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DOE/SC-ARM-TR-179

Ozone Monitor (OZONE) Instrument Handbook

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Revised April 2025

ARM

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Acronyms and Abbreviations

AAF	ARM Aerial Facility
AMF	ARM Mobile Facility
AMF1	first ARM Mobile Facility
AMF2	second ARM Mobile Facility
AMF3	third ARM Mobile Facility
AOS	Aerosol Observing System
ARM	Atmospheric Radiation Measurement
atm	atmosphere
BNL	Brookhaven National Laboratory
C	Celsius
cm	centimeter
diam	diameter
DOE	U.S. Department of Energy
DQPR	Data Quality Problem Report
DQR	Data Quality Report
ENA	Eastern North Atlantic
Hg	mercury
LPM	liters per minute
m	meter
mm	millimeter
NI	National Instruments
NIST	National Institute of Standards and Technology
nm	nanometer
NTP	Network Time Protocol
NYS DEC	New York State Department of Environmental Conservation
o.d.	outside diameter
PFA	perfluoroalkoxy
ppbv	parts per billion by volume
ppm	parts per million
RMS	root mean square
s	second
SGP	Southern Great Plains
UTC	Coordinated Universal Time
UV	ultraviolet
V	volt
VAC	volts alternating current

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Ozone (O_3) monitor

2.0 Mentor Contact Information

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4.0 Instrument Description

Thermo Fisher Scientific Ozone Analyzer instruments are deployed in the U.S. Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) Aerial Facility (AAF), the first ARM Mobile Facility (AMF1) Aerosol Observing System (AOS), the second ARM Mobil Facility (AMF2) AOS, the third ARM Mobil Facility (AMF3) AOS, the Southern Great Plains (SGP) atmospheric observatory, and Eastern North Atlantic (ENA).

Figure 1. Model 49i (AAF, AMF1, AMF2, AMF3, SGP, and ENA,) (from Ozone Manual).

The ozone monitor measures ozone based on the absorbance of ultraviolet (UV) light at a wavelength of 254 nm by ozone molecules. The absorbance is directly related to ozone concentration through the Beer-Lambert Law:

$$I/I_0 = e^{-KLC}$$

where:

K = molecular absorption coefficient, 308 cm^{-1} (at 0°C and 1 atmosphere)

L = length of cell, 38 cm

C = ozone concentration in parts per million (ppm)

I = UV light intensity of sample with ozone (sample gas)

I_o = UV light intensity of sample without ozone (reference gas)

This is a classical measurement technique for ozone measurement. The basic instrument configuration has remained the same for at least 20 years, with minor enhancements of electronics and the user interface. The dual cell configuration with selective removal of ozone in the reference cell reduces any response from interfering species. Following each 4-s measurement cycle, the reference and sample cells are reversed, so optical effects (change in lamp output, detector gain, cell cleanliness, etc.) are rejected.

In addition, the instrument contains an ozone source that can measure response stability over time.

External communication with the monitor is available through an ethernet port configured through the instrument network of the AOS systems. The Model 49i is part of the i-series of Thermo Scientific instruments. The i-series instruments are designed to interface with external computers through the proprietary Thermo Scientific iPort software. However, this software is somewhat cumbersome and inflexible. Brookhaven National Laboratory (BNL) has written an interface program in National Instruments (NI) LabView that both controls the Model 49i monitor AND queries the unit for all measurement and housekeeping data. The LabView vi (the software program written by BNL) ingests all raw data from the instrument and outputs raw data files in a uniform data format similar to other instruments in the AOS and described more fully in Section 6.0 below.

Modifications for the instrument include:

1. Addition of a 47-mm x 5-µm Teflon filter on the inlet line.
2. Internal plumbing changes to allow filtered (to remove ozone) ambient air to be used in the photolysis cell (ozone source) for periodic, automatic span checks.

5.0 Measurements Taken

The primary measurement output from the Thermo Scientific Ozone Analyzer is the concentration of the analyte (O_3) reported at 1-s resolution in units of ppbv in ambient air. Note that because of internal pneumatic switching limitations, the instrument only makes an independent measurement every 4 seconds. Thus, the same concentration number is repeated roughly four times at the uniform, monotonic 1-s time base used in the AOS systems. Accompanying instrument outputs include sample temperatures, flows, chamber pressure, lamp intensities, and a multiplicity of housekeeping information. There is also a field for operator comments made at any time while data is being collected.

6.0 Links to Definitions and Relevant Information

6.1 Data Object Description

6.1.1 Raw Data

The ‘raw’ instrument data stream outputs include all parameters measured by the instrument. Metadata are included automatically in each hourly file.

The metadata are:

Row 1:	Filename
Row 4 (col 1 only):	ARM Climate Research Facility

Row 5:	SitePlatform
Row 7:	Last revised date
Row 9:	Instrument
Row 10:	Instrument Serial Number/ARM Inventory Number (WD#)
Row 13:	Instrument Mentor/Affiliation
Rows 14-19:	Comments (operational conditions, calibrations, etc.)
Rows 21-24:	Constants (usually defined in Comments)
Row 35:	Column title
Row 36:	Column units line 1
Row 37:	Column units line 2
Row 40:	First row of data

Data fields in the raw output begin on Row 40 and are:

Date Time	Primary Date/Time stamp yyyy-mm-dd hh:mm:ss as set by the instrument computer and referenced to the site NTP server (or if unavailable, linked to the 'master' computer in the AOS)
Inst. Time	Time set on the internal instrument computer hh:mm:ss. This should be equal to the primary Date/Time, but can vary if the operator has not set the instrument time. This value is usually discarded.
Inst. Date	Date set on the internal instrument computer mm-dd-yyyy. Note that this is not a standard format. This value should be equal to the primary Date/Time, but can vary if the operator has not set the instrument time. This value is usually discarded.
Flags	%hhhhhhhh (eight hexadecimal digits) showing the state of the instrument. The meaning of individual flags is described in Figure B-1 of the vendor manual, shown here:

