

HOxComp: Formal Blind Intercomparison of Hydroxyl-Radical Measurements at the Atmosphere Simulation Chamber SAPHIR

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Hydroxyl radicals (OH) play a key role in the photochemical degradation of trace gases in the atmosphere. The measurement of OH is an instrumental challenge because of its extremely low ambient concentration (< 1 pptV during the day) and high reactivity. Several measurement techniques have been successfully established: Differential Optical Laser Absorption Spectroscopy (DOAS), Laser-Induced Fluorescence Spectroscopy (LIF), and Chemical Ionisation Mass Spectrometry (CIMS). There have been only few OH instrument intercomparisons in the past. HOxComp is the first formal blind intercomparison involving all three methods. It was supported by the ACCENT integration task 'Quality Assurance' and by EUROCHAMP. The formal part of the campaign included three measurement days outside and six days inside SAPHIR. The measured data was submitted to an independent referee.

Here, we present the OH intercomparison of one DOAS, and three LIF instruments under the controlled conditions within the atmosphere simulation chamber SAPHIR of the Forschungszentrum Jülich. Two different techniques are part of the instrumentation installed at SAPHIR: One active long-path DOAS instrument using a UV-laser light source at 308 nm and a White-cell (2240 m absorption path). And a LIF instrument that excites OH radicals (also at 308 nm) within a low-pressure fluorescence cell followed by detection of the resonance fluorescence (307 - 311 nm) by gated photon counting. Two more LIF instruments were attached to the chamber and operated by the research groups of the FRCGC and of the MPI. All LIF instruments share the same measurement principle but differ in their experimental setup and calibration units and thus differ in their time resolution, precision and accuracies. DOAS is used as a standard for the intercomparison because it is inherently calibrated. The other techniques are more sensitive, but require frequently sophisticated field calibrations. We compared the measurements at SAPHIR using different levels of humidity, ozone, and nitrogen dioxide. We found that all instruments are highly sensitive to OH. The correlation between the different data sets is high, well within the range expected from the precision of the single data point. No significant offset was found, but slopes between the different instrument pairs show a higher variability than the stated accuracy in the datasets. We therefore conclude that the calibration is still an important issue for all OH measurements, except DOAS.