Lab 6
Major Anions In Atmospheric Aerosol Particles

Purpose of Lab 6:
This experiment will involve determining the concentrations of the major ionic chemical components comprising PM2.5 ambient aerosol particles in urban Atlanta. This will involve the use of ion chromotgraphy and the development of calibrations curves following methods similar to Lab 2.

Sources of Anions in Ambient Particles:
One way to identify the source of particles is to measure their chemical composition. Salts such as NaCl, CaCO₃, Ca₂NO₃, (NH₄)₂SO₄, and NH₄NO₃ comprise a large fraction of aerosol particles. Because these salts will adsorb water at moderate RH, the particles take up water and the various salts are often found as solution in particles, where the salts dissociate and form cations (positive ion) and anions (negative ion). Certain salts dominate in different locations due to their differing sources. High concentrations of sodium chloride, NaCl (or Na⁺ and Cl⁻), are found in marine regions due to aerosol formed from sea spray. Calcium carbonate (CaCO₃) and calcium nitrate (CaNO₃), and similar mineral compounds, are found in arid regions from suspension of soils. This is also commonly referred to as mineral dust. Ammonium sulfate ((NH₄)₂SO₄), and ammonium nitrate (NH₄NO₃) are commonly found in air masses influenced by anthropogenic emissions. In the western regions of the U.S. a major anthropogenic aerosol source is emissions from cars/trucks (mobile sources), which lead to high NH₄NO₃ concentrations. NOₓ (NO plus NO₂) formed in high temperature combustion reacts with OH to produce HNO₃ (nitric acid).

\[
\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \quad (\text{OH is formed photochemically involving H}_2\text{O})
\]

Depending on ambient conditions (T, RH) and the composition of the particle, HNO₃ may condense onto existing particles. This gas-to-particle conversion is even more likely if NH₃ is present, forming ammonium nitrate aerosol (NH₄NO₃). In the eastern US where significant power production involves coal combustion, sulfur associated with the coal is released to form sulfur dioxide (SO₂). This SO₂ can form sulfate aerosol (SO₄²⁻) through gas phase reactions,

\[
\begin{align*}
\text{SO}_2 + \text{OH} + \text{M} & \rightarrow \text{HSO}_3 + \text{M} \\
\text{HSO}_3 + \text{O}_2 & \rightarrow \text{SO}_3 + \text{HO}_2 \quad (\text{fast}) \\
\text{SO}_3 + \text{H}_2\text{O} + \text{M} & \rightarrow \text{H}_2\text{SO}_4 + \text{M} \quad (\text{fast})
\end{align*}
\]
The more common pathway, however, is through oxidation in liquid droplets involving hydrogen peroxide (H$_2$O$_2$) or other oxidants.

\[
\begin{align*}
\text{SO}_2 \text{(g)} & \leftrightarrow \text{SO}_2\cdot\text{H}_2\text{O} \quad (\text{SO}_2 \text{ dissolves in the liquid drop and is hydrated}) \\
\text{SO}_2\cdot\text{H}_2\text{O} & \leftrightarrow \text{HSO}_3^- + \text{H}^+ \quad (\text{hydrated SO}_2 \text{ dissociates}) \\
\text{H}_2\text{O}_2 & \leftrightarrow \text{H}_2\text{O}_2 \text{ (aq)} \quad (\text{H}_2\text{O}_2 \text{ is produced from self reaction of peroxy-radicals, HO}_2) \\
\text{HSO}_3^- + \text{H}_2\text{O}_2 \text{ (aq)} + \text{H}^+ & \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + \text{H}_2\text{O} \quad (\text{dissocated SO}_2 \text{ is oxidized})
\end{align*}
\]

