TITLE: Fast-O3 Chemiluminescence Instrument (FO3_CL)

AUTHORS:
Pollack, I.B.; Campos, T.L.; Weinheimer, A.J.
National Center for Atmospheric Research
PI Contact Info:
1) ipollack@ucar.edu, 303-487-1413, NCAR, 3450 Mitchell Lane, Boulder, CO 80301
2) campos@ucar.edu, 303-497-1048, NCAR, 10802 Airport Court, Broomfield, CO 80021
3) wein@ucar.edu, 303-497-1444, NCAR, 3450 Mitchell Lane, Boulder, CO 80301

1.0 DATA SET OVERVIEW

An ozone chemiluminescence instrument was flown onboard the NSF/NCAR C130 aircraft during the PASE field project in Christmas Island during August 2007. Data from 3/3 test flights, 13/14 research flights, and 2/6 ferry flights (HNL – CXI) were recorded from 20070723 to 20070908 (in UTC yyyymmdd format).

Summary of fast-O3 instrument capability:

Time Response	5 Hz (Dt = 0.2 sec)
Sensitivity	~2000 cps/ppbv, ~400 cpDt/ppbv
Instrument Uncertainty	± (2 ppbv + 5% of the ambient measured mixing ratio)
Background	~100 cps, ~20 cpDt
Signal/Noise* (S/N) at 20 ppbv O_3	2000 at 1 Hz, 900 at 5 Hz
Signal/Noise* (S/N) at 100 ppbv O_3	10000 at 1 Hz, 4500 at 5 Hz
Detection Limit†	0.01 ppbv at 1 Hz, 0.025 at 5 Hz

*S/N = (signal-background)/2(background)$^{1/2}$
†Detection limit = 2(Background)$^{1/2}$/sensitivity

2.0 INSTRUMENT DESCRIPTION

The operating principle of the fast-O_3 instrument is the measurement of chemiluminescence from the reaction of nitric oxide (NO) with ambient O_3 using a dry-ice cooled red-sensitive photomultiplier employing photon counting electronics. This O_3 instrument has participated in numerous field campaigns (as a 1 Hz instrument) prior to the PASE project and is described in detail in previous publications [Ridley et al., 1992].

The reagent NO (grade >99%) is supplied from a 500 psig lecture bottle purchased from Scott Specialty Gases. Since NO is a toxic gas, the small high pressure cylinder, its regulator, and several safety features are contained inside a specially designed

pressure safe vessel that is vented overboard the aircraft. This reagent NO gas supply is sufficient for 5 flights plus a couple of ground-based calibrations.

Ambient air was sampled through a forward-facing inlet protruding roughly 10" from the skin of the aircraft so that ambient air can be confidently sampled from outside the aircraft boundary layer. This inlet was made up of ¼" o.d. PFA tubing and supported within a stainless steel tubing gooseneck. A bypass flow of ~ 4 slm at 200 torr was maintained through the inlet using a MKS 640 pressure control valve with a 200 torr downstream set point, ¼" o.d. PFA tubing, and two Vacuubrand MD1 diaphragm pumps. A pick-off line made of a 2" long segment of 1/8" o.d. PFA tubing allows an ambient air sample flow (flow controlled to 500 ± 10 sccm using a temperature controlled metering valve) to the instrument. The flow is monitored using a 0-2 slm range Sierra brand mass flow meter. The reagent NO gas is introduced to the reaction vessel in near-excess flow of ~ 4 sccm using a Tylan brand mass flow controller (0-10 sccm range). Gas flows as well as the reaction vessel temperature (35 ± 0.1˚C) and pressure (10 ± 0.05 torr) are all controlled at constant conditions resulting in maximum stability of the detected signal and instrument sensitivity.

