The Picarro G2302: An accurate and stable carbon monoxide analyzer for greenhouse gas monitoring

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Summary: In this white paper, we describe the performance of the carbon monoxide measurement of Picarro's G2302 carbon monoxide, carbon dioxide, and water vapor analyzer. Precisions of better than 2 ppb are routinely achieved in a five minute measurement time. We also present a careful study of the cross-interference of other common atmospheric constituents with the measurement of carbon monoxide. Through use of the appropriate methods, one can achieve excellent performance that meets and even exceeds the WMO inter-laboratory comparability standard of ± 2 ppb for trend detection of the marine boundary layer and ± 5 ppb for continental sites experiencing the influence of regional pollution (CO > 250 ppb). The G2302 enables high-quality measurements of both the well-mixed atmosphere as well as pollution plumes downwind of urban centers.

The importance of carbon monoxide to greenhouse gas monitoring science

Although carbon monoxide is not considered a significant greenhouse gas, it is an important atmospheric tracer and it plays a critical role in atmospheric chemistry. Major sources of atmospheric CO include anthropogenic emissions and biomass burning. Measurements of CO at Global Atmosphere Watch (GAW) stations focus on understanding the role of CO in the atmospheric photo-chemically driven cycle involving methane, formaldehyde, ozone, and OH. GAW measurements are made in the well-mixed atmosphere in remote locations far from anthropogenic sources. For this type of measurement, the World Meteorological Organization has placed a strict requirement on the inter-laboratory comparability of CO of ± 2 ppb[a] for trend detection of the marine boundary layer and ± 5 ppb for continental sites experiencing the influence of regional pollution (CO > 250 ppb)[b]. This requirement is difficult to achieve in practice, using standard carbon monoxide instrumentation. Common techniques for measuring CO are GC-HgO (Gas Chromatography with a mercuric oxide detector), GC-FID (Gas Chromatography with a Flame Ionization Detector), NDIR (Non-Dispersive Infrared

[a] we use 'ppb,' or parts-per-billion, as a convenient shorthand for nmol mol^{-1}.

[b] See, for example, GAW Report No. 192, Guidelines for the Measurement of Atmospheric Carbon Monoxide, 2010.

Absorption), Gas Filter Correlation, and VURF (Vacuum Ultra-Violet Fluorescence). While it is possible with all these techniques to perform high-quality CO measurements, they all present difficulties for field deployment, either because they suffer from poor reliability, they require frequent human intervention, and/or they require consumables.

An emerging field of greenhouse gas measurement science is focused on understanding the so-called urban metabolism [reference], with the goal of quantifying the emissions of carbon dioxide and other greenhouse gases from urban centers on as small a spatial scale as is possible. A key challenge for these types of measurements is to correctly distinguish anthropogenic, particularly petrogenic, emissions from biogenic sources. Radiocarbon analysis is the gold standard for this type of measurement, but because radiocarbon analysis of sufficient accuracy can only be performed at core Accelerator Mass Spectrometry (AMS) laboratories, it is prohibitively expensive. However, it has been shown [reference] that carbon monoxide is well-correlated with petrogenic emissions, because in urban centers it is produced primarily through combustion of fossil fuels. While the requirements for measurements of carbon monoxide in these measurements have not yet been established, they are likely to be relaxed relative to the WMO inter-laboratory comparability standard.

In this white paper, we describe in detail the performance G2302 CO / CO_2 / H_2O analyzer. Through use of the appropriate methods, one can achieve excellent performance that meets and even exceeds the WMO inter-laboratory comparability standard. The white paper is organized into the following sections:

The near infrared spectroscopy of the G2302 analyzer

We begin with a discussion of the near-infrared spectroscopy that lies at the heart of the G2302. We have selected one of the strongest CO lines in the near-infrared region, which is (nearly) free of spectral interference from other atmospheric species. Unfortunately, the spectrum is not completely free of interfering lines. Within a fraction of a wavenumber of the CO line are several features associated with H_2O and CO_2. This spectrum can be seen in Figure 1. The

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primary CO feature is a single $^{12}C^{16}O$ line, nestled between a set of carbon dioxide and water vapor lines. Clearly, there is a significant possibility of spectral interference in the CO measurement from carbon dioxide and water vapor. We will carefully study the effects of both of these gases on the measurement of CO.

For these purposes, it is important to quantify the cross-talk for all important isotopologues of carbon dioxide and water vapor, so that in real world applications, we can quantify the effect of variations in the stable isotope ratios on the measurement of CO. The spectra of the isotopologues are sufficiently well-known that the HITRAN database can be used to make absorption line assignments. The situation for carbon dioxide is straightforward, since all of the carbon dioxide lines in the immediate vicinity of the CO line are associated with $^{12}C^{16}O_2$ lines. The other stable isotopologues of CO_2 will have a negligible effect on the measurement of CO.

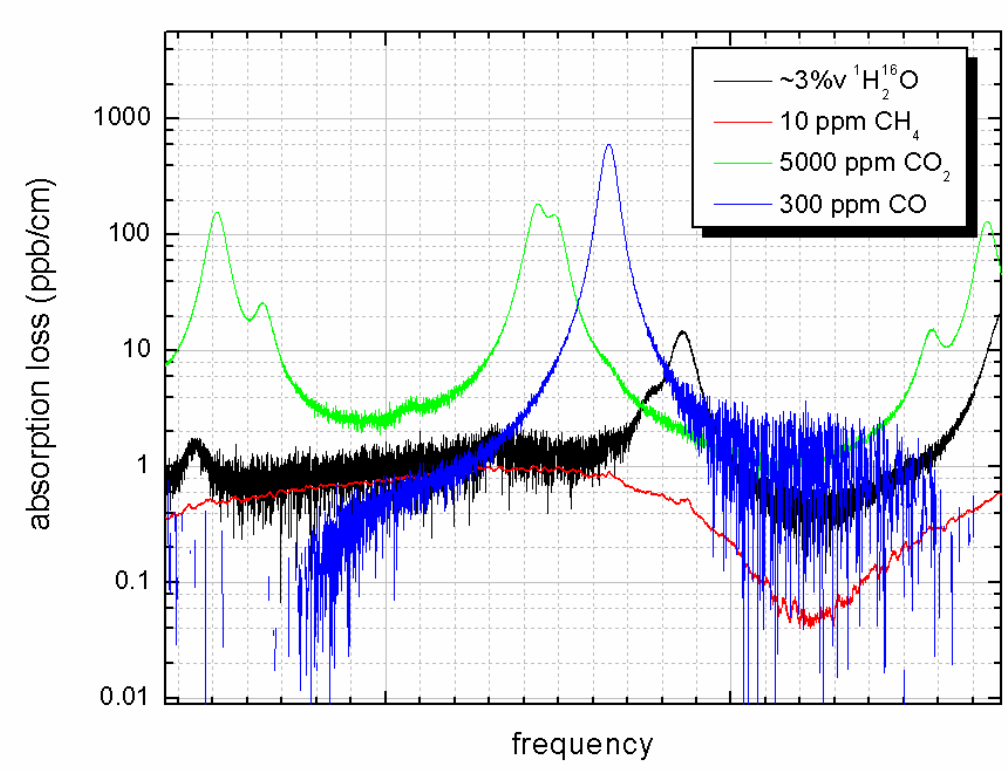

Figure 1: spectrum of CO, CO_2, CH_4, and H_2O. The spectroscopic structure below about 1 ppb/cm is an artifact of the spectral acquisition (for example, there are no distinct lines visible due to methane)

The spectra of the water isotopologues in the real world often deviate significantly from what is reported in the HITRAN database. For this reason, we have made careful experimental spectra on water vapor of differing isotopic composition. The following waters have been used for this study:

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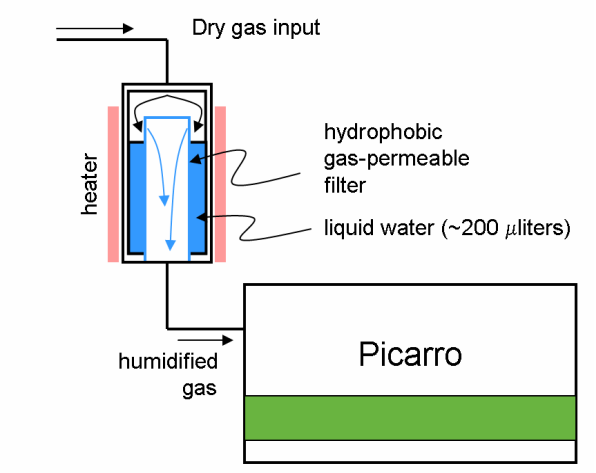

Figure 2: set-up for humidifying dry gas standards.

- **Picarro00 water:** This water is an internal working standard at the Picarro factory, of near meteoric water with measured delta of -9.6 ‰ and -62‰ permil in $\delta^{18}O$ and δD, respectively.
- **Picarro33 water:** This water is also an internal working standard at the Picarro factory, which has been enhanced by +1000 ‰ in δD and +100 ‰ in $\delta^{18}O$.
- **+5000 ‰ $\delta^{18}O$:** This test water was prepared by adding a small volume of ~ 10 atom % $H_2{}^{18}O$ to Picarro00 water, to generate water that is highly enhanced $H_2{}^{18}O$. The +5000 ‰ assignment is only approximate, due to the large uncertainty of the 10% sample.
- **+5000 ‰ $\delta^{17}O$:** This test water was prepared by adding a small volume of ~ 10 atom % $H_2{}^{17}O$ to Picarro00 water, to generate water that is highly enhanced $H_2{}^{17}O$. Similarly, the +5000 ‰ assignment is only approximate, due to the large uncertainty of the 10% sample.

We generated vapors from each of these waters using the apparatus shown in Figure 2. Zero air was used as the gas input. Fine spectra were collected for each of these waters, and the results are plotted below, along with the carbon monoxide peak. Identification of the peaks is noted directly on the graph. Fortunately, the important water peaks in the vicinity of the carbon monoxide peak are all associated with the most common isotopologues of water, which simplifies the spectroscopy substantially. The $^1H_2{}^{18}O$ peaks just to the right of the carbon monoxide line are sufficiently distant, and sufficiently small, that no correction for this isotope will be required. $^1H^2H^{16}O$ are even further away from the CO line.