The predominance of mobile source emissions (cars etc) in the west and coal combustion emissions in the east results in a dominance of NH$_4$NO$_3$ aerosol particles in the west and (NH$_4$)$_2$SO$_4$ aerosol particles in the eastern U.S. Atlanta is ringed by large coal-fired power plants, and is also impacted from more distant power plants in Tennessee (TVA) and power plants along the Ohio River. The result is that the PM2.5 mass in Atlanta is typically about half ammonium sulfate. The other half is carbonacous material, with smaller amount of minerals, ammonium nitrate, and various metals.
Collection of Particles on Filters for Chemical Analysis.
In this lab we will collect particles on filters, extract the filters for compounds soluble in water, and then analyze the extract for anions. As a method to capture particles for analysis, particle filtration is much more complex than expected. The mechanism by which particles are captured is not straight forward and potential interferences during the particle collection is large.

Filters are constructed of a variety of materials that include borosilicate glass, quartz, teflon, cellulose, polyvinyl chloride, polyester, polycarbonate, nylon, silver, etc. Filter structures also vary. The most common are fibers, membranes, and pore filters. Fiber and membrane filters capture particles by providing a convoluted flow path and large surface area. The figure shows an example of membrane filter. A teflon membrane filter will be used in this experiment. Pore filters are very different and are used for collecting particles on a flat surface for single particle analysis (e.g., electron microscopy). The type of filter structure and filter material must be carefully considered and will depend on the type of compounds to be analyzed and by what method. Pertinent issues include, filter pressure drop, interferences due to absorption of gases onto filter material, and possible interferences of the filter material with the measurement method.

When analyzing how filters capture particles it is useful to think of one particle interacting with a single filter fiber (or element). The particle collection efficiency of a single fiber is determined and then contributions for all fibers (or elements) are considered to get the overall filter efficiency. Particles are capture on filters by two main mechanisms; by inertia and by diffusion. The figure shows a schematic of a particle trajectory as is approaches a fiber and is carried along by the gas (air). As the air approaches the fiber along a given streamline it is deflected. “Large” more massive particles have
more inertia than small particles (both have more mass, and hence inertia, than the gas molecules) and do not following the curved gas streamline. This results in the particles impacting the filter element and they are collected. “Small” particles will behave more like the gas and flow around the fiber without intercepting it. However, smaller particles have much higher diffusivities than large particles. This means that they will randomly deviate more from the gas streamline as they move around the particle (see figure). Thus, the filters large surface areas serve to collect small particles (Dp < 0.1 µm) by diffusion. The tortuous (highly curved) flow path of air through the filter leads to collection of large particles (Dp > 1 µm) by inertia. Interestingly, the hardest particles to capture have sizes between 0.1 to 1 µm diameter, the size corresponding to most fine (PM2.5) particle mass. (It is also noteworthy that these “most penetrating particle sizes” are the easiest to transport through tubing). Most filters are designed so that their collection efficiencies are greater than 99%. Thus we can assume they collect all particles of all sizes.

Artifacts can be a large problem when collecting particles on filters for analysis. These artifacts lead to either an over or under-measurement of the compound or parameter of interest, and are respectively referred to as positive or negative artifacts. Many compounds found in particles are semi-volatile (e.g., have fairly high vapor pressures). These compounds exist in the particles due to an equilibrium between the vapor and particle phase. Take for example nitric acid (HNO₃) and nitrate aerosol (NO₃⁻). Nitric acid will condense in a liquid particle to form particulate nitrate. Equilibrium shifts to the particle phase at lower temperatures, whereas at higher temperatures the vapor phase is favored. Higher ambient humidities (RH) lead to more condensed water, which favors the condensed phase. (Note, the situation is actually more complicated since droplet pH is also a significant factor; pH depends on the availability of neutralizing cations, such as ammonia, NH₃). The problem with filter measurements is that sampling can occur over long periods (hours to days). Particles that are collected on the filter, say at night when it is cooler and higher RH, will be exposed to higher temperature and dryer air during sampling the next morning and day. This can lead to a negative artifact due to evaporation loss of HNO₃. Other artifact problems include adsorption of gases onto particles collected on the filter and onto the filter media itself. As discussed in Lab 5 regarding mass measurements with the TEOM, absorbion or desorption of water vapor (a semi-volatile compound) onto the TEOM filter can lead to inaccurate mass measurements. Loss of semi-volatile material from the TEOM filter occurs and results in an under-measurement of PM2.5 mass. Accounting or eliminating this artifact is an active area of current research. For compounds that are not volatile, such as sulfate (the corresponding gas phase compound is sulfuric acid, which has a very low vapor pressure), filter sampling artifacts are minimal.
Experiment 6

