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1. Introduction

Pressure dependent calibrations of a FAGE HO_x instrument have been carried out using the Highly Instrumented Reactor for Atmospheric Chemistry, HIRAC (see poster A21-0206). Fluorescence Assay by Gas Expansion, FAGE, is a low pressure, on-resonance laser induced fluorescence technique used for the detection of HO_x (=OH+HO₂) radicals. FAGE is not an absolute technique requiring calibration to convert measured signals into concentrations, $S_{OH} = C_{OH}[OH]$ and $S_{HO_2} = C_{HO_2}[HO_2]$. The sensitivity, C_{OH} and C_{HO_2} , is dependent on pressure (Fig. 3) and therefore airborne and pressure variable chamber instruments require pressure dependent calibrations.

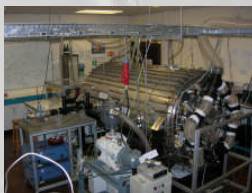


Fig. 1: A picture of HIRAC

2. Traditional FAGE calibrations

A range of [OH] and [HO₂] are produced using the photolysis of H₂O vapour at 185 nm (Hg pen-ray lamp) at various [H₂O] and Hg lamp intensities (Fig. 2). Pressure dependent calibrations are carried out by changing the size of the inlet pinhole to replicate the changes in internal detection cell pressures which occur with changes in external pressure. This may change the flow dynamics within the detection cell and the OH transmission.

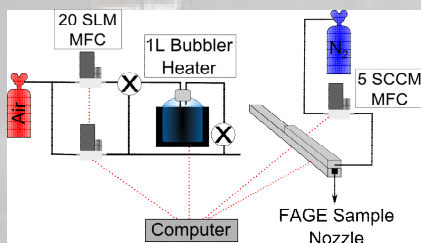


Fig. 2: A schematic of the traditional H₂O vapour photolysis calibration set-up

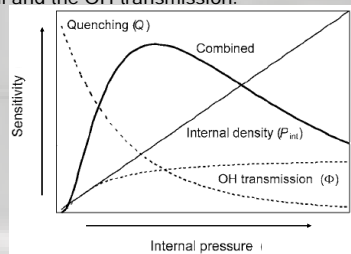


Fig. 3: Theoretical pressure dependence of FAGE sensitivity and pressure dependent parameters contributing to this dependence adapted from Faloon et al., J. Atmos. Chem., 2004.

Two new and independent methods for calibrating FAGE Instruments for OH and HO₂ over a range of external pressures have been developed using HIRAC. These methods can be used to validate the traditional pressure dependent calibration method as well as improve confidence in FAGE HO_x measurements.

5. Uncertainties and Conclusions

The uncertainties in the two new pressure dependent calibration methods are shown in the tables below. They have comparable uncertainties to that from the traditional H₂O photolysis / changing pinhole method which is ±16% (1σ).

a)

Parameter	Uncertainty (±1σ)
[HC] _{calc} / molecule cm ⁻³	5%
k _{OH+HC} / molecule ⁻¹ cm ³ s ⁻¹	4-7%
-d[HC] / dt / molecule cm ⁻³ s ⁻¹	9%
Online position / cts s ⁻¹ mW ⁻¹	2%
Laser power / mW	3%
C _{OH} / cts s ⁻¹ molecule ⁻¹ cm ³ mW ⁻¹	12-13%

b)

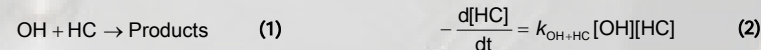
Parameter	Uncertainty (±1σ)
k _{loss} / s ⁻¹	20%
k _{HO2+HO2} / molecule ⁻¹ cm ³ s ⁻¹	7 - 15%
Fit	6%
Online position / cts s ⁻¹ mW ⁻¹	2%
Laser power / mW	3%
C _{HO2} / cts s ⁻¹ molecule ⁻¹ cm ³ mW ⁻¹	22 - 26%

Table 1: A summary of uncertainties associated with a) HC decay OH calibration and b) HCHO photolysis HO₂ calibration.

The HC decay and HCHO photolysis pressure dependent calibrations yield results which are in good agreement with and have uncertainties of similar magnitude those from the traditional method and with. We now plan to use this method to calibrate the Leeds aircraft instrument.

