

TITLE: Hydrogen Peroxide and Methylhydroperoxide by HPLC

AUTHOR(S):

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1.0 DATA SET OVERVIEW:

Hydrogen peroxide (H₂O₂) and methylhydroperoxide (CH₃OOH) data for the Pacific Atmospheric Sulfur Experiment (PASE). Collected on the NCAR C-130 in Aug-Sept, 2007 from Kiribati (Christmas) Island, Republic of Kiribati.

2.0 INSTRUMENT DESCRIPTION:

The named peroxides were quantified using the method of Lee et al. (*J. Atmos. Ocean Tech.*, 12, 1060-1070, 1995). Gas phase peroxides are collected in an aqueous solution, injected onto a reverse phase C-18 chromatography column, separated, derivatized to a fluorophore, and quantified using fluorescence. Samples represent 30 s and are injected periodically with a cycle time between 75 and 150 s.

3.0 DATA COLLECTION AND PROCESSING:

Air sample flows are established using mass flow controllers calibrated volumetrically with Biospherics DryCal. Aqueous collection flows are established using gravimetrically calibrated peristaltic pump tubes. Temperatures are measured using resistance thermistors. Sample air pressure and differential pressure are measured using MKS baratron gauges. All housekeeping data is sampled at 1 Hz, averaged and recorded every 10 s.

H₂O₂ is quantitatively collected. CH₃OOH is collected at its thermodynamic equilibrium value and corrected. Mass flow, temperature, and pressure from the collection stream are used to determine this collection efficiency. The Henry's Law values from O'Sullivan et al. (*J. Phys. Chem.*, 1995) are used to calculate collection efficiency.

Chromatograms are analyzed using EZChrom software and peak height analysis, manually reviewed and baselines corrected as need – about 1 in 10 injections require baseline adjustment. Aqueous calibrations are performed preflight. Zero air is introduced to the collection system to determine fluorescence blanks.

The detection limit for H₂O₂ is 15 ppt (parts per trillion mole mixing ratio) and that for CH₃OOH is 30 ppt. These are based on three times the standard deviation of the fluorescence blanks. Estimated accuracy for H₂O₂ is ±(15 ppt + 0.1*value) and that for CH₃OOH is ±(30 ppt + 0.15*value).

4.0 DATA FORMAT:

Data for each flight is supplied in its own file. Filenames are structured as (for example):
RF03_C130_20070813_09_HPLCPEROXIDES_V1.txt
RAF flight number _ platform _ date of flight measured parameter _ index _ version . file type
ascii text

Standard EOL data archive header information is first followed by a NASA-NOAA header information style precluded by “REMARKS =” identifier.

EXAMPLE HEADER and 3 lines of data

```
PI/DATA CONTACT = Heikes, Brian (Univ Rhode Island), O'Sullivan, Daniel W. (US Naval Acad.)
DATA COVERAGE = START: 20070901191424; STOP 20070902025954 UTC
PLATFORM/SITE = C-130
INSTRUMENT = HPLC PEROXIDES
LOCATION = mobile
DATA VERSION = 1.0 (20080124)
REMARKS = Pacific Atmospheric Sulfur Experiment (PASE)
REMARKS = H2O2 in parts per trillion by mole, ppt
REMARKS = CH3OOH in parts per trillion by mole, ppt
REMARKS = Sample start time in yyymmddhhmmss, UTC
REMARKS = Sample stop time in yyymmddhhmmss, UTC
REMARKS = missing data -9999
REMARKS = level of detection data -8888, nominally 15 ppt H2O2 and 30 ppt CH3OOH
REMARKS = level of overrange data -7777, nominally 10000 ppt H2O2 and 10000 ppt CH3OOH
REMARKS = NASA-NOAA HEADER INFORMATION FOLLOWS
REMARKS = 47 1001
REMARKS = Heikes, Brian
REMARKS = University of Rhode Island
REMARKS = Hydrogen Peroxide and Methylhydroperoxide, Gas-Phase, C-130, PASE
REMARKS = PASE: Pacific Atmospheric Sulfur Experiment - Local and Global Reserach observations
REMARKS = 1 1
REMARKS = 2007 09 01 2008 01 24
REMARKS = 0
REMARKS = Start_UTC, sec
REMARKS = 4
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REMARKS = -9999 -9999 -9999 -9999
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REMARKS = CH3OOH, ppt
REMARKS = 1
REMARKS = Julian Day 244
REMARKS = 28
REMARKS = Filename: RF11_C130_20070901_17_HPLCPEROXIDES_V1.txt
REMARKS = Modified NASA-GTE NOAA-AL Data File Format -> ICARTT Format (http://www-air.larc.nasa.gov)
REMARKS = PI_CONTACT_INFO: Brian Heikes, URI/GSO, South Ferry Rd, Narragansett, RI 02882-1197, USA
```

