

PI2114: Traceable Calibration of Hydrogen Peroxide (H₂O₂)

PICARRO

WHITE PAPER

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Abstract

In this white paper, we discuss the calibration of Hydrogen Peroxide in Picarro's Cavity Ring Down Spectrometers. Because hydrogen peroxide is a reactive species, instrument calibration becomes a difficult challenge. For this reason, and because Picarro's CRDS instruments are both highly precise and very stable, we have defined the following calibration strategy for the PI2114 analyzers:

1. Careful Calibration of a "Golden" PI2114 H₂O₂ analyzer.
2. Factory calibration of all PI2114 analyzers, using the Golden analyzer as a transfer standard.
3. Field Validation of PI2114 analyzers in the field using non-reactive methane as a proxy for H₂O₂ calibration.

Each of these steps are described in detail in this white paper.

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Spectroscopy

Hydrogen Peroxide (H_2O_2) is measured in the near infrared region of the spectrum. Figure 1 shows the spectral region that the instrument uses to quantify H_2O_2 , H_2O , and CH_4 . The CRDS instrument rapidly (in about 1-2 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_2O_2 , H_2O , and

CH_4 are reported by the instrument on the user interfaces and the data logs. Hydrogen peroxide is a highly reactive species for which it is difficult to prepare traceable gas standards. Unlike H_2O_2 , CH_4 is a non-reactive species that can be accurately prepared and stably stored in high pressure cylinders. It is therefore an attractive species to use as a proxy calibration for the optical spectrometer, with a factor of 70 between the line strength of the two species.

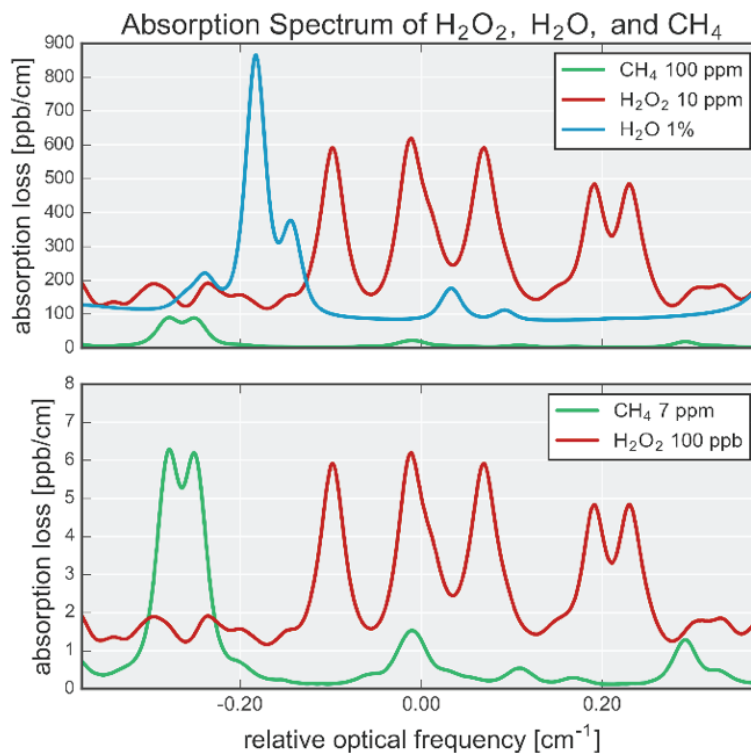


Figure 1. H_2O_2 spectral region, showing major features for H_2O and CH_4 . CH_4 can be used as a 'proxy' for the calibration and proper operation of the instrument. In the bottom panel, note that the strongest H_2O_2 peak at 100 ppb has the same peak absorption loss as the largest CH_4 peak at 7 ppm, for a factor of 70 between the line strengths of the two gases in this region.

Calibration of the Golden H_2O_2 Analyzer

Picarro has developed a method called the Total Droplet Evaporation (TDE) test to calibrate our H_2O_2 instruments. In the TDE test, the H_2O_2 instrument monitors the evaporation of a droplet of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ solution of a known weight. The setup is shown in the Figure 2.

In the TDE test, a controlled flow of humid H_2O_2 free air is directed through a beaker containing a droplet of an aqueous H_2O_2 solution. As the droplet evaporates, the H_2O_2 and H_2O are carried by the flow to the instrument. Any excess flow beyond what the instrument needs for sampling is vented

to atmosphere. In the past, we have diluted a high concentration solution of H_2O_2 ; in this white paper, we describe direct measurements, which have improved repeatability. The molar flow controlled by the MFC and the mole fraction of H_2O_2 as measured by the instrument are combined to measure the total number of moles of H_2O_2 in the sample. This value can be compared to the known amount of H_2O_2 in the aliquot to calibrate the instrument.

The TDE test is not without uncertainty. The cascaded uncertainty of a) the assigned value of

the concentration of the high concentration H_2O_2 solution, b) the optional initial dilution gravimetry step, c) the gravimetry of the droplet, and d) the accuracy of the mass flow controller all contribute to the overall uncertainty of the method. The uncertainty of the solution concentration ($\pm 5\%$) is a large fraction of the overall uncertainty of the method; we have therefore devoted a significant effort to quantifying the concentration of the source solution.

