

Laboratory Manual for Chemistry and Public Policy

Fall 1999

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Keeping a Lab Notebook

The notebook—Get a cheapo "composition" book, you do not need the expensive hardback kind or the kind with carbon paper.

The purpose of keeping a lab notebook is to record why you tried something in lab, what you did (in excruciating detail), what you observed, how you interpret your observations, and what you think it all means in relation to the chemical concepts and the policy issues you are studying in class.

Proper care and feeding of the lab notebook

- 1) Leave several pages blank for a table of contents.
- 2) Each lab period start a new page in your notebook. At the top of the page goes a working title, the date, and a reference for the lab manual procedure that you will follow. You don't need to rewrite the procedures in your notebook.
- 3) Your lab book is your friend, your confidante. Tell it what you really do at each step, not what you were supposed to do. Talk to your notebook--write down your thoughts & ideas, draw pictures of your experiment, confess your bafflement, guess what will happen next in the experiment.
- 4) Despite what you were told in high school, you may use first-person narrative in your lab book. ("After I added the philosopher's stone, the lead turned to gold. I plan to patent this procedure pronto.")
- 5) Spectra & graphs must be labeled with your initials, lab page number, and a sample description. Thus, if I measured the IR spectrum of CO₂ on p. 6 of my notebook, I would label the spectrum ML6-CO₂. Spectra should be taped inside the notebook.
- 6) At the end of the lab period, go back and check that you have answered all the questions posed in the lab manual. Make sure your answers are legible, make sense, and are easy for the TA to find (draw a box around them or something).
- 7) Write a couple of sentences describing what you liked and disliked about the lab work, what you found easy or hard, and any ideas for improving the lab.
- 8) Turn in your notebook to the TA.

Grading of the notebook—you will get feedback from me and from the TA about how well you are accomplishing the objectives stated above and suggestions for how you could improve your notebook. After two lab periods, your lab notes will be graded along with your answers to specific questions posed in the lab manual.

Safety Practical

There will be a short lecture/demonstration/question session the first day of lab.

1) At the back of your lab book, draw a plan of the part of the lab where Chem 191 will meet (the three lab benches to the north of the room, plus the instrument room at the northeast corner). Include on your plan the location of: all exits, telephone, fire alarm, eye wash, emergency shower, your lab drawer, your assigned balance, Reagent Central, broom and dustpan, fire extinguisher, nearest bathroom.

2) Accident Info:

- 1) decide if lab must be evacuated (only for big fires or a large release of noxious gases)
- 2) apply copious amounts of water to victim (sink, eyewash, or emergency shower)
- 3) notify TA of accident
- 4) evaluate injuries (TA will do this) followed by appropriate treatment: a Band-Aid, an escorted trip to the campus medical center (you do know where that is, don't you?), or summoning of emergency assistance.
- 5) help clean up spills or broken glass and dispose in appropriate containers.

3) Fire or Flood Info:

- Large or spreading fires, noxious fumes, or a risk of explosion (e.g. a fire that is near bottles of flammable solvents) warrant evacuation of the lab. Pull the fire alarm.
- Small fires: Notify TA, stay between an exit and the fire, try to smother the fire or use a fire extinguisher to put it out. Fire extinguishers release messy white powder.
- Flood: Try to turn off water, notify TA. Clean up spilled water to prevent slips.

The Test: You will be randomly assigned one of the following situations. In order to pass the safety practical, you must demonstrate the correct course of action and answer any questions the TA may ask.

- 1) You have just dropped an empty flask on the floor, where it shatters into a million pieces.
- 2) The wastebasket is on fire.
- 3) You feel a painful burning sensation in your right eye.
- 4) Your lab partner gives a yell of pain; the bottle of sulfuric acid he was using cracked and he is drenched from the waist down.
- 5) There is a loud beeping sound coming from a nearby hood.
- 6) You notice that a fire is raging at the south end of the lab, where the analytical students work.
- 7) Your lab partner's test tube breaks; she has a small cut on her hand and complains that it stings.
- 8) The sink on your bench is plugged up and overflowing, there is water all over the floor.
- 9) The sleeve of your long shirt is smoldering.
- 10) You just put your elbow in a puddle of liquid on the bench, and now your skin feels funny.

