Evaluation of the Frequency Response of a Chemiluminescence Ozone Sensor Developed for the NSF/NCAR Gulfstream-V Airborne Platform

Ilana B. Pollack*, Andrew J. Weinheimer†, Teresa L. Campos, Wengang Zhang, David J. Knapp, Denise M. Montzka, Frank M. Flocke, and Marcel Foecki

National Center for Atmospheric Research, Boulder, CO, USA

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†Corresponding authors address:

National Center for Atmospheric Research, Atmospheric Chemistry Division, 3540 Mitchell Lane, Boulder, CO, 80301. E-mail: wein@ucar.edu

*Present address:

NOAA Chemical Science Division via the Cooperative Institute for Research in Environmental Studies, University of Colorado, Boulder, CO. E-mail: ipollack@ucar.edu

ABSTRACT: A fast-response ozone instrument based on chemiluminescence detection (CLD) was developed as part of the HIAPER Aircraft Instrumentation Solicitation (HAIS) for use onboard NSF/NCAR research aircraft. A detailed description of the CLD instrument design and basic operating principle are presented along with an extensive account of laboratory and airborne tests performed to characterize the instrument's frequency response. The resulting frequency response measurements from laboratory tests are reported and discussed in terms of three different analysis methods. The best analysis method for the laboratory tests yields an 8 Hz response for the basic instrument. A reduction in frequency response to 5 Hz was observed from the laboratory data when the aircraft inlet and downstream pressure control components were placed in the flow path just upstream of the basic instrument. A frequency response between 5 and 7 Hz was observed when the pressure upstream of the aircraft inlet was varied over the ambient pressure range expected during a research flight (600 to 200 Torr, respectively). The impact of instrument design choices on time response will also be discussed. Airborne measurements of the instrument frequency response were obtained during test flight opportunities onboard the NSF/NCAR C-130. Analysis of fast step-like changes in the flight data, ozone power spectra, and co-spectra of ozone with a fast humidity sensor acquired while making flight measurements in the boundary layer confirms that the instrument has at least a xx Hz frequency response. Laboratory results indicate the present design is likely capable of detecting even faster transients in the atmospheric ozone field, even though atmospheric events on the time scale of the laboratory measurements were not observed during these specific flight opportunities.

KEYWORDS: Time Response, Frequency Response, Ozone, Chemiluminescence, HIAPER

1. Introduction

This publication highlights the development and evaluation of a facility airborne fast-response ozone instrument for use onboard the new NSF/NCAR Gulfstream V High-performance Instrumented Airborne Platform for Environmental Research (HIAPER) research aircraft. HIAPER, with a roughly 15 km operational ceiling and a nominal air speed of 200 m/s, provides a new tool for characterization of a large and in some cases an under sampled region of the upper troposphere and lower stratosphere (UT/LS). The new instrument is designed to meet the needs of the atmospheric science community to investigate two-way stratosphere/troposphere exchange, gravity wave or other tropopause perturbations, and turbulence over a range of smaller scales perhaps induced by deep convection{Lane, 2003 #46; Pavelin, 2002 #47}. High sensitivity and fast-response ozone measurements are required to elucidate these physical, dynamical exchange, and chemical processes common to the UT/LS region.

Ozone has been classified as a standard measurement for understanding gas phase chemistry, clouds, and climate; and thus will likely be required on all such HIAPER programs. The new instrument will be based on a chemiluminescence reaction of ozone in an ambient air sample with reagent nitric oxide, and have the ability to provide high sensitivity and precision while operating at a minimum time response of 5 Hz corresponding to horizontal scales of about 40 m. Although slightly larger and more complex than UV absorption instruments, the chemiluminescence ozone instrument will provide users with a unique tool for studies requiring high sensitivity and precision {Proffitt, 1983 #42} as well as high rate measurements {Pearson, 1990 #9; Pearson, 1980 #19; Faloona, 2005 #27}.

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The development of CL instruments for high sensitivity and high rate measurements is not a new concept. The majority of past laboratory experiments were aimed at characterizing an instrument's time response to a simple step change in concentration. As Pearson {Pearson, 1990 #9} comments, "there is no universally employed definition of the bandwidth or response time for this class of instrument. The transient response to a step-function change in concentration is probably the most commonly reported measure of response time."

Several methods for creating a step change in concentration have been explored in the laboratory. In 1990, Pearson {Pearson, 1990 #9} reported the frequency response of an O_3 CLD instrument similar to the one described in this work. The major differences between Pearson's instrument and the one presented here are reaction vessel shape and internal volume, percentage mixture of reagent NO gas, air sample and reagent NO flow rates, reaction vessel pressure, and the collection mode in which the photomultiplier (PMT) is operated. Pearson used a Teflon three-way switching valve, square-wave function generator, and a transistor switch to produce nearly square-waves of O_3 in zero air. The frequency response of his O_3 CLD instrument was measured by activating the valve up to 30 Hz using the wave function generator and observing attenuation of the O_3 signal to -3 dB. The -3 dB cutoff frequency was observed near 12 Hz consistent with a 4^{th} order Butterworth electronic filter inherent to the detection system.

In 1992, Gusten et al. {Gusten, 1992 #48} reported laboratory tests of an O_3 CLD instrument based upon reaction of ozone with an organic dye adsorbed on a dry silica gel surface. A blue-sensitive PMT was used to monitor the resultant chemiluminescence in the 400 to 500 nm range. Again, a Teflon 3-way switching solenoid valve was employed to produce square pulses of ozone in a constant background. A large air sample flow rate (> 100 l min^{-1})

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similar to that used by Pearson, but significantly larger than that reported in this work was required to produce the best time response of the detector. A 90% response time of $\leq 60 \pm 10$ ms was reported by comparing ideal square waves with waveforms that were generated in the laboratory and recorded with an oscilloscope.

In 1999, Civerolo {Civerolo, 1999 #22} used a step change in NO gas concentration to measure the response time of a nitric oxide CLD instrument, which operates based on the same O_3 + NO chemistry reported here although under reverse titration conditions. Civerolo produced a periodic input pulse using two different methods: 1) a series of three-way solenoid valves and timed contacts were used to switch between gas flows with 0 and 5 ppbv of NO while maintaining constant pressures and flows with multiple vent ports and flow controllers, and 2) by chopping the flow of a 3 ppmv mixture of NO gas through a 0.4 cm separation in a length of Teflon tubing as the gas sample was being delivered to the detector. The time response for Civerolo's NO detector was defined in terms of a 1/e time, which was consistently characterized as 0.3 sec using either method.

Frequency response of O_3 CLD instruments have also been measured in the field via tower or airborne measurements. Field experiments performed by Gusten et al. {Gusten, 1992 #48} involved mounting the ozone sensor along with a three-axis sonic anemometer, which measured wind and temperature on a 10 Hz scale, on an 8 m high tower. A fast Fourier transform was applied to ozone field data sampled at 200 Hz to determine how much of the variance in a time series of ozone concentration is associated with a particular frequency. Gusten et al. report that the resulting energy spectrum, which truncates at the expected Nyquist frequency of 100 Hz, yields a -5/3 slope in the inertial subrange between 1 and about 20 Hz.

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In contrast to tower measurements, Pearson and Steadman {Pearson, 1980 #19} performed aircraft measurements using their O_3 CLD instrument to detect sharp decreases in ozone mixing ratio upon sampling plumes rich in NO from internal combustion sources. A single fall time of 50 ms was observed and is correlated with the sharpest observed ozone decrease upon plume entry.

In 2005 Faloona {Faloona, 2005 #27} reported cospectra obtained in aircraft measurements using an O_3 CLD instrument similar to that used by Pearson and Steadman.