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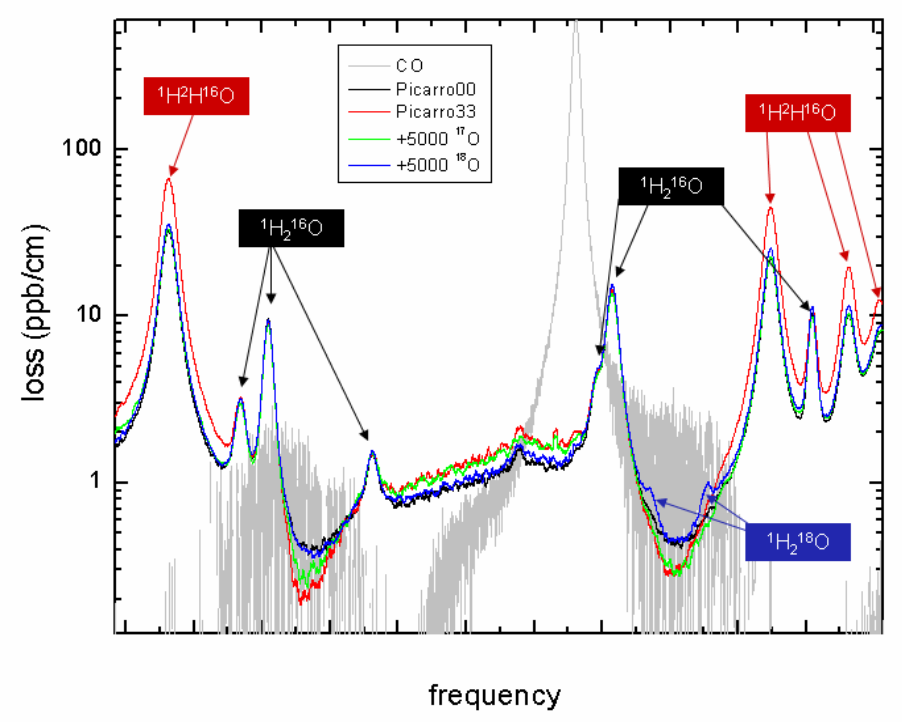
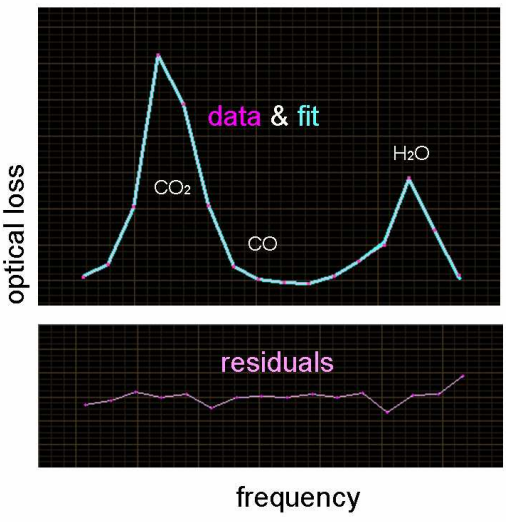


Figure 3: the spectra of the principle water vapor isotopologues in the vicinity of the carbon monoxide line. Note the logarithmic scale. The small deviations on the baseline are not important to this analysis.

Study of these spectra reveals several interesting and important considerations. First, the spectroscopy of the carbon monoxide region requires careful real-time spectroscopic quantification of two additional species: the most abundant isotopologues of carbon dioxide and water vapor. There are a total of five distinct spectral features that need to be included in the spectroscopic fitter: the target carbon monoxide line, and two lines each for carbon dioxide and water vapor. Furthermore, we note that for typical ambient concentrations of 100 ppb of carbon monoxide, 380 ppm of carbon dioxide, and 15,000 ppm of water vapor, the ratios of the largest line for each species in this immediate spectral region are 1:66:32 for $CO:CO_2:H_2O$. This places very stringent requirements on precision and accuracy on the spectrometer and on the nonlinear analysis that converts the measured spectra and converts these spectra into concentration values.



A typical spectrum, along with the full spectroscopic fit, is shown in the figure at the left (there is less than 10 ppb of CO in this gas sample, along with about 0.5% water and 200 ppm CO_2). The residuals are shown on a ~15X magnified scale. The interfering lines are modeled quite well by the spectroscopic fitting algorithms. But it is the small

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drifts in the exact locations of the spectral points (drifts either in frequency or in optical loss) that can cause small distortions of the spectra, which can in turn cause small distortions in the reported residuals. It is drift in the residuals which can cause cross-talk of CO_2 and H_2O to the reported CO values. We will discuss this cross-talk in detail later in this white paper.

Carbon Monoxide: Performance under Dry Gas Conditions

In the GAW Report No. 192, Guidelines for the Measurement of Atmospheric Carbon Monoxide, the data quality objectives for carbon monoxide measurements are as follows:

- Mole fractions of one and the same air sample determined by different laboratories and/or monitoring stations should be ± 2 ppb (95% confidence level or coverage factor of k=2), with averaging time of 1 hour.
- For CO measurements above 250 ppb, the required uncertainty is ± 5 ppb (95% confidence level or coverage factor of k=2).

These uncertainties include random sources of noise as well as biases and systematic errors that can and do occur under real-world conditions, and proving that the Picarro G2302 achieves these very challenging data quality objectives will require the patient efforts of many laboratories studying many instruments, and is beyond the scope of this white paper. However, we have performed experiments on one instrument over a period of several days that clearly demonstrates the potential of this technology to achieve the carbon monoxide data quality objectives set out by the WMO[c].

Single Bottle Measurements

In a first step, we directed gas from a single bottle containing compressed air containing approximately ambient levels of carbon dioxide and methane, and an unspecified amount of carbon monoxide[d]. For the purposes of determining precision and drift, the exact amount of carbon monoxide is not important; we will deal with the absolute calibration of the instrument later in this white paper. We performed this test in our laboratory for about three consecutive days. The results are shown in Figure 4.

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[c] As a proxy for a complete assessment of the inter-laboratory comparability of the G2302, we will analyze and report twice the standard deviation of our measurements, corresponding to the k=2 requirement spelled out in the GAW report.

[d] The vendor did not provide analytical analysis of carbon monoxide in this bottle, and Picarro does not maintain traceable standards for carbon monoxide.

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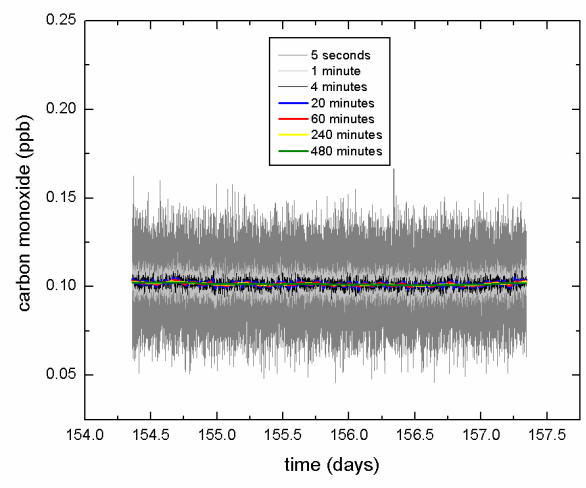

Figure 4: single bottle test of a G1302 CO analyzer, for different window averages.

Below, we tabulate the statistical variation of the data for these three days:

Table 1: measured 2σ for a 3 day test. All three days of data were used for calculation of the standard deviation.

Averaging window	precision (2σ) (ppb)
5 seconds	29.26
1 minute	8.34
4 minutes	4.32
5 minutes (not shown)	*3.90*
20 minutes	2.16
60 minutes	1.54
240 minutes	1.14
480 minutes	0.99

First, it is important to point out that this instrument has a five minute standard deviation of 1.95 ppb, which just meets 2 ppb in a five minute average, which was the Picarro guaranteed specification for the G1302. In other words, the instrument that we used for this work was not an ideal instrument, but was a relatively poor unit from the standpoint of precision. The findings described in this white paper therefore do not represent a best-case scenario, but a realistic estimate of what can be achieved with the G2302.

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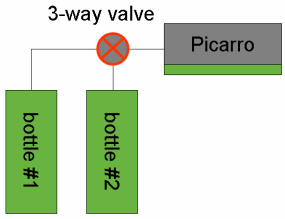
Clearly, these data are quite encouraging; the precision (2σ) of the 60 minute average is well below the inter-laboratory comparability of ± 2 ppb. Yet, while these data look very promising, there are many reasons to caution against over-confidence, for several reasons:

- These data were collected in a laboratory setting – in the field, where temperatures may vary more dramatically, the measurement statistics, especially for long averages, may degrade significantly
- These data were collected over a period of a few days to a week of data collection. For larger time periods, precision and drift will only be degraded from these reported numbers

CO Measurements Using a Secondary Gas Standard

The results demonstrate above, while demonstrating great promise, do not yet provide a reliable path to a method that consistently and robustly provides carbon monoxide data that meets the WMO inter-laboratory comparability standard over all conditions, all time, and all instruments. We then pose the question: can a method be devised that *can* robustly delivery WMO-quality CO results using a secondary gas standard?

We expect that the drift in the CO measurement of the G2302 is dominated by zero drift. Fractional span drift for the G2302 should be similar to the fractional span drift on carbon dioxide, which is less than 0.1% of reading even over long periods of time; for CO levels below 500 ppb, this corresponds to an error of just 0.5 ppb of CO[e]. Thus, the best approach is to use a working standard to track the drift of the zero in the CO measurement[f].



To investigate this possibility, we performed an experiment (depicted in the figure at right) in which we alternated between two bottle sources every two minutes. We wanted to select a fast interval so that any possible drift can be tracked, but slow enough that the dead time during switching (about 30 seconds in these measurements) is not a significant fraction of the duty factor. We do not believe that such a fast switching speed, or high duty cycle, is required to achieve the ± 2 ppb (2-σ) standard. These two bottles have two different carbon dioxide concentrations, and again unknown carbon monoxide concentrations.

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[e] Due to the hazards of handling high levels of carbon monoxide, this span drift test has not yet been performed. These conclusions are based on experience with the G1301 and G2301 analyzers for carbon dioxide and methane.

[f] an alternative to a bottle is to use a catalyst to remove the CO (e.g., Sofnocat) from the sample gas stream. More work is required to validate the efficacy of catalytic removal as a referencing method for the G2302.

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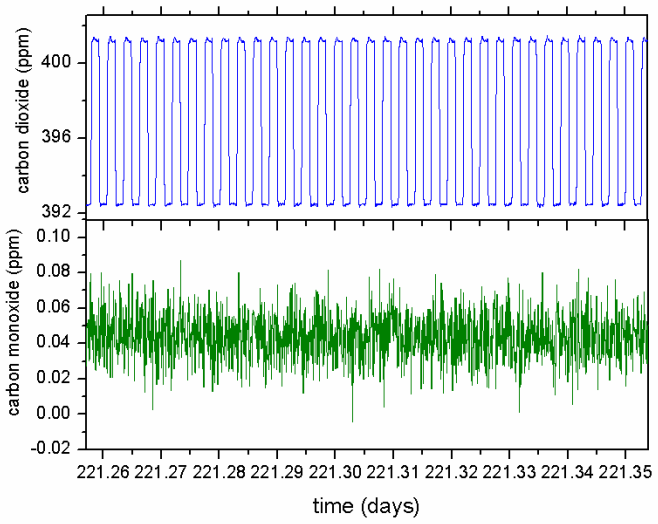

Figure 5: time series showing the concentration of carbon dioxide and carbon monoxide from the analyzer.

A short segment of time, about two hours long, is shown in Figure 5. For two-minute segment, the averages of the reported carbon monoxide and carbon dioxide readings are calculated, excluding a 30 second segment at the transition point between the two gases. We first report the carbon dioxide readings for each bottle over the full seven-day period of the test.