Lab Check-in

Name _____ Date _____

Drawer number _____ Safety practical _____

Item	Number	Check in	Check out
600 ml beaker	1		
250 ml beaker	1		
250 ml conical flask	3		
50 ml conical flask	1		
small spatula	1		
glass stirring rod	1		
10 ml graduated cylinder	1		
100 ml graduated cylinder	1		
10 ml plastic syringe	2		
1 ml plastic syringe	2		
Reaction well plate	1		
Graduated plastic pipets	12		
Micro plastic pipets	12		
Petri dish with lid	2		

Other items available in lab include:

Test tubes—boxes of disposable test tubes are located at Reagent Central

Test tube racks—stored beneath hoods along E wall of lab

Analytical balance--use the balance that is on your lab bench (shared by 8 people)

Ring stands and clamps--stored underneath sinks

Hot plates--stored underneath hoods along E wall of lab

Sinks with regular water and DI (deionized, pure) water, soap solution, and brushes.

Computer--corridor near W wall of lab--this machine has no printer. Additional computers plus a printer are located in 132 Nieuwland.

"Consumables" are stored in the hood in the NE corner of lab.

Kimwipes, disposable plastic pipets, disposable plastic gloves, labels

Reagents (solids and liquids) and waste bottles will normally be placed at Reagent Central--the hoods on the E wall of the lab.

Air Pollution

Air pollution is caused by tiny amounts of reactive gases. The goal of this lab is to give you some insight into how common air pollutants react with the environment and with living organisms. Three three-hour lab periods are allowed to carry out all the suggested experiments.

The first part of the lab is the preparation of pure samples of nitrogen, oxygen, carbon dioxide, sulfur dioxide, and NO_x . Each of these gases will be tested to determine whether it supports combustion, dissolves in water, affects the acidity of water, and whether it is toxic to plants and animals. Each gas will be examined by infrared (IR) spectroscopy to see if it is a potential greenhouse gas. There are also two rather free-form investigations on the pollutants NO_x and carbon dioxide, in which you will learn something about cloud formation, acid rain, and natural sinks for carbon dioxide.

Flowchart

A.1 Preparation of samples of gases in Zip-loc® baggies¹				
Nitrogen N_2	Carbon Dioxide CO_2	Oxygen O_2	Sulfur Dioxide SO_2	Nitrogen Oxides NO_x
A.1a Get from tank	A.1b Get from dry ice	A.1c Synthesize in baggie	A.1d Synthesize in baggie	A.1e Synthesize in baggie

- A.2** Does the gas support combustion?
- A.3** Is the gas soluble in water?
- A.4** Characterize indicator solution as a probe for acidity/alkalinity
- A.5** Does the gas alter the acidity of water?
- A.6** Does the gas damage plants?
- A.7** Does the gas damage brine shrimp?
- A.8** Is the gas a potential greenhouse gas?
 - A.8a** Taking IR spectra
 - A.8b** Interpreting IR spectra

- B.** Additional experiments on Nitrogen Oxides (NO_x)²
 - B.1** A chemical reaction source for NO_x
 - B.2** How is NO_x transported through the air?
 - B.3** Aerosol formation by reaction with ammonia
 - B.4** Cloud scavenging of NO_x
 - B.5** Acid rain

- C.** Additional experiments on Carbon Dioxide (CO_2)
 - C.1** Density of carbon dioxide gas
 - C.2** What affects the solubility of carbon dioxide in water?

¹ Adapted from Chemistry in Context Lab Manual, R. Silberman, Ed., 1994

² Adapted from ChemTrek, S. Thompson, Colorado State U. 1990

A.1 Preparation of samples of gases in Zip-loc® baggies—Some of the gases react with water, so be sure your baggies are clean and dry. The baggies are airtight for hours when properly sealed, but gases cannot be stored from one lab period to the next.

A.1a—Nitrogen (N_2)—The nitrogen inside the tank is at a pressure of about 2000 psi. A two-stage regulator reduces the pressure to 5-10 psi. To withdraw gas from the nitrogen tank, open the thumbscrew so nitrogen flows through the plastic hose (this flushes all the air out of the hose). Squeeze the air out of your baggie, open the zip just a bit, and fill the baggie with nitrogen. Zip it shut and squeeze gently to see if it's airtight.

1) What volume of gas do you estimate is inside the bag?