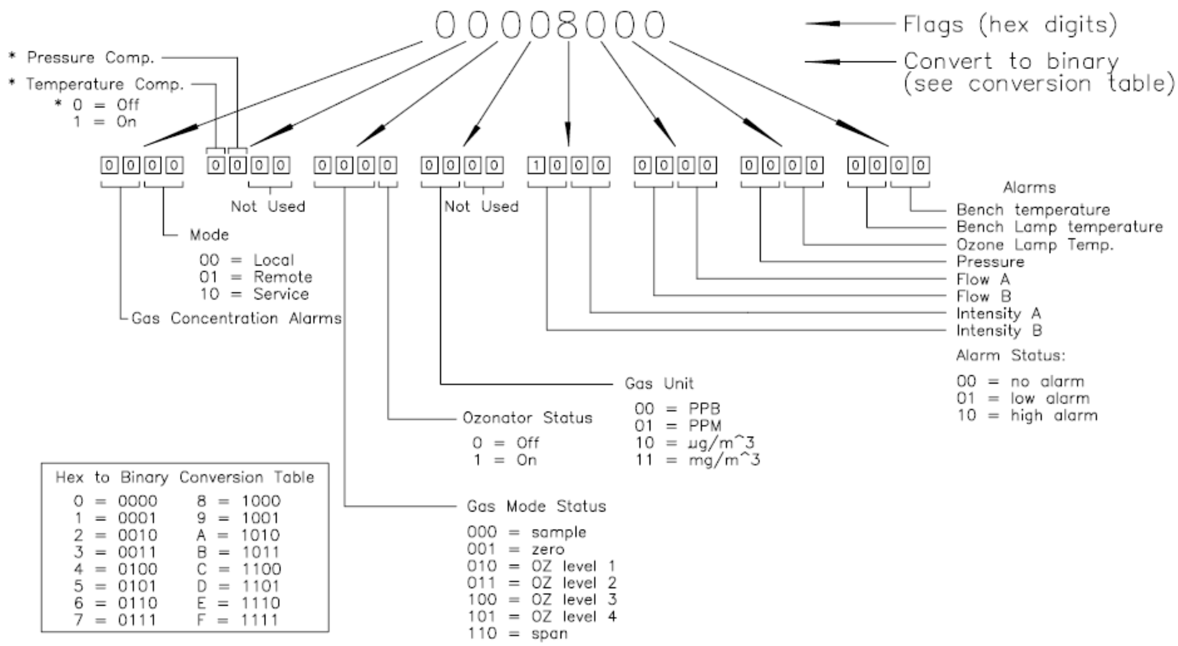

Figure 2. Bit-by-bit meaning of status flag.

O3	Mixing ratio (in ppbv) of ozone corrected to STP (O°C, 1 atm) based on instrument measurement of temperature and pressure.
Pres	Pressure inside the measurement cell (mm Hg).
Bench Temp	Temperature (°C) of the measurement cell. The bench is temperature-controlled by a heater in a feedback loop.
O3 Lamp Temp	Temperature (°C) of the ozone lamp (the lamp used to measure ozone, NOT the other lamp used to generate calibration gas. The lamp block is temperature-controlled by a heater in a feedback loop.
Flow A	Flow through cell A (SLPM). This flow is not calibrated. It is useful to indicate a dirty or blocked inlet filter.
Flow B	Flow through cell B (SLPM). This flow is not calibrated. It is useful to indicate a dirty or blocked inlet filter.
Noise A	Electronic noise in channel A. This value is normally < 10. Excess values can indicate the need to clean the cell or replace the lamp.
Noise B	Electronic noise in channel B. This value is normally < 10. Excess values can indicate the need to clean the cell or replace the lamp.

Avg Time	Time in seconds that gas flows through the reference and sample cells before switching the cells. If the instrument is set for fast response (default for AOS systems), the value reported is 2.5X the actual averaging time. Thus, all measurements in AOS systems are reported as 10 s when the averaging time is actually 4 s.
Cell A Int	The raw detector value in Hz. This is a measurement of lamp throughput for the system. When the Intensity goes below ~60,000, the lamp voltage must be increased or the lamp replaced.
Cell B Int	Same as Cell A Int except for Cell B.
Lamp temp	Temperature (ºC) for the ozonizer lamp. This temperature is controlled in a feedback loop.
Lamp Volt Bench	Control voltage driving the main (analytical lamp)
Lamp Volt OZ	Control voltage driving the ozonizer (calibration lamp)
Range	This controls the analog output and is not germane to the digital recording.
Lamp	Percentage setting of the ozonizer lamp. It should not be changed.
O3 Coef	A nominal slope coefficient to the nominal ozone value to a calibrated ozone value. This coefficient should not be changed. Calibrations are done relative to the ‘nominal’ ozone signal output.
O3 Bkg	A nominal offset to the nominal ozone value to a calibrated ozone value. This offset should not be changed. Calibrations are done relative to the ‘nominal’ ozone signal output.
Diag Volt mb 24	Diagnostic point for the 24V PS on the motherboard
Diag Volt mb 15	Diagnostic point for the 15V PS on the motherboard
Diag Volt mb 5	Diagnostic point for the 5V PS on the motherboard
Diag Volt mb 3.3	Diagnostic point for the 3.3V PS on the motherboard
Diag Volt mb -3.3	Diagnostic point for the -3.3V PS on the motherboard
Diag Volt mib 24	Diagnostic point for the 24V PS on the measurement interface board
Diag Volt mib 15	Diagnostic point for the 15V PS on the measurement interface board
Diag Volt mib -15	Diagnostic point for the -15V PS on the measurement interface board
Diag Volt mib 5	Diagnostic point for the 5V PS on the measurement interface board

Diag Volt mib 3.3	Diagnostic point for the 3.3V PS on the measurement interface board
L1 – L5	These are levels (in %) to drive the calibration lamp during span checks. These values were set after calibration against the New York State DEC calibration of the individual instruments.
Pres Comp should be on	On/Off Flag to determine whether pressure compensation is applied. This flag
Temp Comp	On/Off Flag to determine whether pressure compensation is applied. This flag should be on
OZ Status	On/Off Flag to determine the ozonizer status
Gas Units	Units of measurement. It should always be ppb
Gas Status	Instrument output. Sample, Zero, Levels 1-5
Comment	This field is the last field in the data stream. It allows operators to enter free-form text from the graphical user interface at any time. Operational notes or disruptions may be entered here.

These data are saved unaltered from what is produced by the instrument. Processing of the raw data must be able to deal with more than 1 record per second and time periods with either no data or only a date/time stamp in the record. If the instrument does not put out a number, the instrument computer can include a record of empty fields. Since neither the instrument clock nor the instrument computer clock are perfect, minor irregularities (dithering) in the output data stream can occur.