The instrument sensitivity (~2000 cps/ppbv) is determined from calibrations performed on the ground several times during the project using a commercial, UV based, O_3 generator and calibrator unit (TECO model 49PS) operated with high-quality ultra-pure air. According to the manufacturer, the UV-based O3 calibrator unit (TECO, model 49PS) has the following specifications:

Photometer:
- Response time = 20 seconds
- Lag time = 10 seconds
- Precision = 2 ppb
- Linearity = ± 1 ppb
- noise = ± 1 ppb
- Minimum detection limit = ± 2 ppb

Ozonator:
- Stability = ±4 ppb or ± 1%, whichever is greater

The frequency response of the instrument has been determined as 5 Hz from laboratory and airborne testing prior to the PASE project. (Pollack *et al.*, Manuscript in preparation.) At 5 Hz, the instrument sensitivity is ~400 cpDt/ppbv.

3.0 DATA COLLECTION AND PROCESSING

The "raw" O_3 mixing ratio is determined from fitting the PMT signal minus the "background" count rate to a linear expression representative of the instrument sensitivity. A linear calibration curve is generated in intervals of 10 ppbv over the range of 0 to 80 ppbv. The calibrator is allowed to warm up for 2 hours before a calibration measurement is made. The calibrator is also run at each interval for 5

minutes or more to let the internal ozonator stabilize before a calibration measurement is made. The last two minutes of each interval are averaged for both the TECO calibration unit signal and the corresponding counts from the fast-O3 instrument PMT to produce a single data point in the calibration curve. Prior to determining a linear regression to this curve, the average values recorded from the TECO calibrator are corrected to our lab UV-based O3 analyzer as well as the NOAA and NIST standards.

The TECO 49PS calibrator has been recently checked over the project calibration range (0-100 ppbv) against our "lab" TECO model 49 analyzer. Our calibrator reported a lower mixing ratio than our lab analyzer by ~1.3%.

$$\text{Model 49 lab analyzer} = (1.01352 \pm 0.00375 * \text{49PS calibrator}) + 0.25466 \pm 0.118$$

Our TECO analyzer has been compared to the ESRL/GMD Network Standard (Provided by Sam Oltmans of the NOAA ESRL Climate Monitoring & Diagnostics Laboratory) over its full operation range (0-1000 ppbv) in September 2006. A single comparison run over this range shows that the analyzer yields a lower mixing ratio than the ESRL/GMD Network Standard by ~0.5%.

$$\text{ESRL/GMD Network Standard} = (1.0054 \pm 0.00104 * \text{Model 49 lab analyzer}) + 0.062284 \pm 0.236$$

The calibration of the ESRL/GMD Network Standard was compared to the NIST photometric standard in 2004. The ESRL/GMD Network Standard reads about ~1% lower than the NIST standard. The following average linear regression equation was obtained for the GMD Network Standard from ten comparison runs over the 0-1000 ppbv range:

$$\text{NIST Standard} = (1.011 * \text{ESRL/GMD Network Standard}) + 0.04$$

After the TECO 49PS calibrator measurements were adjusted to reflect the NIST standard, a linear fit of the final calibration curve is generated. The fit is weighted to the 1s standard deviation from the average of 2 minutes of counts from the PMT per interval, and the y-intercept is forced to zero to reflect the true instrument zero which is acquired by subtracting a constant value of background counts from the PMT signal at each interval.

Calibrations performed on the ground every 5-7 days throughout the course of the project provided fast-O3 sensitivities stable to within 5% (corresponding to the 1 σ standard deviation of sensitivity measurements). From the stability of fast-O3 sensitivities from successive ground calibrations, the overall uncertainty of the fast-O_3 instrument is ± 5% of the ambient measured mixing ratio. The background

measurement provides a true zero of the fast-O3 instrument therefore the precision of the TECO calibrator is not relevant.

The background count rate from the detector is very close to the dark count rate of the PMT, which is sensitive to altitude due to secondary cosmic ray events. [Ridley (1992)] However, the background count rate did not exceed 100 cps, even at the highest altitude of ~22 kft. At 5 Hz, the instrument background is ~20 cpDt/ppbv. This background level is insignificant (less than 0.5%) of the nominal signal count rate in ambient air (8,000 cpDt at a typical ambient ozone level of 20 ppbv during PASE) given the high level of instrument sensitivity (400 cpDt). Thus only periodic measurements (once every 30 minutes) of the background count rate need be made. Background levels are determined throughout the flight by computer-controlled switching of a solenoid valve to flow high quality ultra-pure nitrogen to the instrument.

