

Assessment of interferences during field measurements of OH using a laser-induced fluorescence instrument equipped with a scavenger injector

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The hydroxyl radical is the most important atmospheric oxidant controlling the lifetimes of the majority of trace gases, including the greenhouse gas methane, and initiates the formation of harmful pollutants such as ozone and secondary organic aerosol. It has a very short lifetime of typically a second or less and hence its concentration is controlled by local in situ chemistry rather than transport, and hence is an ideal target for models containing detailed oxidation mechanisms. However, its accurate measurement in the atmosphere is extremely challenging, and despite having been measured in the troposphere for ~ 30 years there remain uncertainties surrounding potential interferences in its measurement, which have been reported recently in some environments for some instruments. A new inlet pre-injector (IPI) has been developed for the Leeds FAGE (fluorescence assay by gas expansion) instrument which allows removal of ambient OH by addition of a chemical scavenger prior to the fluorescence detection cell. In this manner the background is determined and is subtracted from the OH signal determined during field measurements leading to a measurement of OH referred to as OH-CHEM. In the more traditional method the background is determined by tuning the wavelength of the laser away from the OH transition leading to a measurement of OH referred to as OH-WAVE.

A detailed laboratory characterization will be presented of the IPI using OH removal using either propane or perfluoropropane (C₃F₆) as scavengers, with the presence of the IPI reducing the instrument OH sensitivity by $\sim 30\%$. There was no removal of OH within the fluorescence cell itself, and the IPI did not reduce the sensitivity of the instrument towards HO₂. Results will be presented during deployment of the Leeds FAGE instrument equipped with the new IPI at a coastal location in Norfolk, England in the summer of 2015, and also in central Beijing, China in the winter of 2016. For both sites, which span a very wide range of NO_x and VOC concentrations, OH-CHEM and OH-WAVE in general agreed well, within measurement uncertainties, demonstrating that at least for these locations there was no significant observed OH interference. Some results of further laboratory tests to investigate the potential presence of OH interferences formed during the ozonolysis of alkenes will also be presented.