The raw data is processed by the ARM. The processed data files include information such as the site, platform (Aerosol Observing System or Aerosol and Cloud and Precipitation Spectrometer), subsite (m1 or s1), species measured (CO), and processing level (a1 or b1). At the "a" level of processing, data are typically ingested hourly and added to output NetCDF files. These files are then split daily at midnight UTC. Data quality officers (DQO) perform the first quality control (QC), which includes comparison, persistence, standard deviation, and flow rate tests. At the "b" level, a1-level data undergoes further processing. This involves applying instrument calibration data and correction factors provided by mentors. It's important to note that spans and zeros are NOT removed from the data streams, and users should be aware of this when utilizing the data for analysis. The instrument's primary measurement of the mixing volume of O3 in ambient air has no water vapor correction.

6.2 Data Ordering

Ozone data collected are distributed through the ARM Data Discovery or can be ordered from https://www.arm.gov/capabilities/instruments/ozone. Data are organized by campaign or site.

6.3 Data Plots

The mentor provides monthly data plots of raw, housekeeping, and final data sets. Typical plots, with explanations, are shown below.

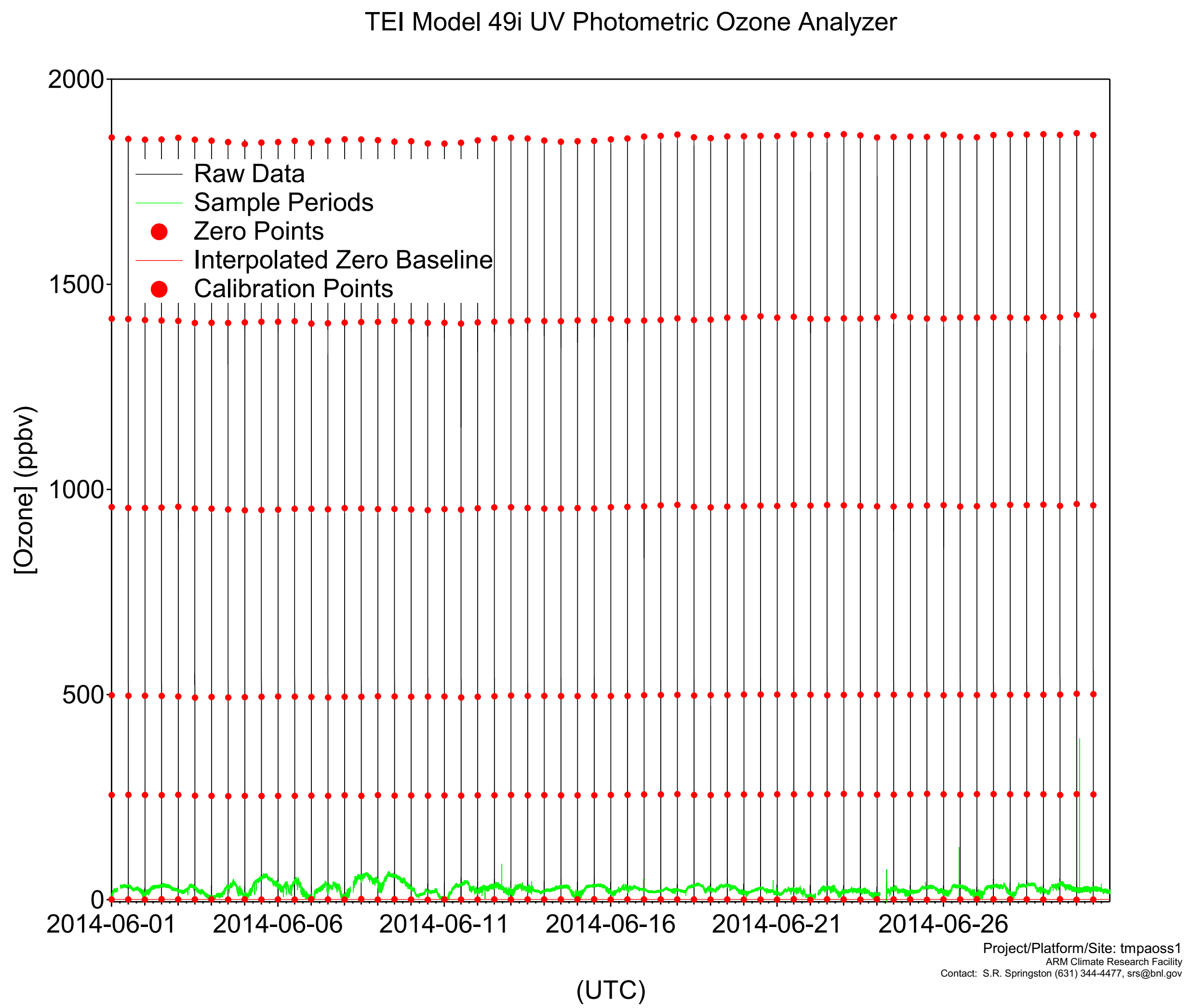

Figure 3. Raw ozone data for one month.

The raw data plot shows all signal data recorded from the instrument. Processing software is used to parse the data into sampling and zero/calibration periods. Every midnight and noon (00:00:00 and 12:00:00 and last for four [4] minutes), the instrument goes into an automatic zero and span check. A blow-up of one of these periods is shown here:

