In the following experiment you will calibrate an ozone analyzer and run O$_3$ and NOx instruments for 1 day to determine ambient concentrations. An uncertainty analysis should be applied to all calibrations and resulting ambient data.

Ozone Instrument Calibration

In this lab we will assume that the PS (Primary Standard) Calibrator produces an accurate O$_3$ concentration, when in reality the primary standard must be verified and recalibrations with a NIST traceable standard. Both instruments need approximately 30 minutes to warm up and stabilize from being off/cold start.

- Connect the output of the O$_3$ PS to the input of the O$_3$ detector (the T prevents pressurizing the O$_3$ detector as the O$_3$ PS Calibrator delivers a higher flow).
- Supply zero air to the O$_3$ PS.
- Open the DAQFactory program for ozone monitoring and start recording the values by clicking the indicated start/stop button. The program is currently set to record raw voltage (V) without applying a calibration correction to ppb. You may view these values by clicking on the “CHANNEL”, “AIN1” in the right menu, and then on the Table tab, where they will be displayed in a running log.
- Deliver O$_3$ concentrations of 180, 120, 80, 40, and 0 ppb from the O$_3$ PS Calibrator to the O$_3$ Analyzer.
  - Make sure screen says LOCAL (if not push ENTER)
  - Push RUN until you see up/down arrows which change the preset calibration levels
  - Using the up/down arrows select a calibration concentration
  - Press ‘ENTER’, the “?” goes away and the generator changes the ozone concentration output). You will see the ozone concentration as reported by the generator start to change at this point, shortly followed by the concentration measured by the analyzer.
- For each O$_3$ concentration setting, let the instrument stabilize for ~ 3 minutes (may be more) before making a measurement. For roughly two minutes, record start and stop time, record the O$_3$ output concentration from the Calibrator screen, (estimate the average – we will not consider the variability in the O$_3$ generator in the overall uncertainty analysis).
- The corresponding output voltage from the O$_3$ Analyzer will be saved to a file on the computer. You will identify the voltages by the time you were performing each experiment. There will be a difference between the log timestamp and the computer time – note it when selecting the time periods for which to average the voltages. You will use this data to construct a calibration curve to determine ambient O$_3$ concentrations.
• The DAQFactory program used to display the O3 and NOx concentrations uses the calibration curve previously constructed to change displayed and recorded values, measured in voltage, into ppb. View the existing calibration curve by clicking on the left menu option labeled Calibrations. Record the existing calibration function for ozone from the program to compare with your calculations.

**NOx Analyzer**

We will not calibrate the NOx instrument and instead just operate the NOx analyzer along with the ozone analyzer and compare the values recorded against the values measured by another instrument.

**Basis for operation:**

The NOx analyzer directly measures NO via a photomultiplier tube, which actually measures the light intensity from the reaction of the NO with O3 generated by the instrument:

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2^* + \text{O}_2
\]

\[
\text{NO}_2^* \rightarrow \text{NO}_2 + h\nu
\]

The sample stream is then routed through a molybdenum converter to reduce any NO2 to NO.

\[
3\text{NO}_2 + \text{Mo} \rightarrow 3\text{NO} + \text{MoO}_3
\]

The sample stream is then re-measured for NO, a value which represents a total NOx concentration. The internal computer then subtracts the final NO (NOx) reading from the initial NO reading to determine the amount of NO2 in the sample stream.

The same DAQFactory program that records the ozone concentrations in voltage is recording 3 channels of NOx analyzer information, converted into ppb. The same data file that will contain the raw voltage for your ozone concentration calculations will have pre-converted NO/NO2/NOx concentrations.

Allow the NOx analyzer to warm up from an off position/cold start until all alarms/warnings have cleared. You may wish to do this while calibrating the ozone analyzer.
Ambient Measurement

Disconnect the sample line delivering O\textsubscript{3} calibration gas from the O\textsubscript{3} PS Calibrator. Shut the instrument off. Connect the ambient sample line to the sample inlet port on the O\textsubscript{3} (Stop and start the data log for ambient measurements so as to exclude the startup values from the NOx analyzer and the calibration information from the ozone analyzer.)