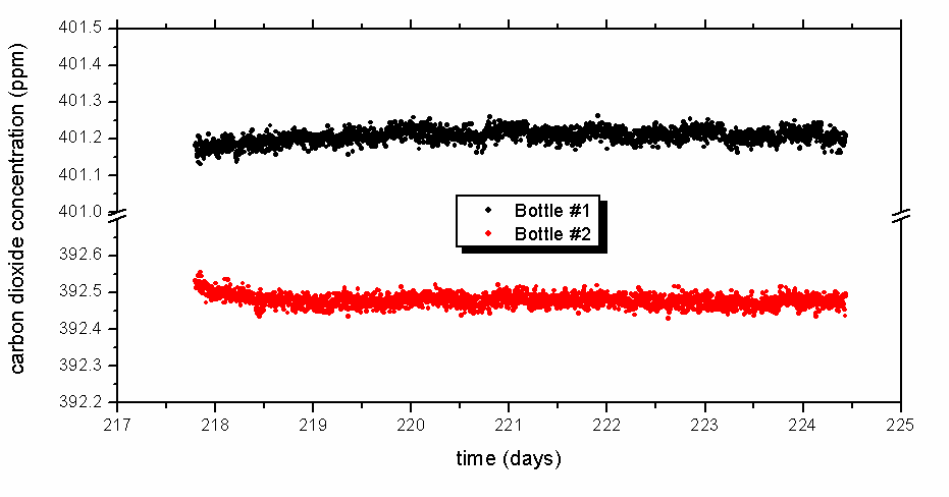

Figure 6: reported carbon dioxide concentrations from each of the two bottles over a 7-day period.

The readings are extremely stable, with just a small drift the order of 50-100 ppb across the full duration of the experiment.

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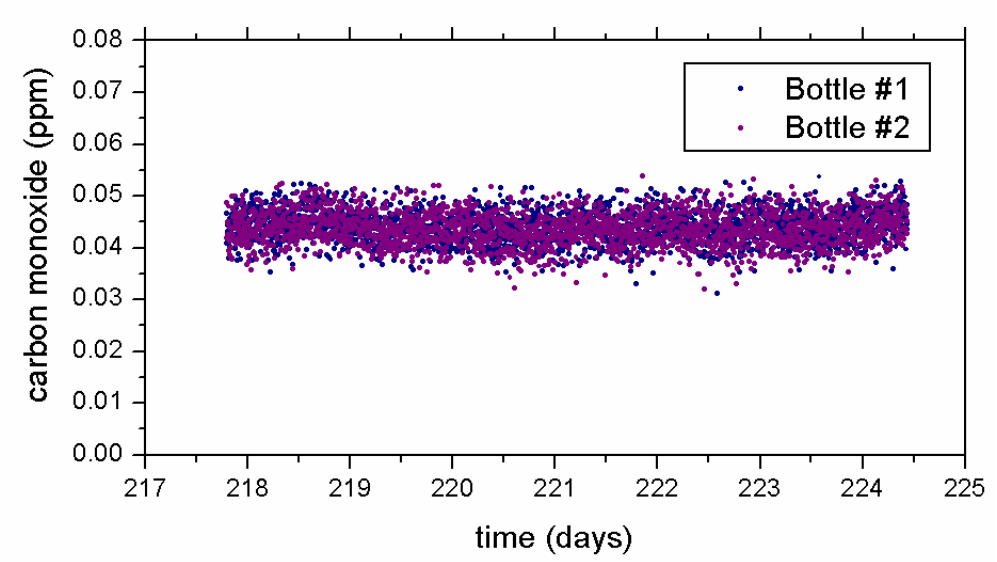

Figure 7: reported carbon monoxide concentration from two bottles, switched every two minutes.

In Figure 7, we display the carbon monoxide from each 2 minute segment on bottle #1 and bottle #2. Clearly, the carbon monoxide readings are almost identical, with the data sets almost completely overlapped. We will now perform further analysis on these data. First, we analyze the results from a single bottle. These results are shown in Figure 8.

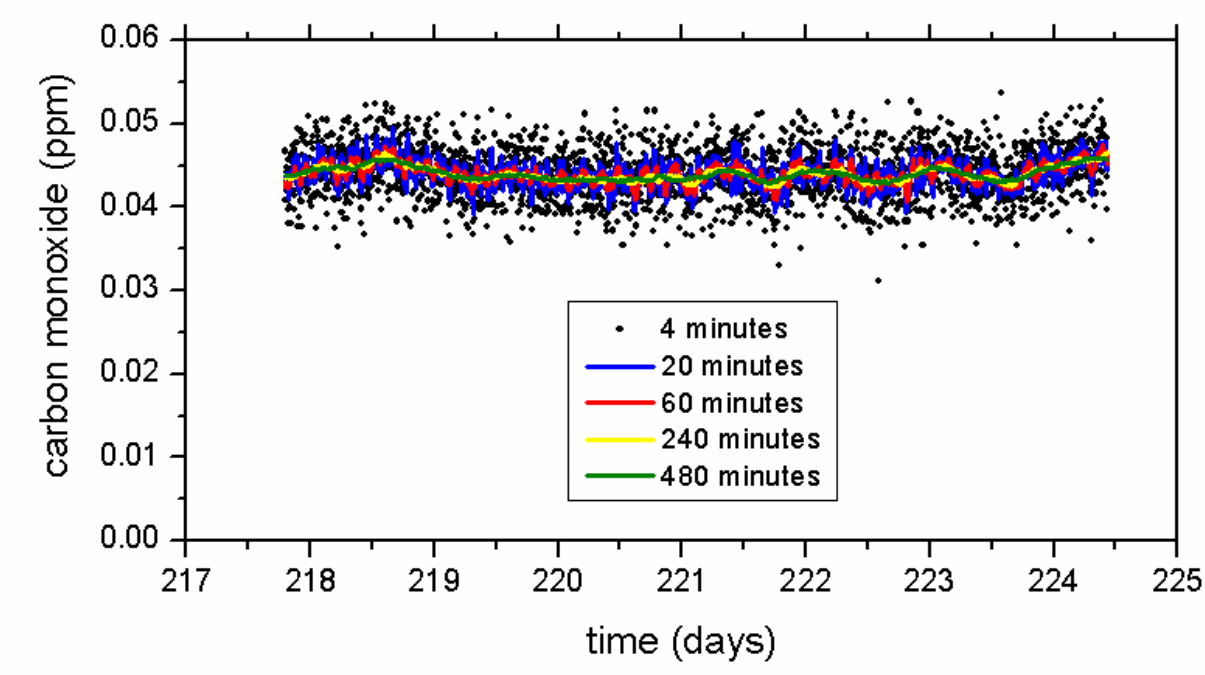

Figure 8: Carbon monoxide measurements on bottle #1, with different averaging windows. The times are total elapsed times – measurements are made on bottle #1 with a 50% duty cycle during this time.

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We summarize the precision and standard deviation, calculated over the full week of data with no data removed. These data are collected with a duty factor of less than 50%, so we expect some degradation of precision relative to the data obtained in the previous, single bottle test.

Averaging window	precision (2σ) (ppb)
4 minutes	6.12
20 minutes	3.14
60 minutes	2.24
240 minutes	1.70
480 minutes	1.52

Consider the processed data series from each two minute segment. We label the resulting concentration series from the 'sample' bottle and 'reference' bottle as *S* and *R*, respectively. The concentrations for the i^{th} segment are thus just S_i and R_i. The simplest analysis would simply calculate the difference between sample and reference, and add the known reference value R_{true} to the resulting data to calculate S_{corr_i}:

$$S_{corr\_i} = R_{true} + (S_i - R_i)$$

The average over time can then be calculated by taking the mean of S_{corr_i}. For example, a 60 minute average would take the mean of 15 bins of sample and reference (each cycle is four minutes in duration, or 15 cycles in an hour). We define the 60 minute average centered at the j^{th} bin as being the average of the period of time from 30 minutes before this bin to 30 minutes after this bin. Therefore:

$$^{60}\overline{S}_{corr\_j} = R_{true} + \left(\frac{1}{15} \sum_{i=j-7}^{j+7} (S_i - R_i) \right)$$

Or, more generally, for an *N* bin average,

$$^{N}\overline{S}_{corr\_j} = R_{true} + \left(\frac{1}{N} \sum_{i=j-n}^{j+n} (S_i - R_i) \right), \text{ where } N = 2n+1$$

These averages are shown in the following figure, for *N* = 1, 5, 15, 60, and 120.

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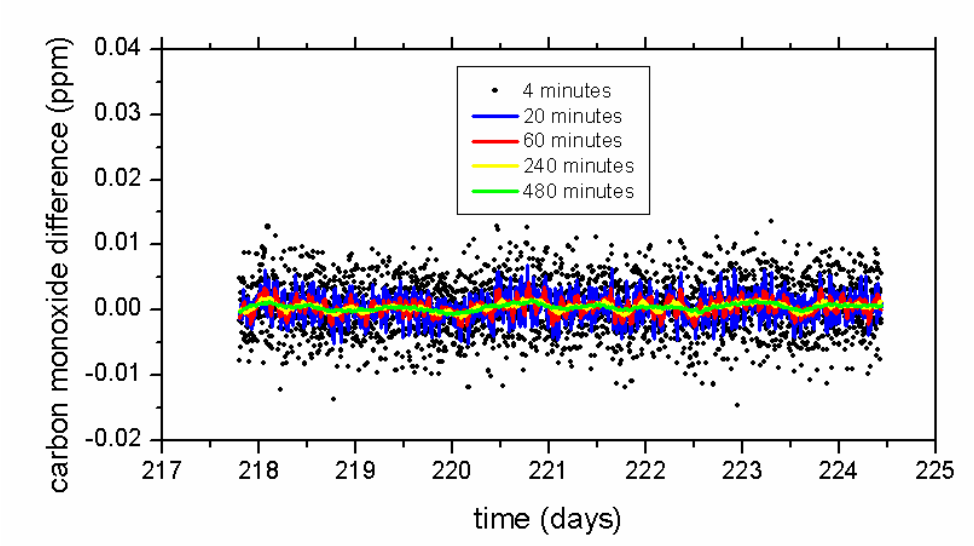

Figure 9: simple averages of the difference between sample and reference.

The statistics generated from this averaging process are expressed in the following table:

Averaging window	precision (2σ) (ppb)
4 minutes	8.52
20 minutes	3.96
60 minutes	2.24
240 minutes	1.31
480 minutes	0.87

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Again, these results are quite good. The sixty minute average very nearly meets the data quality objective for CO of ±2 ppb on an hourly average. But, comparing these data to the single bottle statistics, it is interesting to note that these statistics are *worse* than those for the single bottle data, for all averages except the longest time period average. Why is that? There are three reasons:

- In any given time period, only half of the time is spent collecting CO data. For a 50% duty factor, this increases the noise by the square root of 2.
- The corrected concentration is calculated from the difference between two numbers (which have equal statistics in this instance). These noises (assuming that they are uncorrelated) sum in quadrature, which increases the noise by and additional square root of two.
- Finally, in each 4 minute segment, about 1 minute is dead time during the switching events that is not included in either the reference or the sample measurement. This effect degrades the noise by $\sqrt{4/3}$.