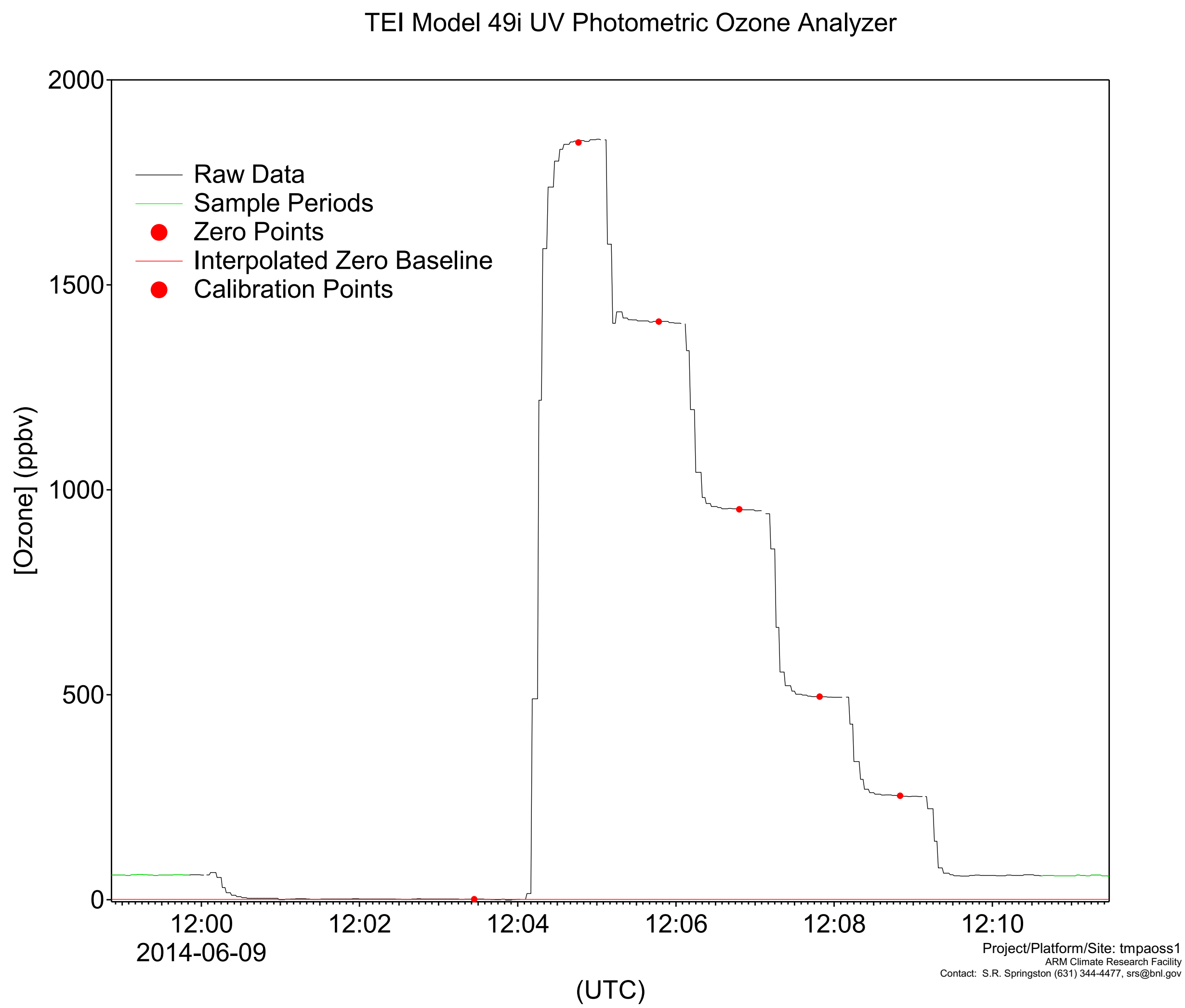

Figure 4. Typical zero, span check.

Sample periods are automatically delineated with time allowed for measurements to re-stabilize. The centroids (numerical averages) of zeros and span checks are shown by the red circles.

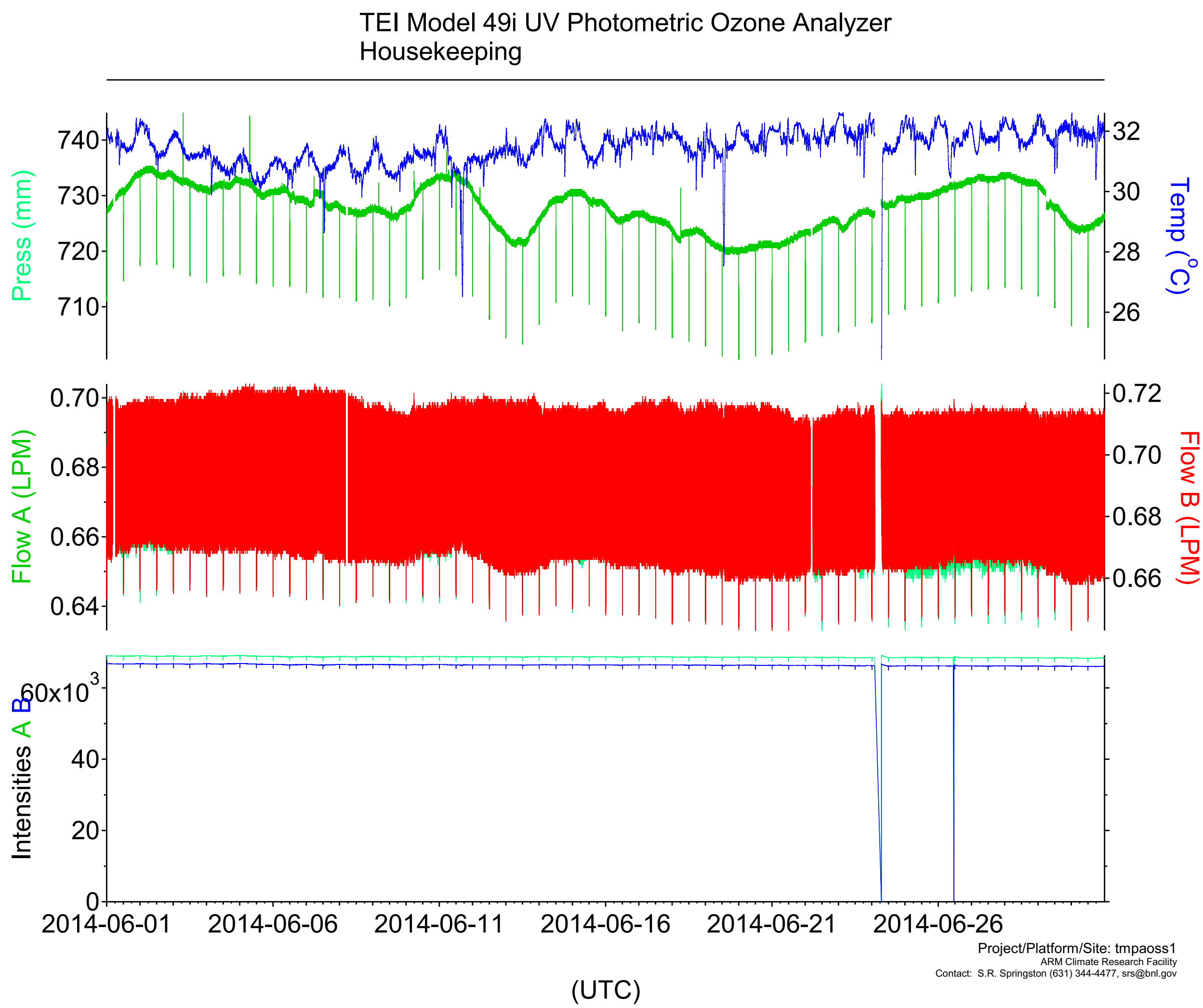

Figure 5. Housekeeping data for one month.

