NOxy OPERATION MANUAL

Two-channel Snooper

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TABLE OF CONTENTS

Section **Page**

1. GENERAL SYSTEM DESCRIPTION

1.1 THEORY OF OPERATION

The detection mechanism for the measurement system involves the oxidation of NO (nitric oxide) by an excess of O_3 (ozone).

$$NO + O_3 \rightarrow NO_2^* + O_2.$$

The chemiluminescence from the relaxation of the electronically excited NO_2 (nitrogen dioxide) is measured with a photomultiplier tube. The background signal, which arises from a variety of sources, is accounted for by using a pre-reactor volume. The difference in signal observed between the measure mode (ozone added to the reaction volume) and the zero mode (ozone added to the pre-reaction volume) is proportional to the NO concentration in the air. In this way the concentration of NO can be measured directly. The concentration of NO_2 is determined by first converting the NO_2 to NO photolytically using LED lamps, followed by chemiluminescence as described above. The concentration of NOy is measured using a heated molybdenum catalyst to reduce NOx, HNO_3, organic nitrates, etc., to NO.

1.2 SYSTEM DESCRIPTION

The NOxy system is comprised of six separate components, including the NO snooper, an ozonizer, a calibration/control box, an inlet instrument, a pure air generator, and a data acquisition computer. In addition there is an external vacuum pump for the system. The NO detector, data system, calibration box, ozonizer, and pure air generator are housed in a 19-inch rack along with a main power distribution box. The vacuum pump and inlet instrument are external to the rack. An overview photograph of the system identifying the major components is shown in **Figure 1**.

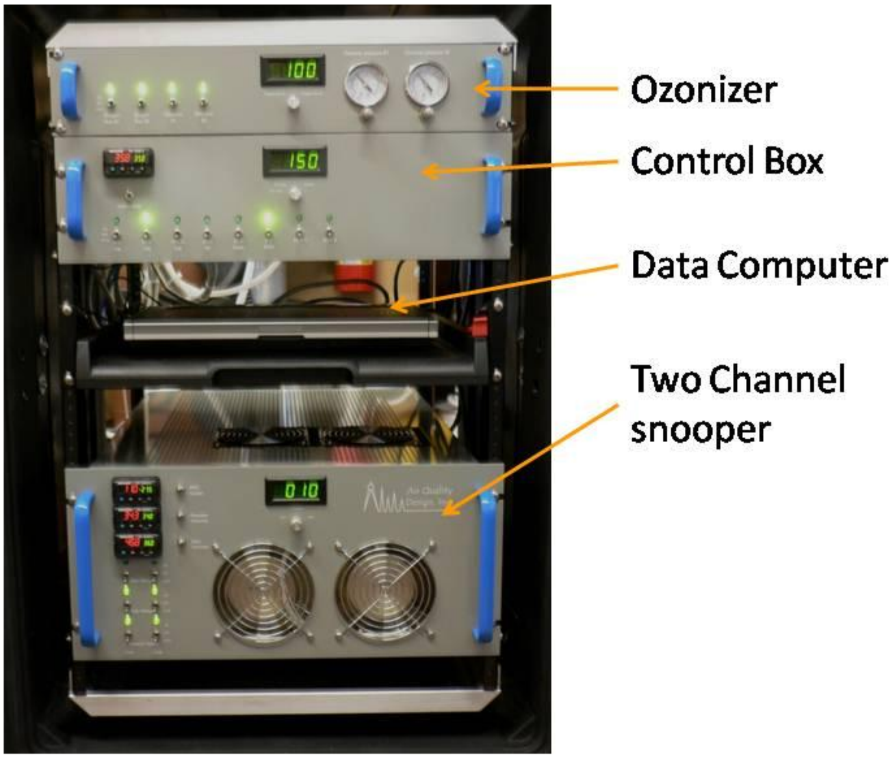


Figure 1. Photograph of the NOxy system.

A description of the different system components is presented in Sections 1.2.1 through 1.2.4.

1.2.1 INLET BOX

The inlet box includes calibration and zero air valves, the NO_2 and NOy converters, and the sample mass flow controllers. A photograph of the sample inlet is shown in **Figure 2**.

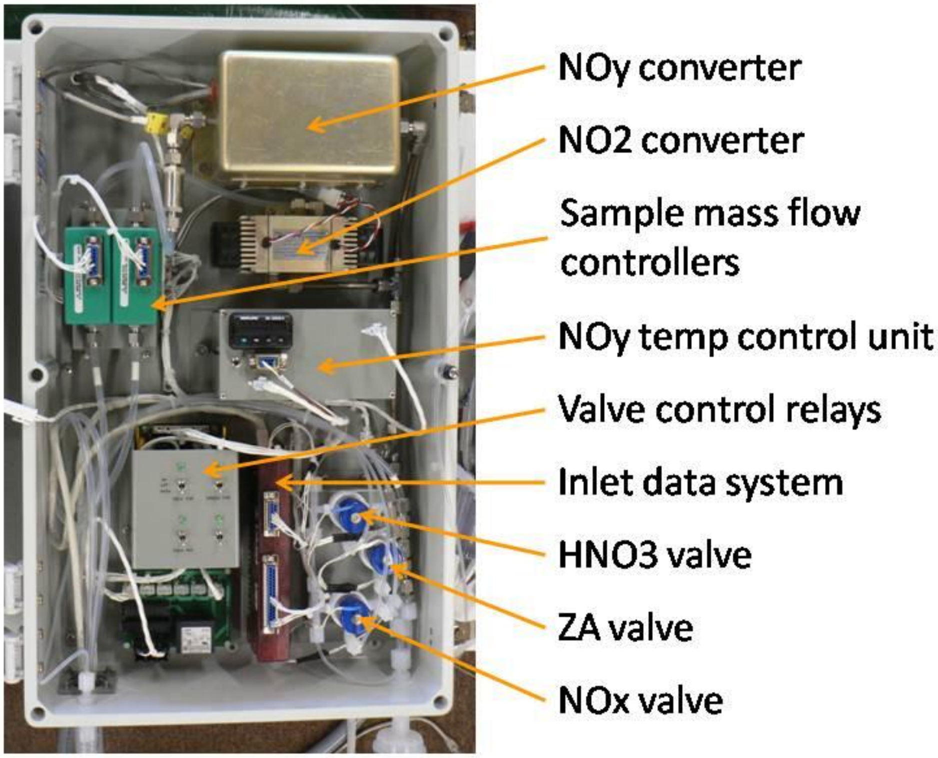


Figure 2. Photograph of the NOxy inlet box.

CALIBRATION VALVES

There is one calibration valve for NO and NO_2 and one calibration valve for HNO_3 on the inlet panel that serves both channels. The NO_2 titration lamp (located in the calibration box) is switched on in order to achieve the NO_2 cals, and is left off for the NO calibrations. The zero air valve allows zero air displacement calibrations and zero air artifact tests.

PHOTOLYTIC NO_2 CONVERTER

The photolytic NO_2 converter is a Blue-Light-Converter (BLC) manufactured by Air Quality Design, Inc.

MOLYBDENUM NOY CONVERTER

The molybdenum NOy converter is a manufactured by Thermo Environmental, Inc..

MASS FLOW CONTROLLERS

There is one mass flow controller in the inlet that regulates the sample flow rate through the Snooper. The mass flow controller is manufactured by Pneucleus. A separate manual for this instrument is attached as an appendix to this manual.