The total noise on short time scales should increase by the product of these factors, or about 2.3. This is roughly the case. The four minute average for the single bottle is 4.53 ppb, and the 4 minute average for the referenced output is 8.52, for a ratio of 1.88. The improvement over this theoretical number comes from the fact that even at fast time scales; we are already seeing the benefit of the referencing method to remove instrument drift.

It is important to remember that the simple averaging formula, with a 50% duty factor between sample and reference, has equal contributions to the noise coming from the sample channel and the reference channel. However, while there is a limit of maximum of one hour specified in the WMO guidelines for the measurement of CO, there is no reason to limit the averaging on the reference channel to one hour. By extending the average on the reference over a longer time period, we can improve upon the statistics of the referencing method without significantly sacrificing the drift correction capabilities inherent in this method.

There are many potential formulations for this averaging, but we have chosen the following recipe: to calculate the corrected concentration over a time period *T*, calculate the average of the sample concentration over that time period, and subtract from it the average of the reference value over the time period *3T* centered on this same time period. In other words, for a one hour

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sample average, calculate the average reference value from the hour before through the hour after the time period in question. Or, using the formulation used above in terms of bins, where *N* bins correspond to a time period *T*, we find:

$$ {}^{N}\overline{S'}_{corr\_j} = R_{true} + \left(\frac{1}{N} \sum_{i=j-n}^{j+n} S_i - \frac{1}{3N} \sum_{i=j-m}^{j+m} R_i \right), \text{ where } 3N = 2m+1 \text{ and } N = 2n+1. $$

Using this expression, we can calculate the statistics for the corrected sample concentration for the same exact data set as we used above. The results are tabulated below, along with the previous result for the simple referencing method, and also the single bottle data, for comparison.

Averaging window on sample	**precision (2σ) (ppb) – single bottle**	**precision (2σ) (ppb) – sample channel @ 50% DC**	**precision (2σ) (ppb) – simple reference method**	**precision (2σ) (ppb) – ext. average on reference**
4 minutes	4.53	6.12	8.52	7.00
20 minutes	3.90	3.14	3.96	3.16
60 minutes	1.54	2.24	2.24	1.68
240 minutes	1.14	1.70	1.31	1.09
480 minutes	0.99	1.52	0.87	1.00

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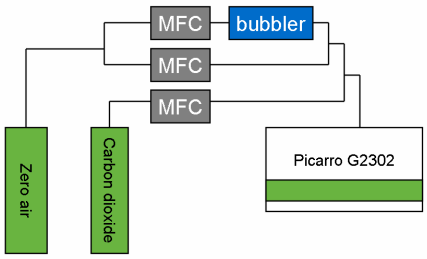
We highlight the fact that the 60 minute measurement using this new referencing calculation easily achieves the 2 ppb WMO data quality standard over a seven day measurement. There are still improvements to be made in this method --- it is not necessary to spend 50% of the time measuring the reference gas, nor is it necessary to switch every two minutes. We will continue to further develop these methods.

In summary:

- Without applying a referencing method, the G2302 is capable of achieving the WMO inter-laboratory data quality standard for CO of ± 2 ppb (k=2) for short periods of time (days).
- By applying an aggressive referencing method to a working standard, improved long-term drift of 1 ppb can be demonstrated, at the expense of some increase in the shorter term noise due to the reduced duty factor of measurements on the sample gas.
- The combination of these two results demonstrates that the G2302 is suitable for measurements that meet the WMO data quality standard for CO over long periods of time.

Carbon Dioxide Measurement, Interference, and Correction

Calibration of the G2302 Carbon Dioxide Measurement



The CO region has a small but significant carbon dioxide ($^{12}C^{16}O_2$) line immediately adjacent to the primary carbon monoxide line. This line is a clearly interfering line. We begin by assessing our ability to quantify this interfering line. The experiment we have performed is to challenge the instrument with variable carbon dioxide and water vapor concentrations, using the apparatus shown. Mass Flow Controllers (MFCs) are used to vary the concentration of water vapor and carbon dioxide. We have then compared the resulting carbon dioxide measurements using two outputs of the G2302:

- the primary carbon dioxide output, which is identical to the G2301. This line has been carefully validated over the course of multiple experiments at multiple laboratories. To

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facilitate the comparison, the *reported* carbon dioxide measurement is used, prior to any water vapor correction for dilution or spectroscopic broadening.

- the secondary carbon dioxide output from the CO region – this line is not used anywhere in the G2301.

The two outputs are shown in Figure 10, below. Although the secondary carbon dioxide line is much noisier (a standard deviation of several ppm, rather than 10s of ppb), it agrees reasonably well with the primary concentration reporting over the full range of conditions.

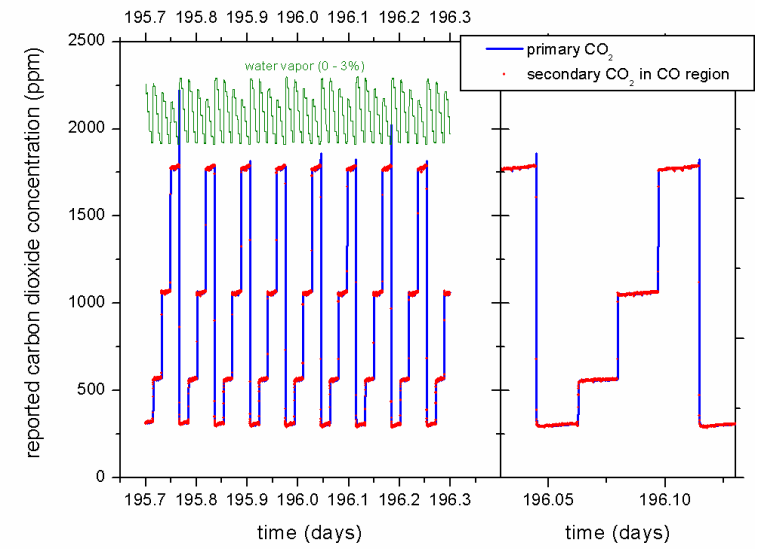

Figure 10: Reported primary and secondary concentration reported from the G2302. The secondary line is much noisier than the standard carbon dioxide line, but agrees well with the primary line.

Cross-interference of carbon dioxide on the carbon monoxide measurement

Next, we have performed an experiment to measure the dependence of the reported carbon monoxide on carbon dioxide. In this experiment, we exposed the instrument to concentrations ranging from 400 – 5000 ppm of carbon dioxide, and measured the reported carbon monoxide. We used a precious metals catalytic filter (25 cc of Sofnocat 514) to scrub any residual CO from the gas delivered into the instrument. The resulting data are shown below.

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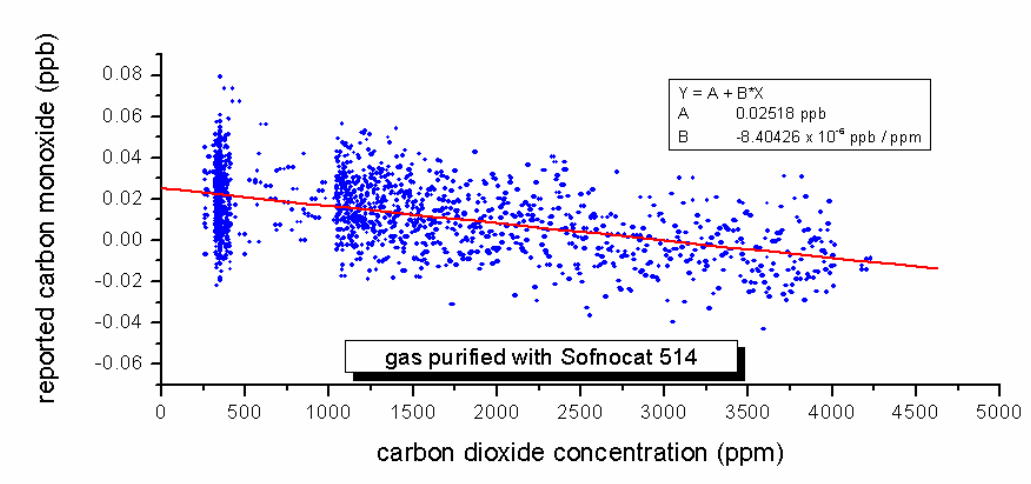
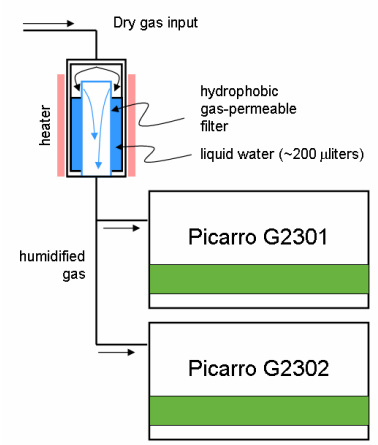


Figure 11: dependence of the reported carbon monoxide signal on carbon dioxide concentration.

The instrument demonstrates a very weak dependence of -8.40 ± 0.25 x 10^{-6} ppm CO / ppm CO_2, or about 0.8 ppb CO per 100 ppm of CO_2. The intercept of 25.2 ± 0.4 ppb of CO is the offset to the zero of this instrument.

Water Vapor Measurement, Interference, and Correction

Calibration of the G2302 Water Vapor Measurement



In the G2302, the water vapor line shown in Figure 1 is used as the primary water vapor measurement. This is a different line than is used in the G2301, and therefore needs to be calibrated against our standard water line. Our first step is to cross-calibrate the G2302 water vapor measurement against the G2301 water vapor measurement, which was calibrated against a NIST-traceable dew-point meter at the Max Planck Institute for Biogeochemistry in Jena, Germany[g]. In this experiment, two instruments were used to measure the same humid gas stream, each measuring one of the two water lines. The humidity was varied by changing the temperature of the filter, which increases the evaporation rate from the water.

The data reported from each instrument have been plotted in the same graph, in Figure 12. Prior to plotting, the data from the G2302 have been adjusted using the following expression:

[g] Calibration courtesy of H. Chen and C. Gerbig at MPI-Jena.