3. OH calibrations - Hydrocarbon decays

Measurement of the decay of a hydrocarbon (HC) in the presence of OH has been used in HIRAC to calibrate a FAGE instrument for external pressures between 300 and 1000 mbar



OH was produced in the chamber by the photolysis of methyl nitrite, and the decay of 1 - 2 HCs with well known rates of reaction with OH, k_{OH+HC} , were measured by GC-FID whilst simultaneously measuring the decay in OH by FAGE. A first order exponential fit to the measured [HC] decay (Fig. 4) was used to calculate [HC] at the frequency of the OH measurement (1 s). By rearrangement of equation (2) the [OH] can be calculated from the rate of decay of [HC], $-d[HC]/dt$, and literature k_{OH+HC} .

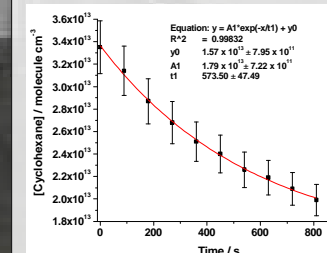


Fig. 4: Decay in [cyclohexane] through reaction with OH.

Average C_{traditional} / C_{HIRAC} of 1.07±0.07

$$[OH] = \frac{-d[HC]/dt}{k_{OH+HC} \times [HC]} \quad (3)$$

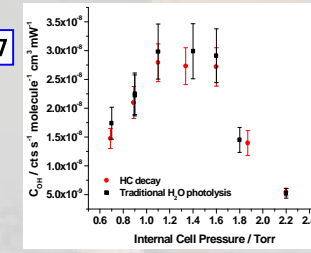


Fig. 5: OH sensitivity as a function of cell pressure from the HC decay and traditional calibration methods.

Measured OH signals were plotted against calculated [OH], and C_{OH} determined from the gradient at each chamber pressure. The results from the HC decay method were compared to data from the H₂O photolysis / changing pinhole technique (Fig. 5).

4. HO₂ calibrations - HCHO photolysis

Measurements of the loss of HO₂ through self-reaction following photolysis of HCHO in air have been used to determine C_{HO_2} between 300 and 1000 mbar and with 0 - 0.8% [H₂O]. The loss of HO₂ is due to mixed first and second order process and can be analysed as follows:

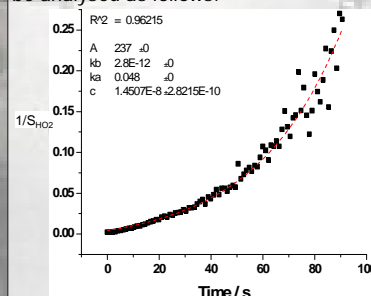


Fig. 6: Experimental HO₂ decay data taken inside HIRAC during a HCHO photolysis calibration of FAGE for HO₂.

$$\frac{d[HO_2]}{dt} = -(k_{loss}[HO_2] + 2k_{HO_2+HO_2}[HO_2]^2) \quad (4)$$

$$[HO_2] = \frac{S_{HO_2}}{C_{HO_2}} \rightarrow \frac{1}{(S_{HO_2})_t} = \left(\frac{1}{(S_{HO_2})_0} + \frac{2 \times k_{HO_2+HO_2}}{k_{loss} \times C_{HO_2}} \right) \exp^{(k_{loss}t)} - \left(\frac{2 \times k_{HO_2+HO_2}}{k_{loss} \times C_{HO_2}} \right) \quad (5)$$

A simple FACSIMILIE model was used to determine $k_{loss} = 0.048 \pm 0.005 \text{ s}^{-1}$ (independent of pressure, [HCHO] and %[H₂O]). Experiments without the chamber mixing fans on ($k_{loss} = 0 \text{ s}^{-1}$) illustrate that k_{loss} is due to loss of HO₂ on the chamber walls. Using the model determined k_{loss} along with pressure and %[H₂O] dependent $k_{HO_2+HO_2}$ (Stone and Rowley, PCCP, 2005), experimental HO₂ decay data were fitted using equation 5 yielding pressure dependent C_{HO_2} .

Average C_{traditional} / C_{HIRAC} of 0.95±0.08

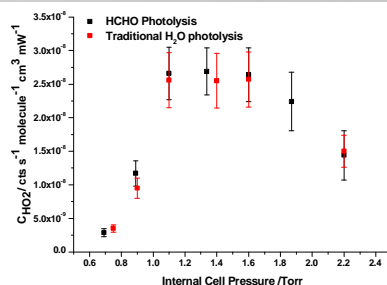


Fig. 7: HO₂ sensitivity as a function of detection cell pressure from the HCHO photolysis and traditional calibration methods.