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Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment

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Abstract. Data from a recent field campaign in Mexico City are used to evaluate the performance of the EPA Federal Reference Method for monitoring the ambient concentrations of NO_2. Measurements of NO_2 from standard chemiluminescence monitors equipped with molybdenum oxide converters are compared with those from Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS) and Differential Optical Absorption Spectroscopy (DOAS) instruments. A significant interference in the chemiluminescence measurement is shown to account for up to 50% of ambient NO_2 concentration during afternoon hours. As expected, this interference correlates well with non-NO_x reactive nitrogen species (NO_z) as well as with ambient O_3 concentrations, indicating a photochemical source for the interfering species. A combination of ambient gas phase nitric acid and alkyl and multifunctional alkyl nitrates is deduced to be the primary cause of the interference. Observations at four locations at varying proximities to emission sources indicate that the percentage contribution of HNO_3 to the interference decreases with time as the air parcel ages. Alkyl and multifunctional alkyl nitrate concentrations are calculated to reach concentrations as high as several ppb inside the city, on par with the

highest values previously observed in other urban locations. Averaged over the MCMA-2003 field campaign, the chemiluminescence monitor interference resulted in an average measured NO_2 concentration up to 22% greater than that from co-located spectroscopic measurements. Thus, this interference has the potential to initiate regulatory action in areas that are close to non-attainment and may mislead atmospheric photochemical models used to assess control strategies for photochemical oxidants.

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