup>3</sup> were used to prepare the gas mixtures. The total flow from the dilution system always exceeded the  $\sim 2$  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:

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

We ran the dilution system at  $f_1 = 32$  sccm,  $f_2 = 500$  sccm, and  $f_3 = 2, 3, 4, 5,$  and  $8$  slm, with steps 400 seconds long. The rated cylinder value is  $49.0$  ppm<sup>4</sup>. 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.

<sup>3</sup> 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.

<sup>4</sup> Ammonia in balance air (Cyl #: ALM057277, Air Liquide, Paris, France),  $49.0$  ppm, accuracy  $\pm 2\%$ .

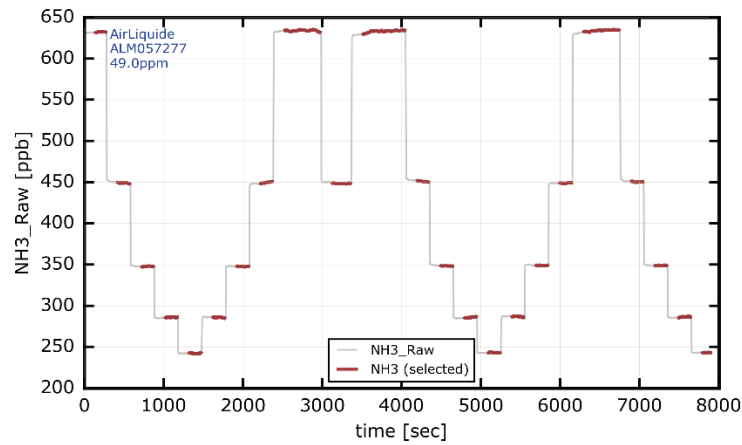


Figure 3: time series with  $f_1$  set to 32.0 sccm.

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.

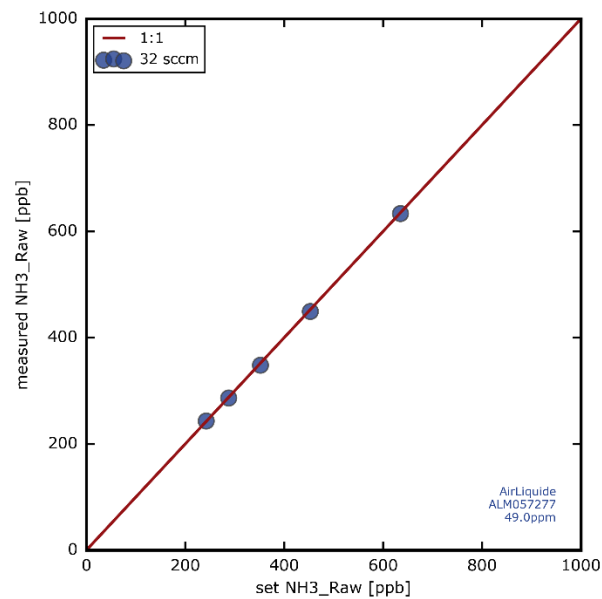


Figure 4: Measured  $\text{NH}_3$  signal as a function of the expected value.

We then plot the ratio of the measured signal to the expected signal for the two data sets, as is shown in Fig. 5.

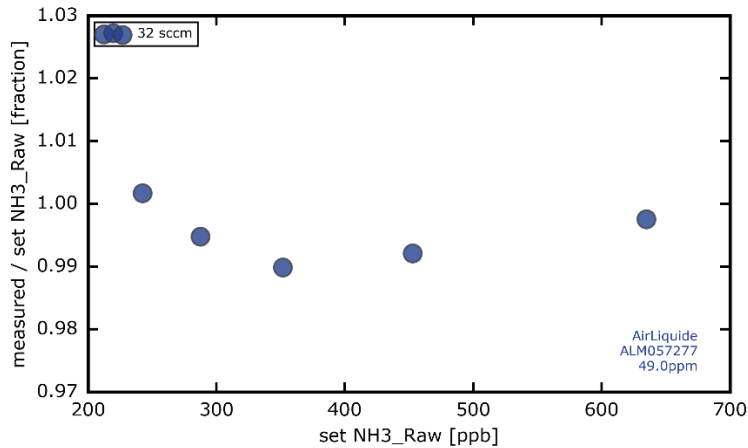


Figure 5: ratio of the measured NH<sub>3</sub> signal to the set point.

The agreement between the measured and expected NH<sub>3</sub> concentration is good, with a ratio of  $1.0 \pm 0.01$ .

We summarize the NH<sub>3</sub> calibration slope measurement of the ‘Golden’ NH<sub>3</sub> instrument below:

Method	Relative Slope
2010 Direct Cylinder Calibration	1.0
2012 HITRAN	0.977
Martin et al. 2016	0.99
Cylinder Dilution Experiment	0.99

**Final Conclusion: We have decided to retain the calibration constant as defined by the 2015 Direct Cylinder Calibration; i.e., a calibration constant of 8.75 ppb NH<sub>3</sub> per ppb/cm. This calibration factor will be applied to all SI2103 and SI2306 instruments.**

## Method for Calibration of Individual Instruments

Because it is difficult to prepare and deliver a constant and known concentration of NH<sub>3</sub>, 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 NH<sub>3</sub>, this proxy gas is CO<sub>2</sub>.