Determining the Concentration of Chloride, Nitrate, and Sulfate in the Ambient PM2.5 Aerosol

In this first experiment, you will use ion chromatography to determine the concentration of anions chloride, nitrate, and sulfate in water extracts from a filter loaded with ambient particles.

Particle Collection Procedure

In the previous lab, the setup was used for collecting particles on filters for subsequent chemical analysis is shown above. The particle size selector is a PM2.5 cut cyclone. To control the flow rate in this experiment we use an appropriate size (near 16.7 L/min) critical orifice. You measured this flow in the last lab.

Do the following steps to determine the concentrations of ions in the ambient aerosol:

1. **Extract the ions from the filters:**
   Use a clean (rinse 3 times with ultrapure water) graduated cylinder to measure and transfer 30 ml of ultrapure (20 Mohm) water into the bottle containing your filter. Do the same for the bottle with the blank. Place the bottle in ultrasonic bath and sonicate until ready for analysis later in the lab (approximately 60 minutes). Determine the relative uncertainty associated with the 30 ml, record in lab writeup.

2. **Calculate How to Prepare Standards to Calibrate the IC for Chloride, Nitrate, and Sulfate (DO THIS SECTION BEFORE YOU COME TO THE LAB)**
   To improve the accuracy of the calibrations, we will use commercially available liquid standard stock solutions. The concentrations of Chloride, Nitrate, and Sulfate in the stock solution are:
   - Chloride = 200 mg/L
   - Nitrate = 400 mg/L
   - Sulfate = 400 mg/L
The goal is to prepare 4 standards that will roughly cover the range of expected ambient concentrations of chloride, nitrate, and sulfate. Each of the four standard solutions you prepare will contain known concentrations of chloride, nitrate, and sulfate that will be used to create separate calibration curves for each compound (ie Conductivity vs Liquid Concentration).

Ambient concentrations of most compounds in the aerosol typically range from 10 µg/m$^3$ to below the instrument detection limit of 0.1 µg/m$^3$ (if you are very careful a detection limit of 0.01 µg/m$^3$ is possible). Calculate the liquid concentration if your filter contained 10 µg/m$^3$ of each analyte (Cl$^-$, NO$_3^-$, SO$_4^{2-}$) by:

$$C_{\text{liq}}(\text{mg/L}) = (10 \, \mu\text{g/m}^3) \times (Q \, \text{L/min})(t \, \text{min}) \times (F) / (V \, \text{ml})$$

Where
- Q is the sample flow rate in L/min (what you measured in the last lab)
- t is the time the filter was loaded in min
- F is a conversion factor to make the units work out
- V is the volume of liquid used to extract the filter (mL)

Show an example of this calculation in your writeup with all units.

Make a table as shown below and add this data to the first column of the table. Repeat this calculation with appropriate ambient concentrations (eg, 1, 0.5, 0.1 µg/m$^3$) to fill in the rest of the first column.