The sample cell pressure and temperature are shown in the top panel. These values are used internally by the instrument to report ozone concentrations at STP (1 atm, 0ºC). The twice-daily negative spikes in pressure are momentary and due to flow interruptions proximate to the zero/span checks. The flows in the two cells are shown in the middle panel. While this technique is fundamentally a concentration-sensitive detector (independent of flow rate), the flows affect the ozone concentration generated for the span checks. The raw lamp intensities for the two channels are shown in the bottom panel. When these decrease below 60,000 Hz, the lamp intensity is raised by the mentor to 110-120,000 Hz. (Intensity does not affect the instrument response).

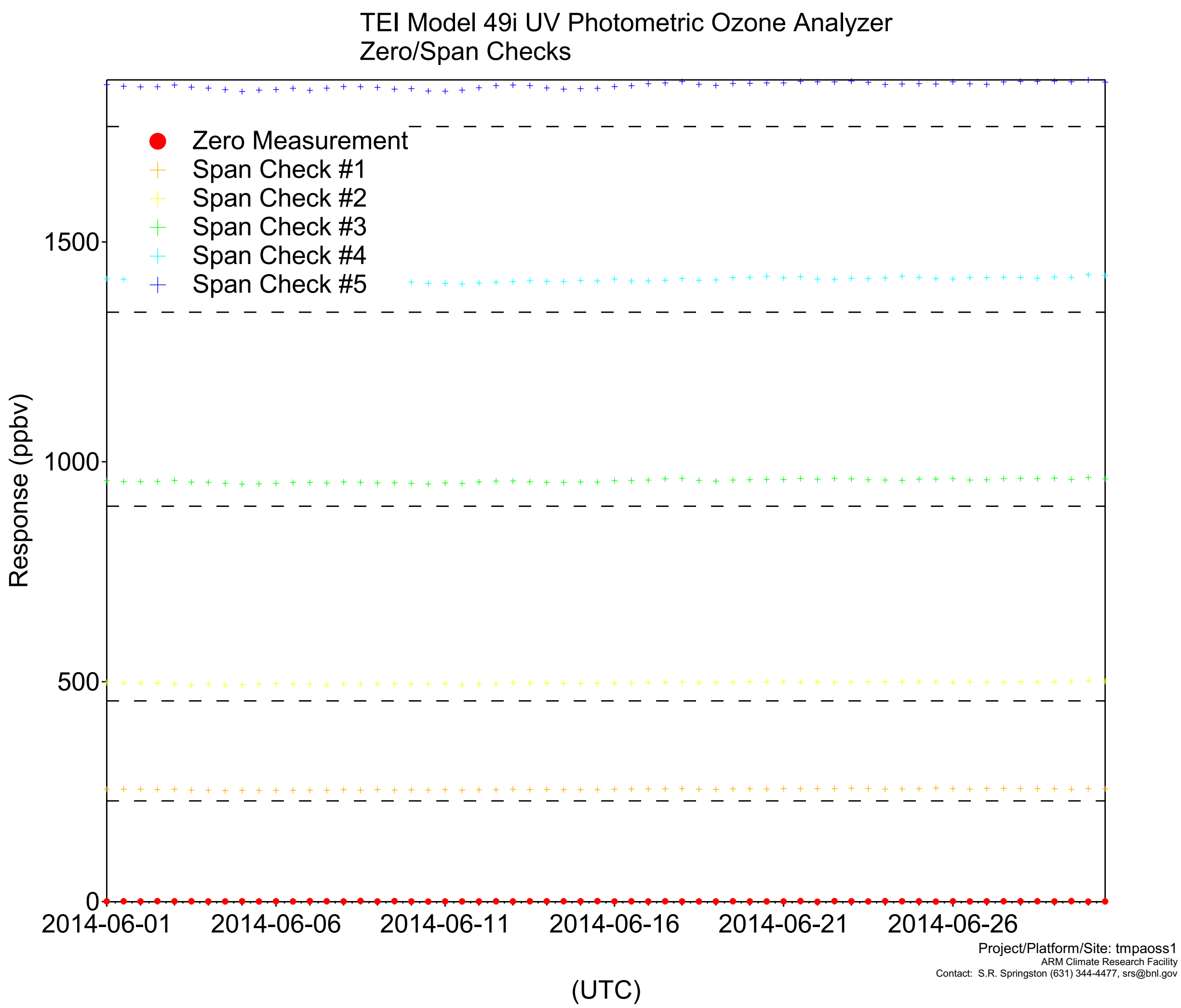

Figure 6. Zero and span check stability over one month.

A one-month record of zero and span checks is shown above. The dotted lines are the responses for the five span checks measured at the New York State Department of Environmental Conservation (NYS DEC) standards laboratory after receipt of the instrument. The difference between the measured span and the calibrated span value is usually less than 5%. This difference is judged to be instability and drift in the photolysis lamp and NOT in the measurement cell. Drift in the span response is monitored over long periods (> 1 year) and drifts of more than 5% indicate need for recalibration at the NYS DEC laboratory.

Finally, a plot is produced of the entire month (and also weekly plots) of the reported, ambient ozone concentrations adjusted for any baseline drift.