The detector sensitivity can be affected by changes in ambient water vapor, as described by Ridley (1992, 1990). The "Raw" O_3 data from each flight was multiplied by $(1 + 4.3 \times 10^{-3}[H_2O])$ where $[H_2O]$ is the mixing ratio of water vapor in the reaction vessel in parts per thousand by volume to correct for the effect of water vapor. Water vapor mixing ratio (MRLA) obtained from the fast humidity sensor has been used for the $[H_2O]$ term of this equation. The correction will be insignificant for normal water vapor mixing ratios anticipated for the middle to upper troposphere and lower stratosphere. However, the correction can be significant in continental boundary layer or warm marine areas, as is the case for PASE research flights.

All fast-O_3 data is internally recorded by our own data system at a 200 Hz sampling rate. (A 1 Hz averaged output is provided to the RAF data system for in-flight use and flight planning during the project. The real time FO3_CL output to the RAF data system is preliminary data only.) The 200 Hz data is averaged down to 25 Hz during post processing analysis. The final fast-O_3 data is provided as 25 Hz to facilitate merging with the aircraft dataset released by RAF. **Note that the true frequency response of the instrument has been determined at 5 Hz from laboratory and airborne testing prior to the PASE project.**

4.0 DATA FORMAT

The fast-O_3 data has been merged with the 25 Hz RAF/C130 data set. The fast-O_3 mixing ratio is reported in units of ppbv.

5.0 DATA REMARKS

Eliminated Data Points:

The O_3 instrument recorded data for the full duration of 13 out of 14 research flights and 2 out of 6 ferry flights. The time vector is continuous with start and stop times

(in UT sec) corresponding to those in the RAF/C130 aircraft data set. Bad data points are flagged as -32767 according to the following criteria.

1) The reagent NO gas delivery system was kept closed during take-off and landing for safety concerns. Thus, a short section of fast-O_3 data has been eliminated from the very beginning and end of each flight corresponding to times when there was no reagent NO gas flow.
2) Short sections of data points corresponding to times when the instrument was recording the "background" count rate are also eliminated from the final data, although this information has been incorporated into the final calibration.
3) In some instances, values greater than ± 4% of the flow setting were recorded by the mass flow meter on the fast-O3 instrument pick-off line. This was a common occurrence during two specific events: 1) when the CO instrument (which shared an inlet with fast-O3) had initiated a calibration sequence and 2) when sampling at high altitudes where ambient pressure is lower than the MKS 640 pressure control valve set point of 200 torr. Since sensitivity is dependent on inlet flow, values recorded by the mass flow meter outside the 500 ± 4% (or 20 sccm) range were eliminated.
4) Short segments of fast O3 data from some flights also needed to be eliminated when there was no mixing ratio for water vapor available for the water correction described above. Bad data points in MRLA are flagged as -32767 in the final RAF dataset.

Summary of Eliminated Data Points:

Local Date	Data Type	Remarks
8/4/07	FF03 (HNL to CXI)	
8/8/07	RF01	
8/11/07	RF02	
8/13/07	RF03	
8/16/07	RF04	MKS 640 pressure control valve lost some control at the extreme ends of altitude range. Segments of data eliminated where MFM reports flow outside 500 ± 20 sccm. Segments also eliminated due to lack of MRLA data for water correction.
8/19/07	RF05	Variability in MKS 640 pressure control and MFM due to CO instrument calibration sequence early in flight. Data eliminated where MFM reports flow outside 500 ± 20 sccm.
8/21/07	RF06	
8/24/07	RF07	
8/26/07	RF08	
8/28/07	RF09	
8/30/07	RF10	No data recorded for entire flight due to data system problem.
9/2/07	RF11	
9/3/07	RF12	Gap in O_3 data from 10:23-10:34 UTC due to data system reboot.
9/5/07	RF13	
9/7/07	RF14	
9/9/07	FF04 (CXI to HNL)	Ambient pressure went below MKS 640 pressure control valve set point during latter portion of flight while at high cruising altitude. Data eliminated for latter 2/3 of flight where MFM reports flow outside 500 ± 20 sccm.