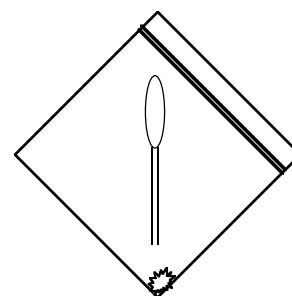
A.1b—Carbon Dioxide (CO_2)—Dry ice is frozen carbon dioxide gas. Its temperature is about $-90^\circ C$, so it can give you a "cold burn" if you touch it with your bare skin. Hold it with the ski gloves or tweezers instead.

1) Slip a piece of dry ice about the size of a pea into a baggie and close the zip.

Record what happens.

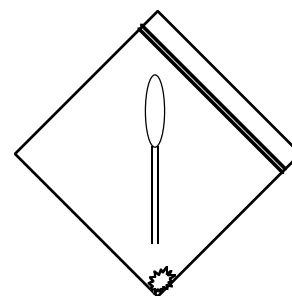
A.1c—Oxygen (O_2)—Oxygen can be made from hydrogen peroxide according to the following balanced equation: $2H_2O_2 \rightarrow O_2 + 2H_2O$. Normally this reaction is slow. A solution of 3% hydrogen peroxide can sit around in your medicine chest for years without decomposing to oxygen. In order to speed things up, a **catalyst** is added. Catalysts increase the rate of a reaction without being used up in the reaction. Many catalysts generate oxygen from hydrogen peroxide—for example, baker's yeast has an enzyme that does the job, as does blood (that's why hydrogen peroxide fizzes when you put it on a scratch). For this lab, manganese dioxide, MnO_2 , is used as the catalyst.

- 1) Weigh about 0.5 grams of MnO_2 and place it into the bottom corner of the baggie.
- 2) Fill a graduated pipet with 6% H_2O_2 . (**caution: corrosive**)
- 3) Put the pipet into the baggie as shown at right, gently smooth the baggie to remove as much air as possible, then seal the baggie.
- 4) slowly drip the hydrogen peroxide solution onto the catalyst. Record what happens in your lab notebook.
- 5) You should now have a baggie partially filled with O_2 .



A.1d—Sulfur Dioxide (SO_2)—This smelly and irritating gas should be produced and sampled in a fume hood. It is generated by the action of acid on sodium sulfite (Na_2SO_3).

- 1) Weigh about 2 grams of Na_2SO_3 and place it into the bottom corner of the baggie.
- 2) Bring the baggie to a fume hood. Fill a graduated pipet with sulfuric acid solution (6M H_2SO_4 , **caution: corrosive**)
- 3) Put the pipet into the baggie as shown at right, gently smooth the baggie to remove as much air as possible, then seal the baggie.
- 4) slowly drip the acid onto the Na_2SO_3 . Record what happens.
- 5) You should now have a baggie partially filled with SO_2 .

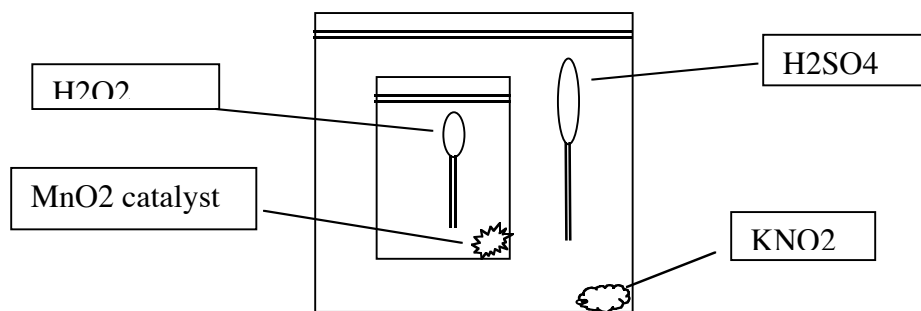


A.1e—Nitrogen Oxides (NO_x)-- This smelly and irritating mixture of NO and NO_2 should be produced and sampled in a fume hood. NO_x is generated in two steps. Nitrogen oxide (NO) and oxygen are generated in separate containers. Then they are mixed to give NO_x .

1) The nitrogen oxide generating bag: Weigh out 1.5 g of potassium nitrite (KNO_2) and place in the corner of a large baggie. In a fume hood, fill a graduated pipet with sulfuric acid solution (6M H_2SO_4) and put it in the bag.

2) The oxygen generating bag: Use a small baggie. Place 0.5 g of MnO_2 in the corner of the baggie. Fill a micro pipet with 6% H_2O_2 and slip it into the bag. Smooth out as much air as you can, then seal the bag.