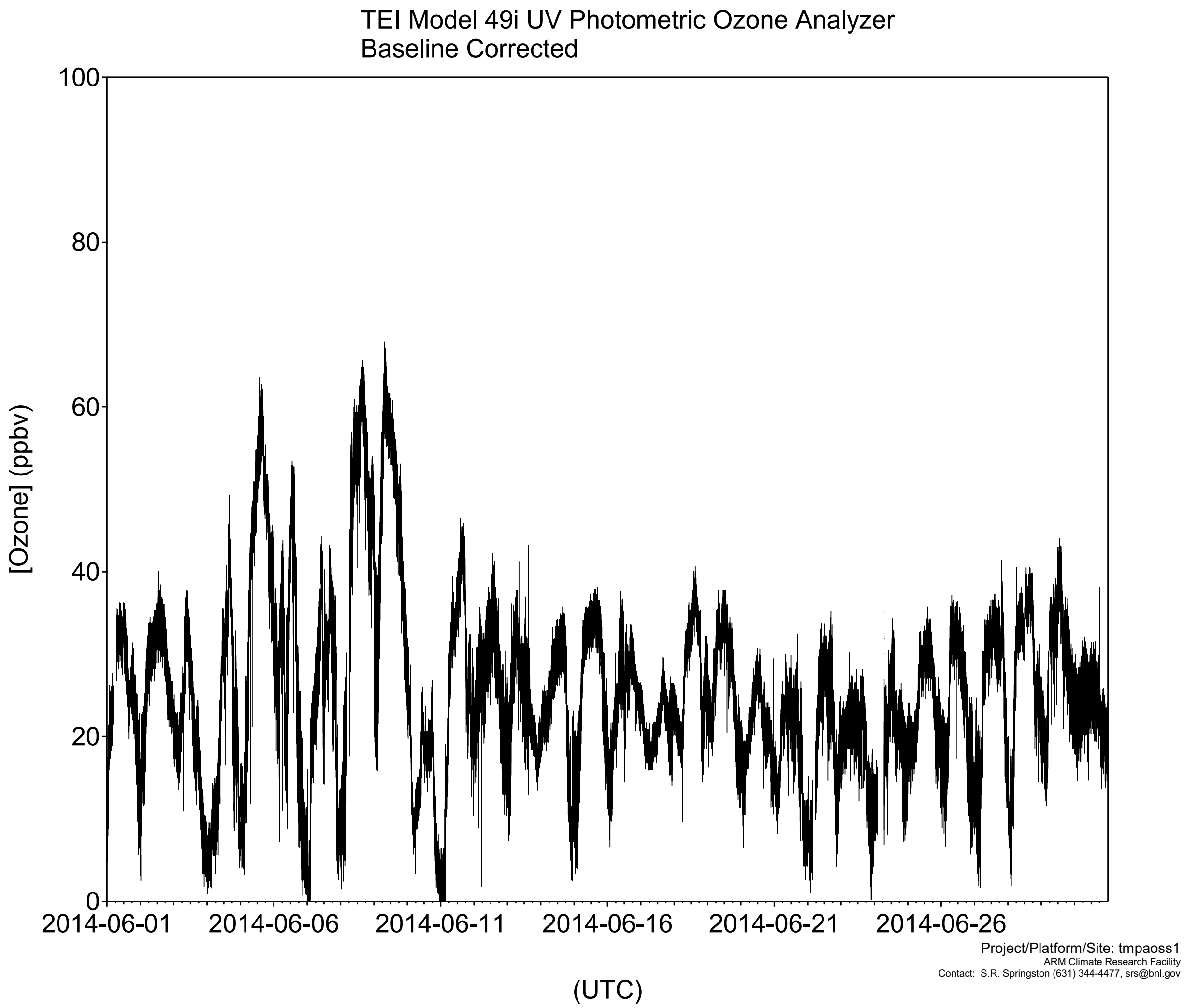

Figure 7. Processed data for one month.

This plot shows a typical month's ambient data record. Since ambient ozone is predominantly produced by photochemistry, a diurnal pattern is (usually) present. Night-time ozone removal occurs by dry deposition, dilution, and reaction with other trace gases.

6.4 Data Quality

The first level of data quality is automatic flagging of data when instrument changes states during zero and span checks. Normally, this eliminates the first 105 seconds after the zero is actuated and then the first 30 seconds after each span level. The 'centroid' of each state is taken as an average of ~30 seconds once a stable level has been achieved.

The second level of data quality is inspection of the 2X daily zeros and span checks. A time series plot over the course of the month typically shows <1-2% relative standard deviation and minimal drift (<2%). Values greater than this indicate the need for instrument recalibration at the NYS DEC. (At present, there is no capability within ARM to deliver a calibration source for ozone to remote field sites.)

Instrument flow rates do not directly affect the instrument response but do affect the span check values. Under normal operation, two factors can change the instrument flow rate: dirt accumulation on the inlet filter or degradation of the internal diaphragm pump. Given the two-week filter change schedule, dirt accumulation is not observed to reduce flow. Pump life under continuous operation is 2-3 years.

The third level of data quality and assessment deals with visual inspection of the output data stream.

Periods of instrument in-operation are identified and flagged. Either instrument failure or inlet failure causes such periods. In some cases, operators note occurrences, but more often, it is up to the mentor to recognize nonsensical values and determine the cause(s). The complete recording of all instruments and inlet housekeeping aids in this diagnosis. Except for pump/inlet failures and several instances where the inlet filter was replaced with an impermeable spacer (documented below), mentors have not experienced any pattern of failures that could be algorithmically identified. Failures, their identification and remedy, and the mentor write-up in the DQPR/DQR system tend to be unique individual events.

One phenomenon requiring visual inspection involves short aberrations in the output signal. These are primarily of 4-s duration (one measurement cycle) and can be positive or negative. Because of the mixing ratio in the inlet, sample lines, and instrument dead volume, a step function on this time scale is nonsensical. However, a 20-40 ppbv spike can dramatically affect daily max/min readings. So, these excursions are flagged for deletion. Note that these instrumental spikes are visually quite distinguishable from negative peaks of 30-s to 10-min duration from local internal combustion sources that produce nitric oxide (NO), which titrates (reduces) the local ambient ozone. Note that negative peaks from titration represent real changes in the ambient ozone concentration and are not flagged. Distinguishing ambient (negative) ozone spikes from spurious instrumental spikes requires a certain amount of experience and judgment. Local sources can, in some instances, be identified by referring to the wind direction measured at the point of sampling. HOWEVER, the identification of local interference is quite subjective.

6.5 Calibration Database

The Thermo Scientific ozone monitors are calibrated for response upon receipt from the manufacturer. This is done by the mentor at the NYS DEC testing laboratory in Albany, NY. These results are tabulated by the mentor and shared with ingest after cross-reference measurements are completed in Albany and/or before a campaign starts. The DEC reference standard is used only for calibration of ozone instruments and is certified by the U.S. Environmental Protection Agency with a National Institute of Standards and Technology (NIST)-traceable reference.

7.0 Technical Specification

7.1 Units

The measured quantity of interest is the mixing volume of the analyte. This is reported in units of parts per million (ppm) by the instrument.

7.2 Range

The full range of this model is somewhat arbitrary. It extends well past conceivable ambient levels. Linearity up to 1500 ppbv is demonstrated with the automatic span checks done twice daily. The zero baseline is assessed in two ways. First, the instrument cycles alternately between reference and sample cells with valving. The only difference is the removal of ambient ozone by a proprietary catalyst (presumably a Hopcalite-type substance that is a mixture of copper and manganese oxides). Second, the zero level is further checked twice daily with a charcoal removal catalyst. All zero and span checks are done through the ambient inlet filter, so should buildup on the filter cause ozone destruction, it would be obvious in the span checks.