This publication highlights the design, development, and evaluation of the frequency response of our new fast-ozone CLD instrument. A detailed explanation of our instrument's basic operating principle and layout are presented along with a description of the laboratory test method used for evaluation of the fast-ozone instrument's time response. The resulting frequency response measurements from laboratory tests are reported followed by a brief discussion about the differences in the observed frequency responses with respect to 1) the three different analysis methods, 2) changes in instrument operating conditions, 3) implementation of the aircraft inlet and related components, and 4) the ambient pressure changes upstream of the aircraft inlet expected during flight.

Despite the new instrument being developed for use onboard HIAPER, flight test opportunities were only available onboard the NSF/NCAR C-130 aircraft during the time between instrument completion and this publication. Airborne tests of the frequency response of the new fast-O_3 instrument from C-130 test flights are also reported and discussed here.

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2. Instrument Description

The basic operating principle of the fast-O_3 instrument reported here is the measurement of chemiluminescence detection (CLD) from the reaction of reagent nitric oxide (NO) with O_3 in an ambient air sample using a dry-ice cooled red-sensitive PMT employing photon counting electronics. The O_3 CLD technique has its roots in the work of Eastman and Stedman {Eastman, 1977 #39} and Pearson and Stedman {Pearson, 1980 #19} for O_3 flux measurements at the surface or about stratus clouds over the Pacific and in our long experience with NO-O_3 CLD instruments for measurements of both reactive nitrogen constituents and ozone {Jaegle, 1998 #43; Ridley, 1994 #41; Weinheimer, 1998 #44}. Ridley et al. {Ridley, 1992 #28} describes in detail the chemistry and basic design inherent to the O_3 CLD instrument.

a. Instrument layout

Figure 1 depicts a flow diagram of the fast-O_3 CLD instrument. According to the figure, ambient air is passed through the reaction vessel at 500 sccm by "picking off" a pumped bypass flow. Ambient air for the bypass flow is sampled through a rear-facing inlet positioned outside the aircraft boundary layer. The aircraft inlet consists of ¼" PFA tubing inserted through a bored-through fitting into a stainless steel, gooseneck-shaped, support tube. PFA tubing and fittings are used whenever possible to minimize loss of O_3 due to contact with metal surfaces. A pressure control valve (MKS 640A, #5 orifice) is placed along the bypass line as close to the inlet as possible (typically 2 to 3 feet from the tip of the inlet). The control valve regulates the downstream pressure of the bypass flow to 200 Torr. A downstream pressure of 200 Torr was chosen for two reasons: 1) to reduce the gas residence time in the ¼" tubing, and 2) it is below

the minimum pressure given the altitude range for the C-130 where our flight test opportunities took place. The bypass flow system is driven by two small diaphragm pumps (Vaccubrand, MD1) placed in parallel at the exit of the bypass line a few feet downstream of the pickoff to the reaction vessel. With both diaphragm pumps running, the bypass flow was measured to be a little over 3 slpm. A sample of ambient air is directed from the bypass flow to the reaction vessel via a short (6") segment of 1/8" PFA tubing. The reaction vessel pressure and flow are maintained using a throttling pressure control valve (MKS, model 153D), a stainless steel metering valve (Hoke, 1300 Series), and a small scroll pump (Synergy Vacuum, ISP-90). The metering valve acts as an orifice restricting sample flow to the reaction vessel to 500 sccm. A mass flow meter (Sierra, model 830D) is placed in line downstream of the metering valve and upstream of the reaction vessel to monitor sample flows to the reaction vessel. The metering valve, mass flow meter and reaction vessel are individually controlled at a constant temperature of 35ºC. A 2 foot long segment of ¼" PFA tubing then delivers the air sample to the reaction vessel. The PFA tubing is covered in aluminum foil to block ambient light from entering the reaction vessel and impinging on the PMT lens which can create an overwhelming number of background counts.

The reaction vessel of the fast-O_3 instrument is a duplicate of the reaction vessel shown in Figure 1 of Ridley et al. {Ridley, 1992 #28} with two exceptions: 1) 1/4" plumbing for the inlet connection rather than 1/8", and 2) a removable inlet flange that bolts with an o-ring seal to the body of the reaction vessel and includes the point of injection for the reagent NO gas. The former was implemented to allow a larger possible range of air sample flows to the reaction vessel and to keep a consistent inner diameter of PFA tubing all the way from the inlet to the

reaction vessel. The latter was implemented to aid in future studies regarding optimal introduction of NO gas into the reaction vessel since the inlet flange can be easily replaced by another flange with a different configuration for reagent gas introduction. The figure shows a schematic of the heart of the detector, which consists of a highly polished, conical-shaped, gold-coated, stainless steel reaction vessel of height 2.5 cm and base of 5 cm (volume 17 cm^3). The volume is coupled to a dry-ice cooled red-sensitive PMT (Hammamatsu, R1333) of 5 cm diameter through a thermopane window glued to a red cutoff filter. The thermopane window acts as a thermal buffer between the heated reaction vessel and the dry-ice cooled PMT to minimize water vapor condensation on the red filter and the lens of the PMT. The red filter transmits wavelengths greater than 610 nm, which is near the onset of the NO-O_3 chemiluminescence (600 nm < l < 2800 nm).

Reagent NO (grade >99%) is supplied from a commercially purchased (Scott Specialty Gases) stainless steel lecture bottle (500 psig). Since NO is a toxic gas, the small high pressure cylinder, the pressure regulator, and several safety features are mounted inside a specially designed pressure safe vessel that is vented overboard the aircraft. The NO gas delivery line is constructed of 1/8" stainless steel tubing and fittings up to a 2-way, normally closed solenoid valve positioned inside the instrument just upstream of the reaction vessel. The solenoid valve acts as an automatable ON/OFF switch for introduction of NO flow to the reaction vessel. Reagent nitric oxide is introduced to the reaction vessel downstream of the solenoid valve via a short segment of 1/16" stainless steel tubing that is welded into the removable inlet flange. On the reaction vessel side, the 1/16" tubing protrudes perpendicularly into the 1/4" bore of the inlet flange and has a 45º cut at the tip to flow reagent NO in the opposing direction to ambient air

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flow in hope of maximizing mixing between the two reactants before the mixture expands into the reflective cone of the vessel. When the reagent NO flow is controlled at a low flow (typically 2 sccm), this supply is sufficient for roughly 13 aircraft flights of 9 hour duration plus a few ground calibrations. Reagent NO flow control is provided by a 0-10 sccm range flow controller (Tylan, FC-260).

b. Instrument sensitivity and calibration

The PMT signal resulting from the chemiluminescence reaction is proportional to the mixing ratio of O_3, and the sensitivity (e.g., counts per Δt per ppbv) is proportional to the sample "mass" flow (e.g., sccm) divided by the reaction vessel pressure provided less than a few percent of the ambient O_3 is unreacted within the view of the PMT {Ridley, 1992 #28}. Typical operating conditions in the laboratory and onboard the aircraft include an ambient air sample flow controlled to 500 sccm with the reagent NO flow at 2 sccm (standard $cm^3\ min^{-1}$ at $0^{\circ}C$ and 1 atm.), a controlled reaction vessel pressure of 10 Torr and a controlled reaction vessel temperature of $35^{\circ}C$. Gas flows as well as the reaction vessel temperature and pressure are all controlled at constant conditions resulting in maximum stability of the detected signal and instrument sensitivity. Table I provides a summary of the above operating conditions which were optimized for sensitivity, signal to noise ratio, and detection limit of the instrument at 1 Hz and 5 Hz operation while maintaining minimal usage of reagent NO gas. In the table, the signal to noise ratio, $S/N = \frac{Sensitivity * \overline{O_3}}{\sqrt{2 * Bckgrd}}$, the smallest change in mixing ratio given a mean value of

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O_3, $\Delta O_3 = \frac{\sqrt{(Sensitivity * \overline{O_3}) + Bckgrd}}{Sens}$, and the detection limit, $DL = \sqrt{2 * Bckgrd * Sensitivity}$, are calculated given 20 and 100 ppbv as exemplary mean mixing ratios of O_3.