Measurement of the Standard 30% H_2O_2 wt/wt Solution

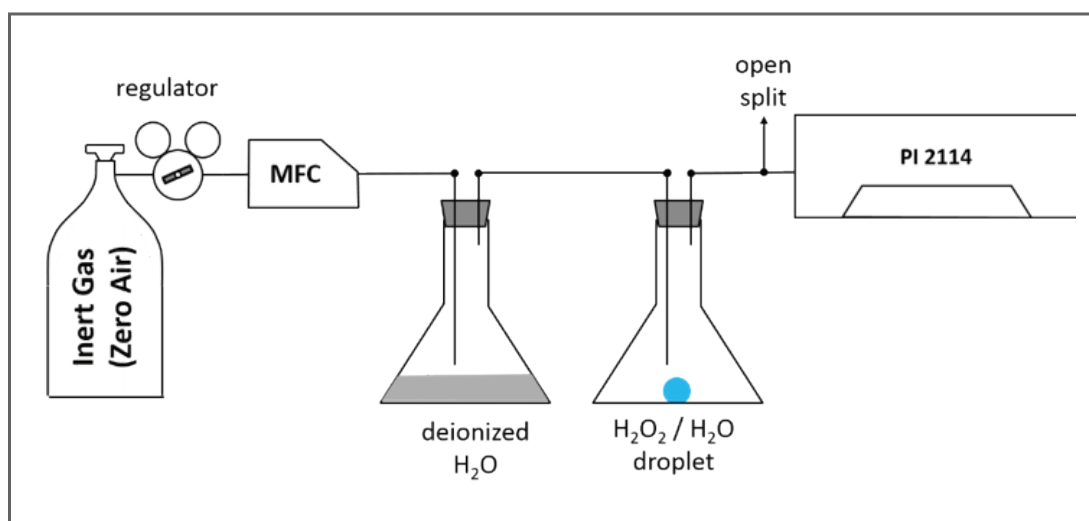
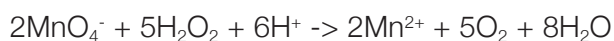


Figure 2. Test schematic for the total droplet evaporation test.

A certified bottle of H_2O_2 in water with a 30.0% concentration (by weight) (H1009-100mL, Sigma Aldrich, St. Louis, MO, USA) is used as a source solution. We have undertaken a series of three experiments to better constrain our measurement of the concentration of this 30% wt/wt H_2O_2 solution.

Titration Experiment

The concentration of hydrogen peroxide in solution can be quantified through a titration experiment with KMnO_4 . The titration reaction is:



500 μL of nominally 30% wt/wt solution of H_2O_2 was weighed and diluted with about 25 mL of deionized water. This solution was placed in a beaker on a magnetic stirrer. Because the reaction must take place in an acid environment, 5 mL of concentrated sulfuric acid was added to the solution prior to each titration. A 25 mL buret was used to deliver standardized 1 N KMnO_4 as titrant; 1 mL of titrant is equivalent of 17.01 mg H_2O_2 . The pink color of excess permanganate was used as a visual end point indicator. Six repetitions of the titration experiment were performed, from which the solution was determined to be $31.36 \pm 0.239\%$ H_2O_2 wt/wt.

A second series of five titrations were performed on the same batch of H₂O₂ about three months after the first run. The resulting concentration was 31.62 ± 0.189% H₂O₂ wt/wt, which is within the repeatability of the individual measurements, indicating the stability of the high concentration source material and the titration procedure. We did not separately confirm the normality of the 1 N KMnO₄ titrant, which has a manufacturer's specified tolerance of ±0.5%. The manufacturer specifies the titrant as standardized at 25C against sodium oxalate obtained from NIST.

Hydrogen Peroxide Solution Density Analysis

The concentration of hydrogen peroxide / water solutions can be determined from density measurements. The concentration of hydrogen peroxide / water solutions can be determined from density measurements. The density of the solution was computed by pipetting and weighing a known aliquot (200 µL) of solution. The balance calibration was verified using known masses with better than 0.1% accuracy traceable to NIST standards. Two runs of ten measurements were performed on the same solution over two days, resulting in a density of 1.1115 ±0.0040 g/mL and 1.1074 ±0.0071 g/mL, where the errors are the standard deviation of the individual measurements. As a test of the accuracy of this measurement, the density of deionized water was measured using the same methodology immediately after the H₂O₂ density measurement, with a density of 0.9955 ±0.0035

g/mL and 0.9933 ± 0.0067 g/mL. The known density of pure water at 22C (the temperature at which these measurements were performed) is 0.9978 g/mL¹, which is slightly higher (by about 0.2%) than our measurements, though it is within the standard deviation of the measurements. If we remove this small bias, and take the weighted mean of the two H₂O₂ measurement runs, we determine that the density of the source solution is 1.1136 ± 0.0013 g/mL at 22C, which corresponds to 30.98 ± 0.33% H₂O₂ wt/wt (1-sigma). This value is consistent with the measurements using the titration.