Unexplained step changes:

Over the 120 research flight hours, there have been roughly 15 random instances where unexplained step changes were observed in the fast ozone signal. The magnitudes of these step changes are small and in all cases, less than 1.7 ppbv. In 10 out of these 15 cases, there is no direct correlation with changes in the TECO O3 mixing ratio, step changes in fast sensors such as MRLA and ATX, or other aircraft and tracer measurements (including Theta, WIC, CO, CONCN, OH, HO_2, HO_2RO_2, CH_3OOH, DMS, H_2O_2, H_2SO_4, and SO_2).

During each flight a set of ~20 housekeeping signals are simultaneously recorded at a 1 sec rate by the fast-O3 instrument's dedicated data system to monitor pressures, flows, temperatures, power supply voltages, etc. A change in one of these signals must occur for there to be a change in the instrument's sensitivity, as outlined in the section above regarding bad data points and data eliminations. No evidence has been found in any of the housekeeping signals to suggest a reason for these step changes to have occurred. In addition, successive calibrations performed on the ground every 5-7 days between research flights do not show any observable drift in instrument sensitivity over the course of the project. It is, however, possible to imagine these offsets as arising from an electronic or grounding issue while onboard the aircraft in flight; a phenomenon of which may not be reflected in the recorded housekeeping signals.

Features considered to be non-real, electronic-based offsets are characterized according to the following criteria: 1) mixing ratio change on a sub 0.2 second time scale corresponding to rise times faster than the time resolution of the instrument and 2) no direct correlation with simultaneous changes in the other chemistry or aircraft measurements. On the contrary, the other 5 step changes are considered to be actual atmospheric features having rise times $\geq$ 0.2 seconds and display some correlation or anti-correlation to features in SO_2, MRLA, and theta.

None of the 15 unexplained step changes were eliminated from the data set since there was no obvious criterion for how they should be removed. Additionally, there was little substantiation to eliminate these data points even for cases believed to be associated with an electronic offset, since the magnitude of the step change is on the same order of magnitude as the overall instrument uncertainty of $\pm$ 5% of the ambient measured mixing ratio.

Summary of unexplained step changes:

Local Date	Flight #	Time (UTC)	Magnitude (ppbv)	Rise time (sec)	Remarks
8/8/07	RF01	None			
8/11/07	RF02	None			

8/13/07	RF03	19:14:36 20:02:04 20:25:08	1.7 1 1.7	0.12 0.50 0.08	Possible electronic offset Likely real atmospheric feature Possible electronic offset
8/16/07	RF04	None			
8/19/07	RF05	19:00:43	1.7	0.23	Possible electronic offset
8/21/07	RF06	17:39:21	0.7	0.50	Likely real atmospheric feature
8/24/07	RF07	23:43:47 00:32:47 01:24:51	1.2 0.7 1.4	0.20 0.50 0.12	Likely real atmospheric feature Likely real atmospheric feature Possible electronic offset
8/26/07	RF08	None			
8/28/07	RF09	None			
8/30/07	RF10	No fast-O3 data this flight.			
9/2/07	RF11	01:55:58	1.5	0.12	Possible electronic offset
9/3/07	RF12	18:57:41 21:08:35 22:02:15	1.7 1.2 1.4	0.04 0.08 0.04	Possible electronic offset Possible electronic offset Possible electronic offset
9/5/07	RF13	16:16:04	1.3	0.20	Undetermined
9/7/07	RF14	22:27:12 00:51:28	1 1	0.04 0.60	Possible electronic offset Likely real atmospheric feature

Comments regarding fast-O3 measurements with respect to the onboard TECO UV-based O3 analyzer:

This section is to clarify some of the confusion with respect to the ozone measurements provided by the CARI group – and to make it clear that the fast ozone data is at least as reliable as promised – in the case of PASE actually better than promised.