Table I: Basic Ozone Instrument Operating Conditions and Performance at 1 Hz and 5 Hz.

	1 Hz, Δt = 1 sec	5 Hz, Δt = 0.2 sec
Sample flow (sccm, cm^3/min at 0ºC, 1 atm)	500	
Reaction Vessel Pressure (torr)	10	
Reaction Vessel Temperature (ºC)	35	
Pure NO Flow (sccm)	2	
Background counts per Δt	200	40
Sensitivity, counts per Δt per ppbv	2200	440
Signal to Noise Ratio at 20 ppbv O_3	1550	690
Signal to Noise Ratio at 100 ppbv O_3	7770	3475
Smallest Δ in mixing ratio (ppbv) at 20 ppbv O_3	0.10	0.21
Smallest Δ in mixing ratio (ppbv) at 100 ppbv O_3	0.21	0.48
Detection Limit (ppbv)	0.01	0.02

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The "raw" O_3 mixing ratio is determined from the PMT signal minus the "background" count rate divided by the instrument sensitivity. 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 #28}. However, the background count rate in the UT/LS region will not exceed ~500 cps. Even with O_3 as low as 20 ppbv in the UT, the background will only be ~ 0.5 % of the signal count rate. Thus only periodic measurements (~every 30 minutes) of the background count rate need be made by computer-controlled addition of an excess flow of high quality zero air to the sampling inlet. In flight, a 2-way solenoid valve and a tee along the pick-off line to the reaction vessel introduces a slight overflow of zero air (typically 700 sccm) at reference marker B in figure 1.

The instrument sensitivity is determined from routine calibrations performed on the ground between research flights. The instrument is calibrated using a UV based ozone generator/calibrator (TECO, model 49PS) operated with ultrapure air. Excess flow containing O_3 from the calibrator is plumbed to the aircraft inlet using a vented tee and with the instrument operating at its normal controlled flows and reaction vessel temperature and pressure. Thus any O_3 losses due to components positioned along the flow path upstream of the reaction vessel are included in the calibration. A calibration range of 0-1000 ppbv is used to characterize the ozone instrument for use onboard HIAPER where sampling stratospheric air is likely. A 0-200 ppbv calibration range generally suffices for the C-130 aircraft given its maximum altitude ceiling of 27 kft. Calibration is not required for every flight since multiple calibrations throughout the course of a field project have given sensitivities stable to within 5%.

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c. Instrument uncertainty

The overall uncertainty of the fast-O_3 instrument is best represented as a propagation of errors (combined in quadrature) of the factors that affect the O_3 CLD sensitivity. Important contributions come from: 1) the manufacturer's specifications for the mechanical components that measure flows, pressures, and temperatures, 2) the 1σ deviation of successive ground calibrations performed in the field, 3) the stability of the O_3 UV-based field calibrator used for ground calibrations, 4) the stability of the NOAA GMD Network Standard used for comparing the O_3 instrument to the NIST standard, and 5) uncertainty in the water vapor measurement used for the quenching correction of the O_3 instrument sensitivity. Given these combined contributions, the overall uncertainty of the O_3 CLD instrument has been determined as ± 5 % of the ambient measured mixing ratio or less depending on the 1σ deviation of successive ground calibrations performed during a specific field project.

3. Evaluation of instrument frequency response

a. Laboratory measurements

1. Test method

In our laboratory's attempts to measure the frequency response of the fast-O_3 instrument with respect to a step change in O_3 concentration, an optical shutter was designed and built to create pulses of ozone in a length of UV transmitting quartz tube. However, a fast time response for the ozone instrument was never observed using this shutter apparatus. Appendix A describes these efforts in more detail.

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A 3-way switching solenoid valve similar to that employed by Pearson (1990) was found to be the best test method for evaluating frequency response of the fast-O_3 instrument in the laboratory. Near-square pulses of O_3 in a flow of high quality zero air (ZA) were produced using a Teflon 3-way switching, DC solenoid valve (General Valve, type 001-0210-900) which can be switched in 10 ms or less according to the manufacturer's specifications. PFA tubing (1/4") was used to deliver the O_3 and ZA to the 3-way valve. A ¼" PFA tee (Galtek) with additional ¼ PFA tubing was used to vent overflow of the O_3 and ZA just upstream of the valve body to reduce the effect of pressure transients as the valve is switched. A square-wave function generator (Tektronix TM 504) and DC relay (Opto-22, G4 O5DC) were used to switch the valve at frequencies up to 20 Hz. An oscilloscope was used to view the square wave signal produced by the wave generator in order to ensure an integer frequency and 50% duty cycle setting. Photon counts from the PMT were recorded at a rate of 200 samples per second (0.005 sec). Ozone mixing ratios from 20-100 ppbv were used in the lab studies, and generated using the UV-based ozone generator/calibrator unit.

Laboratory measurements were consistently collected in the same manner for all laboratory tests. The wave generator was held fixed at 0.25 Hz to obtain near-perfect square waveforms at a very low frequency setting, and then the wave generator was increased in 1 Hz intervals from 1 to 20 Hz. The wave generator was held constant for a period of time sufficient to capture at least 10 square pulses at each interval before changing to the next frequency setting.

2. Tests performed

a. Laboratory frequency response measurements

1. Basic instrument

The frequency response of the "basic" instrument including the metering valve, mass flow meter, and reaction vessel was characterized by placing the test method at reference marker B in Figure 1. A comparison of the frequency response for the basic instrument was also done with and without the mass flow meter upstream of the reaction vessel. For measurements without the mass flow meter, a ¼" Swagelok stainless steel union was used in its place.

2. Effects of operating conditions on the basic instrument's frequency response

The effects of changes in operating conditions (flow, pressure, temperature) on the basic instrument's frequency response were characterized. According to a plug flow calculation,

$$t_{residence} = \frac{V}{F \times \frac{760}{P} \times \frac{T}{273} \times \frac{1}{60}}$$

the residence time ($t_{residence}$) in the reaction vessel is dependent on the volume (V) of the vessel in cm^3, the air sample flow plus the reagent NO flow (F) in sccm, reaction vessel pressure (P) in Torr, and reaction vessel temperature (T) in Kelvin. The plug flow calculation yields the time required for one full volume of the reaction vessel to be completely evacuated or exchanged assuming specific pressure, temperature, and flow conditions. For these tests, the 3-way valve was positioned at reference marker B to understand the effects of these parameters on the residence time through the reaction vessel uncomplicated by the aircraft inlet system. Each of the above parameters was adjusted individually with respect to the operating conditions (Table I) for all other parameters which were initially optimized for instrument sensitivity.

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3. Instrument plus aircraft inlet

The effect of the aircraft inlet system with respect to the basic instrument was characterized by placing the test method at reference marker A in Figure 1. The inlet configuration is expected to play a critical role in the ability of the fast-O_3 instrument to operate at 5 Hz or better. Due to changes in pressure with aircraft altitude, an automated pressure control valve needed to be placed in the flow path to maintain a constant pressure downstream of the inlet and upstream of the stainless steel metering valve. Without the pressure control valve, changes in ambient pressure would affect the flow rate through the metering valve to the reaction vessel, thereby changing the instrument's sensitivity. Past studies have also shown that additional components, bends in the tubing, and telescoping changes in tubing diameter along the gas pathway can affect instrument time response {Massman, 1991 #20}, therefore it was necessary to test the true time response of the instrument with the inlet and the pressure control valve with and without the bypass flow system and as the instrument plus inlet it would be implemented into the aircraft. In addition, it was suspected that the pressure control valve would significantly reduce the frequency response of the instrument due to the complexity of the gas pathway through the body of the valve. A manual 1/4" turn, 1/8" PFA stopcock valve (Swagelok), which has a much simpler gas pathway, was used in place of the automated pressure control valve in a specific test in to distinguish the difference between effects from the valve versus the inlet tubing. However, automated pressure control is critical for aircraft application, specifically for accommodating changes in pressure with altitude. Therefore, it is important to also test the performance of the automated pressure control valve over the pressure range anticipated for aircraft applications. For this particular test, two components (not illustrated in

