Calibration of ATHOS for Detecting Tropospheric OH and HO_2

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Description of Instrument

- *The Penn State ATHOS (Airborne Tropospheric Hydrogen Oxides Sensor) is used to measure OH and HO_2.*
- *The technique is Laser Induced Fluorescence (LIF) at low pressure (3~10 hPa).*
- *OH and HO_2 measurements:*

  OH + *hν*1 (laser) → OH* → OH + *hν*2 (fluorescence)

  $HO_2 + NO \rightarrow OH + NO_2$
- *Measurement time resolution: 20 s*
- *Detection limit: OH: 0.012 pptv; HO_2: 0.1 pptv*

Calibration Methods

- *The calibration is based on a known concentration of OH by the photolysis of H_2O at 185 nm*

$$H_2O + h\nu\ (\lambda=185\ nm) \longrightarrow OH + H$$
$$H + O_2 \longrightarrow OH + HO_2$$

- *The concentration of OH in the photolysis region is given by*

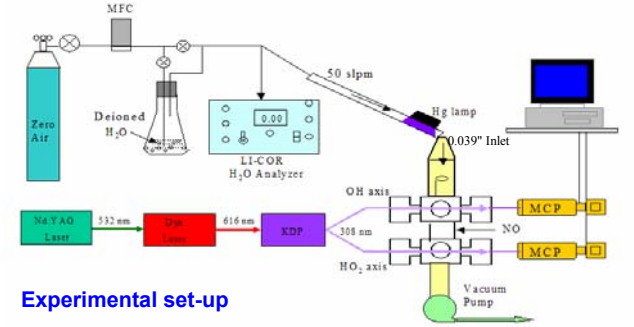
$$[OH] = [HO_2] = \varphi_{OH}\sigma_{H_2O}[H_2O]F_{185}t$$

where:
φ_{OH} is the quantum yield of OH (=1)
σ is the water vapor absorption cross-section (=7.2x10^{-20} cm^2)
t is the photolysis exposure time
F_{185} is the photon flux of the lamp at 185 nm

- *The ATHOS signal, S, is proportional to the OH concentration with the calibration factor C:*

$$S = C[OH]$$

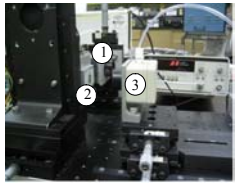
- *Calibrations are performed regularly both in laboratory and in field and the sensitivity of the ATHOS as a function of inlet pressure (altitude) is also calibrated.*



Experimental set-up

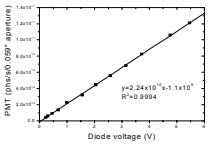
Absolute Hg flux measurement with a calibrated Cs-I PMT

Step 1. Calibration of photodiode

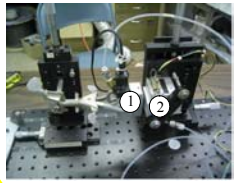


① : *Cs-I photomultiplier tube (primary calibrator)*
② : *Photodiode (secondary calibrator)*
③ : *Hg lamp*

Calibration of photodiode against PMT

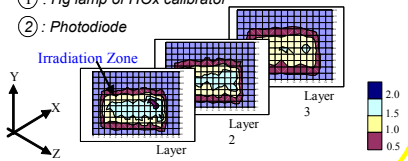


Step 2. Mapping of the flux from the Hg lamp of calibrator



① : *Hg lamp of HOx calibrator*
② : *Photodiode*

Irradiation Zone



Example of flux profiles

Actinic calibration with N_2O and O_2

N_2O Actinometry:

		k(cm^{3}molecule^{-1}s^{-1})
$N_2O + h\nu$	$\rightarrow N_2 + O(^1D)$	$j_{-(N_2O)}$; Φ_{O^1D}=1
$O(^1D) + O_2$	$\rightarrow O(^3P) + O_2$	$k_{(O_2+O^1D)}$ = 4.05E-11
$O(^1D) + N_2$	$\rightarrow O(^3P) + N_2$	$k_{(N_2+O^1D)}$ = 2.61E-11
$O(^1D) + N_2O$	$\rightarrow 2NO$	k_2 = 6.70E-11
$O(^1D) + N_2O$	$\rightarrow N_2 + O_2$	k_3 = 4.90E-11

$$F_{185}t = \frac{(k_{(O_2+O^1D)}[O_2] + k_{(N_2+O^1D)}[N_2] + (k_2 + k_3)[N_2O])[NO]}{2k_2\sigma_{N_2O}\varphi_{O^1D}[N_2O]^2}$$

where
$\sigma_{N_2O} = 1.43x10^{-19} cm^2$
[NO] is the generated concentration of NO (0.3 ~ 3 ppbv)

O_2 Actinometry:

$O_2 + h\nu \rightarrow 2O$ $\quad j_{-(O_2)}$

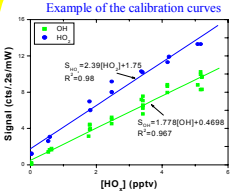
$O + O_2 + M \rightarrow O_3 + M$ $\quad \varphi_{O_3} = 2.0$

$$F_{185}t = \frac{[O_3]}{\sigma_{O_2}\varphi_{O_3}[O_2]}$$

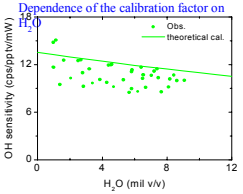
where
$\sigma_{O_2} = \sim 1.12x10^{-20} cm^2$
[O_3] is the generated concentration of O_3 (1 ~ 5 ppbv)

Results

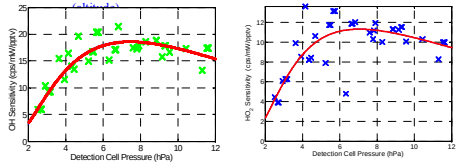
Example of the calibration curves



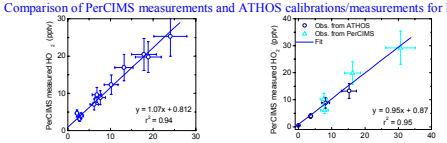
Dependence of the calibration factor on H_2O



Dependence of the calibration factor on the cell pressure



Comparison of PerCIMS measurements and ATHOS calibrations/measurements for HO_2



Typical values of F_{185} acquired by the three calibration methods

Technique	F_{185} (photns/s/cm^2)	2σ relative uncertainty
Absolute method	1.3x10^{12}	20%
N_2O actinometry	1.6x10^{12}	24%
O_2 actinometry	2.1x10^{12}	56%

Conclusions

- *A developed calibration system which combines photolysis of water vapor and measurement of the UV flux at 185 nm is suited for LIF based tropospheric HOx instrument calibration.*
- *Variations in cell pressure affect the sensitivity of the ATHOS.*
- *Excellent agreement was obtained in the calibration comparisons between the PSU ATHOS and the PerCIMS from the NCAR for HO_2 to within 5%.*
- *As alternative approaches, N_2O actinometry gives a typical value of F_{185} that agrees within 23% with the absolute flux technique, while typical F_{185} for O_2 actinometry is* 1.6 times higher than the absolute flux method.

References & Acknowledgments

- Faloona et al., J. Atmos. Chem., 47, 139-167, 2004
- Edwards et al., Anal. Chem., 75, 5317-5327, 2003
- Ren et al., J. Geophy. Res., 108 (D19), doi:10.1029/2003JD003644, 2003

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