

Implementation of a chemical background method (OH-CHEM) for field measurements of OH using the Leeds FAGE instrument: Characterisation and observations from a coastal location

Robert Woodward-Massey^{1,*}, Leanne M. Stimpson¹, Danny R. Cryer¹,
Lisa K. Whalley^{1,2}, Trevor Ingham^{1,2}, Paul W. Seakins^{1,2} and Dwayne E. Heard^{1,2}

¹ School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

² National Centre for Atmospheric Science, University of Leeds, Leeds, LS2 9JT, UK.

* Corresponding author: cmrwm@leeds.ac.uk

The removal of pollutants and greenhouse gases in the troposphere is dominated by reactions with the hydroxyl radical (OH), which is closely coupled to the hydroperoxy radical (HO₂). Comparisons of the levels of OH and HO₂ observed during field campaigns to the results of detailed chemical box models serve as a vital tool to assess our understanding of the underlying chemical mechanisms involved in tropospheric oxidation. Recent measurements of OH radicals are significantly higher than those predicted by models for some instruments measuring in certain environments, especially those at low NO_x influenced by high emissions of biogenic compounds such as isoprene, prompting intense laboratory research to account for such discrepancies. While current chemical mechanisms are likely incomplete, it is also possible that, at least in part, these elevated radical observations may have been influenced by instrumental biases from interfering species.

Recent studies have suggested that some fluorescence assay by gas expansion (FAGE) instruments may be susceptible to an unknown interference in the measurement of OH. This hypothesis can be tested through the implementation of an alternative method to determine the OH background signal, whereby OH is removed by the addition of a chemical scavenger prior to sampling by FAGE (known as OH-CHEM). The more established method to determine the background is to move the exciting laser wavelength to a value where OH does not absorb (OH-WAVE). The Leeds FAGE instrument was modified to facilitate OH-CHEM by the construction of an inlet pre-injector (IPI), where OH is removed through reaction with propane. Results from laboratory characterisation experiments and details of the IPI design will be presented.

The modified Leeds FAGE instrument was deployed at a coastal location in Norfolk, England during summer 2015 as part of the ICOZA (Integrated Chemistry of OZone in the Atmosphere) project. Measurements of OH made using both background methods will be presented, alongside FAGE observations of HO₂, alkylperoxy radicals (RO₂), formaldehyde (HCHO) and OH reactivity. Calculations of the *in situ* ozone production rate, made using measurements of HO₂ and RO₂ will also be shown.