3) Go to a fume hood. Place the oxygen-generating bag inside the nitrogen oxide-generating bag. Smooth out the bag to expel air, then seal the nitrogen oxide-generating bag. Your assembled NO_x generating system should look like this:



4) Without opening either bag, generate oxygen in the small bag by dripping the H_2O_2 onto the catalyst. Generate nitrogen oxide (NO) in the large bag by dripping the H_2SO_4 onto the KNO_2 . Record your observations. When the reaction is over, you will have a small bag filled with oxygen inside a larger bag filled with nitrogen oxide (and possibly some nitrogen dioxide).

5) Without opening the large baggie, open the small bag containing the oxygen. Record your observations.

6) The large bag now contains a mixture of nitrogen oxides, usually called " NO_x ". Please keep it in the fume hood since the NO_x slowly diffuses through the plastic bag.

A.1 con'd Obtaining gas samples from baggies: To get a sample of a particular gas, squeeze the bulb of a graduated pipet to expel the air inside. Keep squeezing the bulb as you push the tip of the pipet against the zip seal. With a bit of practice you will be able to open the seal just enough to admit the pipet tip. Do not touch the pipet to the liquid or solid chemicals inside the bag! When the bulb is released, a sample of the gas will fill the pipet. As you remove the pipet, reseal the zip seal.

A.2 Does the gas support combustion?

1) Prepare a pipet containing a gas sample. Ignite the end of a toothpick, let it burn a few seconds, and blow it out. Continue to blow on the embers so they glow.

2) Hold the pipet tip next to the ember and squeeze a quick puff of gas onto it. Observe and record the results.

A.3 Is the gas soluble in water?

1) Put 5 ml of water into a test tube. Prepare a pipet filled with the gas. Immediately plunge the end of the pipet into the water. Does anything happen right away? Does anything happen over 10 minutes or so? Record your observations and save the test tube & pipet for **A.5**

2) Which gases are soluble and which are not? Why does their solubility matter?

A.4 Characterize indicator solution as a probe for acidity/alkalinity—Chemists measure acidity and alkalinity on the pH scale. For now, all you need to know is that pH 7 is neutral pH (neither acidic nor basic), pH values below 7 are acidic, and pH values above 7 are basic. Most living organisms prefer pH values between about 6-9. At pH values of less than 4, most aquatic life cannot survive.

1) Take your reaction well plate to Reagent Central and place 1 ml of each of the pH standards into a separate large well. You should have six of them: pH 2, 4, 6, 7, 8, and 10. Draw a diagram in your notebook so you can remember which solution is in which well.

2) Place about 1 ml of "universal indicator" solution into an empty well. Take the reaction well plate back to your bench.

3) Add 1 drop of universal indicator to each pH standard. Record your observations.

4) Write down a procedure to find the approximate pH of an unknown water sample. Show it to a TA before proceeding.

A.5 Does the gas alter the acidity of water?

1) You will need the test-tube/pipet setup from **A. 3**. Slowly squeeze the pipet out, bubbling the gas through the water. Mix well.

2) Find the pH of the water using the procedure you developed in **A.4**. Record the result.

3) Which gases alter the acidity of water? What consequences could this have?

A.6 Does the gas damage plants? The colors of many plants & flowers come from natural pigments called anthocyanines. If atmospheric pollutants get into the plant's cells, the reactive gases can react with these pigments, often causing interesting color changes. If pigment molecules react, other cell components can probably react; thus, the color change is an indicator for more serious cell damage which can harm or kill a plant.

1) Get some flower petals and/or vegetable pieces from Reagent Central. Put the plant sample you wish to test into a small beaker.

2) Make a lid for the beaker out of a plastic weighing boat.

3) Prepare a pipet filled with the gas to be tested. Puff the gas into the beaker and put the lid on. Record what happens over the next ten minutes or so. Compare the samples with those which were not exposed to the gas and record your observations.

4) Which gases harm plants? Why does this matter?

A.7 Does the gas damage brine shrimp?

1) Get about 10 ml of brine shrimp in sea water from Reagent Central. Put 1 ml into each of two clean test tubes. Take a moment to watch the brine shrimp and describe them and their behavior in your notebook. They are quite small, so you may need to try some different backgrounds and lighting conditions. There should be at least 5 brine shrimp in each test tube.

