Experiment # 3 Aerosol and Trace Gas Sampling

The purpose of this experiment is to teach you a common method for sampling inorganic atmospheric aerosols and trace gases for chemical analysis. Ambient air is drawn through a cyclone (D_{50} = 2.5 µm), and along etched glass denuder walls (air passes through two denuders in series) which have been coated with chemicals that absorb the gaseous species of interest. The remaining air stream is then filtered through 37mm Teflon and nylon filters in series. The Teflon filter is used to collect particulate matter. The nylon membrane filter is used to capture nitric acid which can be volatilized from particulate matter collected on the Teflon filter. A final back-up denuder is used to capture any gaseous ammonia volatilized from particulate matter collected on the Teflon filter.

After sampling the annular denuders are extracted with deionized water. The extract solution is analyzed for ions corresponding to the collected gaseous species. The first denuder is for gaseous HNO_3, and the second denuder for gaseous NH_3. Aqueous extracts of the Teflon filters will be analyzed by ion chromatography for concentrations of SO_4^{-2}, NO_3^-, Cl^-, NH_4^+, K^+, Ca^{+2}, Na^+, and Mg^{+2}. The extract from the nylon filter will be analyzed for NO_3^-. The back-up denuder is analyzed for NH_4^+. The analysis of anion and cation concentrations will be made using standard techniques of ion chromatography on two Dionex model DX-500 ion chromatographs.

Results from the measurements will be used to examine the major inorganic composition of Ft. Collins aerosol and associated trace gas species.

Materials Needed:

- URG automated denuder/filter sampler
- Filter holder
- Denuders
- Latex gloves
- Teflon filters (Gelman Zefluor, 1.0 µm pore size)
- Nylon filters (Gelman Nylasorb)
- Denuder coating solutions (Na_2CO_3 and phosphorous acid)
- DI water
- Ethanol
- Anion eluent
- Ultrasonic bath
- IC autosampler vials
- 5 ml cryovials
- Pipettes and tips
- Tweezers
- Aluminum foil
- 16 ml test tubes
- Denuder drying system
- URG sampling log sheet

- Christman field weather (T and RH) data may be interesting to examine (may be obtained from: http://ccc.atmos.colostate.edu/~autowx/fccwx_current.php)

Procedure:

1. You will do this experiment in groups. This experiment will be conducted during two weeks of class. You will work with the same lab partner(s) during both weeks. During the first week, two groups will prepare filters and denuders for this experiment. The other two groups will prepare the MOUDI impactor for sampling (Lab #4). The following week the groups will swap duties.

Loading filters

1. Each group will prepare two denuder/filter-pack sampling trains. Each sampling train includes a 2-stage 37 mm filter pack. Obtain sufficient filters to load them (to be explained). The filters are stored in petri dishes labeled T# (Teflon filters) and N# (Nylon filters). Record which filters go into which filter pack. One filter pack will be used as a blank.
2. Spread aluminum foil over your work surface (a 2' length should be sufficient). Be sure to keep the foil clean (i.e., don't touch it except near the edges). Rinse your tweezers in Nanopure water and shake/air dry. Put on latex gloves; rinse them with DI water and shake/air dry.
3. Open one filter holder assembly and load the appropriate Teflon and Nylon filters. The instructor or TA will demonstrate this procedure. Be sure that the Teflon filter is located in the upstream position with the Teflon side facing into the air flow. There is no orientation requirement (front/back) for the Nylasorb filter. ***Cleanliness is critical.*** Do not touch or breathe on the filters. Handle them only with clean tweezers near the edges.
4. Ensure the filter pack is sealed with appropriate plugs and set it aside until it is ready to be attached to the denuders. Load the other filter pack following the procedure above.

Preparing denuders

1. Each group should obtain denuders from the TA or Instructor. One sampling train will use two ammonia denuders and one nitric acid denuder. A second (blank) sample train will use one denuder of each type. Clean the denuders and their caps as follows:

- Rinse insides of denuder caps with DI water. The inside of the cap should be treated as a "clean" surface and should never contact anything but DDW, clean aluminum foil, or a denuder. The outside of the denuder cap does not need to be extremely clean and can be handled with bare hands or gloves.

- Clean denuders with DI. Denuder ends and interiors should be treated as "clean" surfaces.
    - With both caps removed, allow water to flow through denuder, alternating ends.
    - Replace bottom cap.
    - Partially fill denuder with DI, close open end and shake.
    - Repeat 5 times.

- Remove bottom cap and run DI through denuder again.
- Shake off excess DI and replace caps.

2. Coat denuders with Na_2CO_3 coating solution (for HNO_3 collection) or with phosphorous acid coating solution (for NH_3 collection) as follows:

A. Use 5 mL of coating solution to wash denuder.

- Remove top cap of clean denuder (leave bottom capped) and set denuder upright on capped end.
- Slowly pipette 5 mL of appropriate coating solution so that it will cover all surfaces.
- Replace cap.
- Hold denuder horizontally and rotate while lifting one end then the other for 2 minutes to distribute the coating solution evenly.
- Remove top cap and decant excess coating solution into chemical waste container.
- Return denuder to upright position, then decant excess coating solution again; repeat until no solution is decanted.