<table>
<thead>
<tr>
<th>Std 1: 10µg m$^3$</th>
<th>Calculated Conc., mg/L</th>
<th>Vol to Pipette, mL</th>
<th>Relative Uncert. In Pipetted Vol.</th>
<th>Relative Uncert in Volum. Flask</th>
<th>Relative Uncert in Concent.</th>
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</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
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<tr>
<td>NO$_3^-$</td>
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<td>SO$_4^{2-}$</td>
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<td>Std 2: 1µg m$^3$</td>
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<td>Cl$^-$</td>
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<td>NO$_3^-$</td>
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<td>SO$_4^{2-}$</td>
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<td>Std 3: 0.5µg m$^3$</td>
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<tr>
<td>Cl$^-$</td>
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<td>NO$_3^-$</td>
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<td>SO$_4^{2-}$</td>
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<td>Std 4: 0.1µg m$^3$</td>
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<td>Cl$^-$</td>
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<td>NO$_3^-$</td>
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<td>SO$_4^{2-}$</td>
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</table>

Knowing the concentration of the analyte in the stock solution determine the volume of stock solution that must be pipetted into a 100 ml volumetric flask to make the desired first standard...
(Std 1 in the table) for Cl\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−} (see Lab 2).

Now calculate the amount to pipette from Standard Solution 1 to make Standards 2, 3, and 4. The first two columns in the above table should be completed.

3. **Prepare Standards to Calibrate the IC for Chloride, Nitrate, and Sulfate**

Pour a small (roughly 5 ml) of standard stock into a disposable cup. From this dish pipette the calculated volume of stock into a pre-cleaned (rinse 3 times with ultrapure water) 100ml volumetric flask. Fill the volumetric flask to the 100ml mark with ultrapure water. Record the uncertainty in each step of this process (pipette volume uncertainty, volumetric flask uncertainty, and record in table above).

Transfer a portion of the first standard into a disposable cup and make standards 2, 3, and 4 using 3 clean (rinse 3 times with ultrapure water) volumetric flasks and the pipettes following the procedure above. Determine the total relative uncertainty in the volume measurement using quadrature sum of squares. Assuming no uncertainty in the stock concentrations this will equal the total relative uncertainty in the standards concentration.

Run the anion IC and record the peak areas and retention time for each analyte for each of the 4 standards.

4. Transfer a portion of the loaded filter extract and blank filter extract into separate disposable cups. Use a disposable syringe to draw 10 mL of the extract sample into the syringe. Then, attach a disposable filter to the syringe tip, and force the sample through the filter into a pre-cleaned disposable cup. Load the sample loop by drawing liquid from the disposable cup using the other syringe, making sure to wipe clean the tube prior to inserting in the cup and not drawing any air into the sample loop. Run the sample on the IC and determine the conductivity, based on peak area, for each analyte.

**Data Analysis and Interpretation**

1/ Graph the calibration curve for each anion and calculate the slope of the regression line which passes through zero. Determine the uncertainty in the regression slope from ANOVA and include on the equation with your plot.

2/ Calculate the concentration of chloride, nitrate, and sulfate in your sample and the blank using the calibration curves above.

3/ Consider any correction to the data, such as
   - Contamination (ie, a blank above the limit of detection)
   - Losses in sample lines

4/ Convert the liquid concentrations to ambient aerosol mass concentration in µg/m\textsuperscript{3} for Cl\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}.

5/ Provide an estimate of the measurement uncertainty for each analyte and how it was
determined (eg, use quadrate sum of squares for uncertainty in sample air flow rate (gas meter and stop watch), uncertainty in liquid added to extract filter, uncertainty in standards concentration (use an average of the four standards from the table), and uncertainty in the slope of the regression.

6/ Comment on the ability of the filter to capture particles. We are assuming that all particles are captured by the filter. Is this a good assumption, is it a good assumption for all particle sizes?

7/ For each ion measured, comment on possible inaccuracies associated with filter artifacts.

8/ Compare the fraction of the three measured anions to the PM2.5 total mass measured in the previous lab (give the fraction of Cl⁻, NO₃⁻, SO₄²⁻, to total mass). You will have to average the TEOM data to the filter integration time. Are your results consistent with previous studies in this region of the U.S.

9/ List possible sources for Cl⁻, NO₃⁻, SO₄²⁻. Use results and analysis from the previous lab.