DAQ SYSTEM

The inlet instrument includes a LabJack UE9 DAQ device to control the various inlet valves. The device is connected via Ethernet to the system computer. A plumbing diagram for the inlet instrument is shown in **Figure 3.**

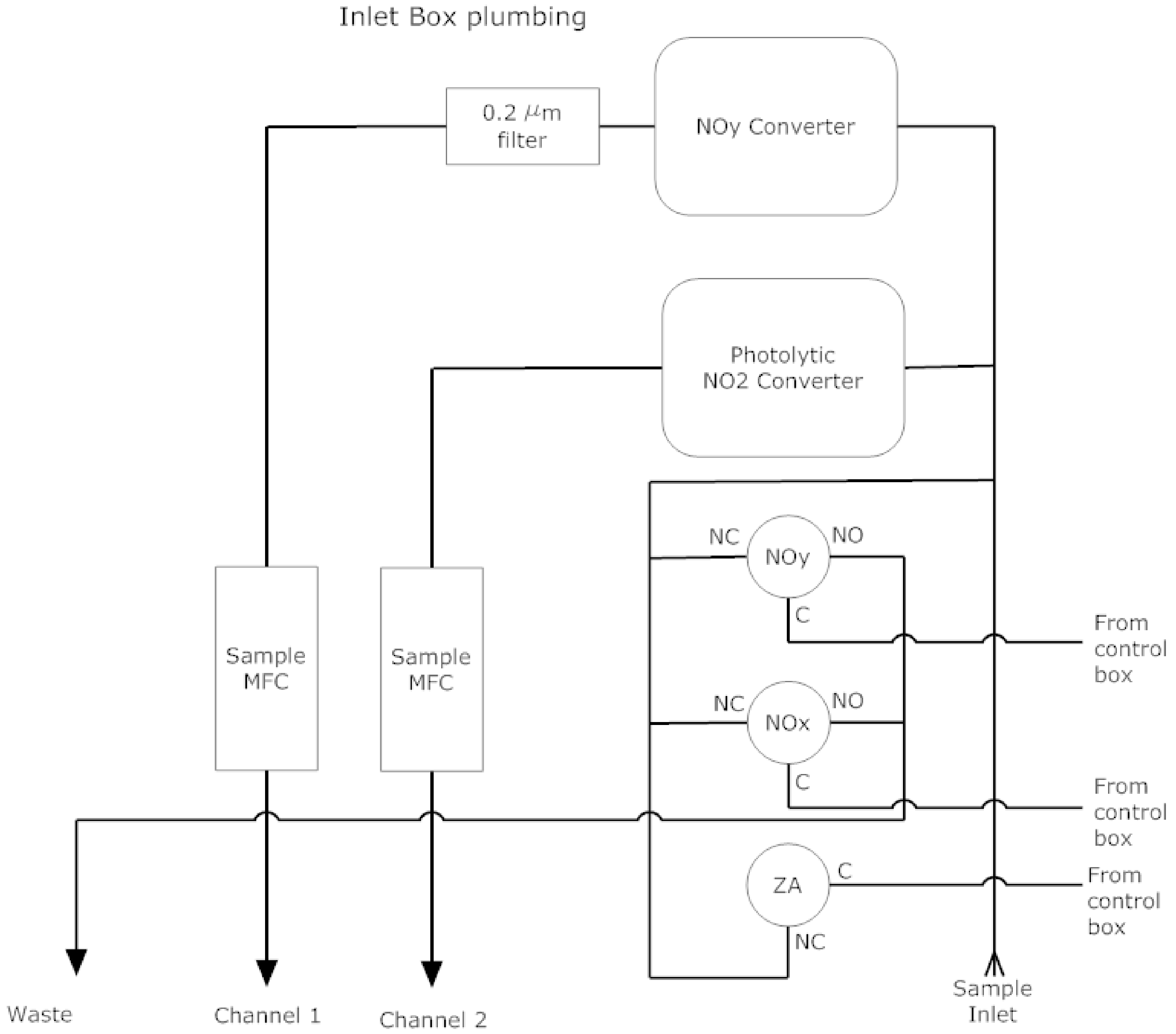


Figure 3. Plumbing diagram for the NOxy inlet.

1.2.2 CALIBRATION/CONTROL INSTRUMENT

The calibration/control instrument includes the mass flow controller for the NO calibration gas, a temperature controller for the HNO_3 permeation tube, the gas phase titration cell, and front panel controls for the inlet valves. A photograph of the control box is shown in **Figure 4**.

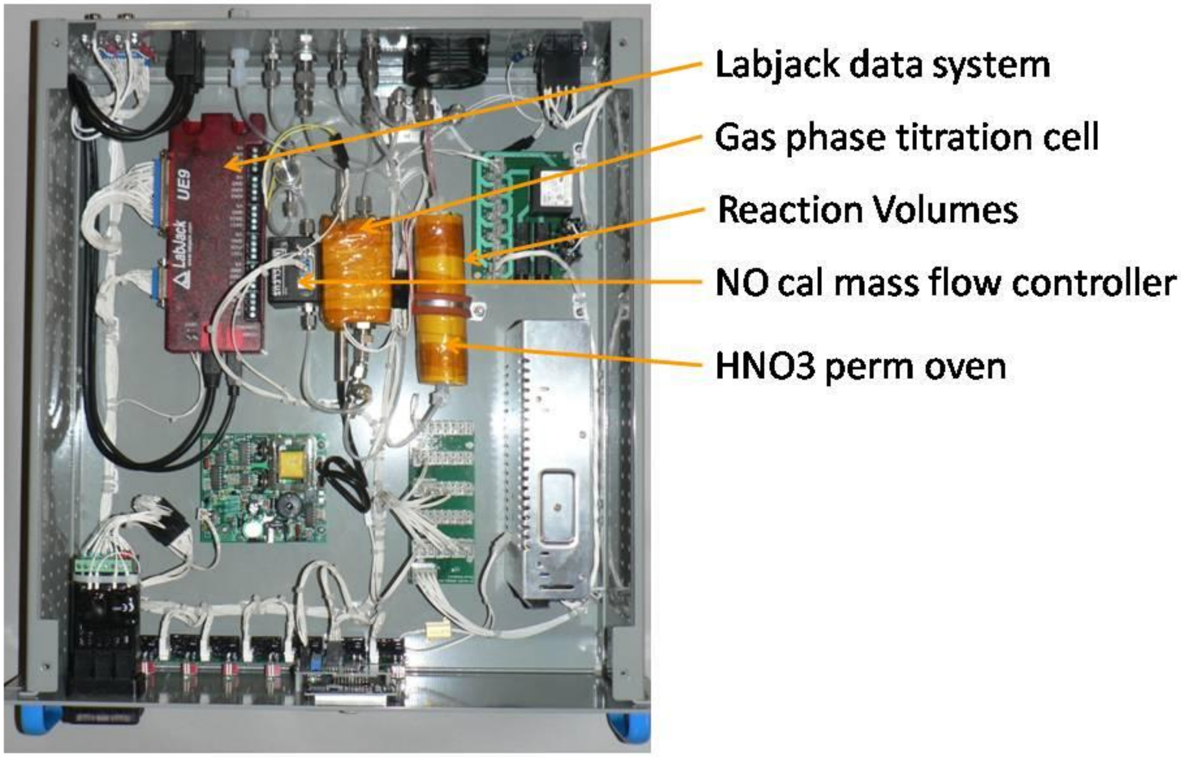


Figure 4. Photograph of the control box identifying the major components.