Figure 1) were added respectively along the gas flow path between the test method and the MKS 640 pressure control valve: 1) a 1/8" PFA (Galtek) needle valve to select the upstream pressure, and 2) a 1/4-1/8-1/8" PFA tee (Galtek) to a 0-1000 torr baratron pressure transducer to measure the upstream pressure set with the needle valve.

b. Aircraft frequency response measurements

Airborne testing of the fast-O_3 instrument took place during two separate field projects. Test flights onboard the NCAR/NSF C-130 took place prior to the Pacific Atmospheric Sulfur Experiment (PASE) in summer 2007 and prior to the VAMOS Ocean-Cloud-Atmosphere-Land Study (VOCALS) in fall 2008. In both projects, flight testing was done in the continental boundary layer over the Colorado Front Range during summer and early fall to maximize chances of sampling high frequency atmospheric turbulent eddies. The two projects are similar in that the instrument was operated under the same conditions as in Table I, and differ only by the use of a rear-facing (VOCALS) versus a forward-facing (PASE) aircraft inlet. The instrument plus inlet are integrated onto the aircraft in the same configuration as how they were tested in the laboratory.

4. Results

a. Laboratory tests

1. Basic Instrument

Figure 2 shows the near-square O_3 waveform observed with the wave generator set at 0.25, 3.0, 5.0, and 10.0 Hz. Waveforms in this figure are representative of laboratory tests made

when operating the instrument with its simplest inlet configuration, specifically with the 3-way valve placed at reference marker B, thereby capturing the frequency response through the reaction vessel within the basic instrument without interference from aircraft inlet related components. A nearly square waveform is observed at frequencies ≤ 0.25 Hz. The inherent rise and fall time of the not perfectly square pulse start to distort the edges of the waveform at 3.0 Hz. At frequencies above 10.0 Hz, the pulse starts to exhibit a sinusoidal waveform with attenuation of the pulse amplitude as the combined rise and fall time begin to exceed the pulse period.

Three different methods of analyzing the near square waveforms for determining the frequency response of the instrument are described here. For comparison of the different analyses, each method is applied to the same data set collected for the basic instrument with the mass flow meter. One method is to analyze the attenuation of the maximum amplitude of the near-square O_3 pulses to -3 dB as the switching frequency of the 3-way solenoid valve is increased over the 0.25 to 20 Hz range with the wave generator. This is the primary method of analysis employed by Pearson {Pearson, 1990 #9}, and will be referred to as the "-3 dB attenuation" method throughout the text. A plot of the normalized amplitude from this attenuation (figure 3) reveals the frequency response of the instrument to a -3 dB cutoff. The error bars reflect the average and 1 σ standard deviation of the maximum amplitude and baseline of five consecutive O_3 pulses that were obtained at each frequency interval. The 1 σ standard deviation from these measurements has been propagated throughout the calculation of the normalized amplitude. Given the vertical error bars in the normalized amplitude one can estimate a frequency error of about 1 Hz. The data points (solid circles) are fit well by a 3rd order polynomial function (solid line through solid circles), where the fit is weighted to the error

in the normalized amplitude. Extrapolation from the fit reveals an 8 Hz frequency cutoff at -3 dB for the basic instrument. A similar 3rd order polynomial fit of the data points (not shown) for the basic instrument without the mass flow meter in the flow path results in a slightly improved response of 9 Hz. Thus, the presence of the mass flow meter just upstream of the reaction vessel indicates a small limitation in the frequency response of the basic instrument, even though the difference lies within the 1 Hz error bar for this analysis method.

Another method of analysis utilizes the relationship for a one-stage low pass RC network in electronics, which is commonly used first-order description of frequency response for a step change in mixing ratio. The rise time of a step-like function generally refers to the time required for a signal to change from a specified low value to a specified high value. Typically, these values are 10% and 90% of the step height. Using a 10-90% rise time (t_r) and an exponential growth function,

$$\frac{V(t)}{V_0} = (1 - e^{-\frac{t}{\tau}})$$

$$0.1 = (1 - e^{-\frac{t_1}{\tau}}) \qquad 0.9 = (1 - e^{-\frac{t_2}{\tau}})$$

$$t_1 = \tau(\ln 10 - \ln 9) \qquad t_2 = \tau \ln 10$$

$$t_r = t_2 - t_1 = \tau * \ln 9 \cong \tau * 2.197$$

and the network time constant relationship for an RC circuit,

$$\tau = RC = \frac{1}{2\pi f_H}$$

the following relationship for frequency can be expressed as,

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$$t_r \cong \frac{2.197}{2\pi f_H}$$

$$f_H \cong \frac{0.349}{t_r}$$

where f_H is the high frequency cutoff (to -3 dB) of the analyzed system in Hz.

Using this relationship we can simplify our data analysis to looking at either the rising or falling edge of the O_3 pulse. In this analysis, the 10-90% rise time was determined by calculating the 10% and 90% values from the difference in the average maximum signal amplitude and the average baseline of the square waveform recorded at 0.25 Hz. It is important to include the average baseline in this calculation since the instrument background, while very small at the 200 Hz sampling rate, is non-zero. The resulting rise time for the basic instrument is 0.06 seconds corresponding to a high frequency cutoff of 5.8 Hz. Our ability to determine t_1 and t_2 is limited to the uncertainty in the 200 Hz sampling rate, such that the individual determinations of these times have a ± 0.005 sec uncertainty. Considering the combined uncertainty in the rise time measurement, t_r ± 0.01 sec, the frequency response can be bracketed between $5.0 < f_H < 7.0$ Hz. As expected, the fall time of this symmetric pulse yields a consistent result within the error bars of this measurement. The "rise time" analysis (as it will be referred to in the this work) will reveal itself as a useful tool in later sections when analyzing the airborne data, specifically in the cases of an observed atmospheric step change in O_3 mixing ratio such as one would encounter when crossing a pollution plume or when transitioning through the inversion layer. The instrument frequency response of 5.8 Hz determined from the rise time

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analysis has been marked by a vertical solid line in Figure 3 for comparison to the -3 dB attenuation method.

Fast Fourier transform of the non-perfect square waveforms was employed as a third analysis method. The finite rise and fall time inherent to the non-perfect square waves provide a measure of the finite bandwidth of the instrument. The fast Fourier transform (FFT) routine built-in to a commonly used scientific data processing platform (Igor Pro 5.01) was applied to a segment of laboratory data consisting of approximately nine square-like pulses. To reduce noise in the resultant power spectrum, a symmetric sampling of data points around the nine pulses was used and no padding at the ends of the data segment was added prior to running the transform. Figure 4 shows the resulting power spectrum for the fast-O_3 instrument when operated in its basic configuration (test method at reference marker B). During this data segment, the wave generator was held constant at a 50% duty cycle and a frequency setting of 0.25 Hz, thus there is a large feature in the power spectrum at 0.25 Hz corresponding to the base or fundamental frequency of the square wave. The power spectrum truncates at the expected Nyquist frequency of 100 Hz (half the sampling rate), and clearly displays the odd harmonics as the dominating component of the spectrum beyond 10.25 Hz corresponding to the 41st harmonic of the base square wave frequency. Observation of dominant, higher order odd harmonics (greater than the fifth harmonic) confirms that the waveforms generated in the laboratory at this fundamental frequency are well described by a square-wave function. Some even harmonics are present in the spectrum, and likely arise from limitations in the 3-way switching valve test method to produce perfect square waves as well as imperfections in acquiring an exact symmetric sampling of square pulses for the transform.

