Experiment No 6: Measurement of Ozone

In the following experiment you will calibrate an ozone analyzer. Run the instrument for 1 day and then use the calibration to determine ambient ozone concentrations. An uncertainty analysis should be applied to all calibrations.

First a brief background on ozone formation and description of how the ozone analyzer functions:

Background, Source for O$_3$
In urban areas, tropospheric ozone (O$_3$) is a secondary pollutant that is formed photochemically from chemical reactions involving oxides of nitrogen and hydrocarbons. In this process sunlight (hv) converts NO$_2$ to NO and atomic oxygen. The atomic oxygen then reacts with O$_2$ to produce O$_3$.

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}
\]

\[
\text{O +O}_2 +M \rightarrow \text{O}_3 + M
\]

Note that the major source for NO$_2$ is through combustion (e.g., vehicles). These two reactions, however, do not lead to a net increase in O$_3$ since the O$_3$ formed can rapidly be converted back to NO$_2$ (see reaction below). Hence these three reactions form a closed cycle.

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

Industrial processes, vehicles, and vegetation produce volatile organic compounds (VOCs) that can disrupt this closed loop and serve as the fuel for O$_3$ production. The VOCs, which can be generically represented by RH, consume NO and produce more NO$_2$ leading to a net formation of O$_3$.

\[
\text{RH} + \text{OH} + \text{O}_2 \rightarrow \text{RO}_2 + \text{H}_2\text{O}
\]

\[
\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2
\]

\[
\text{RO} + \text{O}_2 \rightarrow \text{R'}\text{CHO} + \text{HO}_2
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2
\]

The O$_3$ formed is referred to as photochemical smog since key reactions, NO$_2$ conversion to NO, and the production of OH (mechanism is not shown), require energy from sunlight (hv).

EPA standards for Criteria Pollutants O$_3$.
The Clean Air Act, which was last amended in 1990, requires the EPA to set National Ambient Air Quality Standards (NAAQS) for pollutants considered harmful to public health and the environment. The Clean Air Act established two types of national air
quality standards. Primary standards set limits to protect public health, including the health of "sensitive" populations such as asthmatics, children, and the elderly. Secondary standards set limits to protect public welfare, including protection against decreased visibility, damage to animals, crops, vegetation, and buildings. National Ambient Air Quality Standards have been set for six principal pollutants, called "criteria" pollutants. Units of measure for the standards are parts per million (ppm) by volume, milligrams per cubic meter of air (mg/m³), and micrograms per cubic meter of air (µg/m³).

To protect and promote human health and public welfare the EPA attempts to:

- Mitigate potentially harmful human and ecosystem exposure to the six criteria pollutants: CO, NO₂, SO₂, O₃, PM(2.5, 10), and lead (Pb). The EPA must describe the characteristics and potential health and welfare effects of these pollutants.
- Limit the sources of and risks from exposure to hazardous air pollutants (air toxics).
- Protect and improve visibility impairment in wilderness areas and national parks.
- Reduce the emissions of species that cause acid rain, specifically SO₂ and NOx.
- Curb the use of chemicals that have the potential to deplete the stratospheric O₃ layer.

**NAAQS Effective January 2003**

O₃ 0.12 ppm maximum daily 1-hr avg to be exceeded no more than 1/yr averaged over 3 consecutive years
0.08 ppm 3-yr avg of the annual fourth highest daily 8-hr average (new 2008 standard is 0.075 ppm)

See the EPA web site for more details on NAAQS: [http://www.epa.gov/air/criteria.html](http://www.epa.gov/air/criteria.html)

**General Methods for Measuring Trace Gases**

Many techniques exist for measuring trace gases. Two common methods for measuring O₃ are commonly used; both are based on spectroscopic techniques. One method is based on the property that O₃ molecules strongly absorb UV light of wavelength 245 nm. In the other method, O₃ is reacted with NO or ethane, which produces an excited molecule that quickly relaxes emitting a photon of light.

**Model 49C Ozone Analyzer**

O₃ is quantified in this instrument by measuring the absorption of UR light at wavelength of 254 nm. The instrument works on Beer’s Law, which describes how a specific wavelength of light is absorbed by a particular gas molecule over a specified distance.

\[
I = I_0 \exp(-\alpha L C)
\]

where
- I is the intensity after absorption
- I₀ the intensity of the light entering the absorption cell
- α the absorption coefficient (how well the gas absorbs at a specific wavelength
- L the is absorption path length
- C the concentration of the absorbing gas (O₃ in this case).
To determine $C$, the concentration of $O_3$ in Beer’s Law, the instrument measures the ratio of $I$ to $I_0$. The other parameters in Beer’s Law are known, $L = 38$ cm, and the molecular absorption coefficient, $\alpha = 308$ cm (at 0°C and 1 atmosphere). A schematic of the instrument is shown in the Figure below.