B. Use 10 mL of coating solution to coat denuder.

- Remove top cap of denuder.
- Pipette 10 mL of coating solution into denuder as described above, then rotate as described above for 2 minutes.
- Remove top cap and decant excess solution into chemical waste container.
- Return denuder to upright position, then decant excess coating solution again; repeat until no solution is decanted.

3. Dry denuders

NOTE: Drying manifold caps are labeled to match denuder types. Each denuder must be attached to matching labeled manifold cap.

- Remove top cap of denuder and place on clean aluminum foil.
- Attach top end of each denuder to appropriately labeled drying manifold port.
- Remove bottom cap of denuder and place on clean aluminum foil.
- Ask TA to start the denuder drying system and set appropriate flow rate.
- Allow flow to continue for 5-6 minutes.
- Remove each denuder from drying manifold and attach opposite end to same drying manifold port.
- Allow flow from drying system to continue another 5-6 minutes.
- Remove each denuder and replace top and bottom caps, making sure cap numbers match denuder number.
- Once all denuders are dried, shut off drying system.

Assemble denuders and filter packs and prepare for sampling

Assemble each sampling train as instructed by the TA or Instructor. The TA will help you load one of the sampling trains into the sampling box located outside the lab and attach an inlet cyclone. Two class groups will be loading a sampling train. Record which filter packs and denuders are assigned to each sampling channel. The TA will show you the programmable sampling pumps and flow meters. The TA will program the pumps to run during one 48 hour period following class (depending on expected weather/air quality conditions). Two sampling trains will be operated in parallel to obtain a replicate measurement. Following sampling the TA will provide you with the sample time and total sampled flow for each channel.

One filter and denuder of each type will be used as sample blanks. Record which filters and denuders are designated as the blank. Unload the blank filters back into the appropriate Petri dishes. Give the blank deunders and filters to the TA for storage.

Denuder and filter extraction

The TA will remove the sample trains after the sampling period and store until a subsequent lab period, when you will extract them. You are responsible for extracting those samples you prepared. Remember to extract both the actual samples and the blanks.

1. Denuder extraction

- Place clean aluminum foil on work surface.
- Remove top cap of denuder and pipette 10mL of DI water over exposed glass surfaces.
- Replace cap and agitate denuder for 4 minutes by rotating denuder while alternately lifting each end to spread DDW evenly over all interior glass surfaces.
- Decant extraction solution into 5mL cryovial. Label vial appropriately. Decant additional extract solution into waste container.
- From the 5ml cryovial, pipette 600 µl into IC vial, cap and label appropriately.
- Give labeled vials to TA for refrigeration.

2. Filter extraction

Open the filter holder at each union and, using clean forceps, remove each filter individually.

Teflon filters

- Put the Teflon filter into a 16 ml test tube with the sampling side facing the tube interior. Pipette 200 µl of ethanol onto the surface of the Teflon filter one drop at a time. Add the ethanol slowly so that it wets entire surface.
- Add 5.8 ml DI water and cap tube.

Nylon filters

- Pipette 6.0 ml of IC anion eluent ($NaHCO_3/Na_2CO_3$ aqueous solution) onto nylon filter and cap tube.

Ultrasonic bath extraction

- Fill bath with 3-5 cm of water (too much will make tubes float and tip).
- Place filter tubes into rack in bath and run for 30 minutes.
- Remove and dry tubes

Final sample vial preparation

- For each filter: pipette 600 µl of filter extract into IC vial and label appropriately. Pipette 5 ml of filter extract into cryovial and label.
- Provide sample vials to TA for refrigeration.
- These samples will be analyzed later in the semester by ion chromatography.

Questions for Discussion:

Start this and every lab report with a brief summary of the experiment conducted. Use data from both weeks of experiment #2 to answer the following questions.

1. From the blank sample results (from both weeks), calculate detection limits (95% CL) for aerosol nitrate, sulfate, ammonium, sodium and calcium for the filter sampling method. Calculate detection limits (at the 95% confidence level) for gaseous ammonia and nitric acid measurement by the denuders. Make your calculation for hypothetical samples collected in duplicate over 48 hours. Express your detection limits in units of nanomoles/m^3 for the gases and nanequivalents/m^3 for the particle species.

2. Calculate the concentrations of aerosol nitrate, sulfate, ammonium, sodium and calcium and gaseous ammonia and nitric acid for both week1 and week 2 sampling periods. Express your concentrations in units of nanomoles/m^3 for the gases and nanoequivalents/m^3 for the particle species. To do this you will need to consider the sample volume, the extract volume, and the concentrations in the extracts. How do these concentrations compare to the detection limits? Determine the total particle mass concentration represented by the measured species for each sampling period.

3. Using the concentration values obtained from the sample duplicates, calculate a pooled standard deviation for each species examined in part (2) above. Using this information, determine whether the species concentrations measured in the two (week 1 and week 2) sampling periods are significantly different from each other at the 95% confidence level.