The front panel controls and readouts on this instrument include:

Temperature controllers – The temperature controller for the HNO_3 permeation oven is located on the front panel of the calibration box. Operation of the temperature controller is presented in a separate manual.

Valve switches – all of the valves/calibration modes can be manually activated using the On/Off/Auto switches on the front panel. In the Auto mode the valves can be controlled by applying a TTL level signal (3.5-5 VDC, 3-15 mA) through the rear panel connector (connector pin outs are described in **Section 7**).

Mass flow controller readout– The digital panel meter and selector switch can be used to view the set point and read voltages from the Channel 1 flow and the calibration mass flow controller.

The rear panel of the calibration/control instrument includes the plumbing, power and signal connections that tie this instrument to the data system, NO snooper, and inlet panel. These connections include:

Power input module – This is a standard 3 prong power plug with an On/Off switch for the instrument and a voltage selectable fuse holder.

Data system connectors – There are two 25-pin D-connector on the rear panel of the calibration/control instrument that is used to connect the ozonizer and Snooper instruments to the data system via a shielded cable. This cables contains both the analog signal and digital control wires. In addition there are Ethernet and USB connectors from the DAQ device to allow connection to the system computer.

The plumbing connections route the calibration gas and zero air to the inlet panel.

In addition to the calibration valves there are two critical orifices used to control zero air flows in the inlet system, including:

1. 10 sccm flow of oxygen through the NO_2 titration cell.
2. 2.5 slpm air flow for zero air displacement tests. (Attached to the Pure Air Generator)

The zero air delivery pressure must be maintained at 3 bar to maintain the appropriate head-pressure for the critical orifices.

NO_2 TITRATION CELL

The NO_2 titration cell is an aluminum block that houses a Teflon tube through which flows a small amount of oxygen. When this mixture is illuminated by the Pen-ray lamp also housed in the block ozone is produced to oxidize the NO calibration gas to NO_2 . The amount of titration achieved is controlled by manually adjusting the cylindrical aluminum shutter that surrounds the Pen-ray lamp. The amount of NO titration should be adjusted to some value between 50-95% of the standard addition NO concentration. This is easily done by manually activating the NO and NO_2 calibration valves with the BLC lamp off and adjusting the titration lamp shutter until the desired level of titration is reached.

A plumbing diagram for the Control box is shown in **Figure 5.**

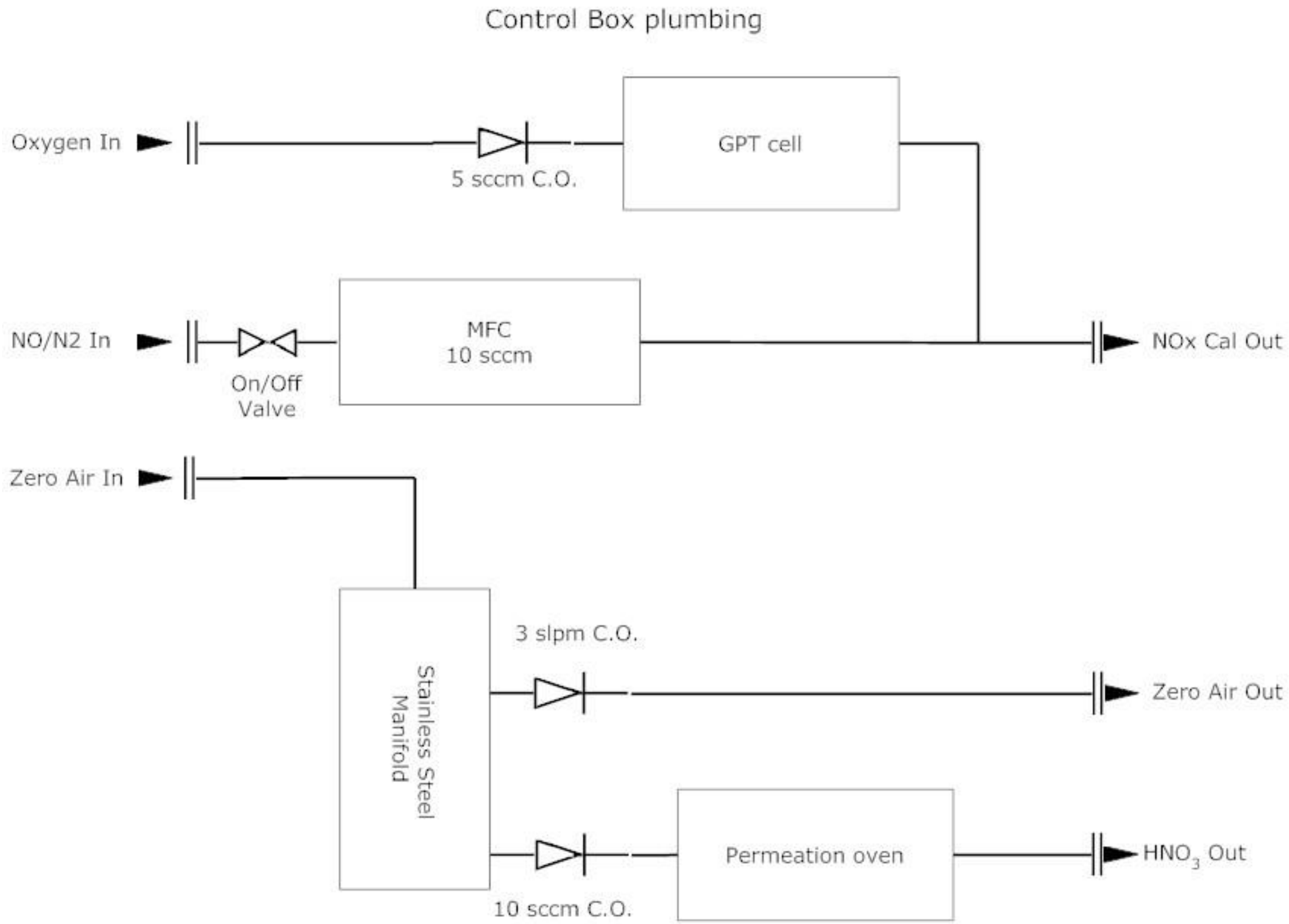


FIGURE 5. PLUMBING DIAGRAM FOR THE CONTROL BOX.

1.2.3 SNOOPER

The NO snooper contains the cooled housing for the photomultiplier tube, the pre-reaction volume and reaction volume, the pulse amplifier/discriminator, a pressure sensor, and the high voltage and DC power supplies for the snooper instrument. The snooper instrument includes temperature controllers for the Reaction volume, Zero volume (pre-reactor), and the PMT cooler. A photograph of the snooper is shown in **Figure 6**.

