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

National Centre for Atmospheric Science NATURAL ENVIRONMENT RESEARCH COUNCIL

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1. Introduction

- The hydroxyl radical (OH) is the most important day time oxidant, and controls the removal of pollutants and the formation of O_3 in the troposphere.
- Comparisons of modelled OH to those observed in biogenic, low-NO_x environments show consistent underpredictions, suggesting missing OH sources.¹⁻⁴
- Recent studies^{4,5} 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,^{4,5} and improved model agreement.⁴
- 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 on-resonance 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).
- Hydroperoxy (HO₂) and alkylperoxy (RO₂) radicals may be measured after conversion to OH by reaction with NO.^{6,7}
- Calibration: known concentrations of OH and HO_2 are formed from the photolysis of water vapour at 184.9 nm in a turbulent flow (40 slm) 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.,⁴ consisting of a 4 cm length, 1.9 cm ID PFA cylinder embedded inside an aluminium housing (Fig. 1), which seals



4. ICOZA I: Introduction and IPI Results

 The ICOZA (Integrated Chemistry of OZone in the Atmosphere) project took place at the Weybourne Atmospheric Observatory, Norfolk, UK, in July 2015.

- 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 turret (Fig. 2).

Propane

Figure 1. Labelled SolidWorks model of the Leeds IPI. The yellow arrows indicate the direction of the sheath flow (see text).



- 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

- Aimed to improve understanding of ozone chemistry through integrated measurements of $P(O_3)$, the *in situ* 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.

8x10[°]



Figure 4. Time series of ambient data obtained between 3-8 (left) and 12-14 July 2015 (right). Top: FAGE measurements of OH-WAVE (blue circles) and OH-CHEM (black squares); solid lines correspond to hourly averages. Bottom: filter radiometer measurements of *J* (O¹D).

Consecutive measurements of OH made using the two background methods

1.6x10⁻

Figure 5 (left). Diurnal profile of measured OH-WAVE (blue),



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



- Simultaneous observations of HO_x and RO_x were made using two side-by-side fluorescence cells:
 - \circ Cell 1 (HO_x) measures OH and HO₂ radicals consecutively
 - \circ Cell 2 (RO_x) measures HO₂* and RO₂ radicals consecutively
 - $HO_2^* = "real" HO_2 + a small interference from certain RO_2$ radicals;^{6,7} differences between RO₂, HO₂* and HO₂ allow forpartially speciated measurements of RO₂,⁷ i.e. between simple(short-chain alkane) and complex (long-chain alkane, alkeneand aromatic) RO₂
- Measurements of total OH reactivity (k_{OH}), 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 main WAO building.



Figure 6. Diurnal profiles of OH, HO₂ and RO₂ radicals (A-C), J(O¹D) (A), and OH reactivity (D) measured between 29 June and 17 July 2015, and HCHO measured between 7-17 July 2015 (D). Error bars correspond to the 95% CI of the ambient variability within each time bin.

- A summary of ICOZA FAGE measurements is provided by the diurnal profiles shown in Fig. 6:
 - High midday OH ($\sim 6 \times 10^6$ molecule cm⁻³)
 - HO₂ and RO₂ radicals exhibit maxima in the afternoon (~15:00)
 - All radical species observed at night (OHwave interference?)
 - \circ RO₂:HO₂ close to 1:1, with RO₂ 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 rises in temperature and O_3 , which eventually reaches ~110 ppbv, accompanied by a reduction in NO
 - Concomitant increases in radical concentrations, with very high levels of OH observed (>1 \times 10⁷ molecule cm⁻³)
 - \circ P (O₃) calculated from radical and NO_x measurements



Figure 7. Time series of various measurements on 30 June and 1 July 2015, showing the O_3 pollution event starting at ~12:00 on 1 July. The solid lines in panels A-C correspond to 30 min averages. Not visible in panel E is a spike in NO to 20 ppbv at ~16:00 on 1 July. Temperature data provided by WAO. HCHO data not available on these days.

6. References and Acknowledgements

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