7.3 Accuracy

Calibrations are done 2 x daily, with an internal zero and 5-level span checks. These reveal short-term (daily) and long-term (annual) drifts. HOWEVER, the stability of the span check source itself is known to be inferior to the stability of the absorbance photometer. After instruments are received from the manufacturer, the internal calibration is checked against the NYS DEC standard. At the same time, the internal span source is also checked. The initial (on receipt) calibration is within 1-2% accuracy. However, field conditions vary substantially. Variation from the original measurement standard would appear to be ~5%.

7.4 Repeatability

Precision (repeatability) is given here as the noise of the 1-s signal (which is actually a 4-s measurement). Under quiet ambient conditions, this has been measured as:

[O_3] σ = 2 ppbv

Therefore, for normally distributed noise, $\pm 2\sigma$ encompasses 95% of the points. The precision of the instrument under average ambient conditions is then given as:

[O_3] 95% Confidence Interval = ± 4 ppbv

Note that these Confidence Intervals represent repeatability over a relatively short period of time. Day-to-day and month-to-month repeatability has a larger confidence interval and approaches the accuracy uncertainties given in the previous section. The manufacturer reports zero noise as 0.25 ppb RMS (for a 60-s average), which is slightly better (smaller) than the values observed under field conditions and reported above.

7.5 Sensitivity

Sensitivity as a lower detectable limit is reported as 95% confidence interval above baseline, which in this case would be 4 ppbv for data as reported to ARM (1 value per second, but each value represents 4 repetitive reports of a 4-s integration time). Assuming the noise decreases inversely with the square of the integration time, the measurement sensitivity under field conditions is similar to the 1.0 ppb 'Lower detectable limit' reported by the manufacturer.

7.6 Uncertainty

Uncertainty is an integral of all errors. It is a combined measurement of accuracy and precision (repeatability) discussed above.

7.7 Output Values

Described in Section 6.0.

8.0 Instrument System Functional Diagram

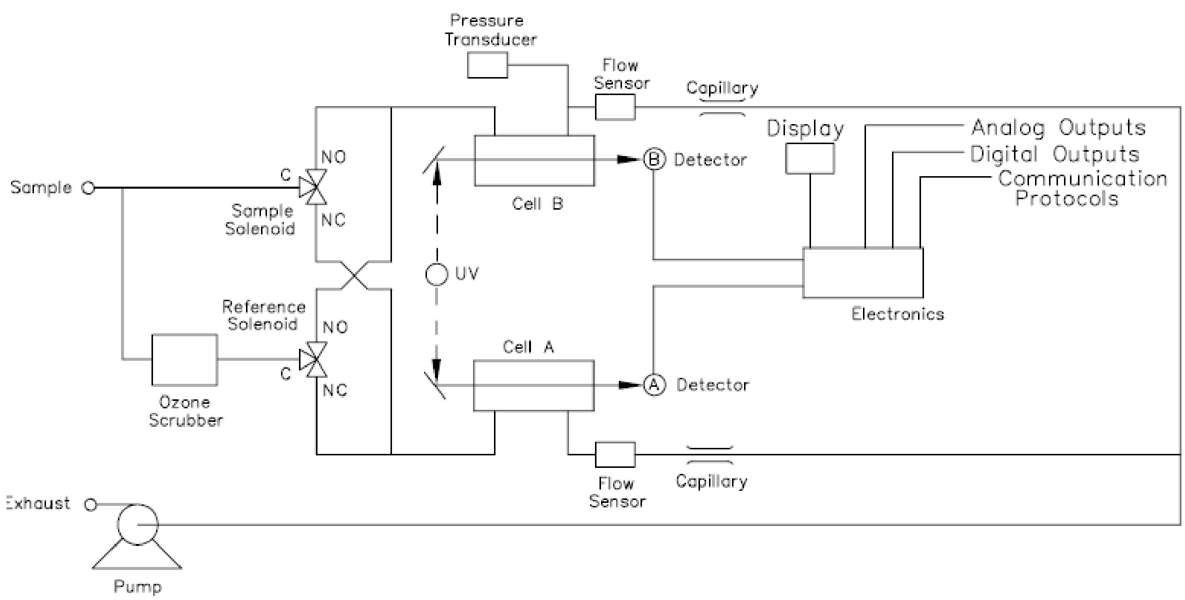

Figure 8. Diagram of flow schematic (from Thermo Scientific manual).

Based on experience, the ozone monitor is modified upon receipt. These changes are shown here:

