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The ICAD NO_2 / NO_x instrument: calibration free in-situ measurements of trace gases for atmospheric and emission studies

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Optical, spectroscopic instrument have the potential to measure quickly and reliably the trace gas concentrations by relying on characteristic absorption features, which reduces potential cross-interferences with other trace gases. They even have the potential to be calibration free. However most instruments need to be calibrated and also rely on stable intensities and are thus sensitive to any intensity fluctuation which does not originate from the trace gas absorption itself. Thus they are difficult to operate mobile or at changing environmental conditions.
In order to overcome these problems, we developed the ICAD instrument (Iterative Cavity Enhanced DOAS) which is a further development of the optical resonator technique CE-DOAS (Cavity Enhanced – Differential Optical Absorption Spectroscopy) or BB-CEAS (Broad Band Cavity Enhanced Absorption Spectroscopy). The optical resonator allows for a long absorption path, and the trace gas analysis relies on the characteristic absorption structure of the trace gases in the UV and visible spectral range (e.g. NO_2, SO_2, O_3, HCHO, HONO, Glyoxal, H_2O). But in comparison to CE-DOAS or BB-CEAS it does not rely on the absolute intensity and thus the system becomes simpler and delivers more reliable results. However, all these systems still need to be calibrated, e.g. with gases, to derive the optical absorption path. To overcome this, we developed a new purely optical calibration method ICOM (Integrated Calibration by means of Optical Modulation). The measurement system can thus avoid any gas calibration.
With these developments a NO_2 ICAD instrument prototype is constructed. It has a high accuracy (0.1 ppb), is relatively small, mobile and has only low power consumption. It is also insensitive to vibrations and thus the perfect tool to perform precise mobile measurements. With an integrated NO to NO_2 converter also the measurement of the total NO_x (NO + NO_2) is possible. An overview of different performed mobile applications will be given.
We focus here on the application of this NO_2 / NO_x ICAD system to investigate NO_2 / NO_x emissions of road traffic. The system is therefore further extended by a CO_2 sensor. The measurement is performed behind the vehicle in the diluted emission plume in a following car based on the plume chasing (sniffer car) principle. Thus remote sensing of emissions become possible. From the ratios of NO_2 or NO_x to CO_2 the emission can be calculated. We validate our measurements to PEMS (Portable EMission Systems) directly measuring on the tailpipe and found a very good agreement within 10%. Our system was used to several vehicle emission studies, especially to investigate emission manipulations of trucks or to investigate high emitters. An overview will be given.