Summary of Standard Solution Analysis

The results of these experiments are shown in the Table 1 (means and 1-sigma uncertainties). The manufacturer specified range on the solution is 29-32% wt/wt. All three assays agree within 4% of each other and are within the certified range, with a mean that is slightly higher than centroid of the manufacturer's specified range. We have no reason to trust one method or set of measurements over the others. For this reason, we have decided to select an assigned value for the standard solution that is the weighted mean of the three assays that we have performed, or 31.43 ±0.13% H₂O₂ wt/wt, where the uncertainty is the 1-sigma weighted standard deviation as determined from the statistical analysis of the individual experiments. We have not attempted to include potential for bias in these measurements, which may increase this uncertainty beyond the value indicated here.

Method	Concentration of Standard 30 % H ₂ O ₂ wt/wt Solution
Manufacturer's Specification	30.5 ± 1.5% H ₂ O ₂ wt/wt
Titration Experiment #1	31.36 ± 0.24% H ₂ O ₂ wt/wt
Titration Experiment #2	31.62 ± 0.19% H ₂ O ₂ wt/wt
Density Analysis	30.98 ± 0.33% H ₂ O ₂ wt/wt
FINAL ASSIGNED VALUE	31.43 ± 0.13% H ₂ O ₂ wt/wt

Table 1: Summary of standard solution analysis

¹As determined on 2 Nov 2017 from <http://active-oxygens.evonik.com/product/h2o2/resources/PeroxideCalculator/calculator.html>, which is based upon Schumb, Walter C., Charles N. Satterfield, and Ralph L. Wentworth. "Hydrogen peroxide." (1955).

Calibration of the Golden Analyzer via the TDE Experiment

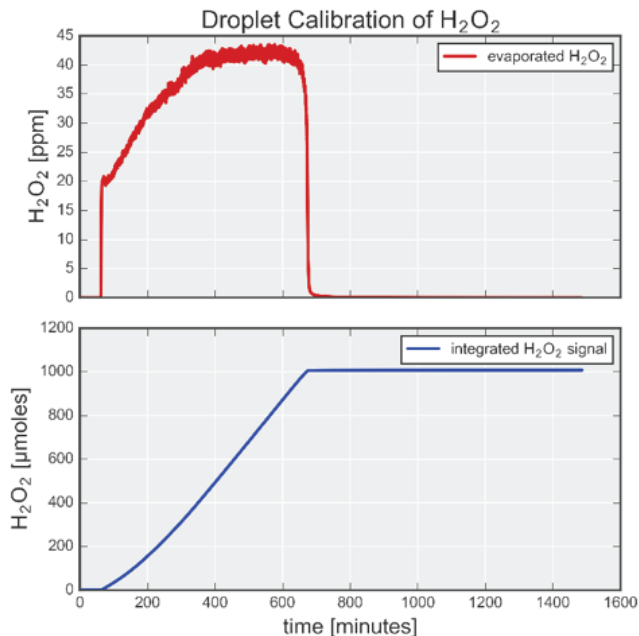


Figure 3: Total droplet evaporation test with a droplet size of 100 μL . Top panel: time series of H_2O_2 after the injection of the droplet. Bottom panel: integrated H_2O_2 measurement.

We now describe the calibration of the golden analyzer using the TDE experiment using the apparatus shown in Figure 2. An aliquot (20–600 μL) of various dilutions (including neat) of the concentrated H_2O_2 solution is injected into a clean glass beaker with a two-port gas tight stopper. A flow of zero air is set using a calibrated mass flow controller (MFC) at 1000 sccm. The gas is directed through the beakers containing first deionized water to humidify the sample stream, and then through a second beaker with the droplet, and finally to the instrument, with an open split to redirect the excess flow not used by the instrument (which has a flow of about 700 sccm).

A typical time series is shown in Figure 3, for the golden analyzer (S/N NBDS-2052), for a droplet size of 100 μL of neat solution. Over a period of several hundred minutes, the droplet evaporates completely. Given the molar flow through the calibrated, traceable MFC (44.6 mmole/min) and the measured concentration profile (where ppm of H_2O_2 corresponds to the mole fraction), the observed concentration pulse can be integrated over the duration of the experiment to arrive at the

total moles of H_2O_2 observed at the outlet of the beaker. In this experiment, 1007.67 μmoles of H_2O_2 were observed using the onboard calibration on the instrument, as compared to the expected 1029.91 μmoles calculated from the analytical analysis of the droplet. This onboard calibration factor, which relates the absorption spectrum model function to the H_2O_2 concentration, was set in 2013 using a single instrument and the total droplet evaporation test with an assumed value for the standard high concentration H_2O_2 solution of 30% H_2O_2 wt/wt. This test indicates that the ratio of the calibration derived from this experiment relative to the onboard calibration is $1029.91 / 1007.67 = 1.022$; in other words, the span calibration of S/N NBDS-2052 would need to be adjusted upward by a factor of 1.022, or 2.2%.

