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Measurement of atmospheric NO_2 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 NO_2 and NO_x. NO_2 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 NO_2 may be useful especially in cases where NO to NO_2 ratios are large such as in freshly emitted plumes from combustion processes. The extinction of ambient air is dominated by the absorption of NO_2 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 (2σ precision) for NO_2 at 1 s time resolution. The accuracy of the NO_2 measurement is given by the uncertainty of the NO_2 absorption cross section to ± 3 %, which was determined by comparing measurements of this instrument with those of a well-established cavity ring-down detector for NO_2 at 532 nm. The sum of NO and NO_2 (=NO_x) is simultaneously measured in a second cavity by quantitative conversion of ambient NO to NO_2 in excess ozone upstream of the cavity. The maximum conversion efficiency of NO to NO_2 is 99 % in 15 ppmv O_3 (at ambient pressure and 298 K) for 1 s reaction time. Because of the formation of undetectable nitrogen species in subsequent reactions of NO_2 with ozone in the NO_x channel, the (1σ) accuracy of the NO_x measurement is increased to approximately ± 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 NO_2, 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.