A 2-channel, UV absorbance based O3 analyzer (TECO, model 49C, $l_{ex,\ photometer}$ = 254 nm) was flown alongside the fast-O3 instrument during the PASE project. The TECO O3 analyzer utilized a dedicated, rear facing inlet made of ¼" PFA tubing roughly 10 feet in length. The TECO was operated in a non-pressure or temperature corrected mode to obtain only the raw, uncorrected TECO O3 signal. The raw TECO signal (TEO3) and pressure output signal (TEO3P) were recorded at 1 Hz by the RAF data system. A pressure correction was subsequently incorporated with the raw O3 TECO signal post-project to provide the corrected TECO O3 data (TEO3C). A constant cell temperature correction was also applied during post-processing. According to the manufacturer, the 49C O3 analyzer has the following specifications.

TECO 49C O3 Analyzer (Photometer):
- Response time = 20 seconds
- Lag time = 10 seconds
- Precision = 1 ppb
- Linearity = ± 1% full scale (where FS = 0-1000 ppbv)

The overall instrument uncertainty for the onboard TECO analyzer data is ± 3 ppbv. Lag time for flight data is 15-20 seconds when considering combined contributions from the inlet and the instrument.

The TECO is indeed a Beer's Law instrument, but it has known interferences with aerosols and toluene, which are captured by the internal scrubber yielding a false reference background measurement compared to air sample. It is also known that strong gradients in humidity can sometimes affect water buildup on window micro-crevices. (Kleindienst *et. al.*, 1993.) In 2000, the onboard TECO 49C analyzer was modified to eliminate this known interference by replacing the original optical cell windows from the manufacturer with 10l flatness sapphire windows. However, interferences from the scrubber remain. Additionally, it was noted post-project that the internal pressure sensor within the 49C analyzer was not comparing well with other aircraft pressure sensors throughout the duration of the project. During post-processing, the pressure correction for the TECO 49C analyzer data was therefore supplied by the aircraft's reference corrected ambient pressure measurement (PSXC) less 30 hPa. The 30 hPa pressure offset arises from a known pressure drop for a rear facing inlet as well as the pressure drop across the 10 foot length of ¼" PFA tubing. The quantitative relationship between fuselage static pressure and TECO 49C analyzer cell pressure has been consistently documented over several field projects.

The fast-ozone data are NOT normalized to the TECO 49C analyzer data, since they are two independent O3 sensing instruments. However, the fast-O3 and the TECO 49C analyzer onboard were both compared and corrected to the same NOAA and NIST standards. The onboard TECO 49C analyzer was compared pre- and post-project to the same TECO 49PS calibrator that was used to do ground calibrations for the fast-O3 instrument. This comparison resulted in the following linear correction for the onboard 49C analyzer to the 49PS calibrator:

$$\text{TECO 49PS calibrator} = (1.0047 \pm 0.00875 * \text{TECO 49C analyzer onboard}) - 0.48879 \pm 0.494$$

As described above in Section 3, the TECO 49PS calibrator has been checked over the project calibration range (0-100 ppbv) against our TECO model 49 lab analyzer which in turn was recently compared to the NOAA ESRL/GMD Network Standard and the NIST Standard. These corrections were applied to the final data from the onboard TECO 49C analyzer.

Within the stated uncertainties, all final fast-ozone data are statistically in full agreement with the onboard TECO analyzer data. Extensive intercomparisons from other projects of the fast-ozone data between NCAR and NOAA's UV-based absorption instrument, as well as between NCAR and NASA, and NOAA and NASA, yield an uncertainty of ± 3 ppbv or 3% of the ambient measured mixing ratio (whichever is greater). This uncertainty is a common and well accepted error bar for ozone measurements in the atmospheric research community. This readme file clearly states the current uncertainties of the fast-O3 measurements during the PASE project as ± 5% of the ambient measured mixing ratio (corresponding to a 1 ppbv error at typical PASE mixing ratios of 20 ppbv) which are based on regular

calibrations with our field calibrator and comparisons of this calibrator to the NOAA and NIST standards. However, a more realistic uncertainty reflecting the magnitude of the unexplained step changes observed should be ± (2 ppbv + 5% of the ambient measured mixing ratio).

6.0 REFERENCES

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