We performed about twenty repetitions of the TDE experiment on the golden instrument; these results are shown in Figure 4. For two experimental runs, we diluted the neat solution further with deionized water, to a level of about 1% wt/wt, from which multiple repetitions were performed. In addition, we did four runs drawing from a neat solution. In the cases of “Full Strength A” and “Full Strength B”, the aliquot was drawn directly from the source flask. In the cases of “Full Strength C” and “Full Strength D,” the neat solution was decanted into two 5 mL glass vials about one week apart, from which multiple aliquots of 20–150 μL volume were drawn.

Figure 4 is a calibration plot of measured moles of H_2O_2 using the onboard calibration vs. actual moles of H_2O_2 in the sample. Fitting the data with a variable intercept and a fixed intercept have nearly the same slope value; we elect to use the fixed slope value for simplicity. The fixed slope of 0.9521 ± 0.015 ($R^2 = 0.997$) indicates that we need to increase the calibration factor on the golden instrument by $5.0 \pm 1.6\%$ (1-sigma), where we have incorporated the uncertainty in our determination of the standard high concentration solution and the uncertainty of the slope determination into our estimate of the calibration slope.

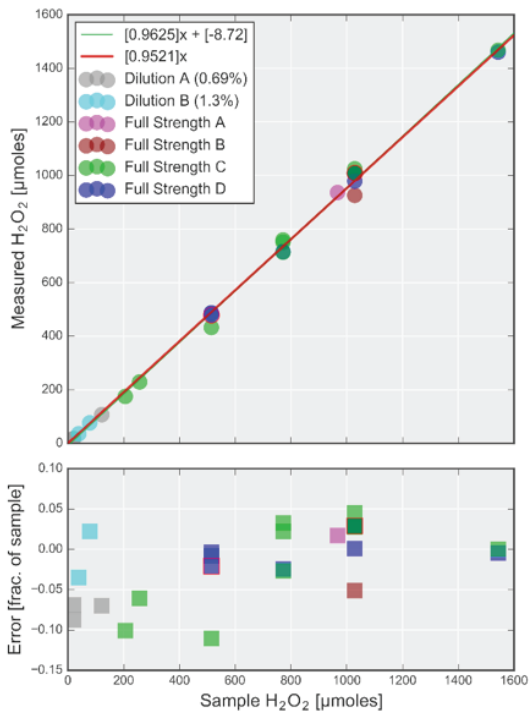


Figure 4: Multiple repetitions of the TDE experiment, using both dilute and neat samples. The top panel shows the measured total moles of H₂O₂ vs known H₂O₂ in the sample. The lower panel shows the residuals from the linear fit as a fraction of the known value.

The vast majority of these experiments were performed in a humid gas stream (~1% mole fraction). Two tests were performed in a dry gas stream (the points at about 500 and 1000 μmoles outlined in red). These data are statically indistinguishable from the humid measurements indicating that the effect of humidity on the measurement of peroxide is minimal.

Calibration Summary

We summarize these results in the Table 2. Most of the adjustment between the 2013 calibration and the final golden calibration is due to the difference between the manufacturer's nominal value of 30% H₂O₂ wt/wt and the experimentally determined value of 31.43% H₂O₂ wt/wt.

Method	Calibration Slope (relative to 2013 value)
2013 Calibration	1.0
Final Golden Instrument Calibration	1.050 ± 0.016

Table 2. Summary of calibration results

Final Conclusion: Picarro will apply the new calibration factor 1.05 to all PI2114 instruments from February 2018 forward.

Method for Calibration of Individual Instruments

Because H₂O₂ is a reactive gas that can adhere to surfaces, it is difficult to prepare and deliver a constant and known concentration of H₂O₂, 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 the 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, repeatability, and accuracy requirements for sample preparation can be relaxed dramatically.

3. Ensure the calibration of the Golden instrument and all instruments in the field over time by checking the calibration of this instrument with a non-reactive proxy gas, which can be routinely obtained with 1-2% accuracy from commercial suppliers, and stably stored in high pressure gas cylinders for years. In the case of H₂O₂, this proxy gas is CH₄.

The apparatus used for performing the cross-calibration experiment is shown in Figure 5. Ambient air flows over a bed of urea hydrogen peroxide to create a humid gas stream containing H₂O₂. This gas source is diluted using the same ambient air. 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, variability of H₂O₂ delivered by this system do not affect the ultimate calibration of the Device Under Test (DUT).