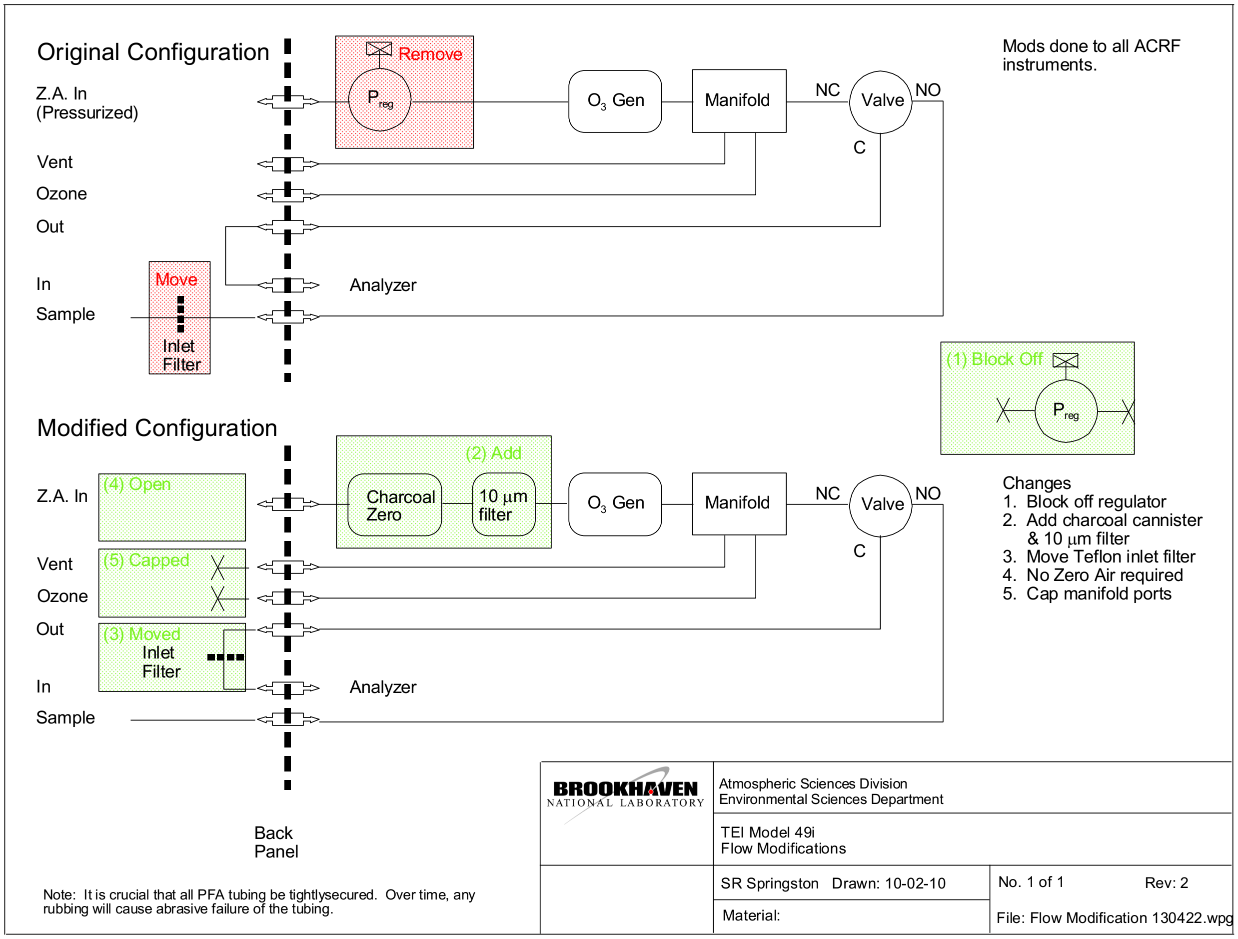

Figure 9. Modifications to the TEI Model 49i by the mentor.

Red boxes indicate components that are removed, and green boxes indicate components added. The original (as received) configuration is shown in the top and the current configuration is shown in the bottom panel. The changes are summarized as follows:

1. The 5-µm Teflon filter (47-mm diam) is moved so that ambient sample AND zeros/spans go through the same flow stream (as recommended by the manufacturer).
2. Instead of supplying zero air to the ozone span generator, the instrument pump draws ambient air through a zeroing charcoal canister and metal filter. This means that the pressure in the ozone generator varies with atmospheric pressure and the output concentration can vary (since it is a function of both pressure and residence time, the variation is with the inverse square of the ambient pressure). However, the supplied pressure regulator only supplies consistent gauge pressure, not absolute pressure and the effect is similar.

The trace-gas inlet used in the AOS systems consists of a high-flow ½” o.d. PFA tubing sampling from under the aerosol inlet rain hat at ~10-m above ground level. Air is pulled into the container at 30 LPM as controlled by a rotometer. The residence time to the back of the instrument is ~1-2 s.

9.0 Instrument/Measurement Theory

The following description is taken from the Thermo Scientific manual:

"The sample is drawn into the Model 49i through the sample bulkhead and is split into two gas streams, as shown in Figure 9. One gas stream flows through an ozone scrubber to become the reference gas (Io). The reference gas then flows to the reference solenoid valve. The sample gas (I) flows directly to the sample solenoid valve. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A contains reference gas, cell B contains sample gas and vice versa. The UV light intensities of each cell are measured by detectors A and B. When the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for several seconds to allow the cells to be flushed. The Model 49i calculates the ozone concentration for each cell and outputs the average concentration to the front panel display, the analog outputs, and also makes the data available over the serial or ethernet connection."

10.0 Setup and Operation of Instrument

The instrument is permanently installed in the AOS systems. This includes:

1. Physical mounting of the instrument in a shock-isolated 19" instrument rack,
2. Plumbing of the sample line into the fast flow ½" PFA trace gas manifold line with the associated 47-mm PFA filter and filter holder,
3. Connection of the RJ-45 ethernet output to the AOS Instrument Network switch, and
4. Connection of the 110 VAC power line to the appropriate Power Distribution Unit outlet.

Initialization involves only making sure the ½" PFA trace gas manifold line runs up the aerosol stack to under the 14" rain hat and turning on the power.

After power is turned on, the instrument goes through self-checks and commences putting out data. Note that after an extended shutdown, this warm-up period can be 10 minutes or more.

11.0 Software

Instrument control and data acquisition is performed by NI LabView-based software written by Brookhaven National Laboratory.

12.0 Calibration

Calibration procedures are described earlier. These include 2X daily zero and span checks.

13.0 Maintenance

Maintenance is minimal on this instrument. The mentor advises changing the inlet particle filter every two weeks. The filter is a 47-mm diam. 5-µm PFA membrane filter Type LS (Millipore Catalog #

LSWPO4700). Note that the filter is not directional (either side up). The filter is white and is packed in a stack separated by blue plastic spacers. DO NOT USE THE SPACER! USE THE WHITE FILTER. (This error has been made multiple times.)

Figure 10. 47-mm PFA filter holder.

Figure 11. 47-mm filter holder wrenches.

The green filter holder wrenches were delivered with the instrument. One end goes over the orange locking ring and the other (smaller) end goes over the PFA body. When opening the holder note (and report), check if the previous filter appears damaged. The filter being replaced should have, at most, a faint circle of trapped dirt. If the circle is visibly dark, increase the change frequency and notify the mentor.

The ¼" PFA fittings on the ends of the filter have an integral ferrule in the nut (no separate ferrule needed). These are finger-tightened but should be quite snug on the ¼" PFA tubing.

The old filter may be disposed of in regular garbage.

14.0 Safety

This unit has no safety concerns during normal operation. The unit has separate mercury PenRay lamps in the photometer and the ozone span source. Both lamps emit light at 254 nm and should not be viewed directly. The internal instrument pump has an exposed shaft that drives the diaphragm on one end and a hard plastic fan on the other end. Both sides are open inside of the enclosure and pose a hazard to fingers. Older versions of this instrument had exposed electrical terminals on the pump motor. The current ARM version does not seem to have any exposed terminals with 110 VAC, but normal electrical procedures and cautions should be used. The instrument should not be operated with the cover off without proper training, precautions, and approvals.

It has been observed that the PFA tubing inside the instrument can abrade even when rubbing against another PFA tube. Thus, all tubing must be strain-relieved (with tie wraps) to prevent any rubbing.

15.0 Citable References

N/A

www.arm.gov

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