2) Design and write down a procedure for testing the toxicity of a gas sample to brine shrimp. Show it to a TA to make sure there are no problems.

3) Carry out your procedure with your gas sample & record the results.

4) Which gases harmed the brine shrimp? Brine shrimp are not exactly an endangered species, so why are these results important?

A.8 Is the gas a potential greenhouse gas? The greenhouse effect keeps our planet warm enough to support life. The Earth is a warm object—about 16°C average temperature—which radiates heat into space in the form of photons of infrared light. If all these photons escaped into space, the average temperature of the Earth would be below the freezing point of water. Greenhouse gases absorb infrared light and prevent it from escaping to space. The energy of the light heats up the atmosphere; this is called the greenhouse effect.

Infrared light is just like visible light, except the energy range for infrared light photons is lower than the energy range for visible light. There are different "colors" of infrared—we cannot see them, but some animals (like bees) can. We have to use instruments to produce and measure different frequencies of infrared light. An infrared spectrometer shines different frequencies of infrared light through the sample and measures how much of the light is absorbed by the sample and how much is transmitted through the sample at each frequency.

A.8a Taking IR spectra—You only need to take the IR spectrum of one of the air pollutants.

- 1) Make sure that the outside of your gas baggie is completely dry. Inspect your baggie to find a corner which is also dry inside—probably one of the top corners.
- 2) The TA will show you how to use the spectrometer and plot out the spectrum.
- 3) In your notebook, write a list of instructions for how to use the spectrometer which you could give to another student who had never used the instrument.
- 4) What substances are sampled by the spectrometer—in other words, what does the IR beam pass through? Write a list or draw a sketch—include dimensions.
- 5) Label the spectrum with your name and the gas formula and give it to the TA.

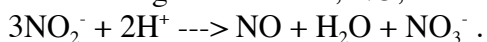
A.8b Interpreting the IR spectra—You will need copies of the IR spectra for each gas, the IR spectrum of air, and the IR spectrum of a baggie. These will be posted on the whiteboard in lab.

- 1) The units of the x-axis are reciprocal centimeters (cm^{-1}). You can think of the x-axis as "how many waves will fit into a centimeter". At the position on the x-axis marked 1600 cm^{-1} there are 1600 waves per centimeter so each wave has a length of $1/1600 \text{ cm}$, or $6.25 \times 10^{-6} \text{ m}$. Figure out which end of the x-axis corresponds to high energy IR light and which to low energy light, then annotate the axis accordingly.
- 2) The units of the y-axis are "% transmission." Annotate the y-axis to show which end means that the sample absorbs most or all of the IR light of a given frequency, and which end means that the sample doesn't absorb the IR light of a given frequency.
- 3) What frequencies or frequency ranges does air absorb strongly?
- 4) What frequencies or frequency ranges does a baggie absorb strongly?
- 5) Why do you need to know the information in steps 3 and 4?
- 6) Identify the characteristic absorbance frequencies or frequency ranges for each gas sample.
- 7) Which gases are potential greenhouse gases? Explain your evaluation.

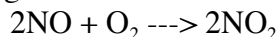
B. Additional experiments on Nitrogen Oxides (NO_x)³

B.1 A chemical reaction source for NO_x

NO_x is actually a mixture of several nitrogen oxides, including NO and NO_2 . Nitrogen oxides can be formed by a chemical reaction between the nitrite ion, NO_2^- , acid, and air. The initial product is nitrogen monoxide, NO, which is not very soluble in water:



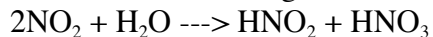
The NO is released as a gas and floats around until it encounters a molecule of oxygen, O_2 , from air. The oxygen oxidizes some of the NO to NO_2 .



The mixture of NO and NO_2 is called " NO_x ".