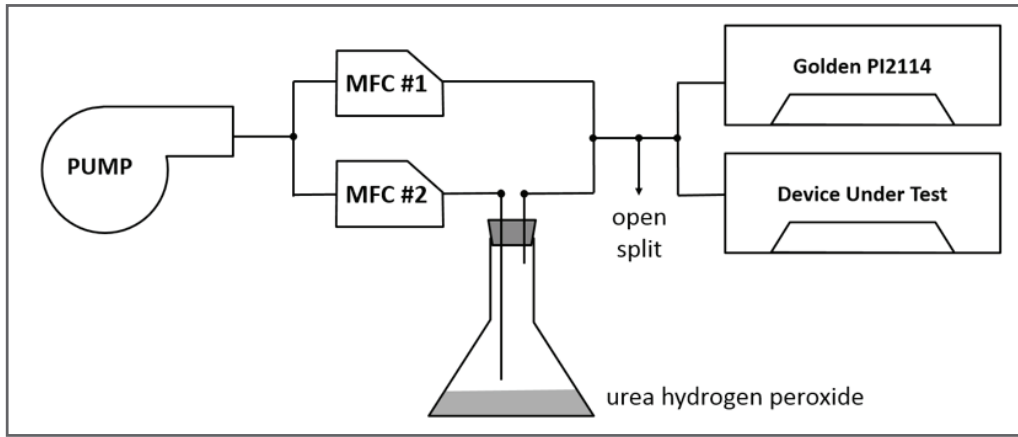


Figure 5. Cross-calibration setup used to transfer the calibration of the Golden instrument onto the DUT.

For a typical dilution profile, we vary MFC #1 and MFC #2 in tandem to create a slowly varying concentration over a period of several hours. This pattern is generally repeated twice. A typical time series is shown in Figure 6.

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 Figure 8. To create this figure, we determine the slope (1.0123 ppb/ppb) and offset (+2.32 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 is plotted in Figure 7.

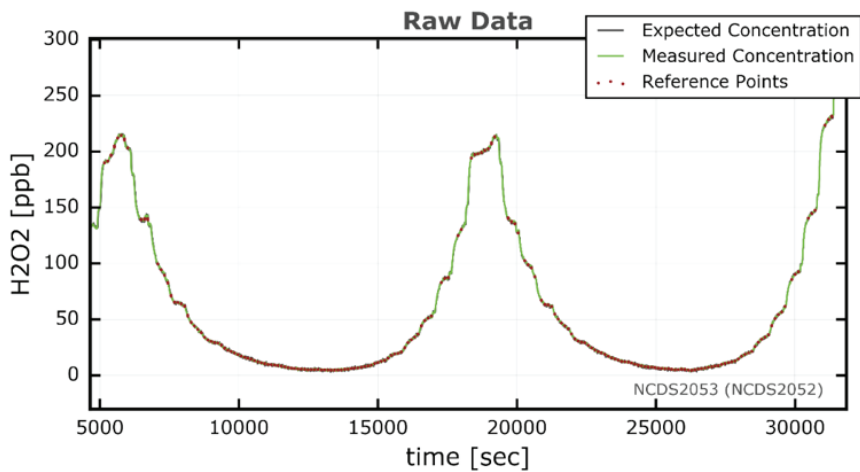


Figure 6. Time series for the Golden Instrument (NCDS2052, in gray) and the DUT (NCDS2053, in green). The reference points (shown in red) are selected from both time series to meet minimum criteria for stability. These points are used in further analysis.

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 that is applied to all instruments, for the following reasons:

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.

- Because H_2O_2 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 H_2O_2 can also distort the calibration curve.

We 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 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 Figure 7.

From this second set of data, we also derive the linearity of the instrument², which is defined as the ratio of the maximum excursion of the residual from a linear fit to the total span of concentration. Figure 8 shows this linearity plot; the gray dotted lines in the lower figure indicate the requirement of 1% for

