1. Introduction

The hydroxyl radical (OH) is the most important day time oxidant, and controls the removal of pollutants and the formation of O₃ in the troposphere. 

Comparisons of modelled OH to those observed in biogenic, low-NOₓ environments show consistent underpredictions, suggesting missing OH sources. 1, 4

Recent studies 3, 4 have suggested that some fluorescence assay by gas expansion (FAGE) instruments may suffer from positive biases in OH measurement, where implementation of a chemical method to determine the OH background signal (OH-CHEM) resulted in substantial reductions in measured OH, 2, 4 and improved model agreement. 3

The Leeds FAGE instrument was modified to incorporate a new inlet pre-injector (IPI) sampling system to allow measurements of OH-CHEM, in order to assess the magnitude of any interference.

2. The Leeds Ground-Based FAGE Instrument

- Ambient OH is measured using laser-induced fluorescence (LIF) at low pressure (~1.5 Torr), where OH fluorescence at 308 nm is detected using a micro-channel plate (MCP), and the signal analysed by gated photon counting.
- The background signal is normally obtained by scanning the laser wavelength off-resonance from the OH transition (OH-WAVE).
- Hydroperoxyl (HO₂) and alkyperoxyl (RO₂) radicals may be measured after conversion to OH by reaction with NO. 2, 7
- Calibration: known concentrations of OH and HO₂ are formed from the photolysis of water vapour at 184.9 nm in a turbulent flow (40 sml) of humidified zero air; radical concentrations are calculated from lamp flux, determined using chemical actinometry.

3. Inlet Pre-Injector (IPI): Design and Characterisation

- Similar to the design of Mao et al., consisting of a 4 cm length, 1.9 cm ID PFA cylinder embedded inside an aluminium housing (Fig. 1), which seals to the FAGE cell via an O-ring base flange (Fig. 2A).
- The chemical scavenger is injected into the centre of the PFA flow tube via four 0.25 mm ID needles.
- In order to reduce radical wall losses, excess ambient air is drawn through the IPI to generate a sheath flow, which minimises the FAGE sampling of air from near the walls of the cylinder, housing and tunnel (Fig. 2).

3.1. Experimental Design

- The presence of the IPI results in reproducible losses in sensitivity of ~40% for OH, and ~20% for HO₂.
- Overall uncertainty in OH measurements is estimated at ~40% (2σ).
- The scavenging efficiency was determined for both propane and hexafluoropropene (C₆F₆), with good agreement between the two scavengers (Fig. 3).
  - The OH remaining is much larger than the theoretical, suggesting the efficiency is limited by mixing.
  - Optimum removal of virtually 100% at k$_{BA}$ = 300 s⁻¹ equivalent to ~110 ppmv propane.
  - No evidence for internal removal.

3.2. Calibration

- Consecutive measurements of OH remaining are made using the two background methods (OH-WAVE and OH-CHEM) generally show very good agreement (Figs. 4 and 5).
- However, some discrepancies are observed for short periods of time (Fig. 4), the reasons for which are subject to ongoing investigation.

3.3. Operational Details

- Simultaneous observations of HO₂ and RO₂ were made using two side-by-side fluorescence cells:
  - Cell 1 (HO₂) = measures OH and HO₂ radicals consecutively
  - Cell 2 (RO₂) = measures HO₂ and RO₂ radicals consecutively
  - Differences between RO₂ and HO₂ allow for partially speciated measurements of RO₂, i.e. between simple (short-chain alkane) and complex (long-chain alkane, aromatic and aliphatic) RO₂

- Measurements of total OH reactivity (kOH$_{total}$), the pseudo first-order loss rate of OH, were made using another FAGE instrument, which sampled from the Leeds container roof, formaldehyde (HCHO) observations were made using a separate LIF instrument situated in the WAO building.

- A summary of ICOZA FAGE measurements is provided by the diurnal profiles shown in Fig. 6:
  - High midday OH (~6 × 10⁶ molecules cm⁻³⁻¹)
  - RO₂ and HO₂ close to 1, with HO₂ dominated by simple RO₂

- Ozone pollution event observed on 1 July 2015 (Fig. 7):
  - Air mass change from ESE to S (i.e. sea to land)
  - Sharp rise in temperature and O₃, which eventually reaches ~110 ppbv, accompanied by a reduction in NO
  - Concomitant increases in radical concentrations, with very high levels of OH observed (>1 × 10⁶ molecules cm⁻³⁻¹)
  - P (O₂) calculated from radical and NO$_x$measurements

4. ICOZA I: Introduction and IPI Results

- The ICOZA (Integrated Chemistry of Ozone in the Atmosphere) project took place at the Wyebourne Atmospheric Observatory, Norfolk, UK, in July 2015.
- Aimed to improve understanding of ozone chemistry through integrated measurements of P (O₂), the eu tropospheric ozone production rate (OPR), with comparisons to a range of other observational and model approaches.
- The WAO site is impacted by a range of contrasting air masses, from clean Arctic air to processed emissions from the UK (e.g. London) and Northern Europe.

5. ICOZA II: FAGE Observations of OH, HO₂ and RO₂ Radicals, OH reactivity (kOH) and HCHO

- Simultaneous observations of HO₂ and RO₂ were made using two side-by-side fluorescence cells:
  - Cell 1 (HO₂) = measures OH and HO₂ radicals consecutively
  - Cell 2 (RO₂) = measures HO₂ and RO₂ radicals consecutively
  - Differences between RO₂ and HO₂ allow for partially speciated measurements of RO₂, i.e. between simple (short-chain alkane) and complex (long-chain alkane, aromatic and aliphatic) RO₂

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6. References and Acknowledgements


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