³ Adapted from ChemTrek, S. Thompson, Colorado State U. 1990

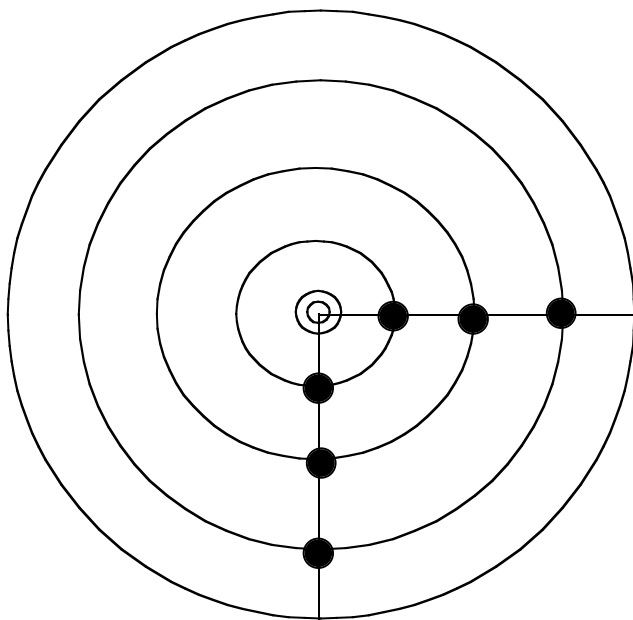
NO_2 reacts with water to form various strong acids:



Drops of indicator solution can be used to "see" the acid that is produced. The acid can be neutralized with a naturally occurring base such as ammonia (NH_3).

B.2 How is NO_x transported through the air?

- 1) Place a clean dry petri dish on the reaction grid below.



- 2) Place small drops of universal indicator solution in the positions shown by the black dots. These drops will show you how NO_x moves out from their source, which will be at the center of the grid.

- 3) Drop one drop of 1M KNO_2 at the center of the grid. Hold the lid over the dish and add one drop of 6M H_2SO_4 . Immediately close the lid. Watch carefully and record what happens. You might even want to time some of the processes.... Refer back to your notes for **A.4** to interpret the color changes you see.

- 4) Use a wash bottle to flood the dish with water, then clean and dry it at the sink.

- 5) If NO were very soluble in water, what results would you have seen in this experiment?

- 6) When you generated NO_x in a baggie in **A.1e**, why were you asked to use separate oxygen and NO generating baggies instead of just using oxygen from air to oxidize the NO ?

B.3 Aerosol formation by reaction with ammonia—An "aerosol" is any small particle or droplet of liquid that is so small it can be suspended in air. Dust, hair spray, and fog are all aerosols. NO_x reacts with ammonia to form an aerosol—believe it or not, the exact chemical formula of this aerosol is not known.

1) Get a dry petri dish with lid. Put a drop of indicator solution at the center of the dish. Place 1 drop 1M KNO_2 at one side of the dish, add 1 drop of 6M H_2SO_4 , and replace the lid. When is the petri dish full of NO_x ? How do you know?

2) Add 1 drop of 2M NH_3 solution to the other side of the petri dish. Watch carefully, first against a white background and then, after 2-3 min, against a black background. Record your observations.

3) What color is the aerosol? Imagine that you had a lot of aerosol particles in the atmosphere. How would they affect the amount of sunlight absorbed by the Earth? Why is this relevant to global climate change?

4) Rinse out the petri dish at the sink and dry with paper towels.

B.4 Cloud formation and scavenging of NO_x —Clouds consist of very tiny droplets of water. Two-dimensional clouds can be created inside a petri dish by cooling the lid so water vapor inside the dish condenses on it. The tiny droplets scatter light, so the cloud is visible against a dark background. What happens when the cloud interacts with atmospheric NO_x ?

1) You will need two clean, dry petri dishes with lids. Put a few drops of KNO_2 solution in the center of each of the dishes, but don't add the H_2SO_4 yet. Place some drops of universal indicator in the dishes so you can monitor the NO_x generation and transport & cover the dishes with their lids.

2) Get a cup of ice from Reagent Central and add some water. Use a pipet to place a small pool of this cold water on top of the lid of one petri dish. Add a few ice chips to the pool. Slide the dish over a dark background and wait 2-5 minutes for a cloud of droplets to form under the cold pool.

3) Gently lift the lid so the cold pool stays on it. Add a drop of 6M H_2SO_4 to the KNO_2 drop and replace the lid. At the same time, add a drop of 6M H_2SO_4 to the KNO_2 in the other petri dish and replace its lid.

4) Wait about 3 min. What happens in the two dishes? Record your observations.