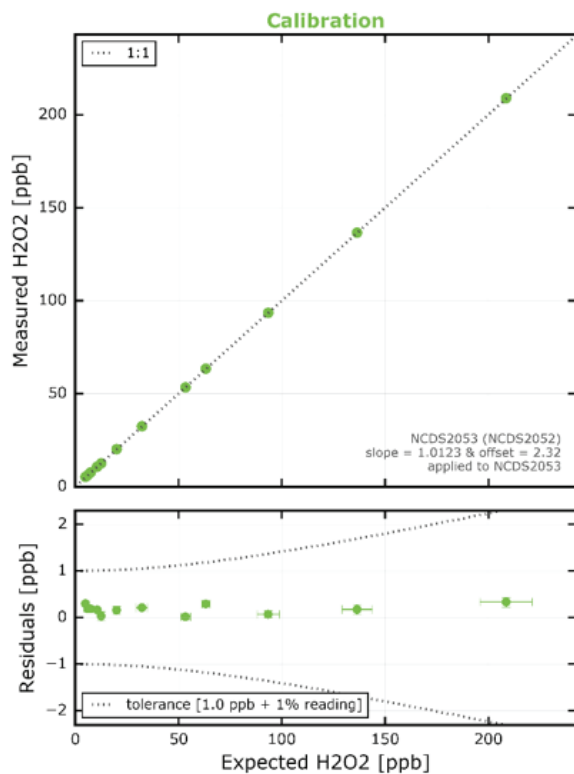


Figure 7. Calibration data derived from Figure 5

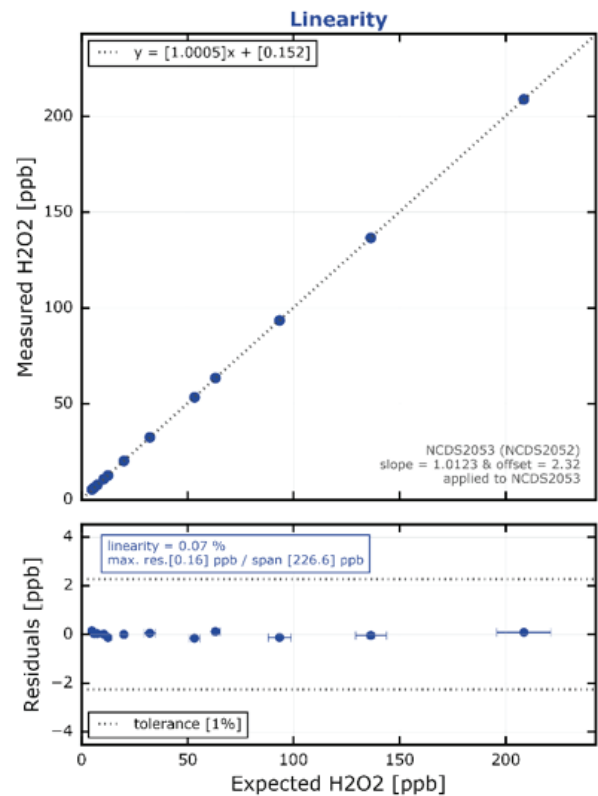


Figure 8. Linearity plot

Finally, from each cycle, we can determine the Method Detection Limit (MDL)³. The MDL data are shown in Figure 9. The MDL must be lower than 1.0 ppb on both cycles for the instrument to pass the test.

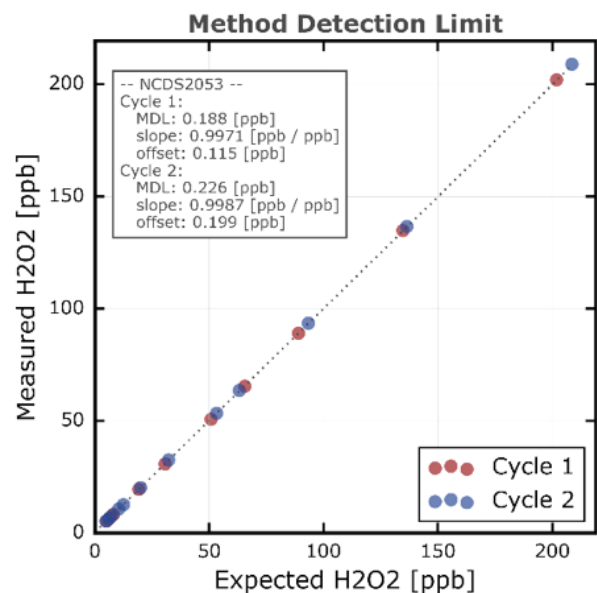


Figure 9. Calibration data derived from Figure 5

² IEC 61207-1

³ SEMI C10-1109

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. As noted above, traceable calibration of H₂O₂ is a difficult process. We therefore have little direct confirmation of the stability of our H₂O₂ 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)⁴, 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 H₂O₂⁵, we may then conclude that the H₂O₂ calibration slope in the PI2114 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 H₂O₂, we recommend a yearly calibration validation, using either the reactive gas H₂O₂ itself, or, more simply, the non-reactive proxy gas CH₄. There is no need to perform a true calibration in which the calibration slope is changed per the results of a direct H₂O₂ calibration experiment.

CRDS: An Inherently Stable Optical Spectrometer

In CRDS, the beam from a continuous wave, single-frequency tunable laser diode enters a cavity defined by three high reflectivity mirrors (Figure 10.) When the laser is on, the cavity quickly fills with circulating laser light. Because the mirrors have

slightly less than 100% reflectivity (99.999%), a small amount of light continually leaks out. This leakage is directly proportionate to the intensity of the light in the cavity, and is continuously measured with a photodetector.

When the photodetector signal reaches a threshold level (in a few tens of microseconds), the laser is abruptly turned off. The light already within the cavity continues to bounce between the mirrors (about 100,000 times). For a Picarro cavity of only 25 cm in length, the effective path length can be over 20 kilometers. As the light continues to circulate it is gradually lost, and the photodetector measures an exponential decay curve. In the absence of absorbing gas, the decay rate is determined solely by the reflectivity of the mirrors. If an absorbing gas is present, a second loss mechanism is introduced resulting in a faster exponential decay rate.

This decay, or “ring-down”, is measured in real-time by the photodetector, producing an exponential decay curve comprised of several thousand individual light measurements. A dedicated signal processor fits this curve to determine a decay rate. Critically, this rate is independent of the initial laser intensity, providing immunity to laser intensity variations. Further, because each fit is made to thousands of sequential measurements, the process is highly resistant to detection system noise.

