1. Introduction

- \( \text{HO}_2 \) (OH and \( \text{HO}_2 \)) are the most oxidising radicals in our atmosphere.\(^1\)
- The sensitivity relationship between \( \text{HO}_2 \) and \( \text{OH} \) gives an insight into the localised atmospheric composition.
- The regional and altitudinal variation in \( \text{OH} \) and \( \text{HO}_2 \), the hydroperoxy radical, can be measured using the airborne Fluorescence Assay by Gas Expansion (FAGE) instrument.
- A new method for calibrating FAGE instruments for \( \text{OH} \) and \( \text{HO}_2 \) has been developed (Fig 4.1) using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC).\(^2\)

2. FAGE

- Fluorescence Assay by Gas Expansion (FAGE) is a low pressure, on-resonance (\( \lambda = 308 \) nm) Laser Induced Fluorescence (LIF) technique.
- Simultaneous OH and HO2 measurement are made where HO2 is titrated to OH using NO.
- FAGE is a non-absolute method and therefore requires calibration.
- Instrument signals due to \( \text{OH} \) and \( \text{HO}_2 \) are converted to concentrations using calibration factors \( C_{\text{OH}} \) and \( C_{\text{HO}_2} \):
  \[
  [\text{OH}] = C_{\text{OH}} \times S_{\text{OH}} \quad \text{and} \quad [\text{HO}_2] = C_{\text{HO}_2} \times S_{\text{HO}_2}
  \]
- Changes in external pressure result in changes in the internal detection cell pressure of the FAGE instrument which affect the sensitivity towards \( \text{OH} \) and \( \text{HO}_2 \).
- The first calibration of a FAGE instrument over a range of external pressures has been completed in HIRAC (see box 3).

3. HIRAC\(^3\)

- 2.25 m\(^3\) steel chamber (Fig 3.2).
- Pressure and temperature variable (up to 1000 mbar, 225 – 325 K).
- 8 rows of internal photolysis lamps (Fig 3.1).
- 4 mixing fans (total mix time of ~70 s).
- Series of instruments including: GC-FID, FTIR, FAGE, CRDS and \( \text{O}_3 \), \( \text{NO}_x \), \( \text{H}_2 \) and CO analysers.
- Steel design allows the calibration of FAGE at varying external pressures.

4. Traditional Calibration Method

- Photolysis of water in a flow of humidified air at 184.9 nm (Hg pen ray lamp, Fig 4.1) produces \( \text{OH} \) and \( \text{HO}_2 \) in a 3:1 ratio via reactions 4.1 and 4.2:
  \[
  \text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H} \quad \text{R} \ 4.1
  \]
  \[
  \text{H} + \text{O}_2 \rightarrow \text{HO}_2 \quad \text{R} \ 4.2
  \]
- A range of [OH] and [HO2] are generated by changing [H2O] and Hg lamp current. Calibration plots are produced by plotting the measure \( S_{\text{OH}} \) or \( S_{\text{HO}_2} \) as a function of \( \text{[OH]} \) or \( \text{[HO}_2\text{]} \) giving the calibration factor, \( C_{\text{OH}} \) or \( C_{\text{HO}_2} \), as the gradient (Fig 4.2).

5. OH Calibrations

- Based on a study by Bloss et al.\(^4\)
- Preliminary results shown here for the HIRAC FAGE instrument only.
- OH reacts with a hydrocarbon (HC) in HIRAC whose rate constant is well understood.
- Photolysis of t-butyl hydroperoxide (\( \lambda = 254\)nm) used to produce \( \text{OH} \).
- The HC decay is monitored using GC-FID (Fig 5.1), whilst \( \text{OH} \) is measured using FAGE.
- [OH] is inferred from the HC decay (see boxed equations below) and temporally matched to \( \text{OH} \) signal, producing a calibration plot (Fig 5.2).
- \( C_{\text{OH}} \) in good agreement with traditional method at STP (3.77 x 10\(^6\) compared to 3.56 x 10\(^6\) counts s\(^{-1}\), m\(^{-1}\) molecule\(^{-1}\) cm\(^{2}\)).

6. HO2 Calibrations

- Monitor decay in \( S_{\text{HO}_2} \) after photolysis of \( \text{HCHO} \) reaches steady state \( \text{HO}_2 \) (Fig 6.1).
- Decay can be described by first order wall loss and second order \( \text{HO}_2 \) self reaction (Eq 6.1 and 6.2).
  \[
  \frac{d[\text{HO}_2]}{dt} = -(k_{\text{loss}})[\text{HO}_2] + 2k_{\text{HO}_2}[\text{HO}_2][\text{HO}_2]
  \]
  \[
  \frac{1}{S_{\text{HO}_2}} = \frac{1}{S_{\text{HO}_2}0} + \frac{2k_{\text{HO}_2}S_{\text{HO}_2}0}{S_{\text{HO}_20}k_{\text{loss}}} \quad \text{exp}(k_{\text{loss}}t)
  \]
- 5 decays recorded per experiment and average \( k_{\text{loss}} \) determined.
- Experiment repeated for various chamber pressures corresponding to internal cell pressures used in the traditional method (box 4).
- Both Aircraft (Fig 6.2) and HIRAC based FAGE instruments calibrated using this method show good agreement with the traditional calibration process.

7. Conclusions and Future Work

- Conclusions
  - First alternative external pressure dependent \( \text{HO}_2 \) FAGE calibration has been completed and has been shown to agree well with the traditional method.
  - Preliminary experiments into an alternative kinetics based OH calibration method using HIRAC have been successful, and are in good agreement with the traditional method.
- Future Work
  - Complete HIRAC based \( C_{\text{OH}} \) pressure dependence experiments.
  - Decide on optimum fitting conditions for HC and \( \text{HO}_2 \) decays.
  - Full uncertainty analysis for both alternative \( \text{OH} \) and \( \text{HO}_2 \) calibration methods.
  - Use the HIRAC temperature control system to investigate possible \( C_{\text{OH}} \) and \( C_{\text{HO}_2} \) temperature dependence.

References