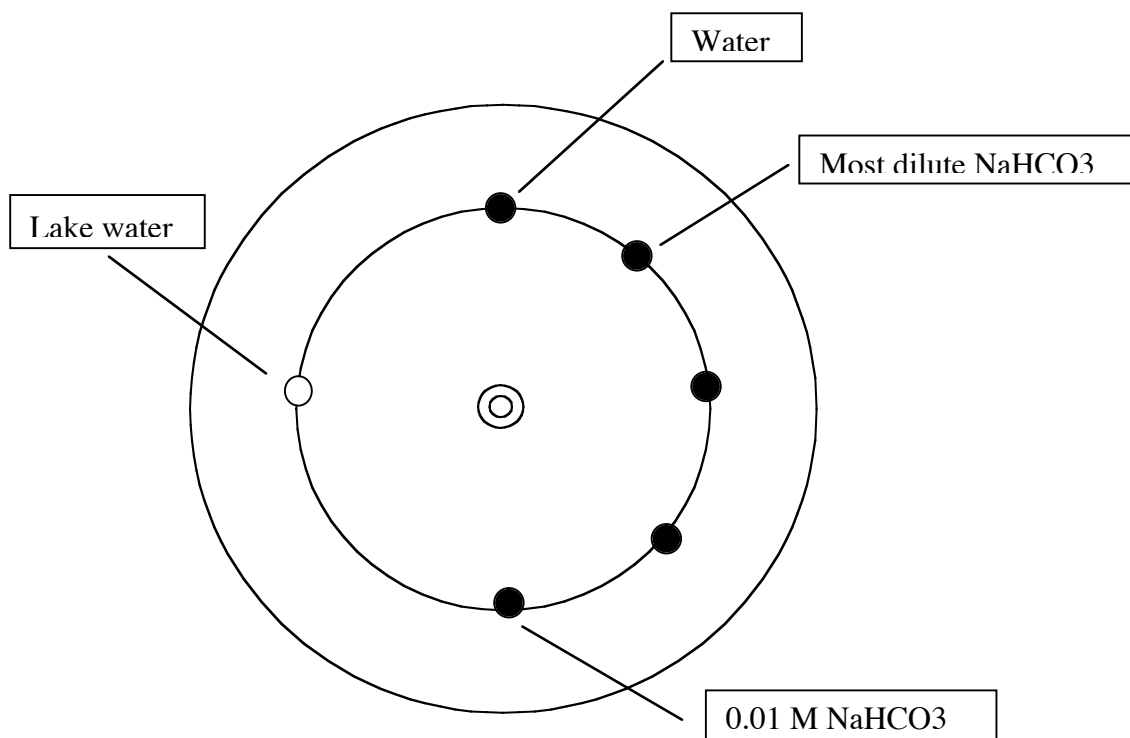
5) Where did the NO_x go in the dish with the cold pool on the lid? Design an experiment to test your hypothesis. Show your procedure to a TA and then carry it out.

B.5 Acid rain—Some lakes seem to be unharmed by acid rain which damages other lakes nearby. One of the most important factors determining the susceptibility of lakes to acid rain is the presence of natural bases in or near the water. The most important natural bases are calcium and magnesium bicarbonates and carbonate minerals.

1) Go to Reagent Central and fill a pipet with 0.01M NaHCO_3 solution.

2) In a clean, dry reaction well plate, place 10 drops of the NaHCO_3 solution in one small well. Place 5 drops in #2, 2 drops in #3, and 1 drop in #4. Now get some deionized water. Add 5 drops of water to well #2, 8 to well #3, 9 to well #4, and ten to an empty well. You now have a series of NaHCO_3 solutions with a different concentrations. In your notebook, calculate the concentration of each solution; if you're not sure of your math, check with a TA before going on to the next step.

3) Place a clean, dry petri dish over the grid below and put 1 drop of water at the position corresponding to 12 o'clock. Place single drops of the various NaHCO_3 solutions as shown below. Get some lake water from Reagent Central and place a drop at the 9 o'clock position.



- 4) Add 1 drop of universal indicator to each of the samples. Record your observations.
- 5) Generate NO_x at the center of the dish in the usual manner and place the lid on the dish. What happens? Record your observations.
- 6) Predict whether the lake you tested would be susceptible to acid deposition from nitrogen oxides.
- 7) Several minerals are available at Reagent Central. Do any of these minerals offer any protection to lakewater from the effects of acid deposition? Write down an experimental procedure that would test the protective ability of these materials against acid deposition. Show it to a TA, and then carry out the experiment.

C. Additional experiments on Carbon Dioxide (CO_2)

C.1 Determine the density of carbon dioxide gas--Density is the mass per unit volume of any substance. In this case, we want to know how many grams of carbon dioxide gas will occupy a volume of 1 liter at room temperature and pressure.