To obtain a spectrum, the laser frequency is tuned over a sequence of steps, and a ring-down rate is measured for each step (Figure 3.) Hundreds of ring-down measurements are made each second. The total absorption of the sample is given by the reciprocal of the product of the ringdown time and the speed of light.

⁴Yver 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.

⁵The 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.

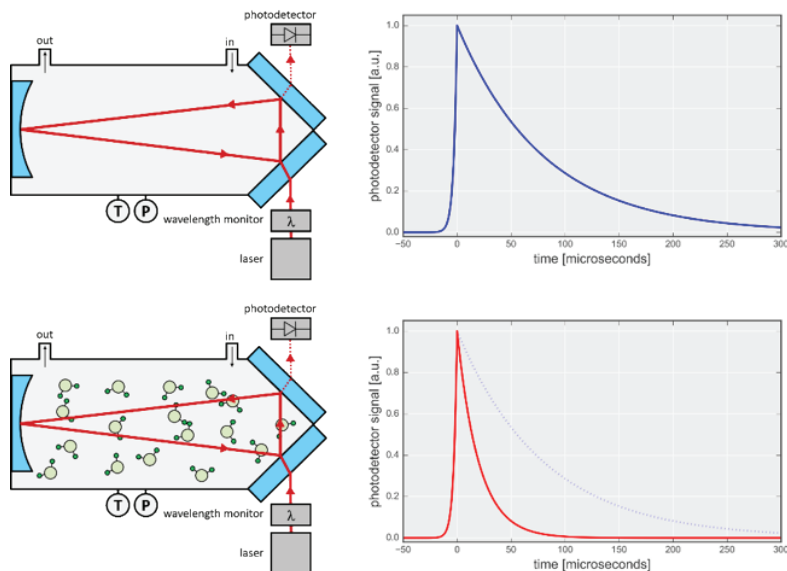


Figure 10. High finesse optical cavity with a three-mirror configuration. Top: no absorbing species in the cavity = long ring-down time. Bottom: absorbing species present in the cavity = short ring-down time

The long-term stability of an optical laser spectrometer depends on the accuracy of primarily four parameters 1) Laser frequency/wavelength, 2) Measured optical absorbance, 3) Cavity pressure, and 4) Cavity temperature. We consider these four parameters below.

At Picarro we developed and patented our own wavelength monitor. This system provides ultra-precise frequency measurements, and real-time feedback control of the laser operating parameters. The result is higher spectral precision than can be found in any other commercial spectrometer-laser-based or otherwise. The optical absorbance as provided by the temporal analysis of the ringdowns; time-based measurements such as these exhibit a high degree of accuracy. This spectral accuracy, both in the wavelength axis and the absorbance axis, is the key to the ultra-precise fitting of line shapes and line heights necessary to reach parts per billion concentration sensitivity.

Since the spectrum for each gas is a function of cavity temperature and pressure, accurate

estimation of gas concentrations therefore requires not only precise wavelength measurements, but also precision measurement and active control of the cavity temperature and pressure, to minimize instrument drift.

In Picarro CRDS gas analyzers, the sample cavity is surrounded by layers of thermally insulating material to provide a high degree of passive thermal stability. The cavity is further actively stabilized by means of a solid-state heating system locked to the output of a thermal sensor. This enables the cavity to be permanently locked to the operational temperature.

The sample pressure in the cavity is sensed using a high-linearity pressure transducer. The system computer uses this pressure data in a feedback loop to control the proportional valves which adjust the inlet and outlet gas flow of the cavity. In this way, the pressure in Picarro analyzers is actively stabilized to better than 1 part in 2000.

Rationale for Calibration Validation using CH₄ as a Proxy Gas

While the PI2114 can be operated for very long periods without calibration, Picarro recognizes that most users will need to periodically validate the

performance and calibration of the instrument to ensure proper operation, and to comply with GMP guidelines or other institutional policies.

Every time the analyzer makes a gas concentration measurement, a spectrum is obtained and interpreted as the summation of background light loss in the analyzer, and gas-specific light loss. These two mechanisms control the zero intercept and slope of the gas concentration calibration respectively. Over time, physical evolution of the state of the mirrors or other optical components can have very small effects on the accuracy of this calibration, which will manifest as slight variation in the zero intercept.

The slope parameter of any gas concentration calibration is related to the fundamental properties of the gas and should never be field calibrated. As we've seen, Picarro instruments maintain exquisite control over temperature and pressure. Inaccuracy in the slope calibration could be caused by physical failure of the temperature or pressure control systems, but in the unlikely event that this happens, the problem should be resolved by repairing those systems rather than adjusting the slope parameter. Therefore, field calibration of the slope is limited to a 'calibration validation' without changing the instrument's factory calibration. There are two options how a 'calibration validation' can be achieved.

The first option is to perform the same type of experiment that was used to generate the fundamental H₂O₂ factory calibration as explained in the above section about the calibration of the Golden instrument. The described TDE approach is time consuming and requires expert knowledge to obtain an accurate instrument validation.