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If one considers the detection limit of the instrument to be 3σ above the magnitude of the noise floor, then the resulting frequency response of the basic instrument from the power spectrum is approximately 12 Hz. However, a more rigorous way of interpreting the instrument's frequency response from the power spectrum is to consider the frequency roll-off of the odd harmonics to half power or -3 dB (referred to as the "FFT" method here). The roll-off curve was generated by multiplying the magnitude squared of each odd harmonic in the spectrum by the square of its corresponding odd harmonic number. This correction factor must be applied to account for the inverse harmonic coefficient preceding each term in the expansion of the Fourier series for a square wave. The normalized power in units of dB was then determined by taking 10 times the $\log_{10}$ of this quantity divided by the corrected power of the fundamental harmonic. A similar curve to that generated using the -3 dB attenuation method can be produced by plotting the normalized power of the odd harmonics (in dB) from the FFT spectrum versus frequency of the odd harmonic (in Hz). Again, the data points are fit well by a 3rd order polynomial function which reveals a frequency response of 5.5 Hz at -3 dB. The normalized amplitude data points from FFT analysis of the square waveform (open diamonds) and the polynomial fit (solid line through diamonds) has been overlaid in figure 3 for comparison to the -3 dB attenuation and rise time results. It is important to recognize that the FFT and rise time methods produce a consistent result for the basic instrument's frequency response within the error bar associated with the rise time measurement.

FFT of symmetric data segments with the wave generator set to 1, 2, and 3 Hz fundamental frequencies produced similar power spectra. Roll-off curves generated from the 1 Hz (open circles), 2 Hz (open triangles), and 3 Hz (open squares) power spectra are also

illustrated in Figure 3, and resulted in a -3 dB frequency cut-off of 6, 6, and 7.3 Hz, respectively, as determined from the 3rd order polynomial fit (not shown) of each set of data points. Again, results from the roll-off curves were consistent with the resulting frequencies determined from the rise/fall time analysis of the same data segments acquired at these fundamental frequencies.

2. Effects of operating conditions on the basic instrument's frequency response

For simplicity and ease of data analysis, only the rise time method was used to obtain frequency response numbers for this comparison. A five-fold increase in sample flow rate over the range of 200 to 1000 sccm showed a two-fold improvement in time response. Increasing the reaction vessel pressure from 5 Torr, which is the minimum pressure of the reaction vessel set by the pump speed and sample flow rate, up to 20 Torr resulted in no change in residence time outside the error bars of the rise time analysis. Likewise, changes in NO flow over the 0-10 sccm range of the Tylan mass flow controller and changes in reaction vessel temperature from 10 to 40ºC also had no appreciable effect on the instrument's time response.

The frequency response of the instrument was also found to be independent of O_3 mixing ratio. Tests done with the UV-based ozone generator/calibrator set to 10, 20, 100 and 1000 ppbv showed no difference in time response outside the error bars of the rise time measurement.

3. Instrument plus aircraft inlet

Laboratory measurements performed with the test method positioned at reference marker A in Figure 1 such that the flow path includes the aircraft inlet and the pressure control valve between the inlet and the metering valve, yet excludes the use of the two diaphragm pumps on

the bypass system, resulted in a dramatic reduction in instrument response to ≤ 0.5 Hz, as expected. Replacement of the automated pressure control valve with the manual 1/4" turn stopcock valve results in only a slight reduction of frequency response (by roughly 1-2 Hz) compared to the basic instrument. Limitations of the automated pressure control valve were only overcome by increasing the flow rate through the pressure control valve. Thus a bypass flow from the inlet through the pressure control valve was created using the two small, identical, diaphragm pumps in parallel. With only one pump running, the bypass flow was measured as 2.9 slpm and the instrument's response was found to be 4.5 Hz. With both pumps running the bypass flow increased to 3.3 slpm, and the response to 5 Hz. The above frequency response measurements are reported in terms of the -3 dB attenuation method of analysis.

Tests were also done to determine the effect of changing pressure at the inlet on the instrument's time response. The frequency response was found to increase from 5 to 7 Hz, when using the -3 dB attenuation method of analysis, with decreasing inlet pressure towards the 200 Torr set point. Table II presents a summary of frequency response measurements obtained in the laboratory as a function of pressure upstream of the inlet. Note the frequency response of 5 Hz determined with the inlet pressure set to 570 torr for later comparison to aircraft measurements obtained in the boundary layer near 2 km.

Table II: Frequency response measurements obtained in the laboratory as a function of pressure upstream of the inlet (in Torr). The test method is positioned at reference marker A in figure 1 for all measurements reported in the table. Frequencies are reported in Hz, with f_H representing the high frequency cutoff determined using the rise time method. Likewise,

$f_{-3\ dB}$ represents the frequency determined using the -3 dB attenuation method of increasing the wave generator in 1 Hz steps.

Pressure Upstream of Inlet (Torr)	t_r **(sec)**	f_H	$f_{-3\ dB}$
570	0.08	4.4	5
400	0.07	5.0	6
300	0.065	5.4	6
200	0.055	6.4	7

b. Airborne frequency response tests

1. PASE test flights

Several fast changes in O_3 mixing ratio (figure 5) were observed while ascending and descending in and out of the top of the continental boundary layer at a rate of ~1000 ft/min during pre-PASE test flight (TF03, 20070731). Correlated fast changes are observed in humidity and air temperature measurements from the standard suite of aircraft sensors, and are also shown in Figure 5. Correlated changes in potential temperature and condensed nuclei concentration as well as anti-correlated changes in carbon monoxide with the O_3 measurement were also observed confirming that a real atmospheric change in O_3 mixing ratio had occurred. However, fast step-like changes were not observed for these later measurements due to either the time resolution of the instrument or the rate at which the data was recorded, thus they are not depicted in the figure. An expanded view (figure 6) of one of the features (17:00:23.5-17:00:25.0 UTC) in figure 5 highlights an exemplary fast step-like change observed in the former three measurements. A fall

time of 0.065 ± 0.01 sec was observed for the ~ 20 ppbv step-like change in O_3. The corresponding frequency response from this fall time is 5.4 Hz. Given the combined uncertainty of ± 0.01 sec for the rise time method, the frequency response can be bracketed between $4.7 < f_H < 6.4$ Hz. Humidity and air temperature also have fast rise and fall time of 0.08 ± 0.04 sec associated with this specific step-like change corresponding to a 4.4 Hz response, bracketed between $2.9 < f_H < 8.8$ Hz.

Periodic in-flight measurements of the O_3 instrument background every 30 min using solenoid valve injection of zero air near reference marker B in Figure 1 resulted in a 7 Hz step-like change, slightly better than that expected from the lab tests (5.8 Hz), when using the rise time analysis method. These background measurements confirm that the basic instrument was functioning properly throughout the course of the flight and provides a periodic in-flight comparison to laboratory frequency response measurements. In addition, a standard set of pitch, roll, side slip, airspeed, and aircraft engine power maneuvers had no measurable effect on the magnitude of the O_3 signal.

Power spectral distributions of ozone measurements (sampled at 200 Hz) are also analyzed for frequency response information. Several segments of boundary layer measurements were recorded in pre-PASE TF04. Figure 7 depicts a plot of the O_3 power spectral density from airborne measurements obtained in the boundary layer near 1.7 km during one segment of pre-PASE test flight (TF03, 20070731, 17:03:06-17:05:33 UTC). A reference line with a -5/3 slope as well as an arrow marking a 5 Hz frequency response has been overlaid on the plot to guide the eye. The power distribution spectrum reveals amplitude roll-off in O_3 before the frequency roll-off of the instrument can be observed. The observation of amplitude roll-off is likely due to

small amplitude O_3 fluxes that could not be detected above the instrument's signal to noise level. Even though the upper limit of the instrument's frequency response cannot be determined from analysis of this power spectrum, it is important to note that the O_3 power distribution intersects the horizontal asymptote, corresponding to the noise floor of the instrument, at 5 Hz.

