Atmos. Meas. Tech. Discuss., 5, C2122–C2126, 2012
www.atmos-meas-tech-discuss.net/5/C2122/2012/

Atmospheric Measurement Techniques Discussions

Interactive comment on "Evaluation of factors affecting accurate measurements of atmospheric CO_2 and CH_4 by wavelength-scanned cavity ring-down spectroscopy" *by* H. Nara et al.

H. Chen (Referee)

huilin.chen@noaa.gov

Received and published: 9 September 2012

Nara et al. 2012 performed laboratory experiments to examine the potential effects on WS-CRDS CO_2 and CH_4 measurements from variations in background gases (N_2, O_2, and Ar), water vapor, and isotopologues. The most important contribution of the paper is to derive the pressure-broadening coefficients (PBEs) due to variations in O_2 and Ar for CO_2 and CH_4, which is very useful in estimating the uncertainty of the WS-CRDS CO_2 and CH_4 measurements of, e.g. purified gas standards. Besides this, the authors also confirmed the theoretical corrections due to changes in CO_2 isotopologues with their experimental results. Furthermore, water corrections for three WS-CRDS analyzers have been derived using a known method, and the transferability was discussed. Overall, the experiments presented in this paper were carefully conducted followed by proper data analyses, and the results and conclusions are valuable. I recommend publication after rephrasing some of the conclusions and addressing my concerns below.

General comments

1) Regarding the PBEs of the WS-CRDS CO_2 and CH_4 measurements, one should be aware that a direct way of removing them is to determine the mole fractions of a species of interest from the integrated absorption area instead of from the absorption peak height, which would be practical when the variations in background gases are unavoidable, and cannot be determined easily. Certainly, the measurement would be less precise (when compared to 0.03 ppm for CO_2 and 0.3 ppb for CH_4), but I wonder whether it will be more precise than the measurement determined from the peak height with the estimated PBEs removed based on the method presented in this paper. Can the authors give a comparison of the estimated uncertainties caused by the two different methods?

2) It may be necessary to reconsider the “accurate measurements” in the context of “transferability” for water vapor corrections for CO_2 and CH_4. The WMO recommended inter-laboratory comparability goal for CO_2 is 0.1 ppm and 0.05 ppm for the northern hemisphere and the southern hemisphere, respectively, and for CH_4 is 2 ppb. I recommend the authors take a different accuracy target than the precision of the measurements when discussing the transferability. Note that the residuals from the fitted water correction functions for the G-1301 (Fig.5.), 0.08 ppm for CO_2, and 0.8 ppb for CH_4, are already larger than the precisions. Furthermore, regardless of the transferability of the water corrections, an alternative way of making high-accuracy measurements of CO_2 and CH_4, rather than performing complete or moderate drying

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

of the air followed by the application of a water vapor correction function, is to develop instrument-specific water corrections, as has been done by the authors and researchers in other labs.

Specific comments

Page 5010 Abstract: It will be helpful to add a sentence like “the pressure-broadening coefficients (PBEs) due to variations in O_2 and Ar for CO_2 and CH_4 are empirically determined, and are linearly correlated with the differences between the mole fractions of O_2 and Ar and their ambient abundances”

Also as mentioned above, I recommend the authors rephrase their conclusions on the transferability and complete/moderate drying of air samples for accurate measurements of CO_2 and CH_4.

Page 5011/Line 20, add “measurements of the total” before “column abundances . . .. . .”

Page 5012 Please also check WS-CRDS measurements of CO_2 (Richardson et al. 2012 in “Journal of atmospheric and oceanic technology”)

Page 5013/Line 23, change “inverse modeling work” to “further investigation”

Line 25, Since the impact on synthetic standard gas measurements is only one application, a sentence like “the correlations between the pressure-broadening effects (PBEs) and variations in background gases N_2, O_2, and Ar” will better describe the section than the original one.

Page 5014/Line 11-12, “. . .by adjusting the flow rate using two solenoid valves placed at the sample inlet and outlet of the cavity” is not true if the WS-CRDS analyzer is a mobile version, which controls a constant flow rate based on a critical orifice. Since the description here is given in general, I would leave out this part of the sentence.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Page 5018
Line 6, change “Thus PBEs . . .” to “Thus the delta coefficients . . .”

Line 19-20, what are the precisions of the mass flow controllers? Are the precisions dominating the errors in the calculated dilution effects in Eq. (10)?

Page 5020
Line 6, change “mixing ratios” to “mole fractions”

Line 14-18, Here the PBE for N_2 is biggest because the abundance of N_2 is biggest, and that a relative increase of 2.5% of the abundance was considered. Given the same absolute increase for all three species, the PBEs are not very different. Especially for O_2 and Ar, the difference might not be significant. Considering the uncertainties in the pressure-broadening coefficients obtained in Nakamichi et al. 2006, the coefficients (0.067±0.002 and 0.062±0.002) are also very close. Then I have a problem understanding why the delta coefficients for O_2 and Ar (in Table 1) are so different?

Page 5021
Line 26-27, it is acceptable to use purified air for gas standards as long as the potential bias due to the removal of O_2 is quantified. It is certainly preferred to synthetic air, but not as ideal as real ambient air.

Line 13, -0.05 ppm for CO_2 is not big, but not negligible. This potential effect should be aware of when making high-accuracy measurements.

Page 5023/Line 13, Eq. (14), change $^{18}R_{std}$ to $^{18}R_{ref}$. And similarly for Eq. (16).

Page 5026/ Line 15, please specify how was 0.16% (below zero dew point) water vapor achieved.

Page 5033/Table 1, what are $CO_2 x 10^7$, and $CH_4 x 10^8$? If they are the magnification factors of the coefficients, seem to be too large.

Page 5041/Fig.6, I suggest plotting the differences against the reported water vapor, since it is the case in Table 3 as well as in available publications. How was the one sigma calculated here? A calibration of the water vapor scale is given in Winderlich et al. 2010, Page 1118, Eq.(1). How do these water vapor calibrations compare?

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 5009, 2012.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper