Atmos. Meas. Tech. Discuss., 5, C3118–C3124, 2012
www.atmos-meas-tech-discuss.net/5/C3118/2012/

Atmospheric
Measurement
Techniques
Discussions

Interactive comment on "Accurate measurements of carbon monoxide in humid air using the cavity ring-down spectroscopy (CRDS) technique" *by* H. Chen et al.

H. Chen et al.

huilin.chen@noaa.gov

Received and published: 1 December 2012

We thank the reviewer #2 for the detailed and helpful comments and give our responses to each of these comments below. Accordingly, changes in the manuscript have been highlighted in the revised version.

Responses to Anonymous Referee #2

The paper demonstrates the possibility to make CO measurements with a CRDS analyzer without the necessity of drying the sample air. This possibility will significantly simplify CO measurements, as drying the air sample is often difficult in field conditions,

and it can be a source of additional errors. Moreover, the fact that sample drying is not necessary allows receiving potentially interesting information on the atmospheric water vapor. Each analyzer has to be characterized individually, for which the present paper provides a clear methodology. The paper is well written and should be published in AMT after minor revisions.

General comments

C1: I think it should be made clear that this paper refers to the CRDS instruments manufactured by Picarro Inc. Also, are there other CRDS instruments available for CO measurements? Would this research be applicable to any CRDS instrument?
R1: We have clarified this point in the introduction as "In this paper, we derive water correction functions for the CO measurements made by the Picarro CRDS technique to account for the dilution and spectroscopic effects." We are not aware of other CRDS instruments available for atmospheric CO measurements. This paper deals with the CO measurements made by the Picarro instrument based on light absorption in the near infrared region, where the signal is very weak with a lot of interferences from other species. It depends on the selected wavelength and the settings for the cavity temperature and pressure. Measurements made at different wavelengths or temperature and pressure may not suffer significantly from line interferences. Therefore, this research cannot be applied directly to any other CRDS instrument for CO measurements. We added a sentence in the discussion "This study applies to the CRDS instruments manufactured by Picarro Inc. that determine the CO mole fractions of air sample in a pressure (∼186 mbar) and temperature (∼40 °C) controlled cavity based on light absorption in the near infrared region (∼1.57 μm)."

C2: The averaged residuals of deltaCO and COdry in Figs. 3, 4 and 6 are compared to the WMO intercomparability goals, and this is mentioned several times through the paper. However the noise in non-averaged deltaCO, COraw and COdry in the same figures is obviously larger than the WMO goals. Please explain why it was considered

that the comparison with the data averaged over H2O and CO2 intervals is correct and meaningful.
R2: What we intend to achieve here is that the uncertainty of the determined water correction function is within the WMO intercomparability goals, and we are able to demonstrate this by integrating the residuals over H2O and CO2 intervals. We can do this because the noise is mostly random, and can be reduced by averaging the measurements, which has been shown in the Allan deviation plot by Zellweger et al. 2012. This verifies that our water correction function meets the WMO intercomparability goals, although the measurements at the reported data frequency (∼0.5 Hz) do not (the measurements need to be averaged to reach the goal).

C3: From Fig. 7, and as stated in Sect. 5, it is clear that different analyzers react differently and need individual water correction functions. It is not clear to me why it is considered that the differences come only from the line interference coefficients (A, B, C, D) and not also from the coefficients for pressure and broadening effects correction a' and b'. These are supposed transferable from one analyzer to another only based on analogy with CO2, since the CO tests were performed on only one analyzer (Sect. 2.1, from line 14). If there is any physical reason to believe this please explain, otherwise state it clearly that this is for now only an assumption. If a' and b' were different for different analyzers, would the differences be (partly) compensated for when fitting the forth degree function for the A – D coefficients?
R3: It is an assumption with high confidence. The dilution effect is the same for all instruments, and the pressure-broadening effect will be very similar since the spectroscopic features for different analyzers are very close, which has been demonstrated by the transferability of CO2 water vapor corrections among the same type of CRDS analyzers. Furthermore, the total water vapor dilution and pressure-broadening effects for CO are relative small (∼5 ppb for 2% water vapor at a level of 200 ppb CO) when compared to the line interference effect (up to ∼20 ppb for the range of 0-2% water vapor). Therefore, the uncertainty that could be caused by potential differences in a'

and b' will be rather small. If a' and b' were different for different analyzers, the differences can only be partly compensated by the A-D coefficients, because the line interference does not depend on CO mole fractions. We have modified the last sentence in Sect. 2.1: "Therefore, these coefficients can be assumed to be transferable to all CO measurements made by the same type of CRDS analyzer to account for dilution and pressure-broadening effects with insignificant transferability errors."

