



Measurement of atmospheric NO₂ and NO_x by a small, sensitive diode laser based cavity ring-down detector at 404 nm

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A new, cavity ring-down detector was developed for the detection of atmospheric NO₂ and NO_x. NO₂ is directly measured by laser diode based cavity ring-down spectroscopy at 404 nm. In contrast to the indirect detection in most commonly used chemiluminescence detectors, the direct measurement of NO₂ may be useful especially in cases where NO to NO₂ ratios are large such as in freshly emitted plumes from combustion processes. The extinction of ambient air is dominated by the absorption of NO₂ so that the instrument does not exhibit significant interferences due to other absorbers such as ozone or water vapor. The limit of detection is 22 pptv (2 σ precision) for NO₂ at 1 s time resolution. The accuracy of the NO₂ measurement is given by the uncertainty of the NO₂ absorption cross section to $\pm 3\%$, which was determined by comparing measurements of this instrument with those of a well-established cavity ring-down detector for NO₂ at 532 nm. The sum of NO and NO₂ (=NO_x) is simultaneously measured in a second cavity by quantitative conversion of ambient NO to NO₂ in excess ozone upstream of the cavity. The maximum conversion efficiency of NO to NO₂ is 99 % in 15 ppmv O₃ (at ambient pressure and 298 K) for 1 s reaction time. Because of the formation of undetectable nitrogen species in subsequent reactions of NO₂ with ozone in the NO_x channel, the (1 σ) accuracy of the NO_x measurement is increased to approximately $\pm 5\%$ depending on the level of NO_x. This instrument was designed as a small, light weighted instrument with limited needs for consumables such as electric power and zero air. Measurements were validated by comparison to measurements from a chemiluminescence detector. Both instruments sampled six days of ambient air with co-located inlets. The correlations of the combined data sets for NO₂, NO and NO_x exhibit good agreements within the combined accuracies of both methods. Linear fits for all three species give similar slopes of 1.04 without a significant intercept.