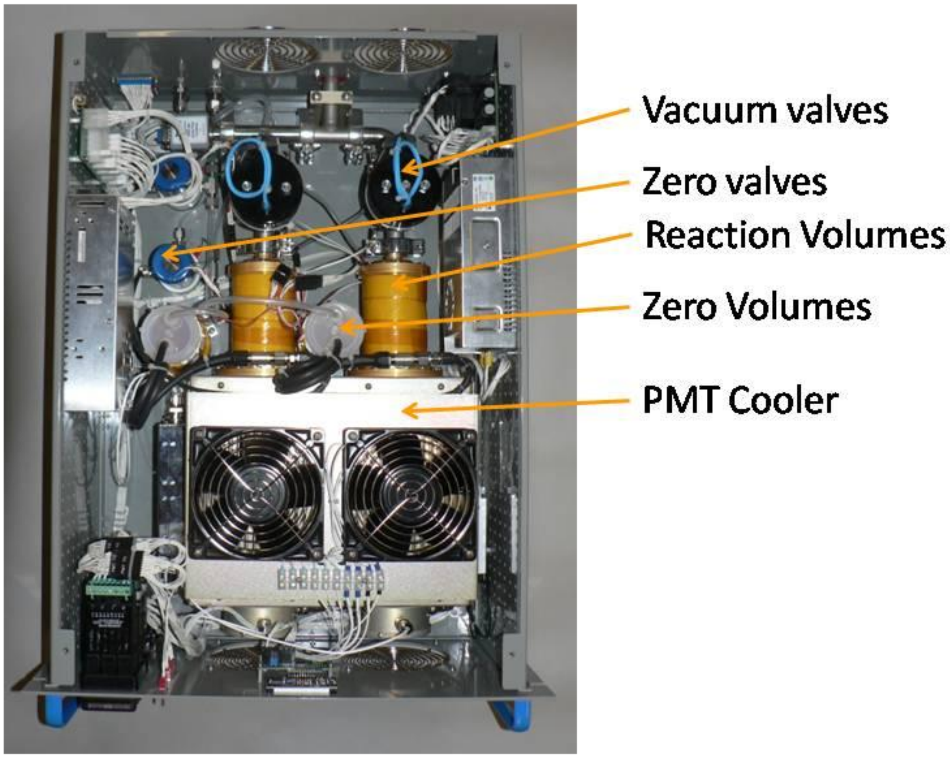


Figure 6. Top view of the Snooper with major components identified.

Snooper Readouts

Main LED display – Includes readouts for the reaction vessel pressure (direct readout in torr), PMT high voltage.

Temperature controllers – Actual and set-point values are displayed for the reaction vessel, zero volume, and PMT cooler. The power to the heaters and the PMT cooler power supply are controlled with the On/Off switch located directly beneath the temperature controllers. This switch is normally left on.

Snooper Controls

HV On/Off/Auto – These switches control the high voltage applied to the PMTs. The Auto position allows control of the high voltage by the data system by providing TTL level signal on the appropriate pins of the 25 pin rear panel data system connector (see section 7, Connector Pin-outs). The front panel includes 2 HV switches, one for each channel.

Zero Valve On/Off/Auto – These switches control the zero valves. The Auto position allows control of the zero valve by the data system by providing TTL level signal on the appropriate pins of the 25 pin rear panel data system connector (see section 7, Connector Pin-outs). The front panel includes 2 zero valve switches, one for each channel.

Vacuum Valve On/Off/Auto – These switches control the vacuum valves. The Auto position allows control of the vacuum valves by the data system by providing TTL level signal on the appropriate pins of the 25 pin rear panel data system connector (see section 7, Connector Pin-outs). The front panel includes 2 vac valve switches, one for each channel.

High voltage and pulse discriminator adjustments

The PMT high voltage and the pulse height discriminator levels can be adjusted for each of the channels via trim pots located on the HV supply and the PAD enclosures, respectively.

Rear panel connections

The rear panel connections for the NO snooper instrument include the following:

Plumbing connections – There are plumbing connections for the sample in, ozone in, and air in on the rear panel of the snooper. The air in (or inert gas in) is used to power the pneumatic vacuum valve.

Signal connections – There is a BNC connector on the rear panel that connect to the output of the PAD located inside the instrument. The signal at this connector is a TTL pulse proportional in frequency to the light measured at the PMT cathode. There is a 25 pin D-connector that contains the analog signals and digital control wires for the snooper that connects to the data system.

There is a standard 3 prong power plug with an On/Off switch for the instrument and a voltage selectable fuse holder. A plumbing diagram for the Snooper is shown in **Figure 7.**

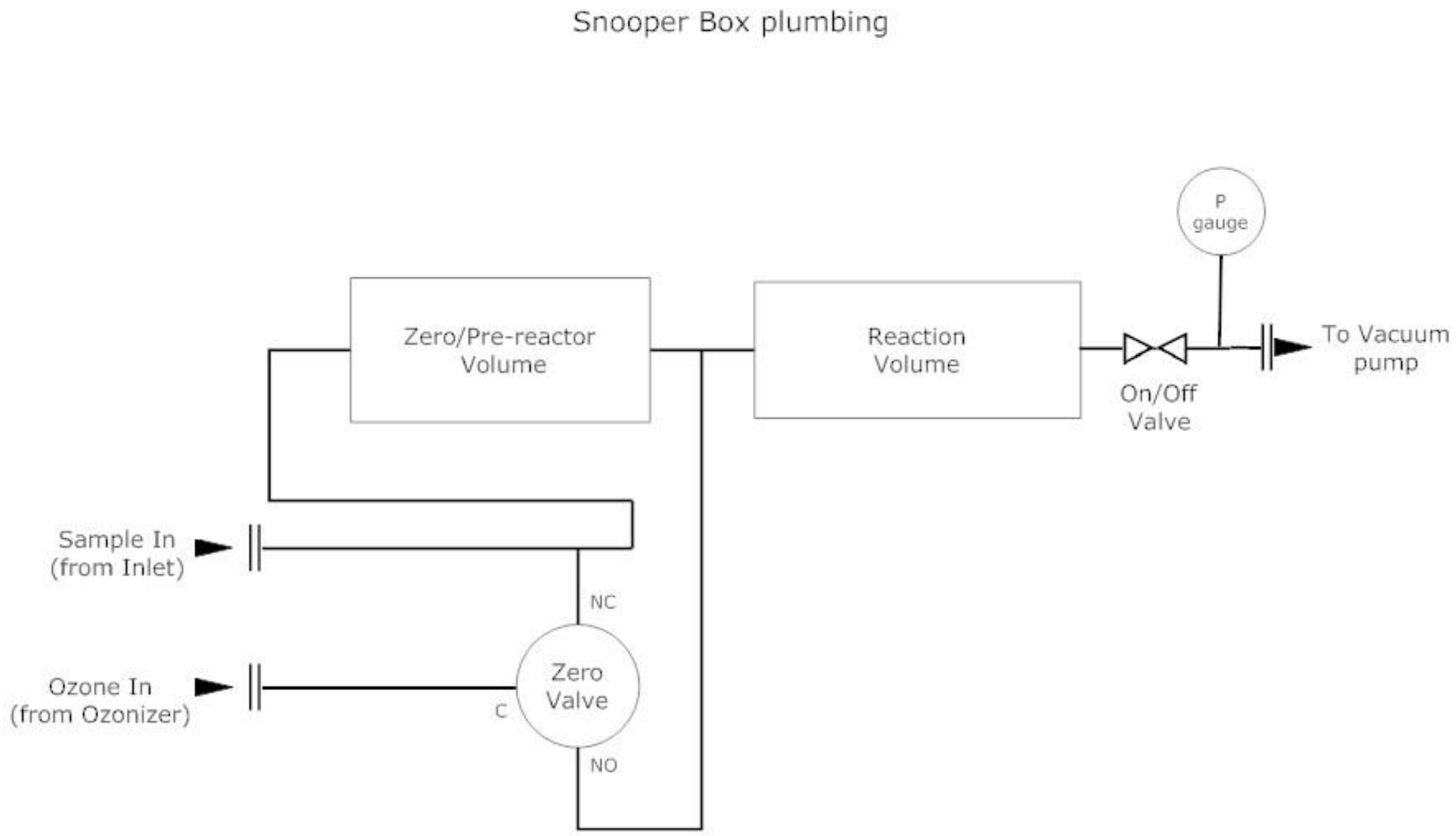


Figure 7. Plumbing diagram for one of the channels in the Snooper box. The second channel is identical and is connected to the same vacuum manifold as the first channel.

