

Pressure broadening effects of inert gases on CO₂ and CH₄ measurements using a wave scan cavity ring down spectrometer

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A wavelength-scanned cavity ring-down spectrometer (CRDS, available from PICARRO, Inc., Santa Clara, CA) is a rapidly spreading observation instrument which can detect atmospheric CO₂, CH₄, and H₂O simultaneously based on the principle of laser absorption technique (Crosson, 2008). Chen et al. (2010) made airborne observations of CO₂ and CH₄ over the Amazonian rain forest using a CRDS and evaluated its performance for CO₂ measurement in comparison to NDIR. These investigators reported the CRDS measurements were affected by the variations in inert gaseous species (N₂, O₂, and Ar) due to pressure broadening effects (PBE) on absorption spectrum of CO₂ and CH₄. However, the magnitudes of the pressure broadening effects were not tested. In this work PBE of N₂, O₂, and Ar on the CO₂ and CH₄ measurements by means of a wave scan cavity ring-down spectrometer was examined through the experimental approach. Our experiments revealed similar PBE behaviour on CO₂ and CH₄. The relative increase of N₂ in the sample gas shows negative PBE while those of O₂ and Ar show positive PBE. Maximum PBE was observed for N₂, followed by O₂ and minimum for Ar. For example, PBE of N₂ on the CO₂ measurement at the 2.5% increase is estimated to be -0.93 ppmv while those of O₂ and Ar is +0.23 ppmv and +0.01 ppmv, respectively. For CH₄, PBE at 2.5% increase is estimated to be -1.08 ppbv while those of O₂ and Ar is +0.22 and +0.02 ppbv, respectively. Based on the experimental results, possible PBE during the synthetic standard gas measurements was considered. We inferred substantial PBE for both CO₂ and CH₄ within +/-0.6 ppmv for CO₂ and +/-0.6 ppmv for CH₄ during the measurement of the standard gas balanced with the synthetic air consists of N₂, O₂, and Ar. On the contrary, negligible PBE was estimated empirically up to -0.05 ppmv for CO₂ and -0.07 ppbv for CH₄ during the measurements of purified air-balanced standard gases. Our results clearly indicated that natural air-based standard gas should be used to remove the possible bias during the ambient air measurements and otherwise purified air-balanced standard gas should be used after the isotope correction

Keywords: cavity ring-down spectrometer, carbon dioxide, methane, pressure broadening, continuous measurements