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 NH<sub>3</sub> in this system do not affect the ultimate calibration of the Device Under Test (DUT).

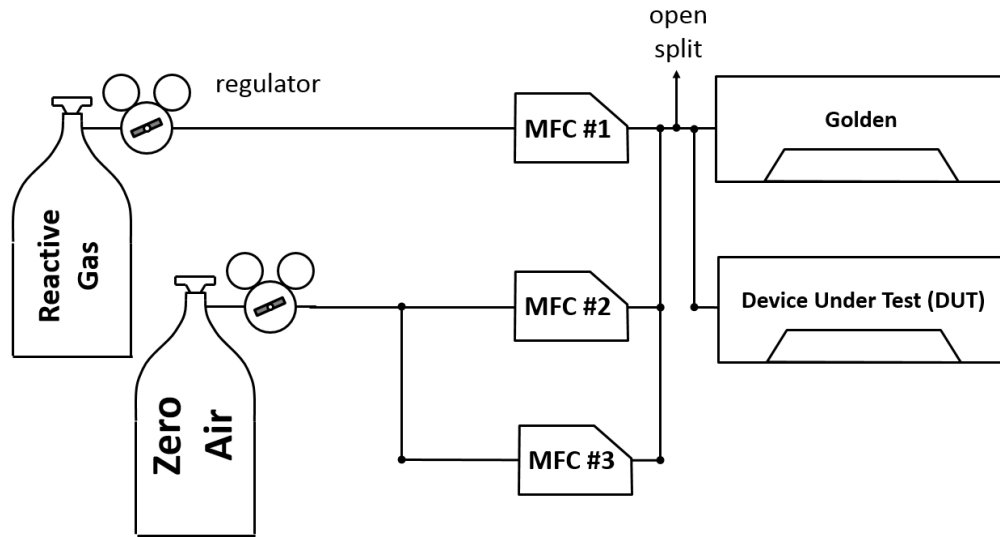


Figure 6: Cross-calibration setup used to transfer the calibration of the Golden instrument onto the DUT.

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.

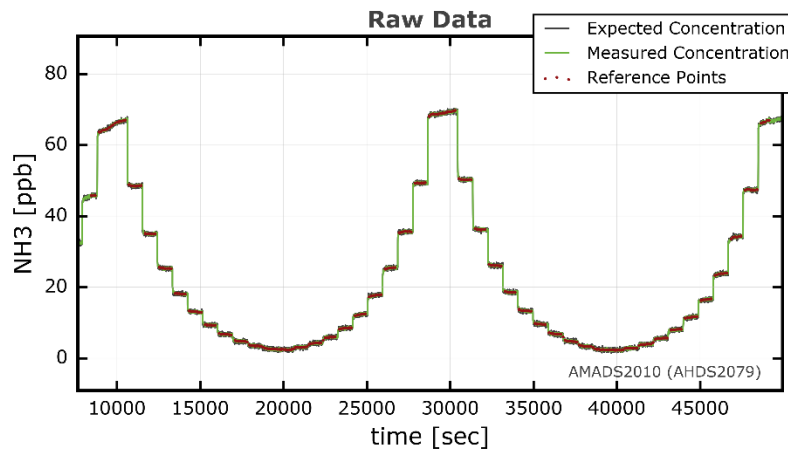


Figure 7: Time series for the Golden Instrument (AEDS2079, in gray) and the DUT (AMADS2010, in green). The reference points (shown in red) are selected from both time series to meet minimum criteria for stability. These points are used in further analysis.

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 (0.9943 ppb / ppb) and offset (0.03 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. 8.

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 8.75 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.
2. Because  $\text{NH}_3$  is retained on the wetted surfaces of the instruments, sometimes for hours or more, the fact that each instrument may have been exposed to differing amounts of  $\text{NH}_3$  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

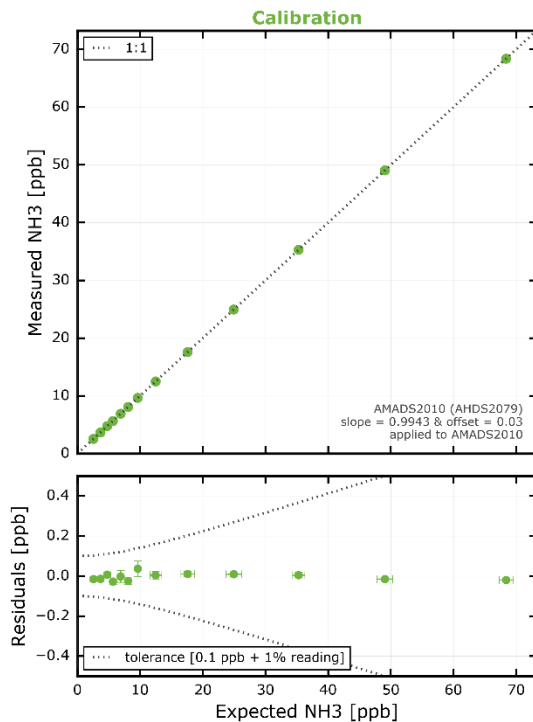


Figure 8: Calibration data derived from Fig. 7.

standard calibration constant of 8.75 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. 8.