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$$^{G2301}H_{rep} = {}^{G2302}H_{adj} = 0.98\,{}^{G2302}H_{rep} + 0.008\,{}^{G2302}H_{rep}^{2}$$

We may then plug this formula into the expression for the G2301 relating the reported water vapor concentration to the actual water vapor concentration[h]:

$$H_{actual} = 0.772\left({}^{G2301}H_{rep} + 0.02525\,{}^{G2301}H_{rep}^{2}\right) = 0.7566\left({}^{G2302}H_{rep} + 0.03291\,{}^{G2302}H_{rep}^{2}\right)$$

This work therefore provides traceability via the spectroscopic lines from the G2302 vapor measurement to the original G1301 vapor calibration performed at the Max Planck Institute in Jena, Germany. In addition, the above expression relating the reported water concentrations from the G2302 to the G2301 allow us to correct obtain the dry gas mixing ratios for carbon dioxide on the G2302 by substituting the G2302 water value into the expressions in the white paper for the G2301:

$$\frac{(CO_2)_{wet}}{(CO_2)_{dry}} = 1 + c\,{}^{G2302}H_{rep} + dG^{2302}H_{rep}{}^{2}$$

parameter	value
c	- 0.01176 ± 0.00009
d	- 3.615 ± 0.24 x 10^{-4}

[h] For more information, please see the white paper "Accurate Greenhouse Gas Measurements in Humid Gas Streams Using the Picarro G1301 Carbon Dioxide / Methane / Water Vapor Gas Analyzer," http://www.picarro.com/assets/docs/White_Paper_G1301_Water_Vapor_Correction.pdf

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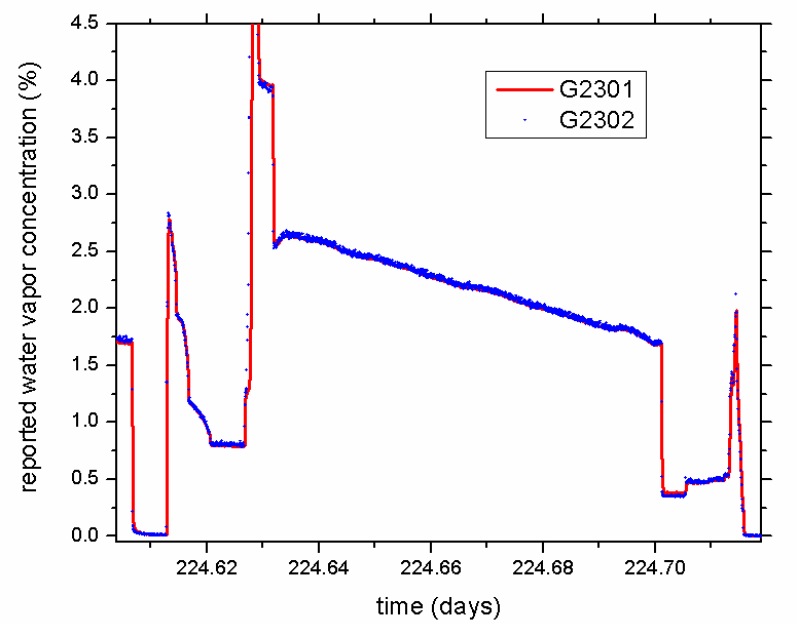

Figure 12: cross-calibration of the G2302 water vapor measurement to the G2301 water vapor measurement. The G2302 data have been adjusted by a small linear and quadratic factor to overlay the two measurements. Please see the text for more information.

Cross-interference of Water Vapor on the Carbon Monoxide Measurement

As mentioned above in the section on the spectroscopy of the carbon monoxide line, for typical ambient concentrations of 100 ppb of carbon monoxide, 380 ppm of carbon dioxide, and 15,000 ppm of water vapor, the ratios of the largest line for each species in this immediate spectral region are 1:66:32 for $CO:CO_2:H_2O$. In other words, under normal conditions, the carbon monoxide absorption line is just a few % in height compared to the other lines in the immediate vicinity. This situation presents a challenge for the spectroscopic fit engine that reports concentrations – it must provide a determination of the carbon monoxide peak height with a high degree of accuracy and precision, in the presence of much larger spectral features.

Water vapor can interfere with the measurement of the carbon monoxide in the following ways:

- **Dilution:** The dilution effect is simply the change in mixing ratio of carbon monoxide caused by variability in the humidity. For example, a dry air mass traveling over warm water will accumulate humidity, and this additional water vapor will dilute the concentration of the other gases. Conversely, a humid air mass that becomes drier (as through precipitation) will cause an inverse dilution effect, increasing the mixing ratios of the other gases. The magnitude of the effect is a 1% decrease in the reported fractional

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concentration for every 1% increase in water vapor concentration. The dilution effect is largely due to the most abundant isotopologue of water ($^{1}H_{2}{}^{16}O$), which is 99.8% of all the water in the world under most conditions. The correction for dilution is proportional to the magnitude of the CO concentration.

- **Spectral broadening[i]:** The Lorentzian broadening of the spectral lines are affected by the presence or absence of water vapor. The magnitude of the effect on the reported concentration is of the order of the dilution effect (though generally somewhat smaller), and, like the dilution, the correction is proportional to the magnitude of the CO concentration. As with dilution, this effect is largely due to $^{1}H_{2}{}^{16}O$.
- **Direct spectral interference:** Direct spectral interferences are caused by any water vapor spectral lines that are in the immediate vicinity of carbon monoxide spectral lines. These interfering lines can cause an offset to the carbon monoxide measurement. Unlike dilution, this effect can depend on whichever isotopologue or isotopologues are interfering with the carbon monoxide line. Unlike the first two effects, direct spectral interference affects the measurement even at zero carbon monoxide concentration.
- **Second-order spectral interference:** Water vapor can also interfere with the carbon monoxide measurement by changing the spectral line broadening of *other species* in the vicinity of the carbon monoxide line. In particular, increasing water vapor concentration can affect the broadening of the nearby carbon dioxide line, which, if not properly accounted for, will cause errors in the reported carbon monoxide concentration. This correction factor can be non-zero even at zero carbon monoxide concentration, but is zero when either carbon dioxide or water vapor is zero.

We begin by performing measurements to quantify the combined dilution and spectroscopic broadening effects. In this experiment, we humidified an extremely high concentration bottle of carbon monoxide (~1000 ppm), using the same type of hydrophobic filter apparatus described above. The results of this experiment are shown in Figure 13. The data are well-characterized by the quadratic equation of the following form:

$$\frac{CO_{wet}}{CO_{dry}} = 1 + a \cdot {}^{G2302}H_{rep} + b \cdot {}^{G2302}H_{rep}^{2}$$, where a = -0.01287 ± 0.00003 and b = -5.365 ± 0.06 x 10^{-4}.

[i] For a more complete treatment of the general theory of spectral broadening, please see the technical white paper, "Accurate Greenhouse Gas Measurements in Humid Gas Streams Using the Picarro G1301 Carbon Dioxide / Methane / Water Vapor Gas Analyzer," available on the Picarro website: http://www.picarro.com/assets/docs/White_Paper_G1301_Water_Vapor_Correction.pdf

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Here, we have noted explicitly the fact that the reported water vapor is uses a different line that the G2301. Comparison between the CO correction factor measured here, and the CO_2 and CH_4 correction factors obtained on the G2301, can only be made after applying the expressions relating the two water vapor measurements.

If we recast the above expression in terms of the reported water vapor from the G2301, we find that the new linear and quadratic terms are $a' = -0.0130$ and $b' = -4.50 \times 10^{-4}$. We may compare these results directly to the values for CO_2 and CH_4 that are used on the G1301 and G2301[j], where $a' = -0.0120$ and $b' = -2.674 \times 10^{-4}$ for CO_2 and $a' = -0.00982$ and $b' = -2.393 \times 10^{-4}$ for CH_4. Not surprisingly, the resulting correction factors are very similar.

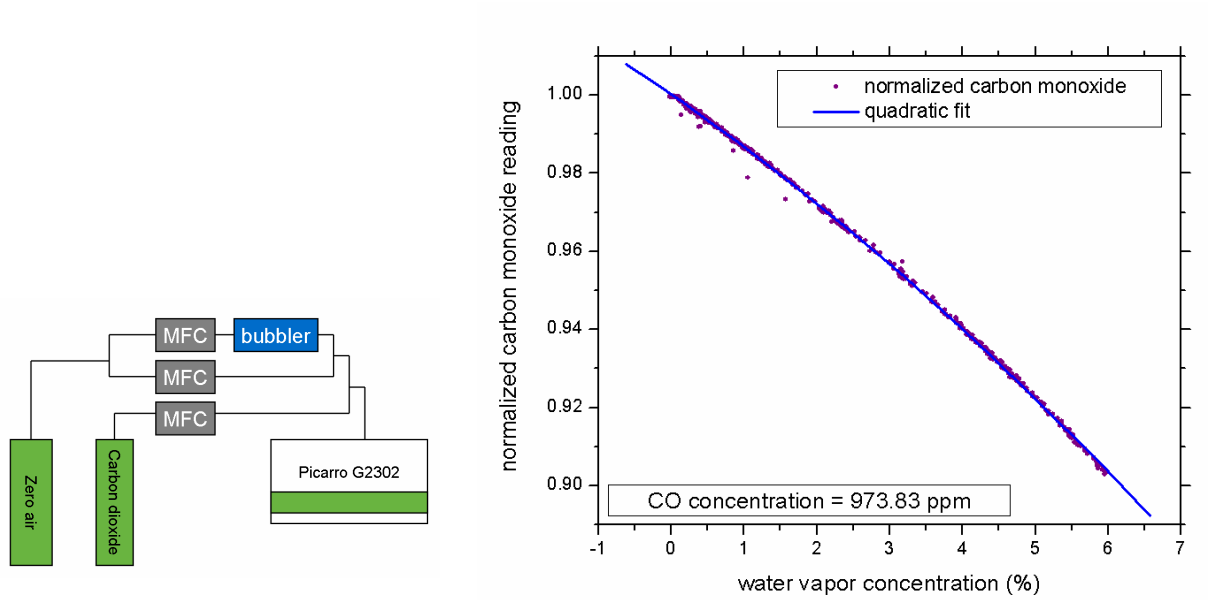

Figure 13: normalized carbon monoxide concentration (normalized to the x-intercept of these data). Water vapor concentrations up to 6% were achieved.

Next, we investigate the any cross-interference effects on the measurement of zero carbon monoxide, due to direct spectroscopic interference or second-order spectroscopic interference. From the detailed spectra, it is clear that both carbon dioxide and water vapor must be included in this analysis. To perform this experimental work, we have generated a gas stream with variable amounts of carbon dioxide and water vapor by two bottles (5000 ppm carbon dioxide and zero air), three MFCs, and a water bubbler to generate a gas stream with a variable amount of water vapor (0 – 3%) and carbon dioxide (0 – 2000 ppm).