1.2.4 OZONIZER

The ozone for the system is generated from oxygen using a corona discharge tube. The ozone generator is a commercial device manufactured by Ozone Services. A manual for this device is included separately. Operation of the ozonizer is controlled by the On/Off/Auto switch on the front of the ozonizer instrument. The oxygen flow through the discharge tube is also controlled by an On/Off/Auto switch located on the front of the instrument. The oxygen flow is controlled by a 500 sccm MFC with a set point of 100 sccm (1.00 volts on the front panel display. The other controls on the front panel of the instrument are needle valves that control the pressure inside the discharge tube. The pressure sensors are the front panel-mounted bourdon gages. The system includes 2 complete ozone cells/power supplies. A photograph of the ozonizer is shown in **Figure 8**. A plumbing diagram for the Ozonizer is shown in **Figure 9.**

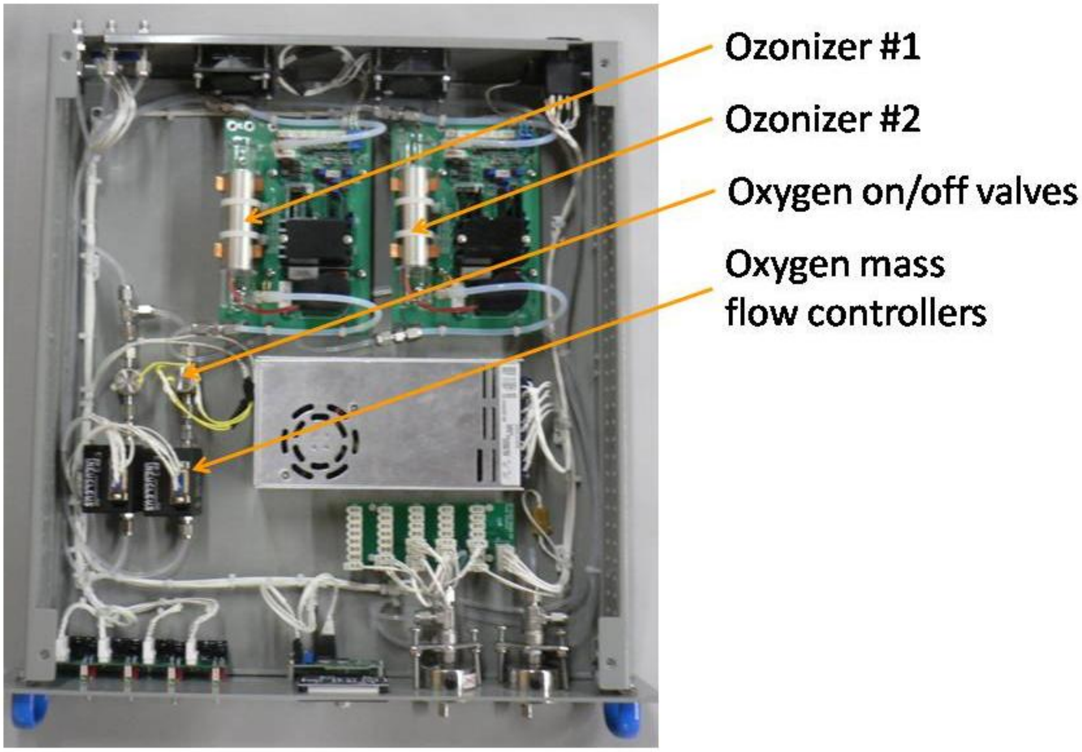


Figure 8. Photograph of the ozonizer identifying the major components.

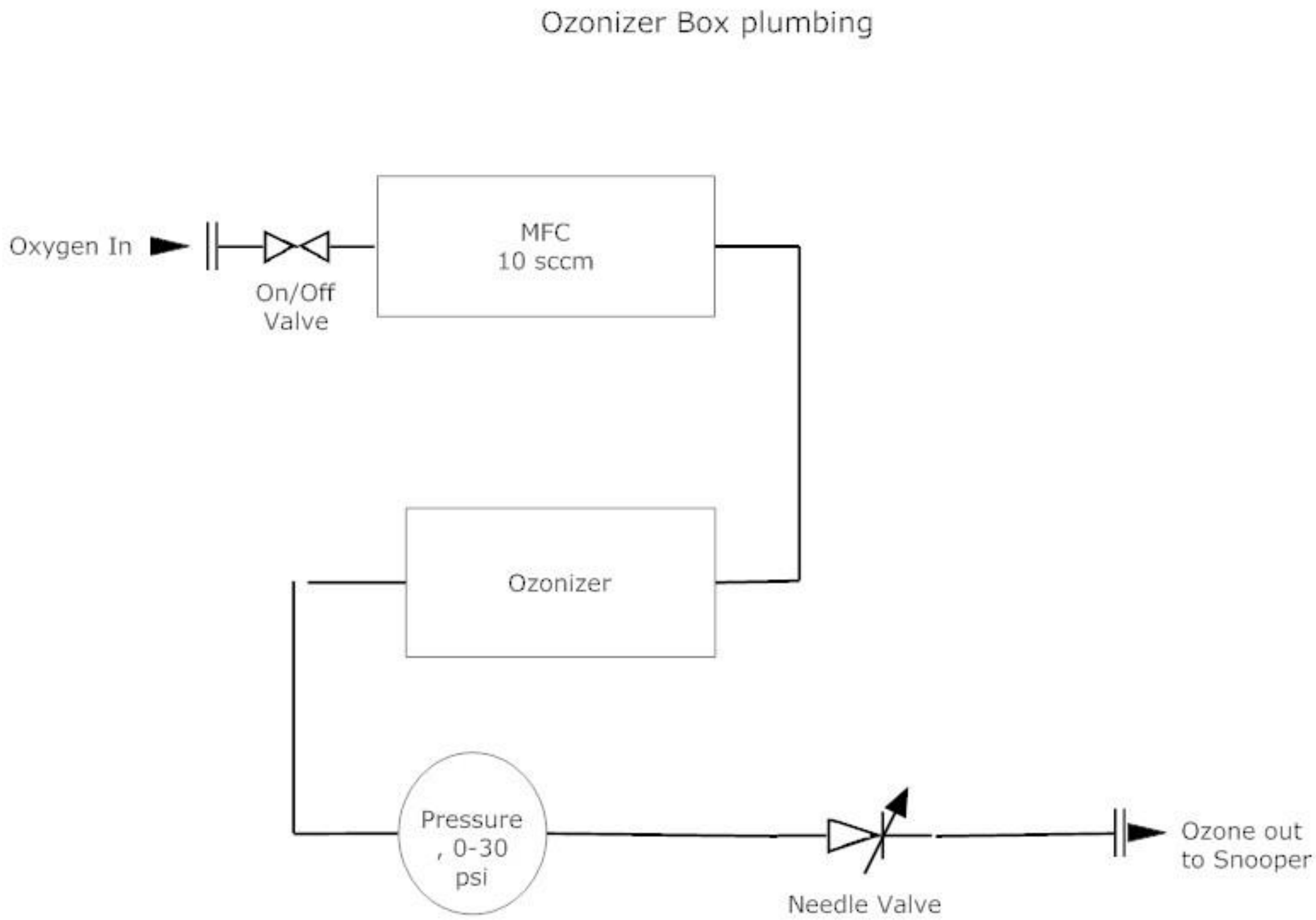


Figure 9. Plumbing diagram for one channel of the ozonizer. The second channel is identical and independent.