To measure $I$ and $I_0$ simultaneously, sample air is split into two streams. One gas stream flows through an $O_3$ scrubber to serve as the reference gas (the $I_0$ measurement) the other flow remains unchanged and is the sample gas (the $I$ measurement). There are two “identical” detection cells (A and B) in the instrument. A solenoid valve alternates the reference and sample gas streams between cells A and B every 10 seconds so that any differences between the cells can be compensated. For example, the solenoid switches and reference gas flows through cell A and sample gas through cell B. The instrument than measures the absorption of 254 nm light in each cell, calculates the $O_3$ concentration for each cell, and outputs the average concentration (volts) to both the front panel display and the analog outputs. After 10 s the solenoid valves switch so that sample gas now flows through cell A and reference gas flows through cell B. The absorption measurement is made and $O_3$ concentration determined and displayed. The cycle is continued. A calibration must be performed to convert the voltage from the photo-detector to $O_3$ concentration.
Experimental Method

First perform the following instrument functionality checks and record the results in your lab notebook.

1. Detector Frequencies: From ‘Main Menu’, select ‘Diagnostics’, then ‘Intensities’ (the values should be between 65000 and 120000 Hz)

2. Lamp Noise (Service Mode must be ‘on’: From ‘Main Menu’, select ‘Instrument Controls’, then ‘Service Mode’, switch on if needed): From ‘Main Menu’, select ‘Service’, then ‘Intensity Check’, do for both A and B (noise should drop below 4 Hz within 20 seconds)

3. External Leaks: Disconnect sample inlet line and screw on a plug fitting. From ‘Main Menu’, select ‘Diagnostics’, then ‘Flows’ (Both flows should drop to zero); From ‘Main Menu’, select ‘Diagnostics’, then ‘Pressure’ (Pressure should drop below 250 mm Hg)

4. Pump Operability (Service Mode ‘on’): From ‘Main Menu’, select ‘Service’, then ‘Pressure Check’, then ‘Pump Check’ (Cell B flow should drop to 0 and the pressure should drop below 390 mm Hg)

5. Internal Leaks: Input 180 ppb O\textsubscript{3} from the O\textsubscript{3} Primary Standard Calibrator and let stabilize for 3-5 minutes; From ‘Main Menu’, select ‘Diagnostics’, then ‘Cell A/B O\textsubscript{3}’ (The average of ten successive simultaneous readings between cells A and B should agree within 3%)

Instrument Calibration

Note, in this lab we will assume that the PS (Primary Standard) Calibrator produces an accurate O\textsubscript{3} concentration. Deliver O\textsubscript{3} concentrations of 180, 120, 80, 40, and 0 ppb from the O\textsubscript{3} PS Calibrator to the O\textsubscript{3} Analyzer (using the ‘_’ ‘_’ ‘ENTER’ keys on the front of the PS Calibrator). For each O\textsubscript{3} concentration setting, let the instrument stabilize for ~ 3 minutes before making a measurement. For roughly two minutes, record start and stop time, record the O\textsubscript{3} output concentration from the Calibrator screen, (estimate the average – we will not consider the variability in the O\textsubscript{3} generator in the overall uncertainty analysis). The corresponding output voltage from the O\textsubscript{3} Analyzer will be saved to a file on the computer. You will identify the voltages by the time you were performing each experiment. (Make sure the computer clock is correct). You will use this data to construct a calibration curve to determine ambient O\textsubscript{3} concentrations.

Ambient Measurement

Disconnect the sample line delivering O\textsubscript{3} calibration gas from the O\textsubscript{3} PS Calibrator. Connect the ambient sample line to the sample inlet port on the O\textsubscript{3} Analyzer and record the time.

A small met station will be operating during your measurements. You can download this data and include in your analysis.
**Discussion/Questions**

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 linear regression. 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$_3$ concentration), 2) the uncertainty associated with the linear regression intercept (use 1 standard deviation). Determine DL using both methods and compare. Also, make sure you explicitly state what the O$_3$ uncertainty is.

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. Investigated the 24-hour variation of O$_3$. Also, you can plot diurnal variations in key meteorological data and compare with the O$_3$ variability. (Since O$_3$ is photochemically produced, solar intensity is one key variable). Explain the cause for any diurnal trends, or lack of trends, or any abrupt changes in concentrations. Support your arguments.

Try to compare your data to other sites in the city or surrounding region (see http://www.air.dnr.state.ga.us/amp/). Do you think the penthouse lab provides a site for a representative measurement of O$_3$ Atlanta, justify your answer.

Only considering the rooftop measurements, would Atlanta be in compliance with the 24-hour air quality standards for O$_3$, for your sampling period? (I.e., check if your measurements exceed the standard).