[j] See the white paper located here:
http://www.picarro.com/assets/docs/White_Paper_G1301_Water_Vapor_Correction.pdf

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We then look for a correction factor for the zero level of carbon monoxide that has the following form:

$$CO_{reported} - CO_{actual} = \Delta_{CO}, \text{ where } \Delta_{CO} = A + BH_{rep} + CH_{rep}^2 + D(CO_2)_{wet} + E(CO_2)_{wet} H_{rep}$$

Each term is associated with the following effects:

- ***A***: The offset to the carbon monoxide reading reported in the absence of carbon dioxide and water vapor; i.e., the 'true zero' of the carbon monoxide measurement for this instrument. This term was determined in the CO_2 correction section to be 25.2 ± 0.4 ppb CO.
- ***B***: The error in the reported carbon monoxide reading that is proportional to the reported water vapor concentration but independent of the carbon dioxide signal. This term is the direct interference of the water vapor spectroscopic line on the reported carbon monoxide peak. This term was also determined in the CO_2 correction section to be -8.40 ± 0.25 x 10^{-6} ppm CO / ppm CO_2.
- ***C***: The error in the reported carbon monoxide reading that is proportional to the square of the water vapor concentration. This is the nonlinear contribution to the direct spectroscopic interference, due primarily to the error in the measurement induced by self-broadening of the water line (which is not captured by the spectroscopic pattern recognition algorithm)
- ***D***: The error in the reported carbon monoxide reading that is proportional to the carbon dioxide concentration. This is due to the direct spectroscopic interference of the carbon dioxide line on the carbon monoxide line.
- ***E***: The error in the reported carbon monoxide reading that is proportional to both the carbon dioxide *and* the water vapor concentration. This error is caused by second order spectral interference, where the cross-broadening of the carbon dioxide line by water vapor (which is not captured by the spectroscopic patter recognition algorithm) causes an error in the fit of the carbon dioxide peaks, and thus an error in the reported carbon monoxide line.
- ***higher order***: we will investigate the necessity of employing any higher-order terms into this equation for the range of concentrations we are likely to see.

The figure below shows the reported carbon monoxide signal as a function of time, along with the water vapor and carbon dioxide concentration reported by the instrument. The carbon monoxide data (which has been averaged by 30 seconds) shows a clear dependence on both the water vapor and the carbon dioxide concentrations, with a full range of reported values of nearly

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100 ppb. Clearly, without correction, this would present a very serious error to the reported values from the instrument[k].

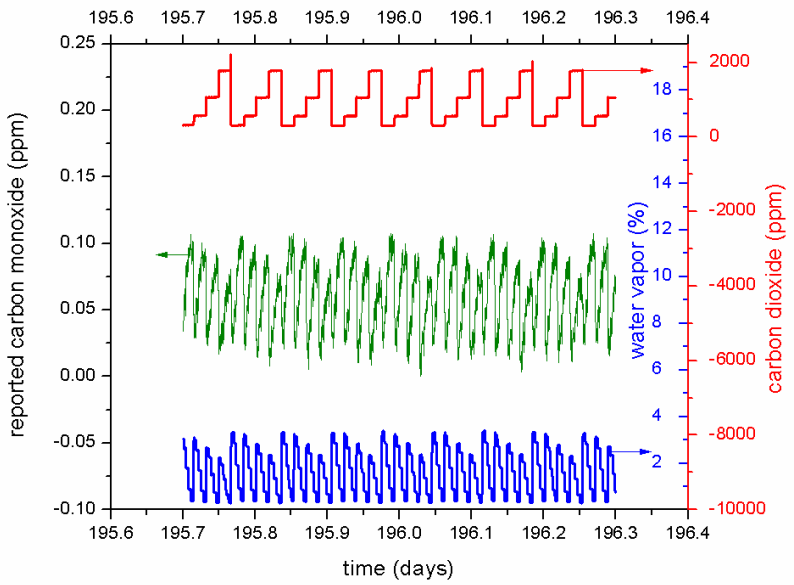

Figure 14: reported carbon monoxide concentration (green) as a function of time, along with water vapor (blue) and carbon dioxide (red). Some of the observed dependence is due to non-zero carbon monoxide in the tanks used to create the mixture. This will be discussed and quantified later in this white paper.

We begin by removing the dependence of water vapor on these data. We analyze each step change (in water vapor and carbon dioxide) in the above data for the average reported value of water, carbon dioxide, and carbon monoxide, after discarding the time immediately after the each transition of the MFCs. Those data are shown in the figure below, where the reported carbon monoxide concentration is displayed as a function of water vapor, for each of the four carbon dioxide concentration steps[l].

[k] Much of this variability is real; that is, there is a varying carbon monoxide concentration in the gas stream generated by the test setup, due to a non-negligible amount of carbon monoxide present in the two cylinders used to prepare the mixture.

[l] It is important to note that the carbon dioxide concentration used here is the corrected dry-gas mixing ratio, not the reported wet mixing ratio. This output was chosen so that the data and correction factors are more easily separable in this experiment. An equivalent set of correction factors could be defined using the wet mixing ratio for carbon dioxide.

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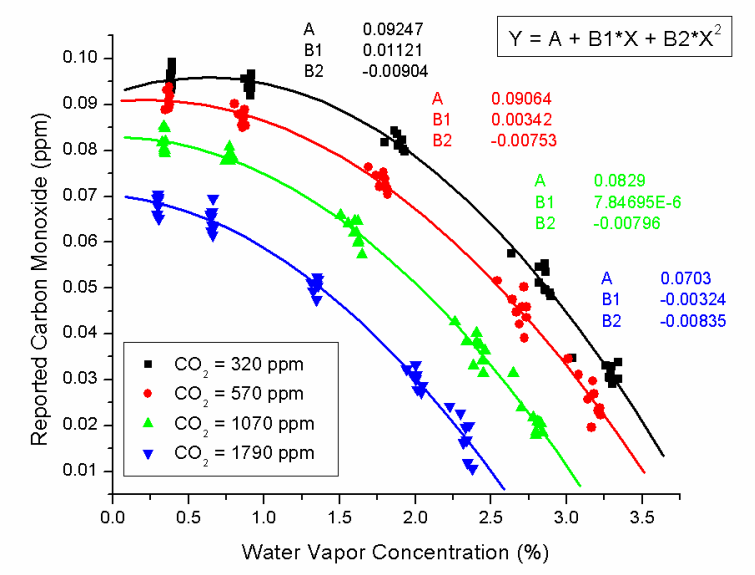

Figure 15: reported carbon monoxide concentration as a function of water vapor concentration, for several different carbon dioxide concentrations. Some of the observed dependence is due to the non-zero levels of carbon monoxide in the zero air tank and the carbon dioxide tank used for this experiment.

We then fit a quadratic function in water vapor to each of the four carbon dioxide concentration steps, letting all three terms vary. We begin by focusing on the quadratic terms from each of the four polynomial fits. Note that there is no clear dependence of this term on carbon dioxide concentration over the full range from 320 to 1790 ppm. The average result from these four fits is -0.00822 ± 0.00064. It is interesting to note that the reported error in this coefficient from each of the least squares fits was reported to be 0.00059 on average, which is essentially the same as the standard deviation of the four quadratic terms. This indicates that within measurement uncertainty, there is no additional dependence of the quadratic term on carbon dioxide concentration. This quadratic term corresponds to term ***C*** in the equation above.

In the next step, we refit the data with a fixed quadratic term of -0.00822, allowing the lower order terms to vary. These results are shown below. The quality of the fits is essentially identical from the previous fits in which the quadratic term was allowed to vary.

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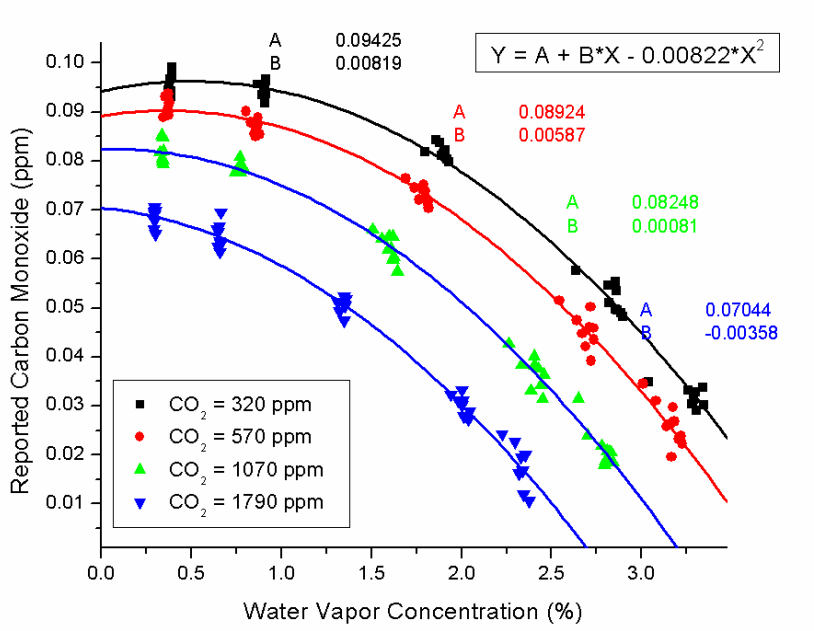
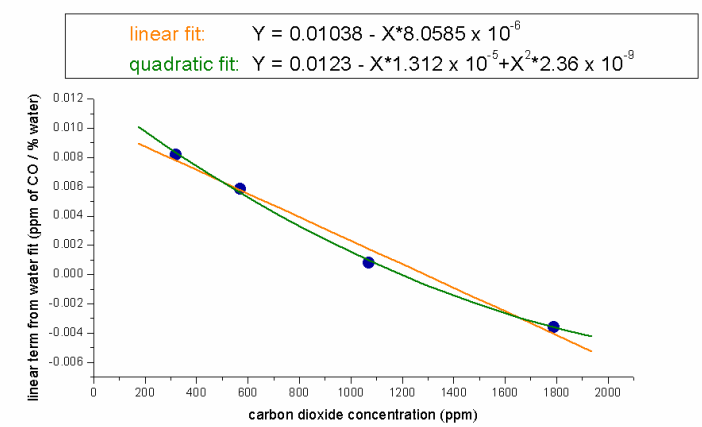


Figure 16: The same data as above, but with the quadratic term fixed at -0.00822 / % H_2O.

From these results, we now study the linear term. Unlike the quadratic term, there is a clear dependence of this linear term on carbon dioxide concentration, as can be seen in the figure below. A quadratic fit is much better, clearly, but there are only four data points, and the magnitude of this correction factor is in fact quite small – just a few ppb / % water. At this time, we will assume the linear fit properly captures the underlying correction. From the data, we can then determine two correction factors from the equation above: the dependence of the reported carbon monoxide concentration on water vapor concentration (***B*** in the equation above, with a value of 0.01038 ± 0.00078 ppm CO / %v), and the cross-term which depends on water vapor and carbon dioxide (***E*** in the equation above, with a value of – 8.0585 ± 0.7 x 10^{-6} ppm CO / %v / ppm CO_2).



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Finally, we look at the carbon monoxide offset term (that is, the extrapolated value of carbon monoxide for water vapor = 0%) as a function of carbon dioxide concentration, shown in the figure below. We have removed from these data the instrument offset ***A*** and the CO_2 concentration dependence ***B***, before plotting it below. These data still show a significant offset at zero carbon dioxide, and a strong dependence on carbon dioxide concentration. Both of these effects are due to the fact that each of the two bottles used for this experiment (zero air and CO) have residual carbon monoxide in them, which shifts the overall level of the measurement.

From the data below, we have determined that the zero air tank has 73.8 ± 1.2 ppb of carbon monoxide, and the 5000 ppm carbon dioxide tank has 37.3 ± 3.0 ppb of carbon monoxide.