1.2.5 DATA ACQUISITION SYSTEM

The data acquisition instrument includes two Ethernet connected data acquisition boards (LabJack UE9 – one located in the Control box and one located in the Inlet), a connection panel that includes connections for each of the instruments, and a laptop computer. The LabJack data acquisition cards are controlled using DaqFactory software as described in section 5 (Software operation). Manual for the LabJack hardware is included separately as a PDF file.

2. SYSTEM SETUP

The NOxy system was shipped in multiple containers, including:

1. The rack mount enclosure that includes most of the instrument as well as the bulkhead connections for power input/output and gases in and out, and

2. A large box that contains the vacuum pump, the NOx inlet box, all of the interconnection cables and tubes, a spare parts box, the system computer, and all of the documentation. This box also contains the wheels for the rack mount box.

Set up

1. The system setup should start by unpacking the large parts box.

2. Set the inlet box on the top side of the rack mount box.

3. Connect the inlet tubing and cables. The inlet tubing connects to the bulkheads on both the back of the instrument housing and on the inlet box. Attach the end with longer 1/8" tubes to the instrument housing. The 26 pin connector attaches to the inlet bulkhead and to the back of calibration box. The power connector for the inlet box attaches via a 3-pin power connector to the inlet bulkhead and to the power distribution box on the instrument enclosure.

4. Connect the vacuum pump. Place the vacuum pump within 2 feet to the rear of the instrument enclosure. Connect the ozone destruction trap to the vacuum pump by the end with the elbow fitting attached (bottom of the trap faces down). Connect the trap to the NO instrument using the 3 ft. flexible stainless steel bellows tube. Connect the exhaust line to the exit of the pump and route the exhaust to a hood or outdoors. Connect the pump power plug to the power distribution box at the rear of the instrument.

5. Connect the gases to the instrument bulkheads.

6. Connect the main power plug to the instrument and to the building power (user supplied plug). The instrument is setup to receive 240 VAC and will require ~ 5 Amps.

7. Remove the system computer from its case and place on the sliding shelf. Plug the power connector into the computer.

8. Place all of the front panel controls of the instrument into the OFF position.

3. START UP PROCEDURE

The instrument Startup procedure is shown on the Signals page of the DaqFactory software and includes:

1. Turn on Main Power, NO Inst, Control Inst., and Ozonizer.
2. Turn on Vacuum pump.
3. Turn on oxygen and NO gases at cylinders.
4. Turn on Instrument with the START button.
5. Turn on manual heater switches.

Once these steps have been followed the user should press the on-screen START button.

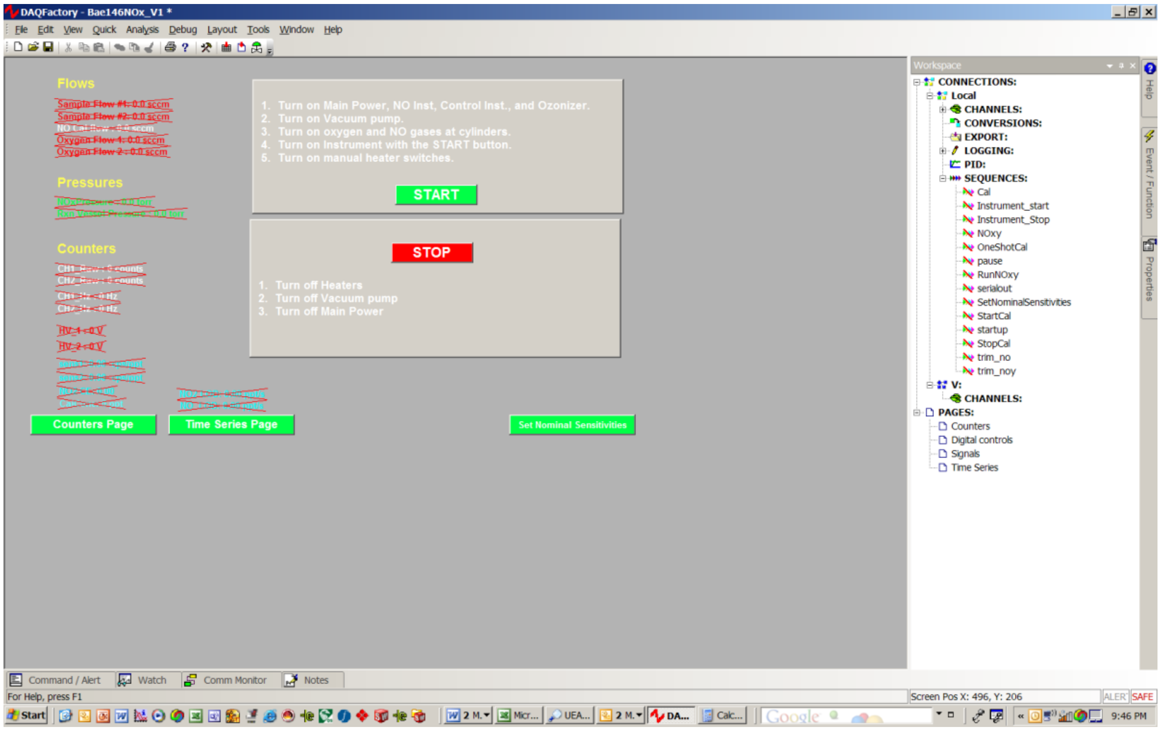
4. SHUT DOWN PROCEDURE

The instrument Shutdown procedure is largely automated and is initiated by pressing the onscreen STOP button, followed by the following actions:

1. Turn off Heaters
2. Turn off Vacuum pump
3. Turn off Main Power

5. SOFTWARE OPERATION

The data acquisition program for the NOxy instrument is written using DaqFactory software. The software is designed for automatic operation of the system and includes automatic control of the zero valves, serial data output, and automatic file save operations. The software contains several pages or screens, including SIGNALS, COUNTERS, and TIME SERIES. The default start page is the SIGNALS page shown below in **Figure 10**.



1. Turn on Main Power, NO Inst, Control Inst., and Ozonizer.
2. Turn on Vacuum pump.
3. Turn on oxygen and NO gases at cylinders.
4. Turn on Instrument with the START button.
5. Turn on manual heater switches.

1. Turn off Heaters
2. Turn off Vacuum pump
3. Turn off Main Power

Figure 10. Image of the Signals page.

The COUNTERS page is a nice diagnostic page since it shows the detectors signals in hertz. An image of the Counters page is shown in **Figure 11**.

