Ambient Air Measurements of Formaldehyde by Near-infrared Cavity Ring-down Spectroscopy

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Formaldehyde (HCHO or H_2CO) is an important species in atmospheric chemistry. There are multiple direct emission sources of HCHO and it is the photochemically-driven decay product of volatile organic compounds from both natural and anthropogenic sources. For this reason, real-time HCHO measurements provide critical insights into the mechanisms of tropospheric ozone formation. Formaldehyde has a clearly resolved ro-vibrational absorption spectrum that is well-suited to optical analysis of formaldehyde concentration. We describe a commercial instrument based on cavity ring-down spectroscopy for the real-time quantitative analysis of HCHO concentration in ambient air. The instrument has a precision (1-sigma) of about 1 ppb at a measurement rate of 1-second, and provides measurements of less than 100 ppt with minutes of averaging. Long-term laboratory measurements of a gas standard demonstrate that the instrument provides stable measurements (drift <1 ppb) over long periods of time (days). Given the difficulty of preparing known concentrations of HCHO, the stability of the instrument often exceeds the stability of prepared standards. Because it is based upon high resolution optical absorption spectroscopy, it does not suffer from cross-talk with other aldehydes or other carbonyl containing compounds. The instrument has been ruggedized for both mobile (ground and flight) applications or for unattended operation at ground monitoring stations, and with a fast response time of a couple of seconds, it is suitable for ground-based vehicle deployments for fenceline monitoring of HCHO emissions. In addition to the laboratory testing described above, we report on ambient atmospheric measurements at a 10 m urban tower, which demonstrate the suitability of the instrument for applications in atmospheric chemistry and outdoor air quality.

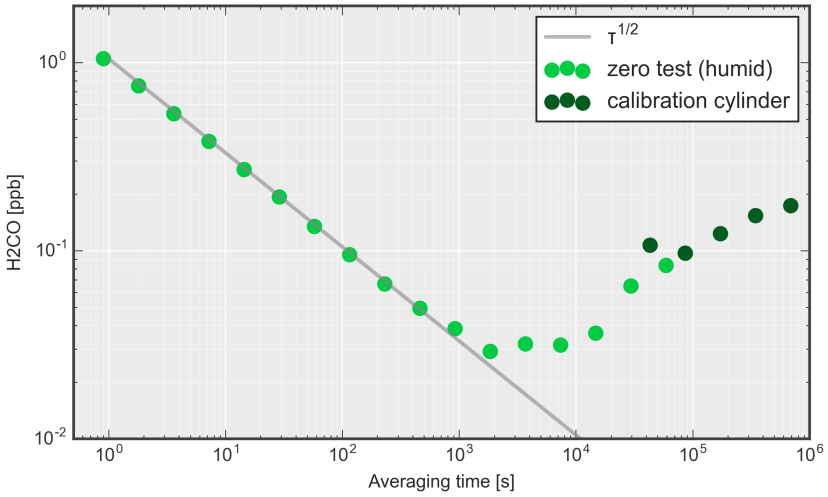

Figure 1. Measured Allan standard deviation indicating precision of 1 ppb in 1 second, 0.1 ppb with 100 seconds of averaging, and stability of about 0.2 ppb (1-sigma) over several days.

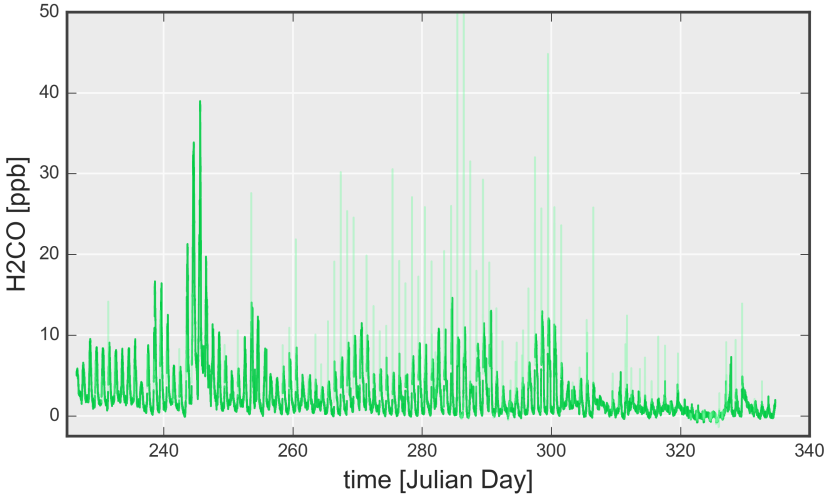

Figure 2. Outdoor ambient air measurements in Santa Clara, CA, from August to December 2017, indicating a strong diurnal cycle and large synoptic scale variability of the peak HCHO concentration.