For comparison, power spectra (also shown in figure 7) were generated for humidity (blue) and ambient air temperature (red) obtained from the same time segment in the boundary layer as ozone. A reference line with a -5/3 slope as well as arrows marking 5 and 10 Hz frequency responses have been overlaid on the plot to guide the eye. The power distribution spectrum reveals frequency response out to at least 10 Hz. Water and air temperature measurements were reported at a lower frequency than the instrument's response, thus frequency roll-off beyond 10 Hz cannot be observed in this plot.

1) VOCALS test flights

5. Discussion

a. Laboratory Tests

1. Basic instrument results: Comparison of analysis methods

The FFT and rise time analysis methods yield consistent frequency responses near 5.8 Hz, whereas the -3 dB attenuation method of increasing the wave generator and looking for pulse amplitude attenuation results in a higher frequency cutoff of 8 Hz, as shown in figure 3. In Pearson's work, a -3 dB cutoff was observed near 12 Hz consistent with a 4^{th} order Butterworth electronic filter inherent to the detection system. The response to ozone was flat out to 8 Hz and

within 0.2 dB of a theoretical curve for the filter between 0.1 and 10 Hz and within 0.5 dB between 11 and 20 Hz. Effectively, Pearson's instrument response was sufficiently fast, thus the signal bandwidth is fixed by the electronic filter such that the shape of the attenuation curve of the instrument's response matches that of the filter. No electronic filters were used in conjunction with the fast-O_3 instrument reported in this work, thus the signal bandwidth is only limited to 1) the true frequency response of the basic instrument and 2) our ability to produce near-perfect square pulses of O_3 in ZA with the test method.

It is possible that differences in the results with respect to analysis method arise from a distortion of the shape of the rising/falling edges of the near-square pulse while having no distinguishable effect on the maximum amplitude of the signal. Any such distortion would affect the 10-90% rise time measurement or FFT without disturbing pulse attenuation, thereby resulting in a different frequency response from the FFT and rise time methods compared to the -3 dB attenuation method. Several factors may be simultaneously involved, some of which include imperfections in the 3-way valve test method, effects from tubing walls, and the geometry of the flow path all of which may only affect the leading and falling edges of the waveform; although the true physical reasoning behind the discrepancy in frequency measurements with respect to analysis method remains unclear. However, one possibility is that the difference in frequency response with respect to analysis method could be a consequence of the square wave nature of the input function. The increase in frequency cutoff observed in the FFT and rise time analyses observed with increasing frequency setting of the wave generator from 0.25 to 3 Hz (figure 3) supports this idea.

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To test this hypothesis, a first–order approximation of the attenuation of a square wave function when run through a low-pass RC network was calculated, and an expression for the output of a Fourier expanded square wave, $x_{output}(t)$, after attenuation by the system was determined. A theoretical curve illustrating the half power attenuation of the signal to 0.707, corresponding to a -3 dB roll-off, was generated by taking the ratio of the output expression to an input expression for the Fourier series expansion of the square wave, $x_{input}(t)$. The input function is derived from the following basic form for the Fourier series expansion of a square wave

$$x_{square}(t) = \frac{4}{\pi}\sum_{k=1}^{\infty}\frac{1}{(2k-1)}\sin((2k-1)2\pi f t).$$

Given that $\omega = 2\pi f$, the amplitude of the square waveform is at a maximum at $\pi/2$. Under this condition, the equation can be simplified to assess the square wave function only at its maximum amplitude. The resulting expression,

$$x_{input}(t) = \frac{4}{\pi}\sum_{k=1}^{\infty}\frac{1}{(2k-1)}\sin((2k-1)\frac{\pi}{2}),$$

is used as the input square waveform. Adding in the effects of a low-pass RC circuit, $\frac{1}{\sqrt{1+\omega^2\tau^2}}$, on the system results in an attenuation factor for the square wave input of

$$\frac{1}{\sqrt{1+((2k-1)^2\omega^2\tau^2)}},$$

where τ is the network time constant and is derived from the instrument's frequency response of 5.8 Hz as determined using the rise time and FFT methods from above. Thus the output can be expressed as the input function multiplied by the attenuation factor,

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$$x_{output}(t) = \frac{4}{\pi}\sum_{k=1}^{\infty}\frac{1}{(2k-1)}\frac{1}{\sqrt{1+((2k-1)^2\omega^2\tau^2)}}\sin((2k-1)\frac{\pi}{2}).$$

The input and output are calculated as finite sums over a range of *k* values from 1 to 10^5 in integer increments, and for frequency values every 0.5 Hz from 0.5 to 20 Hz. The attenuation curve resulting from the ratio of the sums from the output to the input expressions of a square wave (open circles) is illustrated in Figure 9. The data points and 3rd order polynomial fit generated using the -3 dB attenuation method of analysis from laboratory observations for the basic instrument (solid circles) have been reproduced in Figure 9 in terms of attenuation.

For comparison, the output of a pure sine wave through the same first–order approximation for attenuation yields the following expected gain curve

$$Gain = \frac{1}{\sqrt{1+\omega^2\tau^2}},$$

where τ is the same as above. The resulting attenuation curve generated using the sine wave input function (open downward triangles) is also shown in Figure 9. The sine wave input produces the expected gain curve such that the half power attenuation of 0.707 is reached at 5.8 Hz, whereas the theoretical curve generated using the square wave input results in a higher frequency cutoff of 7.4 Hz. While this is still not in perfect agreement with the observed frequency cutoff of 8 Hz determined using the -3 dB attenuation method of analysis, it does result in a frequency cutoff closer to the observed value and within a reasonable margin of error of 1 Hz of the measured response.

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Since the theoretical attenuation of a square wave does not entirely account for the difference in the -3 dB attenuation method of analysis, it is possible that the $\frac{1}{\sqrt{1+\omega^2\tau^2}}$ functional form associated with an RC circuit is not the best way to characterize this system. It is also likely that other factors may affect the rise time or shape of the rising/falling edges of the square pulse while not yet affecting the maximum amplitude of the signal. For instance, the edges of the square pulse might be a convolution of the instrument response time and the open/close time associated with the 3-way valve such that they are best described by a double exponential rather than a single exponential as assumed by the RC network system. Additionally, a first-order approximation may not be adequate to describe this system. However, a higher-order analysis or analysis based on a convolution of rise times is beyond the scope of this publication.

2. Effects of operating conditions on the basic instrument's frequency response

For the reaction vessel volume alone, our plug flow residence time is anticipated to be 24 ms given the operating conditions listed in Table I. The observed frequency responses of 8 Hz via the -3 dB attenuation method and 5.8 Hz via the rise time method are within a factor of 2 and *e* of the plug flow calculation, respectively. The observed two-fold increase compared to an expected five-fold increase from the plug flush calculation as well as no observed change in frequency response with reaction vessel pressure suggests that plug flow may not be a good assumption for our conical shaped reaction vessel such that something other than the operating conditions of the reaction vessel plays an important role in limiting the frequency response of the

basic instrument. The shape and size of the vessel as well as the sample flow rate, which govern the fluid dynamics through the reaction vessel, may play an important role. Previous experiments by Pearson {Pearson, 1990 #9} highlight the use of a cylindrical shaped reaction vessel with a significantly larger inner volume of 139 cm^3. A considerably larger sample flow rate of 3700 sccm was necessary to achieve a similar plug flow residence time (26 ms) given the larger volume as well as a reaction vessel pressure of 10 Torr and temperature of 39 ºC. Pearson's laboratory measurements of the frequency response through this cylindrical reaction vessel yielded a -3 dB frequency cutoff near 12 Hz from, corresponding to a rise time of 29 ms, which is in very close agreement with the plug flow calculation.