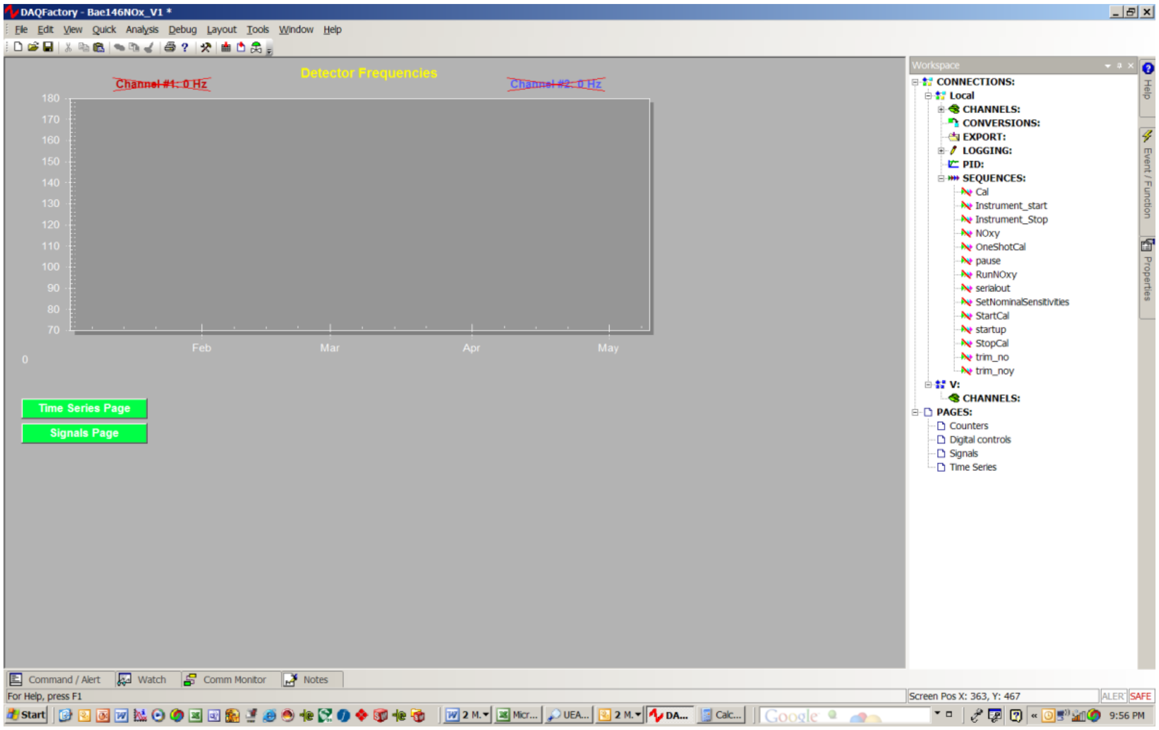


Figure 11. Image of the Counters page

Most of the time the user will use the TIME SERIES page which shows the calculated NOxy concentrations and as well has buttons to start and stop calibrations and to pause the zeros for a defined length of time. An image of the Time Series page is shown in **Figure 12**.

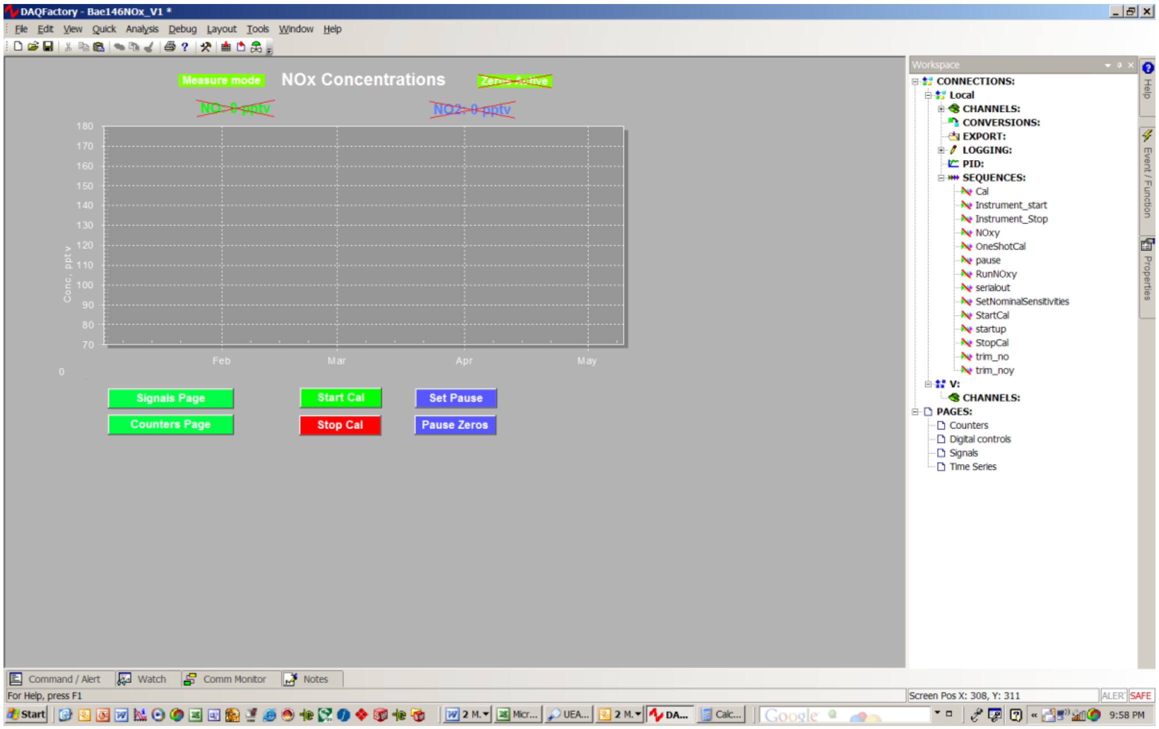


Figure 12. Image of the Time Series page

The DaqFactory program is automatically launched when the computer is turned on and the program worksheet NOxy_V1.ctl is loaded. Once the program has started a control sequence for the various signal controls automatically begins (the control sequences are described below). The display elements of the program show several important instrument parameters (detector frequency), the current state of each of the system valves, and a time series of the last hour of observations. All of the values displayed are also saved to file (located in the desktop folder) every day. The filenames are NOxy_yymmdd_hhmmss.asc.

5.1 INSTRUMENT CONTROL SEQUENCES

The instrument control sequence programmed into the sequence generator module can be examined by clicking on the tab labeled “Sequences” in the Workspace panel of the DaqFactory program. Within that box click on the any of the five sequences present to view the commands. The sequences are:

1. **Startup** – This sequence runs automatically whenever the DaqFactory program begins. It initializes all of the system variables and starts the **RUNNOxy** sequence. This sequence is shown below:

2. **RunNOxy** – This sequence has overall control of the instrument functions of measure, zeroing, and calibration. It simply evaluates whether a calibration of pause has been requested and initiates the appropriate sequence. If no calibrations or pauses are called for it runs the **NOxy** sequence. The sequence is:

3. **Serial Out –** The Serial_out sequence is launched at the start of the DaqFactory program by the **Startup** sequence. It ports the results of the running NOxy calculations and the various instrument states to the computer serial port. The sequence is shown below. The sequence updates the values on the serial port every second in the order shown following the Write command.

4. **Instrument_Start** – This sequence is called when the START button is pressed. It initializes all of the instrument controls and brings the instrument to life in a controlled manner and begins the measurement sequence NOxy. The sequence is shown below:

5. **NOxy** – This is the standard measurement sequence that cycles the instrument through its various measurement and zeroing states. The sequence is shown below. The sequence as shown is on a 240 second zeroing cycle. That period can be lengthened or shortened by changing the value in the "time 240" line.

6. **Cal** – The **Cal** sequence should be run in preflight and post-flight if possible. The sequence takes 10 minutes to complete and set the instrument sensitivities. The sequence cal be started and stopped from the Time Series page of the program. The sequence is as follows:

5.2 DATA FILE FORMAT

The data file format is set to ASCII – readable by most windows programs. There are several alternative formats that are more efficient in terms of file size (binary formats). Changes to the data file format may be made under the “logging” tab in the DaqFactory software.