From this second set of data, we also derive the linearity of the instrument<sup>5</sup>, which is defined as the ratio of the maximum excursion of the residual from a linear fit to the 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.

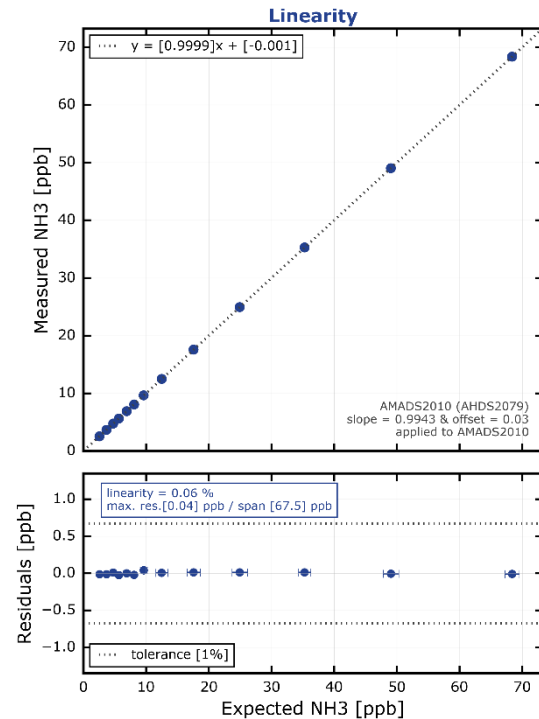


Figure 9: Linearity plot.

<sup>5</sup> IEC 61207-1

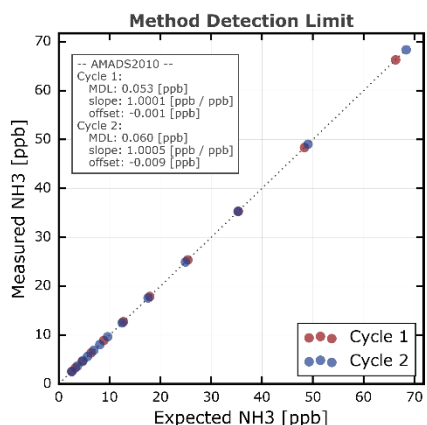


Figure 10: MDL plot

Finally, from each cycle, we can determine the Method Detection Limit (MDL)<sup>6</sup>. The MDL data are shown in Fig. 10. 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 NH<sub>3</sub> standards stable for long periods of time. For example, permeation tubes and gravimetrically prepared cylinders of NH<sub>3</sub> generally have a certified life of no more than 6 months. We therefore have little direct evidence of the stability of our NH<sub>3</sub> 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)<sup>7</sup>, 47 Picarro CRDS instruments that measure CO<sub>2</sub>, CH<sub>4</sub>, 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 NH<sub>3</sub><sup>8</sup>, we may then conclude that the NH<sub>3</sub> calibration slope in the SI2108 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 NH<sub>3</sub>, we recommend a yearly calibration validation, using either the reactive gas NH<sub>3</sub> itself, or, more simply, the non-reactive proxy gas CO<sub>2</sub>. There is no need to perform a true calibration in which the calibration slope is changed according to the results of a direct NH<sub>3</sub> calibration experiment.

## Summary

For all Picarro NH<sub>3</sub> instruments (SI2108):

1. The calibration factor relating the optical absorbance in the measurement cell to the concentration of NH<sub>3</sub> is the same value for all instruments: 8.75 ppb NH<sub>3</sub> per ppb/cm of absorbance.
2. This calibration factor, derived from a gravimetrically prepared cylinder, has been validated against the 2012 HITRAN spectroscopic database, against primary standards prepared by the UK national metrology laboratory NPL, and against a second gravimetrically prepared cylinder standard that was diluted using calibrated mass flow controllers.

<sup>6</sup> SEMI C10-1109

<sup>7</sup> 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 H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub> and CO, Atmos. Meas. Tech., 8, 3867-3892, doi:10.5194/amt-8-3867-2015, 2015.

<sup>8</sup> 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.



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  $\text{NH}_3$  and a non-reactive proxy gas,  $\text{CO}_2$ .
4. While in the field, the calibration of the instrument can be verified using a direct  $\text{NH}_3$  calibration experiment, or, more simply, by testing with  $\text{CO}_2$ .