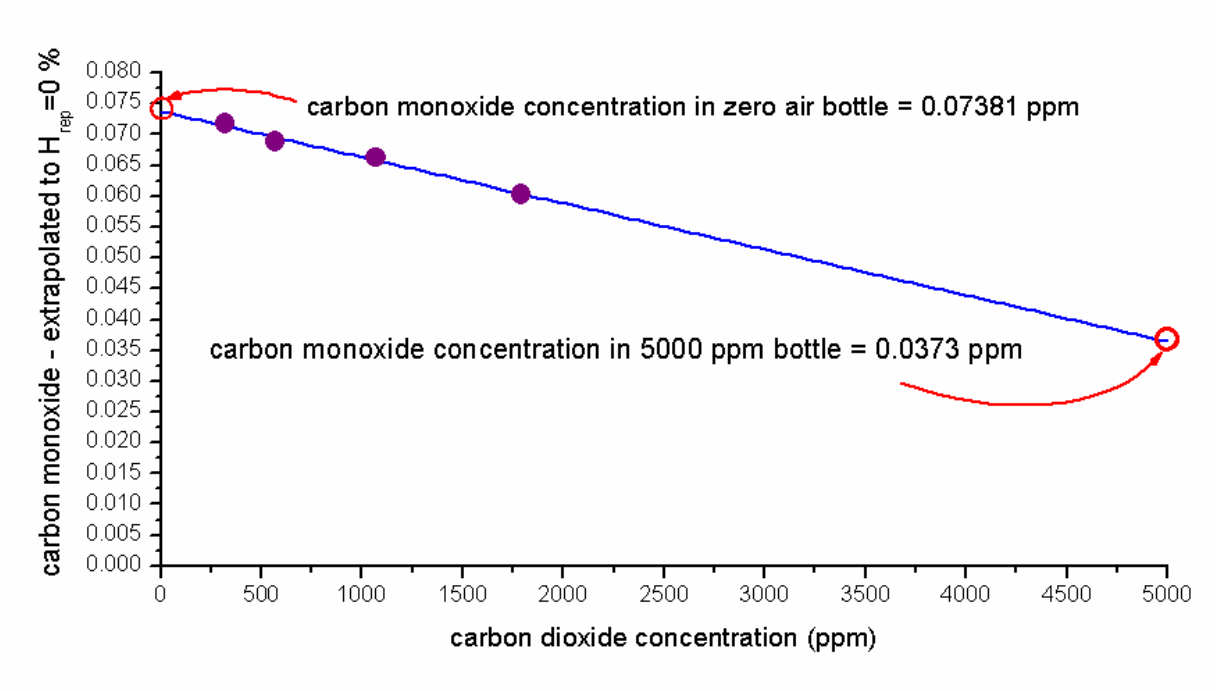

Figure 17: observed dependence of reported carbon monoxide on carbon dioxide, for dry samples. These are the data remaining after applying all water vapor and carbon dioxide correction factors.

In this experiment, the fact that the two bottles have differing, non-zero amounts of carbon monoxide has a slight affect on the correction factors derived above, due to the fact that, in addition to the zero correction, there also needs to be a span correction applied to the data. This correction amounts to about 0.5 – 1.0 ppb CO / % H_2O. In fact, what we have done is 'baked' this span correction into our zero correction factor data. However, it is possible to remove this effect from our correction factors, by using the concentration of carbon monoxide in the gas mixture (which can be obtained from Figure 17) and applying the wet-to-dry water dilution and spectral broadening correction described above. Due to the span correction for water vapor, the

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value for ***B*** must be adjusted from +0.01038 to +0.00943, and the carbon dioxide – water vapor cross term ***E*** must be adjusted from -8.06 x 10^{-6} to -7.96 x 10^{-6}. The adjustment to ***B*** amounts to a correction of 0.95 ppb / % H_2O, and the adjustment to ***E*** amounts to a correction of 0.01 ppb for every % H_2O and 100 ppm change in CO_2. Both of these corrections are small.

Finally, we may apply all the correction factors to the original data, to understand the effectiveness of the correction. These data are shown in the figure. The standard deviation of the five minute data is 2.2 ppb. This can be compared with the standard deviation of the single bottle data of 1.95 ppb. The additional error associated with the water and carbon dioxide correction factors is just the root quadrature difference of these standard deviations, or just 1.0 ppb, over the complete range of water vapor and carbon dioxide.

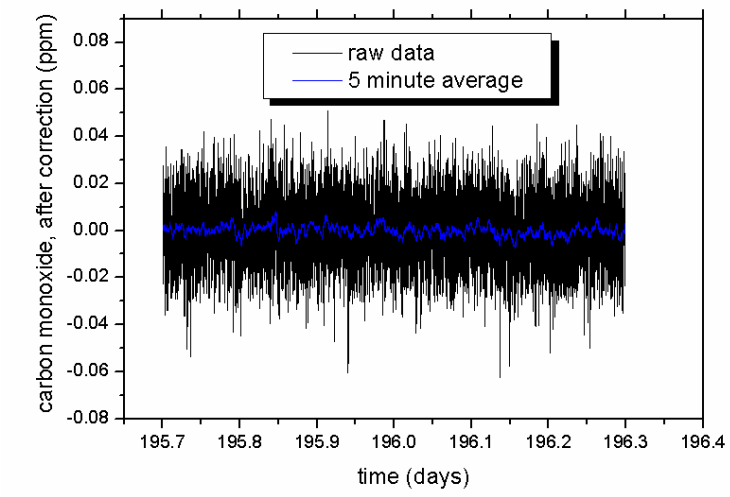

Figure 18: reported carbon monoxide after applying all correction factors *and* removing the effect of the carbon monoxide measured in each bottle.

Summary of cross-interference correction factors

Both water vapor and carbon dioxide have a perceptible effect on the measurement of carbon monoxide in the G2302. Water vapor is by far the stronger effect – the correction factors for water vapor are in general more than 10 times larger than the correction factors for carbon dioxide for typical concentration ranges.

These correction factors have been derived in a single set of experiments performed on a single instrument. It is therefore important to note that we do not yet understand the extent to which these correction factors are stable from instrument to instrument, **or** stable on a given instrument over time, temperature, and other environmental conditions. In particular, the correction to the carbon monoxide value at zero levels is likely to be subject to variability. Unlike the water correction for carbon dioxide, which stems directly from the spectroscopic effects of water vapor

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on carbon dioxide, the carbon monoxide correction at zero is necessary because slight imperfections in our spectrometers that cause our spectroscopic model of this spectral region to have small, but perceptible, errors, which then translate into errors in the reported carbon monoxide. We emphasize that the G2302 measurements must be validated with great care, not only at the Picarro factory with additional measurements, but at leading greenhouse gas monitoring laboratories around the world. As time progresses and further work is done to validate this instrumentation, we will update our testing procedures and documentation to reflect this new work.

Carbon monoxide

The recipe for obtaining the corrected dry-gas mixing ratio for carbon monoxide from the G2302 is as follows. First, correct the reported zero level of carbon monoxide using the expression below.

$$CO_{zero\ adjusted} = CO_{reported} - \Delta_{CO}, \text{ where } \Delta_{CO} = A + BH_{rep} + CH_{rep}^2 + D(CO_2)_{wet} + E(CO_2)_{wet} H_{rep}$$

parameter	value	uncertainty	units	range of correction for 380 – 480 ppm CO_2 and 0 – 1% H_2O
A	+ 0.0252	± 0.0004	ppm CO	N/A
B	+ 0.00943	± 0.00078	ppm CO / % H_2O	10.4 ppb
C	– 0.00822	± 0.00064	ppm CO / %^{2} H_2O	8.2 ppb
D	+ 8.40 x 10^{-6}	± 0.25 x 10^{-6}	ppm CO / ppm CO_2	0.8 ppb
E	– 7.96 x 10^{-6}	± 0.7 x 10^{-6}	ppm CO / % H_2O / ppm CO_2	0.8 ppb

Using this carbon monoxide value, the actual carbon monoxide concentration can be derived using the following expression:

$$\frac{CO_{zero\ adjusted}}{CO_{dry}} = 1 + a \cdot {}^{G2302}H_{rep} + b \cdot {}^{G2302}H_{rep}^2,$$

where a = -0.01287 ± 0.00003 ppm / % H_2O and b = -5.365 ± 0.06 x 10^{-4} ppm / %^{2} H_2O.

Carbon Dioxide

The carbon dioxide reading from the G2302 can be corrected for water vapor concentration using the following equation.

$$\frac{(CO_2)_{wet}}{(CO_2)_{dry}} = 1 + c^{G2302}H_{rep} + dG^{2302}H_{rep}{}^2$$

parameter	value
a	- 0.01200 ± 0.00009

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b	$- 2.674 \pm 0.18 \times 10^{-4}$
c	$- 0.00982 \pm 0.00006$
d	$- 2.393 \pm 0.1 \times 10^{-4}$

Water Vapor

The actual[m] water vapor concentration is related to the reported water vapor concentration using the following expression:

$$H_{actual} = 0.7566\left({}^{G2302}H_{rep} + 0.03291\,{}^{G2302}H_{rep}^{2}\right)$$

Uncertainty in the carbon monoxide correction factors

Clearly, to achieve a high degree of accuracy and precision on the measurement of carbon monoxide using the G2302, great care must be taken to determine the cross-calibration factors to carbon dioxide and especially water vapor, especially at ppb levels of carbon monoxide. It is therefore important to understand both the magnitude of the correction factor throughout the likely parameter space, as well as the uncertainty in these corrections.

We have generated a contour plot of the CO correction factor at zero as a function of water vapor and carbon dioxide. Clearly, water vapor is the worst offender, with an error that grows increasingly more negative at high water vapor concentration. Carbon dioxide exhibits a much weaker dependence.

[m] Traceable via internal Picarro spectroscopic 'standards' to a measurement made on a G1301 at Max Planck Institute for Biogeochemistry in Jena, Germany.

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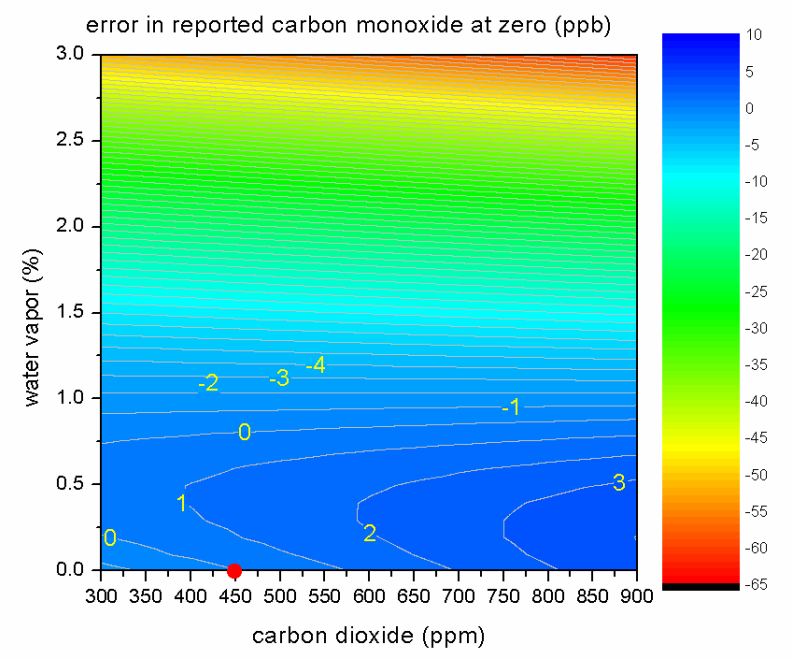

Figure 19: contour plot of the total correction factor for carbon monoxide.

