TITLE: Hydrogen Peroxide by Acridinium Ester Chemiluminescence

AUTHOR(S):

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1.0 DATA SET OVERVIEW:

Hydrogen peroxide (H_2O_2) mixing ratios for the Pacific Atmospheric Sulfur Experiment (PASE). Collected on the NCAR C-130 in Aug-Sept, 2007 from Kiribati (Christmas) Island, Republic of Kiribati determined by acridinium ester chemiluminescence.

2.0 INSTRUMENT DESCRIPTION:

The chemiluminescence determination of H_2O_2 is based the method of *Cooper et al.* (2000) for natual water analysis of H_2O_2 that is free from interferences from most soluble species. The method involves the direct oxidation of 10-methyl-9-(p-formylphenyl)-acridinium carboxylate trifluoromethanesulfonate (AE) by H_2O_2 producing chemiluminescence. *Melamed et al. (2000)* proposed a mechanism for the reaction involving attack of HO_2^- on the acridine moiety under alkaline conditions. The resulting adduct self-reacts to form an unstable six membered ring, which rapidly decomposes into an electronically excited intermediate, N-methylacridone. N-methylacridone relaxes via chemiluminescence with an emission near 470 nm. The chemiluminescence reaction is specific for H_2O_2, since organic peroxides to not form HO_2^- in solution (*King et al. 2007*).

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 thermisters.

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. H_2O_2 is quantitatively collected by partitioning into an aqueous phase. The aqueous collection solution is analyzed for hydrogen peroxide by continuous flow analysis acridinium ester chemiluminescence.

The chemiluminescence system is calibrated during preflight with aqueous hydrogen peroxide solutions. Zero air is introduced to the collection system to determine chemiluminescence blanks during flight, in flight aqueous standards are used to check the span on the system.

The detection limit for H_2O_2 is 40 ppt (parts per trillion mole mixing ratio), based on three times the standard deviation of the chemiluminescence blanks and in flight zeros. Estimated accuracy for H_2O_2 is ±(40 ppt + 0.25*value).

4.0 DATA FORMAT:

Data for each flight is supplied in its own file. Filenames are structured as (for example):
USNA-H2O2_20070804_R1_L1_V1_FF03.txt

USNAdesignator_ date of flight measured parameter _ R1_L1 _ RAFflightdesignator. 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

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PI/DATA CONTACT = O'Sullivan, Daniel (US Naval Acad.), Heikes, Brian (Univ. of
Rhode Island)43 1001
DATA COVERAGE = START: 20070804200203 STOP: 20070805015533 UTC
PLATFORM/SITE = C-130
INSTRUMENT = CHEMILUMINESCENCE H2O2
LOCATION = mobile
DATA VERSION = 1.0 02/14/2008
REMARKS = Pacific Atmospheric Sulfur Experiment (PASE)
REMARKS = Sample start time yyyymmddhhmmss, UTC
REMARKS = Sample stop time yyyymmddhhmmss, UTC
REMARKS = H2O2 in parts per trillion by mole, ppt
REMARKS = missing data -9999
REMARKS = level of detection -8888, nominally 30 ppt
REMARKS = upper limit of detection -7777, nominaly 6000 ppt
REMARKS = NASA header information follows
REMARKS = 1 1
REMARKS = 2007 08 04 2008 02 14
REMARKS = 0
REMARKS = Start_UTC, sec
REMARKS = 3
REMARKS = 1 1 1
REMARKS = -9999 -9999 -9999
REMARKS = Stop_UTC, sec
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REMARKS = H2O2, ppt
REMARKS = 1
REMARKS = Julian Day 204
REMARKS = 25
REMARKS = Filename: C:\dwo\research\PASE\DATA\Postmission\revR1\USNA-
H2O2_20070804_R1_L1_V1_FF03.txt
REMARKS = Modified NASA-GTE NOAA-AL Data File Format -> ICARTT Format
(http:/www-air.larc.nasa.gov)
REMARKS = PI_CONTACT_INFO: Daniel O'Sullivan, USNA, Chemistry Department, 572
Holloway Rd, Annapolis, MD 21402, USA
REMARKS = email: osulliva@usna.edu
REMARKS = voice: 410.293.6636
REMARKS = fax: 410.293.2218
REMARKS = PLATFORM: NCAR C-130
REMARKS = LOCATION: Other PASE data can be found at anonymous ftp web site
(http://catalog.eol.ucar.edu/pase/)
REMARKS = ASSOCIATED_DATA: other observations made in PASE will be made
publically available at: (http://catalog.eol.ucar.edu/pase/)
REMARKS = INSTRUMENT_INFO: H2O2 by aqueous collection followed by
Chemiluminescence detection with acidinium ester.(unpublished method)
REMARKS = DATA_INFO:
REMARKS = 1. sample collection is contiguous, results are reported as a 10 sec
average.
REMARKS = 2. start time is in seconds past mid-night on the day of takeoff,
and will exceed 86400 if midnight UTC is crossed during flight
REMARKS = UNCERTAINTY: +/-(30 ppt + 0.20*value)
REMARKS = ULOD_FLAG: -7777
REMARKS = ULOD_VALUE: N/A; N/A; 6000
REMARKS = LLOD_FLAG: -8888
REMARKS = LLOD_VALUE: N/A; N/A; 30
REMARKS = DM_CONTACT_INFO: N/A
REMARKS = PROJECT_INFO: PASE; 7/15/06 to 9/15/07 field phase, Boulder CO,
Monterey, CA, Honolulu, HI, Christmas Island,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 for February 2008 Data workshop;
REMARKS = Start_UTC_sec Stop_UTC_sec H2O2_pptv
20070804200203 20070804200214 -9999
20070804200214 20070804200224 -9999
20070804200224 20070804200233 -9999
.
.
.
```

5.0 DATA REMARKS:

None

6.0 REFERENCES:

Cooper, W.J., Moegling, J.K., Kieber, R.J., and Kiddle, J.J., A chemiluminescence method for the analysis of H_2O_2 in natural waters., *Mar. Chem*., 70, 191-200, 2000.

King, D. W., Cooper, W. J., Rusak, S. A., Peake, B. M., Kiddle, J. J., O'Sullivan, D. W., Melamed, M. L., Morgan, C. R., and Theberge, S. M., (2007) Flow injection analysis of H_2O_2

in natural waters using acridiium ester chemiluminescence: Method development and optimization using a kinetic model, Analytical Chemistry, 25-Apr, DOI:10.1021/ac062228w.

Melamed, M. L., Bizier, N. P., Lovitz, S. B., Theberge, S. M., and King, D.W., Investigation of the chemiluminescence reaction dynamics of H_2O_2 and acridinium esters for optimization of FIA for natural H_2O_2 samples, 219th ACS National Meeting, American Chemical Society, 2000.