C4: How good is the water vapor measurement of the considered instruments, in terms of precision and accuracy?
R4: For the analyzer (S/N: CFKBDS2007), the standard deviation of H2Opct measurements is less than 100 ppm at the reported frequency (∼0.5Hz) for the reported H2Opct level of up to 3.6%, which is precise enough for the purpose of correcting CO mole fractions. The water vapor measurement provided by H2Opct is about 20% off a scale calibrated by a dew point mirror (the variable "H2O" in the dataset of the CRDS measurement). We want to emphasize that the water corrections for CO presented in this paper do not depend on the accuracy of the H2Opct measurements. However, the stability of the H2Opct measurements may affect the water corrections, and needs to be assessed in future work. We have added a paragraph in the end of Sect. 2.5: "The standard deviations of the CO measurements made by the CRDS analyzers at the reported frequency (∼0.5Hz) are in the range of 4 - 17 ppb. For H2Opct, the standard deviations increase with water vapor levels, and are smaller than 100 ppm for up to 3.6% water vapor. The uncertainty of the CO water corrections due to the precision of H2Opct at the reported frequency is calculated based on Eq. 5 and is less than 0.5 ppb for up to 3.6% water vapor, which is a smaller effect when compared to the uncertainty in the determined water vapor correction function for CO."

C5: Figure 3 suggests that the water correction function may introduce a bias at very low water concentrations. What are the implications for the calibration which is usually done with dry air cylinders - could this lead to a systematic error in reported CO mole fractions?

R5: It is true that the lowest water interval exhibits a bias of $\sim$ -2 ppb, which is caused by the inaccurate determination of dry CO values of the gases used in the experiments. Because we force the curve through zero, this would not lead to a systematic error in reported CO mole fractions at very low water concentrations.

Specific comments

C1: - page 6497, lines 21-24: it is not clear what H2Opct is, and what is its relation to the water vapor content. Could you please give more details.
R1: This is also raised by the Reviwer 1. We have added a sentence to explain H2Opct, and please refer to the responses to anonymous referee 1.

C2: - page 6498, line 21: is the CO mole fraction not affected by silica gel or acidified water?
R2: We have made water droplet tests to demonstrate that the CO mole fractions are not affected by silica gel or acidified water, where the humidified air was passed through a chemical dryer (magnesium perchlorate) and the dry mole fractions of CO were then determined by a second CRDS analyzer. No significant (less than 1 ppb CO on 30-second averaged data) variations/drifts in the dry mole fractions of CO were found. We have added this before Sect. 2.1.

C3: - page 6499, lines 10-11: How precisely are these coefficients determined? It is stated that the coefficients for CO are “very close” to the ones for CO2, but the b and b’ coefficients look quite different. Are these differences not significant?
R3: The targeted precision/accuracy needs to be taken into account when considering the significance of the differences. The differences between the ones for CO and CO2 correspond to a difference of 0.45 ppb in the corrected CO mole fractions at a water vapor level of 2%. Because the water vapor variables used to correct CO2 and CO are different, we expect the differences between the coefficients among different CO analyzers to be smaller than the differences between the ones for CO and CO2.

C4: - page 6500, line 1: five tests were made in total, from which three were used and one (the Feb 2011 one) was not used due to incompleteness of data. What happened to the fifth one?
R4: One droplet test was rejected due to a significant difference between the dry mole fraction measurements of CO before and after the test (probably due to a leak). We have added this to Sect.2.2 as “(one droplet test was rejected due to a significant difference between the dry mole fraction measurements of CO before and after the test, probably due to a leak)”.

C5: - page 6501, lines 1-2: It is stated that there is no evidence for drift in water correction functions from Feb 2011 to Mar 2012. Looking at Fig. 3b, however, the data for Feb 2011 seem positively biased compared to the 2012 data, and the curvature estimated from the 2012 data does not seem to correspond to the 2011 data. Can you explain this? Is this due to different analyzers and/or test methods?
R5: We agree that the residuals of 2011 data are not random, and have a small bias. The experiments were done on the same analyzer with different test methods. The features in the residuals of 2011 data could potentially be explained by different test methods or a drift. However, given the relatively small magnitude of the residuals (all below 2 ppb except one point), we do not think the drift is significant.

C6: - page 6501, line 11: differences in what?
R6: differences “in the CO water corrections from what is determined from a water test using 380 ppm CO2”. We have completed the sentence.

C7: - page 6503, lines 5-6: please see General comment 3.
R7: please refer to the response to the general comment 3. We have modified the last sentence in Sect. 2.1

C8: - Fig. 2d: Were the residuals obtained at 1000 ppm CO proportionally scaled to a CO mole fraction of 200 ppb? The assumption is needed for this that the residuals are

proportional to the CO mole fraction. Is this true and known?
R8: Yes. We did scale the residuals obtained at 1000 ppm CO proportionally to a CO mole fraction of 200 ppb. The dilution effect is proportional to the mole fractions of CO, and the pressure-broadening effect is assumed to be proportional to the mole fractions of CO based on the fact that the coefficients a' and b' are close to those for CO2. We have added the discussion in Sect. 2.1.

C9: - Fig. 8: In this case, binning the measurement results could help detecting possible dependencies.
R9: We have binned the CO biases in time, H2O, CO2, CO, CH4, and pressure bands. We have also removed the lines since the trends are not significant. The corresponding texts are changed accordingly.

Technical corrections

C1: - page 6501 line 8: typo “liner”;
R1: Corrected.

C2: - Fig. 8: a) ... f) are missing in plots.
R2: Corrected.

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 6493, 2012.