The instrument was 'calibrated' (that is, we have set the error to be zero) at 450 ppm CO_2 and 0% H_2O (the red dot in the figure). The size of the correction factor relative to this point is shown by the contours – each contour is separated by 1 ppb of CO. Notice that the magnitude of the correction factor is within ± 2 ppb for 300 – 600 ppm of CO_2 and 0 – 1% H_2O. This fact give us hope that once a correction factor is applied, the instrument can be quite stable over time.

However, in this particular range, the linear and quadratic correction factors for water vapor in particular tend to cancel, leading to a small range of values for the total correction. However, there is nothing to guarantee that these two correction factors will always maintain this fortuitous arrangement. It is for this reason that we cannot use the size of the correction factor as a reliable measure of the uncertainty.

Instead, we may estimate the overall uncertainty of the correction (2-σ) as the quadrature sum of the uncertainties (2-σ) in each of the correction factors ***B*** through ***E*** (we have omitted ***A*** because drift in this parameter is addressed in the discussion on drift and drift correction, above). This uncertainty map is plotted below. Estimating the uncertainty in this way captures the uncertainty in the actual measurement of the correction factors, which has in it both the raw noise of the CO measurement, as well as any drifts that were observed during the calibration test (about 12 hours). Thus, the overall uncertainty of the correction calculated in this manner should a reasonable scenario for the stability of the correction factors over a time period of perhaps a few days to a week. More work is required to assess the stability of the correction factors over time.

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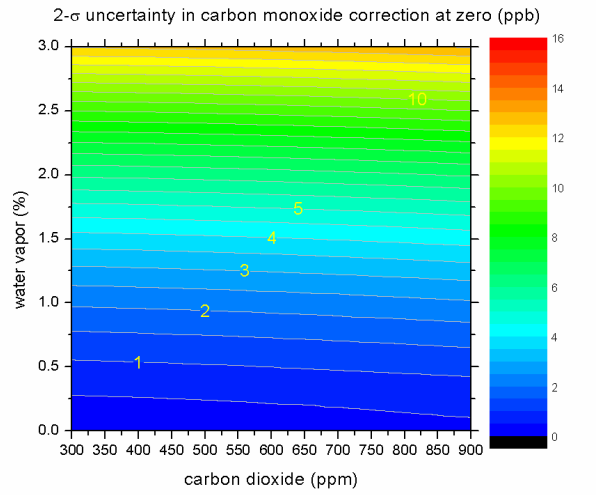

Figure 20: uncertainty in the correction factor, derived from the quadrature sum of the uncertainties of each of the individual correction factors.

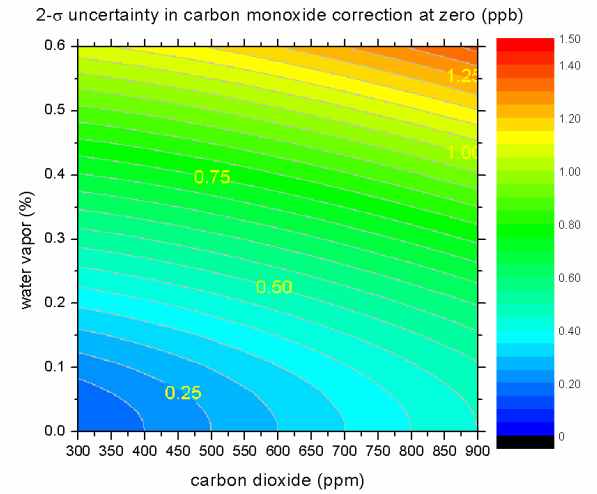

Figure 21: The same as the slide above, but looking at a narrower range of water vapor.

From this graph, we see that the 2-σ uncertainty is within 5 ppb CO for water vapor below 1.5%, 2 ppb CO for water vapor below 0.8%, and below 1 ppb for water vapor below 0.6% and carbon dioxide between 300 and 600 ppm. In the right panel, we provide an expanded view of the correction uncertainty for low water vapor (i.e., dry samples). Even by drying to 0.6 % water (dew point of 0 C), the 2-σ uncertainty under all conditions except high water vapor and high carbon dioxide is less than 1 ppb.

The next important question to answer is to assess the stability of the correction factors. As a simple initial assessment of this stability, we have repeated the previous test and completely re-

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derived the coefficients two weeks after the initial test. The differences between the coefficients derived from the two tests are listed below:

A	0.00116 ppm CO
B	0.00155 ppm CO / % H_2O
C	-7.0×10^{-5} ppm CO / % H_2O
D	2.43×10^{-7} ppm CO / ppm CO_2
E	-1.22 x 10-6 ppm CO / ppm CO_2 / % H_2O

The difference between the complete correction factors over the entire operating ranges of carbon dioxide and water vapor are plotted in the uncertainty plot below. Over the vast majority of the range, the uncertainty is less than 2 ppb of carbon monoxide; this uncertainty includes not only the underlying variability in the correction factors but also the uncertainty in our ability to measure these correction factors, due to the inherent noise in the instrument, and the finite time over which the data are collected. Thus, while this test was only two weeks in duration, it does indicate a reasonable level of stability of the correction, stemming from the inherent stability in the spectrometer. However, there is clearly more work to do to fully assess the stability of the correction factors over time, especially the water vapor correction factor.

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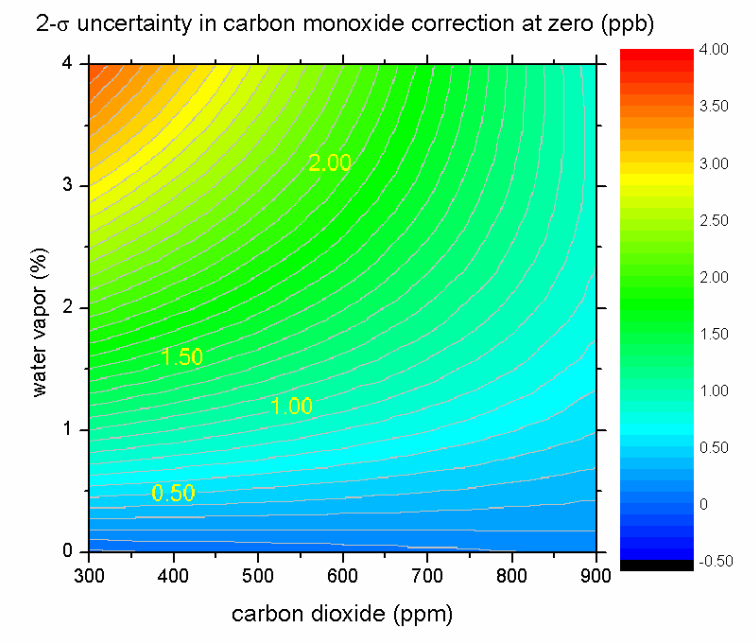

Figure 22: Difference in the correction factors derived two weeks apart using separate data sets.

Putting it all together – making GAW-quality measurements in the field with the G2302

Given these measurements and our understanding of the precision and stability inherent in WS-CRDS analyzers, we make the following recommendations for using the G2302 analyzer for field measurements of carbon monoxide in the atmosphere:

1. The native drift of the instrument can enable carbon monoxide measurements that can meet the WMO standard of ± 2 ppb (2-σ), at least over the short term (hours and days). For more polluted continental air, where the requirement is ± 5 ppb (2-σ), the native instrument performance fares even better. We expect that occasional working standards, applied daily or perhaps even weekly, that are used to track the zero drift in the instrument will be sufficient to achieve WMO levels of performance for continental air. The situation is even better for urban metabolism applications, where the CO levels are even higher and the uncertainty levels are relaxed somewhat further.
2. For measurements that require the utmost in accuracy and traceability, we recommend the use of a working gas standard that contains a constant and known amount of carbon monoxide in a background of ~380 ppm carbon dioxide and nominal atmospheric values

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for oxygen and nitrogen[n]. The purpose of this working gas standard is to track zero drift in the instrument. The precise level of carbon monoxide is not important, as long as it is below about 500 ppb or so. A CO scrubber may be substituted for a working gas standard. Every G2302 instrument at Picarro is tested against the WMO ± 2 ppb (2-σ) standard for 72 hours, during which time the secondary standard is measured for 5 minutes out of every 20 minute period. Data are analyzed using the statistical methods outlined in this white paper. Every G2302 instrument is guaranteed to achieve the ± 2 ppb (2-σ) using this method[o].

3. It is not necessary to verify the span of the carbon monoxide measurement. The drift in the span will be less than 0.125 % of the reading, or 0.25 ppb for 250 ppb of carbon monoxide[p].

4. The cross-talk of carbon dioxide on the carbon monoxide signal is about 0.7 ppb over a range of 380 – 480 ppm of carbon dioxide (and dry gas conditions). We believe that a beginning-of-life calibration of the CO_2 → CO cross-talk (to correct the zero of the instrument) should be sufficient to maintain the ± 2 ppb (2-σ) accuracy over time. This cross-interference will be measured and corrected at the Picarro factory on every G2302 instrument.

5. The cross-interference of water vapor will be measured and corrected on every G2302 instrument at the Picarro factory. The question remains what the stability of this correction method will be over time; unfortunately, not enough work has been done to validate this correction over long periods of time and for many instruments. We can however make a few observations about this correction factor. First, it seems clear that it is not necessary to thoroughly dry the sample when using the G2302. Measuring carbon monoxide in moderately humid gas streams can be accomplished with low uncertainty with the G2302. Exactly how humid 'moderately humid' is will depend both on the required uncertainty of the measurement and on the stability of the correction factors.

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[n] In the absence of water vapor, the G2302 uses the nearby carbon dioxide spectral lines to track small drifts in the on-board wavelength monitor. It is therefore crucial for high quality measurements that more than about 200 ppm of carbon dioxide be supplied to the instrument. If less than 200 ppm of carbon dioxide is not supplied, the instrument will not be damaged, but it may not report accurate CO mixing ratios.

[o] Other methods with different duty factors and time intervals may also meet the WMO standard.

[p] We base this conclusion on the spectroscopic performance of our carbon dioxide measurements, for which we guarantee, and easily achieve, span drift of less than 0.15% on CO_2.

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Given the uncertainty analysis presented above, we expect that drying the sample to below 0.6% (about 0 C dew point) as can be achieved using Nafion dryers should be sufficient to achieve ±5 ppb or even ±2 ppb uncertainty over long periods of time. Even higher water vapor levels may be tolerated while maintaining these low uncertainties if it is proven that the correction factors are stable over time. It also may be possible to measure the water cross-interference in real time by periodically humidifying (using, for example, Nafion) the dry working standard. Contact Picarro to discuss constructing such a method.

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