5.3 DATA REDUCTION NOTES

The basic relationship used to calculate concentration for NO and NO2 is

$$[X] = (\text{X\_meas} - \text{X\_zeroint})/\text{X\_sensint}$$

where [X] is the concentration of X in pptv, X_meas is the counts recorded by the photomultiplier tube while in measure mode, X_zeroint is the interpolated value of the averaged counts recorded while in zero mode and X_sensint is the interpolated value of the sensitivity.

The sensitivity of the X channel for a given species Y (NO or NO2) is given by

$$\text{X\_sens} = (\text{X\_Ycal} - \text{X\_measint})/\text{X\_Ycalconc}$$

where X_Ycal is the average counts recorded by the X channel during a calibration of Y, X_measint is the interpolated value of counts while in measure mode, and X_Ycalconc is the concentration of Y introduced during calibration in units of pptv. This concentration is calculated by the following relationship:

$$\text{X\_Ycalconc} = (\text{cylinder concentration in ppm} * 1\text{e}6 * \text{NOcalQ})/\ \text{Sample flow}$$

Zero mode sequences are usually performed for 15 seconds every 2 minutes, while calibration mode sequences are performed every 5-23 hours. Data obtained immediately after a change in mode should be deleted from all calculations (approximately 10-30 seconds). In the entire notation which follow, a subscript of “int” indicates a linear interpolation between data points, where the first and last data values have been copied and inserted at the beginning and the end of the data column, respectively.

NO CALCULATIONS

The calculation for NO proceeds directly. The equation used is

[NO] = NO_meas - NO_zeroint)/NO_NOsensint.

The sensitivity for the NO instrument is given by

NO_NOsensint = (NO_NOcal - NO_measint)/NO_NOcalconc.

NO2 CALCULATIONS

The method for calculating NO_2 concentration is similar to that of NO,

[NO2] = (NO2_meas – NO2_zeroint)/NO2_NO2sensint,

Where NO2_meas is the number of counts recorded by the photomultiplier tube while in measure mode, NO2_zeroint is the interpolated value of the average counts measured in the zero mode, and NO2_NO2sensint is the interpolated NO2 sensitivity for the instrument. Sensitivity is calculated as

NO2_NO2sens = (NO2cal - NO2_measint/NO2_NO2calconc)

Where NO2cal is the average of counts from the instrument in calibration mode, NO2_measint is the interpolated value of the measure-mode counts and NO2calconc is the concentration of the NO2 calibration.

NOy concentration is calculated in a similar fashion to the NO2 concentration.

CORRECTIONS

Several conditions may contribute to an inaccurate measurement of NO and NOy. While the instrument is designed to keep the post-experiment corrections to a minimum, several important corrections are still necessary.

CALIBRATIONS/SENSITIVITIES

Of major importance is the ability to accurately measure the amount of reference gas added to the sample during calibration. The flow meters for the reference gas need to be calibrated before, during and after the campaign to assure accurate readings. Also, the reference gas concentration needs to be checked against the manufacturer's stated concentration. These corrections were made before any others and come into play only for the calculations of sensitivity.

H_2O

Ambient water vapor is a known quencher of reaction (1). In the presence of water the excited NO2 may transfer its energy to water and thus the amount of NO recorded is less than the actual value. In a similar way, ambient water vapor will quench reactions that give rise to the instrument background signal. The result is that water vapor tends to reduce both the system sensitivity and the system background. For systems operated aboard aircraft, where the water vapor concentration may change more rapidly than the system is zeroed and calibrated correction for the effect is necessary. This effect is made less variable by the addition of water through a capillary tube prior to the zero volume, but is still present. Others have noted this effect and have corrected developed correction algorithms (See for example, Ridley et al.[1]). The algorithms described therein are recommended for correction of both sensitivity and zero levels for rapidly changing water vapor concentrations.

O_3 CORRECTIONS

The reaction of ambient O_3 with NO upstream of the reaction vessel can affect the measured concentration of NO for the NO channel since the residence time is relatively long. For the NOy channel the effect is negligible since ozone is destroyed in the catalytic converter. Correction for the titration of ambient NO is best done by developing a system specific correction algorithm. This can be done by accurately by plotting the NO_NO sensitivity measured over several calibration cycles versus the coincidentally measured ozone concentration.

ARTIFACT

The artifact is the apparent signal measured while the instrument is sampling zero air. Typical artifacts are ca 2 pptv for the NO channel for the NO2 channel. For accurate measurements of very low concentrations the artifact signal should be subtracted from the ambient signal.

[1] Ridley, B.A, J.G. Walega, J.E. Dye, and F.E. Grahek, Distributions of NO, NOx, NOy, and O3 to 12 km altitude during the summer monsoon season over New Mexico, Journal of Geophysical Research, 25529-25534, 1994.

6. ROUTINE MAINTENANCE AND TROUBLESHOOTING

ROUTINE MAINTENANCE

GASES

1. Oxygen. A full oxygen cylinder (nominally 2200 psi) should last 21 days, leaving 100 psi in the tank. To change the oxygen, first turn of the ozonizer HV and O2 flow switches. Replace the tank and turn both switches back on. We have 9.75 tanks of UHP oxygen. Please reserve 2 for the month(s) of sunrise. In the meantime use aviators oxygen if the rest of the UHP does not show up.

2. Zero Air. Two zero air tanks should last for an entire year. Assuming that we get one zero air tank use that first, then switch to UHP nitrogen.

3. Cal gas. We have three NO cal cylinders. The one attached to the system should last for the duration. The others are backups.

FLOWS

The sample and calibration gas flows should be checked periodically to ensure accurate concentration measurements. In addition, the critical orifice controlled flows should be checked periodically to ensure that the nominal flow rates are still correct. These flows should be checked every few months.

TITRATION CELL

The NO_2 titration efficiency should be between 50-90 %. Adjustment of the pen-ray lamp intensity of the titration cell may be necessary (only if the cal tank is changed).

NOY CONVERTER

If the NOy_NO2 calibration indicates that the NOy converter efficiency has fallen below ca. 95% the NOy converter should be baked out under flow of an inert gas (N2 or H2 if desired) at ca. 450 ^{o}C for a couple of hours. This procedure should return the conversion efficiency of the NOy converter to > 95%.

LEAK CHECKING

It is a good idea to periodically leak check the system. This is easily done by sampling zero air and methodically spraying all of the connections from the inlet to the reaction vessel with the NO cal gas. A leak will be readily evident in the detector signal.

TROUBLESHOOTING

The NOxy system is a relatively complex array of plumbing and electrical connections, and troubleshooting this system requires a general familiarity with these types of systems. In most cases an improper flow and a missing signal can be traced to a loose or broken plumbing or electrical connection. The first steps in trouble-shooting are to ensure that the primary system components are operational. These include:

1. Vacuum is operational (nominal 10 torr reaction vessel pressure).
2. Compressed gases are on and at nominal head-pressure.
3. Sample flows are operational (nominal 1 slpm flow)
4. All control switches are in either on or auto position.
5. Calibration flow is operational (nominal 1-10 sccm)
6. Ozonizer is functional (oxygen flow is ca 100 mL/min, ozone cell pressure is nominal 3 psig). Turning the ozone HV on and off while the rest of the system is running should result in relatively large changes in the detector signal.

If these conditions are met and there is still no detector signal please contact Air Quality Design, Inc. for further assistance:

Tel: 303-225-0287
marty@airqualitydesign.com