Make sure that the met station is operating during your measurements. You can download this data and include in your analysis. When you click the link below (and scroll down the page), you’ll see a table of today’s data (and a link at the bottom to download the file—which you can do per day).


Discussion/Questions

1. O\textsubscript{3} Calibration: Construct a calibration curve that you can use to covert the Ozone Analyzer voltage to ozone concentration. This means plotting the calibration data and fitting with a line. From the fit, determine the detection limit (DL) and accuracy (uncertainty) of the instrument. DL can be estimated two ways 1) from the uncertainty in the zero air measurement (e.g., the standard deviation of the zero air readings converted to O\textsubscript{3} concentration), 2) the uncertainty associated with the linear regression intercept (use 1 standard deviation, ie, the results from the regression). Determine DL using both methods and compare. Also, make sure you explicitly state what the O\textsubscript{3} uncertainty is.

2. Data Quality and Diurnal Trends: For O\textsubscript{3}, NO, NO\textsubscript{2} and NOx, check the quality of your data by plotting a continuous time series for the 24-h or longer measurements. Check for extraneous spikes in concentrations. If justified (state reason in lab report), remove spikes. Investigate the 24-hour variation of all species. Also, plot diurnal variations in key meteorological data and compare with the O\textsubscript{3}, NO, NO\textsubscript{2}, and NOx variability. Explain the cause for any diurnal trends, or lack of trends, or any abrupt changes in concentrations. Support your arguments (i.e., O\textsubscript{3} and NO should have strong and different diurnal profiles). Note, that NO\textsubscript{2} data may be noisy and at times negative. Why is this (discuss issues with uncertainty in how NO\textsubscript{2} determined)? Try averaging the data (including negatives) to improve the signal.

3. Determine the NO\textsubscript{2} photolysis rate \( j_{\text{NO2}} \) from steady-state assumptions.
Assuming that the observed O\textsubscript{3} is in photochemical steady-state (PSS) with NO and NO\textsubscript{2}, calculate \( j_{\text{NO2}} \). Apply the PSS assumption below to this data set containing measured ambient O\textsubscript{3}, NO, NO\textsubscript{2}, P, and T.

\[
\begin{align*}
\text{NO}_2 + \text{hv} \ (j_{\text{NO2}}) & \rightarrow \text{NO} + \text{O} & \text{(R1)} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} \ (\text{fast, not rate-limiting}) & \text{(R2)} \\
\text{O}_3 + \text{NO} \ (k_3) & \rightarrow \text{NO}_2 + \text{O}_2 & \text{(R3)}
\end{align*}
\]
With, $k_3 = \left( \frac{2 \times 10^{-12}}{e^{(1400/T)}} \right) \left( \frac{P}{1013.25 \text{ mbar}} \right) \left( \frac{273.15K}{T} \right) \left( 2.687 \times 10^{10} \text{ ppbv}^{-1} \text{s}^{-1} \right)$

Under the PSS assumption:

$$j_{NO_2} = k_3 [NO] [O_3] / [NO_2] \text{ in s}^{-1}.$$ 

Discuss the $j_{NO_2}$ diurnal profile in terms of shape and maximum value. Compare your observations with values to that of the literature.

4. Comparisons of O$_3$ and NO$_2$ to Georgia DNR: Try to compare your data (O$_3$, NO$_2$) to other sites in the city or surrounding region (see http://www.air.dnr.state.ga.us/amp/). Again, you may have to average the NO$_2$ data. Do you think the penthouse lab provides a site for a representative measurement of these species in Atlanta, justify your answer.

5. Compliance: Only considering the rooftop measurements, would Atlanta be in compliance with the air quality standards for O$_3$ (8-hr) and NO$_2$ (1 hr) for your sampling period? (Consider your measurement uncertainties).