In theory, the residence time can be optimized for a reaction vessel of a given volume by increasing the total flow rate, decreasing the pressure, and increasing the temperature in accord with the plug flow calculation. It is obvious from the calculation and the laboratory measurements reported here that an increased time response can be achieved for the basic instrument by simply increasing the sample flow rate through the reaction vessel. However, to implement a higher sample flow rate in our small volume reaction vessel yet maintain instrument sensitivity, an increase in the reagent NO flow rate would be necessary. The increased usage of NO gas would require maintenance to replace NO lecture bottles in the containment vessel or the need to carry a much larger supply of pure NO gas onboard the aircraft. The increased weight, space, and costs associated with such a modification defeat the purpose of the small volume reaction vessel and the ease of operating this instrument onboard an aircraft. All the same, if a faster measurement is required, the system needs only a bit more attention to routine maintenance and to be recalibrated at the higher flow rate.

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3. Influence of Inlet Configuration and Inlet Pressure

It is clear from the results that addition of the aircraft inlet system to the basic instrument dramatically reduces the frequency response of the instrument. The addition of a single diaphragm pump to create a bypass flow of 2.9 slpm significantly improves the response through the inlet system, and it is improved even further when the bypass flow is increased to 3.3 slpm by using a second diaphragm pump in parallel. Indeed, it is crucial to keep the inlet plumbing as short and as simple as possible to achieve maximum frequency response in accordance with plug flow. Along the same reasoning, the increased flow rate through the aircraft inlet and pressure control valve induced by the pumps significantly reduces the residence time in the inlet system. However, even without the bypass flow, the residence time through the inlet system is small given the combined volume of the 3 foot length of ¼" PFA tubing and the body of the pressure control valve. Considering that replacement of the pressure control valve with the manual 1/4" turn stopcock valve does not significantly reduce the frequency response from the basic instrument, it is likely that the complex gas pathway inherent to the automated pressure control valve induces mixing of the gas pulse such that the rising and falling edges of the near-square waveforms are elongated. Further evidence that the pathway through the pressure control valve may be of importance is illustrated in the pressure tests upstream of the inlet. For example, when the inlet pressure is near the 200 Torr downstream set point of the pressure control valve, the valve is fully open allowing a more straightforward gas pathway through the valve body under less constriction. In contrast, when the inlet pressure is near 570 Torr, the pressure control valve is mostly closed thereby restricting and obstructing the gas path through the valve.

Certainly improvements to the fast-O_3 instrument's frequency response can be made simply by using a different pressure control valve. However, time constraints for instrument development and delivery were not conducive to exploration of other automated pressure control options prior to test flights on the C130. Ongoing efforts by this laboratory are aimed at designing and developing a non-commercial system consisting of a Teflon valve body with a simple gas pathway and an actuator for automated inlet pressure control.

b. Airborne and Field Tests

Time response measurements to step change in O3 concentration.

Power spectra

Cospectra

From the 90% response time measurements in the laboratory and the energy spectrum generated using the field measurements, Gusten et al. claim an overall response time for their ozone instrument of 0.05 s or 20 Hz.

In contrast to tower measurements, energy spectra of ozone from aircraft measurements are much more difficult to achieve. A low level of ozone variance upon turbulent eddying in the boundary layer (near 1.7 km) making it difficult to distinguish high frequency events in the spectrum above the instrument's noise floor. In Pearson and Steadman {Pearson, 1980 #19}, where aircraft measurements were performed for field experiments, the author does not report an ozone power spectrum. Instead, plumes rich in NO from internal combustion sources were sampled in order to observe a sharp decrease in ozone mixing ratio. A single fall time of 50 ms was observed and is correlated with the sharpest observed ozone decrease upon plume entry.

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In 2005 Faloona {Faloona, 2005 #27} reported…

c. Influence of Water Vapor

As described by Ridley et al.{Ridley, 1992 #28; Ridley, 1994 #41}, the detector sensitivity can be affected by changes in ambient water vapor. The "raw" O_3 data has to be 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. The correction is negligible for normal water vapor mixing ratios anticipated for the middle to upper troposphere and lower stratosphere, but could be significant within the warm marine or continental boundary layer.

Previous experiments reveal different results for frequency response upon the introduction of water vapor to the instrument. Pearson showed that the presence of water vapor does not interfere with the time response of the instrument {Pearson, 1990 #9; Pearson, 1980 #19}. In his studies of airborne cloud penetration and fair weather cumuli, he showed that neither clouds nor precipitation interfered with ozone measurements except for the small decrease in sensitivity due to the increase in water vapor mixing ratio. On the other hand, Gusten's measurements found that sensitivity was enhanced, albeit non-linearly, with changes in water vapor pressure, and the 90% response time of the sensitivity enhancement after sudden changes in humidity was on the average of 22 ± 5 s, nearly two orders of magnitude longer than the response time to changes in ozone. However, instrument sensitivity, selectivity, and time response is known to be enhanced upon interaction with water vapor in ozone-induced chemiluminescence of dyes adsorbed on silica gel.

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For a complete analysis of our new fast-O_3 instrument, future laboratory experiments should include humidifying the O_3 sample as well as the ZA supplied to the 3-way valve test method to observe any direct changes in time response upon addition of water vapor.

6. Summary and conclusions

Laboratory and airborne testing of an ozone chemiluminescence instrument were performed to measure the instrument's frequency response. A 3-way switching solenoid valve proved to be the best tool for producing near square pulses of ozone in zero air for the laboratory tests. Three different analysis methods were employed to determine the instrument's frequency response from resulting waveforms collected during laboratory measurements: 1) Pearson's method of looking for attenuation to -3 dB upon increasing the switching frequency of the valve with the wave generator, 2) calculation of the one-stage low pass RC network high frequency cutoff from the 10-90% rise (or fall) time of a single square pulse, and 3) FFT of a segment of square pulses then determination of the -3 dB cutoff frequency of the odd harmonics in the resulting power spectrum. Discrepancies in the resulting frequency responses from the different methods of analysis of the laboratory data arise from…

Power spectra generated from ozone measurements in the boundary layer acquired during flight tests yielded a response of xx Hz. Co-spectra of ozone data with a fast humidity sensor yielded a response of xx Hz.

Development of this fast-response O_3 chemiluminescence instrument is part of the HIAPER Aircraft Instrumentation Solicitation (HAIS) which aims to provide a suite of airborne

instruments available for use in any HIAPER project. The HAIS fast-O_3 instrument has met its target delivery date of March 2008. Since then the new O_3 instrument has successfully participated in one field research project onboard the NSF/NCAR HIAPER aircraft and one on the NSF/NCAR C130.

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Funding for the fast-O_3 instrument development as part of the HIAPER Airborne Instrumentation Solicitation was granted by the National Science Foundation. Mechanics, engineers, and technicians at NCAR's Research Aviation Facility provided invaluable ideas and assistance with the design, development, and flight testing of the fast-O_3 instrument with respect to its implementation on the HIAPER and C130 aircraft. Helpful scientific discussions and insights were also provided by Donald Lenschow and Brian Ridley. The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under the sponsorship of the National Science Foundation.

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Appendix A.

In our laboratory's attempts to measure the frequency response of the ozone instrument with respect to a step change in O_3 concentration, an optical shutter was designed and built to create pulses of ozone in a piece of UV transmitting quartz tubing. The shutter housing contained a 6" long segment of ¼ od. quartz tubing and a Hg lamp operating at 254 nm. Small mixing ratios of ozone (roughly 10 ppbv) could be generated inside the quartz tube upon 254 nm photolysis of O_2 from a background source of zero air given the basic instrument's flow rate of 500 sccm. A flat sliding aluminum plate with a 2" long x 1 mm wide slit acted as a manual shutter. In theory, manually opening/closing the shutter should produce near-square pulses of O_3 in zero air if the shutter can be manually operated fast enough. The opening (rise) and closing (fall) time was measured by watching a photodiode's response to ambient room light on an oscilloscope as the shutter was manually slid open and closed. A series of measured pulses resulted in consistent 10-90% rise and fall times of ≤ 10 ms. *(*Ozone production from the Hg lamp occurs on a xx time scale and is thus very fast with respect to the instrument's expected frequency response and the open and close time of the shutter.*)* Despite our extensive efforts, a fast time response for the ozone instrument was never observed when pulses of O_3 in zero air were generated using this shutter apparatus.