REMARKS = email: bheikes@gso.uri.edu
REMARKS = voice: 401.874.6638
REMARKS = fax: 401.874.6898
REMARKS = PLATFORM: NCAR C-130
REMARKS = LOCATION: Other PASE data can be found at EOL.NCAR.UCAR.EDU
REMARKS = ASSOCIATED_DATA: other observations made in PASE will be made publically available through EOL at NCAR...
REMARKS = INSTRUMENT_INFO: H2O2 and CH3OOH by aqueous collection followed by HPLC separation and enzyme...
REMARKS = DATA_INFO:
REMARKS = 1. sample collection interval is NOT contiguous and may vary from approximately 30 seconds every 75 sec to 30 ...
REMARKS = 2. sample start times are irregular in time and not periodic
REMARKS = 3. start time is in seconds past mid-night on the day of takeoff, and will exceed 86400 if midnight UTC is crossed...
REMARKS = 4. sample stop time is approximately 30 seconds after sample start and based upon fluidics
REMARKS = H2O2 UNCERTAINTY: +/- (15 ppt + 0.1*value)
REMARKS = CH3OOH UNCERTAINTY: +/- (30 ppt + 0.15*value)
REMARKS = ULOD_FLAG: -7777
REMARKS = ULOD_VALUE: N/A; N/A; 10000; 10000
REMARKS = LLOD_FLAG: -8888
REMARKS = LLOD_VALUE: N/A; N/A; 15; 30
REMARKS = DM_CONTACT_INFO: N/A
REMARKS = PROJECT_INFO: PASE Base of operations: Boulder Test Flights, Transit Boulder-Monterey-Hawaii-Xmas (return), ...
REMARKS = STIPULATIONS_ON_USE: Use of these data requires PI notification and adherence to the PASE data protocol
REMARKS = OTHER_COMMENTS: N/A
REMARKS = REVISION: R1
REMARKS = R1: Initial Final data file, prior to first data workshop;
REMARKS = Start.UTC_sec Stop.UTC_sec H2O2.pptv CH3OOH.pptv
Start Stop H2O2 CH3OOH
UTC UTC ppt ppt
20070901193224 20070901193254 2433 1492
20070901193354 20070901193424 2515 1454
20070901193524 20070901193554 2562 1494
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5.0 DATA REMARKS:

None

6.0 REFERENCES:

- Lee, M., D. O'Sullivan, K. B. Noone, and B. G. Heikes, HPLC method for the determination of H2O2, C1 and C2 hydroperoxides in the atmosphere, *J. Atmos. Oceanic Tech.*, 12, 1060-1070, 1995.
- O'Sullivan, D.W., M. Lee, B.C. Noone and B.G. Heikes, Henry's law constant determinations for hydrogen peroxide, methyl hydroperoxide, hydroxymethyl hydroperoxide, ethyl hydroperoxide and peroxyacetic acid, *J. l of Phys. Chem.*, **100**, 3241–3247, 1996.