As a second option, with the aim to reduce this burden on our users, we have developed a surrogate gas validation procedure that greatly accelerates the process. In this approach, methane gas is introduced to the system at known concentrations, and a dedicated spectroscopic model is used to evaluate these concentrations. Just as for H₂O₂ (or any other molecule), the slope of the calibration for this gas will not change except in the event of failure of the temperature or pressure control systems. By providing the system with several gas concentrations, the accuracy of the slope and therefore the validity of the instrument can be verified. Since any failure that would compromise the ability

to measure H₂O₂ would also compromise the ability to measure the methane surrogate gas, proper behavior with the surrogate gas also validates performance with H₂O₂.

Methane is an excellent proxy gas for H₂O₂ in this spectral region, as can be seen in Figure 1. Every few seconds, the instrument scans the full spectral region shown in this figure, which includes the spectral features of CH₄, H₂O, and H₂O₂. The primary spectral features of CH₄ and H₂O₂ are just a fraction of a wavenumber from each other; in other words, this difference in the wavelength is just 3 parts in 100,000. Because all the same optics (laser, wavelength monitor, fibers, mirrors, detectors) are used to collect this spectrum, there are almost no conceivable failure modes that affect the wavelength or absorbance measurements that will lead to incorrectly reported H₂O₂ but correctly reported CH₄, and vice versa. Similarly, because the optical beam path samples the same physical gas sample across this spectrum, any errors in temperature or pressure will lead to calibration slope errors in both CH₄ and H₂O₂. Measurements of calibrated methane cylinders is thus an excellent method of validating the proper operation of the PI2114 optical spectrometer.

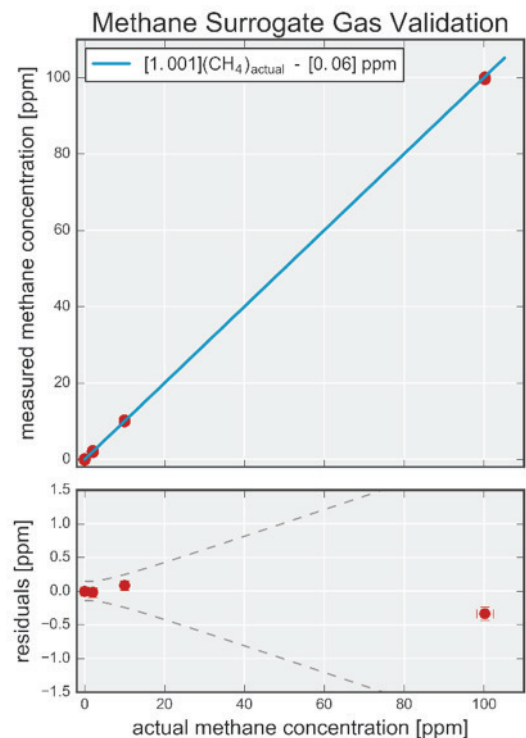


Table 11. Proxy gas calibration, using three gravimetrically prepared

Methane can be prepared gravimetrically at many commercial specialty gas manufacturers, routinely achieving traceable accuracy of $\pm 2\%$. Because the PI2114 also reports methane during normal operation, this output channel can be used to verify proper operation of the instrument, by injecting CH_4 gas standards (balance air) and comparing the measured concentration to assigned values for the cylinders. An example of such a validation experiment is shown in Figure 11. Each point corresponds to a measurement of a single bottle, where the mean and standard deviation of the measurement are recorded after the measurement through the instrument stabilizes. The slope is 1.001, indicating a discrepancy of 0.1% on the span calibration; the offset of -0.06 ppm corresponds to $0.06/70 = 0.86$ ppb of H_2O_2 . The bottom panel shows the residuals of the linear fit, which are well within the target specification of $0.07 \text{ ppm} \pm 2\%$ reading. This procedure can be performed easily whenever one wishes to confirm that the optical spectrometer is operating properly.

Of course, to be certain that the instrument is operating properly, there is no substitute for performing a reactive gas measurement of H_2O_2 , using a total droplet experiment, a comparison experiment with a second H_2O_2 instrument, or similar test. For example, reactivity of H_2O_2 in the instrument sampling system may lead to an under-reporting of the H_2O_2 concentration that the non-

reactive methane proxy would not capture. That having been said, the non-reactive proxy calibration procedure is an excellent, simple method for detecting the most common failure modes that lead to erroneous measurements of H_2O_2 .

Summary

For all Picarro H_2O_2 instruments (PI2114):

1. The calibration factor relating the optical absorbance in the measurement cell to the concentration of H_2O_2 is the same value for all instruments.
2. This calibration factor, derived from three gravimetrically prepared cylinders and zero air, has been determined with a series of careful total droplet evaporation experiments.
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, using both reactive H_2O_2 (about once/year) and a non-reactive proxy gas, CH_4 (about once/quarter).
4. While in the field, the calibration of the instrument can be verified using a direct H_2O_2 calibration experiment, or, more simply, by testing with CH_4 standards.