Additional tests of the shutter apparatus were later performed in the laboratory by passing near-square pulses of ozone in zero air through the quartz tube of the shutter apparatus such that the quartz tube is positioned inline along the flow path. Neither the UV lamp nor the manual sliding shutter was operated during these tests. The near-square pulses were generated using the 3-way switching solenoid valve test method described above which was shown to result is a fast

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response through the basic instrument. With the shutter apparatus in the flow path, a significant increase in residence time was observed. A possible explanation could be ozone adsorption/desorption on the walls of the quartz tube. Slow uptake and release of ozone from the walls of the quartz tube would result in an effective mixing on the rising and falling edges of the square pulses. The overall result was a decrease in the time response of the pulses as they passed through the quartz tubing before entering the reaction vessel where the time response of the pulse is measured. In an attempt to overcome the effects of the quartz tube, a ¼" od. PFA tube was used in its place; however, there was not enough UV light transmission through the thin walled PFA tubing to produce sufficient amounts of ozone. In lieu of these attempts, the 3-way switching solenoid valve test method employed by Pearson {Pearson, 1990 #9} was found to be the best method for evaluating frequency response of the ozone instrument.

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REFERENCES

[Insert Reference List here]

Figure Legends

Figure 1. Instrument flow diagram. A pressure controller (P) downstream of the aircraft inlet and upstream of the two diaphragm pumps used to create the bypass flow. A metering valve (MV) and mass flow meter (F) are positioned respectively along the pick-off line to the fast-O_3 instrument just upstream of the reaction vessel (RV) and photomultiplier (PMT) assembly. An electronic transducer (T) is used to measure the pressure just downstream of the RV. Flow through the RV is generated a scroll pump (SP) and a pneumatic safety valve (SAF) and throttling pressure control valve (PC) allow automated control of pressure and flow through the RV. Diamond shaped reference markers (A and B) callout the two sites where the laboratory test method was employed for frequency response testing.

Figure 2. Time series plots of the observed O_3 square wave with the wave generator set at 0.25, 3.0, 5.0, and 10.0 Hz. Waveforms in this figure are representative of laboratory tests made when operating the instrument in its simplest inlet configuration with the test method placed at reference marker B, thereby capturing the frequency response through the reaction vessel within the basic instrument. A nearly square waveform is observed at frequencies ≤ 0.25 Hz. The inherent rise and fall time of the not perfectly square pulse start to distort the edges of the waveform at 3.0 Hz. At frequencies above 10.0 Hz, the pulse starts to exhibit a sinusoidal waveform with attenuation of the pulse amplitude as the combined rise and fall time begin to exceed the pulse period.

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Figure 3. Comparison of roll-off curves generated using the -3 dB attenuation, FFT, and rise time methods. The -3 dB attenuation method fit with a 3rd order polynomial (solid line through solid circles) reveals an instrument response of 8 Hz. The error bars reflect the average and 1 σ standard deviation of the maximum amplitude and baseline of five consecutive O_3 pulses that were obtained at each frequency from 1 to 20 Hz then propagated throughout the calculation of the normalized amplitude. Four curves illustrate the FFT method, and correspond to four different wave generator settings: 0.25 Hz (open diamonds), 1 Hz (open circles), 2 Hz (open triangles), and 3 Hz (open squares). The resulting frequency roll off to -3 dB is observed at 5.5, 6, 6, and 7.3 Hz, respectively, from the FFT analysis. The solid line through the open diamond symbols represents a 3rd order polynomial fit of the roll-off curve from the FFT method with the wave generator set to 0.25 Hz. The solid vertical line marks the frequency response determined from rise time measurements at 5.8 Hz, and the dashed horizontal line guides the eye to the -3 dB limit.

Figure 4. Power spectrum from FFT of the square wave generated in the laboratory with the test method positioned at reference marker B to capture the response of the basic O_3 instrument. The large feature at 0.25 Hz corresponds to the base square wave frequency set by the wave generator. The noise floor of the spectrum onsets beyond the 41st harmonic at 10.25 Hz.

Figure 5. A four minute window time series of a) humidity (gram/Kg), b) ambient air temperature (°C), c) ozone (ppbv), and d) altitude (km) measurements obtained during pre-PASE test flight (TF03, 20070731, 17:08:15-17:12:15 UTC). Several fast changes in O_3, humidity, and

air temperature were observed while ascending and descending in and out of the top of the boundary layer at a rate of ~1000 ft/min. The arrows point to a specific fast step change that is highlighted in Figure 8.

Figure 6. Expanded view (1.5 second window) of the time series in Figure 7 (TF03, 20070731, 17:00:23.5-17:00:25.0 UTC) to highlight a fast step-like change observed in all three measurements. The frequency response associated with this specific step-like change is ~5 Hz for all three variables. Humidity (a) and ambient air temperature (b) measurements were initially recorded at a 500 Hz sampling rate, but are reported and displayed here at 25 Hz. The ozone measurement (c) is recorded and displayed here at 200 Hz. Symbols have been overlaid on all plots as a 25 Hz reference.

Figure 7. Plot of O_3 power spectral density from airborne measurements obtained in the boundary layer near 1.7 km during pre-PASE test flight (TF03, 20070731, 17:03:06-17:05:33 UTC). A reference line with a -5/3 slope as well as an arrow marking a 5 Hz frequency response has been overlaid on the plot to guide the eye.

Figure 7-2. Plot of O_3 power spectral density from airborne measurements obtained in the boundary layer near 1.7 km during pre-PASE test flight (TF03, 20070731, 16:22:01-16:23:38 UTC). A reference line with a -5/3 slope as well as an arrow at 3 Hz marking the frequency at which the O_3 power spectrum intersects the asymptote of the instrument noise floor have been overlaid on the plot to guide the eye. The true frequency response of the instrument (expected to

be > 3 Hz from lab measurements) is buried within the noise floor in this spectrum since atmospheric changes in O3 mixing ratio are not big enough (not high enough power) above the S/N level of the instrument to determine true frequency roll-off.

Figure 7a. Plot of humidity (blue) and ambient air temperature (red) power spectral densities from the standard suite of aircraft sensors obtained in the boundary layer near 1.7 km during pre-PASE test flight (TF03, 20070731, 17:03:06-17:05:33 UTC). A reference line with a -5/3 slope as well as arrows marking 5 and 10 Hz frequency responses have been overlaid on the plot to guide the eye.

Figure 8. Cospectra of ozone with humidity (solid line) and ambient air temperature (dashed line) obtained from the same data segment as the power spectrum. Data taken in the boundary layer near 1.7 km during pre-PASE test flight (TF03, 20070731, 17:03:06-17:05:33 UTC). A reference line with a -7/3 slope as well as arrows marking 5 and 10 Hz frequency responses have been overlaid on the plot to guide the eye.

Figure 9. Calculated attenuation curves assuming square wave input (open circles) or pure sine wave input (open downward triangles). The observed frequency roll-off for the basic instrument using the -3 dB attenuation method of analysis and the corresponding 3rd order polynomial fit of the data points (solid line through solid circles) has been reproduced for comparison.

Extra Possible Figures:

Evaluation of the Frequency Response of a Chemiluminescence Ozone Sensor Developed for the NSF/NCAR Gulfstream-V Airborne Platform

Figure XX5. Compares plots of O_3 power spectral density from airborne measurements obtained in the boundary layer near 1.7 km during pre-PASE test flight TF03, 20070731 from 17:03:06-17:05:33 UTC (smoothed plot?) and 16:22:01-16:23:38 UTC.

Evaluation of the Frequency Response of a Chemiluminescence Ozone Sensor Developed for the NSF/NCAR Gulfstream-V Airborne Platform