- 1) Get a clean, dry baggie. If the inside or outside of the bag is wet, it will throw off the measurement considerably.
- 2) Weigh out about 0.5 g of dry ice—a piece about the size of a lentil. Try to avoid pieces with a lot of frost on them. Immediately put the dry ice into the baggie, seal the baggie, and wait until all the dry ice has evaporated.
- 3) Hold the baggie in a large beaker and fill the beaker up partway with water. The baggie will try to float up to the surface, so hold it down so it is entirely submerged. Make a mark at the level of the water.
- 4) Remove the baggie. The water level will go down. Add measured amounts of water to fill the beaker back to the mark. This is the volume of the baggie + gas.

5) Calculate the density of CO₂. In your lab book, explain how to do this calculation.

6) If you were to repeat this measurement with a different weight of dry ice, what value of the density do you think you'd get? Try it at least once and see (be sure to use a dry baggie...)

7) Write your name and CO₂ density values on the blackboard.

C.2 What affects the solubility of carbon dioxide in water?—The oceans are the second-largest sink for carbon dioxide. The carbon dioxide does not just dissolve in the water, it undergoes a reaction with water molecules to form bicarbonate ion (HCO₃⁻) and acid (H⁺). The bicarbonate and acid can in turn react with other ions that are in the water. The goal of this part of the lab is to test some of the factors that influence CO₂ solubility so that oceanographers will know what is important to measure for climate change studies. Some factors that might influence the solubility of carbon dioxide include salt content, water temperature, presence of metal ions such as Ca²⁺, Fe³⁺, and Mg²⁺, and acidity/basicity of the water.

1) A method for measuring gas solubility: Take a plastic baggie, add 50 ml of water (possibly containing other ions too), press out the air. Weigh out 0.5 g of dry ice & add it immediately. Seal the bag. Let the dry ice evaporate, then measure the volume of the bag. Use the density of carbon dioxide from **C.1** to calculate how much volume the dry ice *should* have occupied. Any difference between this "theoretical" value and the actual volume of the bag must be due to the carbon dioxide dissolving in the water. Calculate how many grams of carbon dioxide dissolved in the 50 ml of water.

2) The following materials will be available at Reagent Central:

Dry baggies (3 per person), dry ice chips, ocean water (37g sea salt per L water), ice, solutions of Ca²⁺, Fe³⁺, and Mg²⁺ ions, and solutions with pH 2, 4, 6, 7, 8, and 10.

3) Design an experiment to test the influence of any *one* factor on the solubility of carbon dioxide in water. Show your procedure to a TA, then carry out the experiment.

4) Describe your experiment, results & conclusions on a large piece of paper (tape it next to the whiteboard).

5) Can you think of ways to improve your experimental procedure? What other questions should be investigated to learn more about this sink for carbon dioxide?

Modeling Climate Change (1 period)

Climate is what we expect, weather is what we get.
--Mark Twain

Part I: Observed climate data—past 100 years

Go to http://ipcc-ddc.cru.uea.ac.uk/cru_data/visualisation/visual_index.html
The Intergovernmental Panel on Climate Change operates an extensive data distribution center at the above web address. Here you can access climate information from thousands of weather stations all over the world, in addition to simulation results that will be used later in this lab.

Click on **observed regional time series**. This will call up a Java program that allows you to graph different weather anomalies for any region of the world, averaged over any month, season, or yearly, for the period 1900-1999.

1) Set the season to summer by selecting June for the first month and August for the last month. On the world map at the bottom of the screen, click and drag the cursor to select a region in the Continental US. Select "temperature anomaly"—this means the deviation of the observed summer temperatures, averaged over the region, from the average summer temperature for that region in the period 1960-1980. Record the latitude & longitude of the region in your lab notebook. Run the program and print out the resulting graph (black and white is fine).

- Explain what a "10-year moving filter" does and why it is a useful treatment for this climate data.

- In the 30's, a drought struck most of the US. Describe in your notebook the temperature anomaly for this time period, corresponding to the Dust Bowl. Now run the program again, and this time look for precipitation anomalies. Describe what you find in your notebook.

2) Reset everything to the default values, then run the program again. This will calculate global temperature anomalies in the past century—it takes 2-5 minutes to run. Print out the resulting graph (black and white).

- In your notebook, describe the observed trends in global mean temperature over the past 100 years. Be as precise as you can—imagine you're describing the graph to someone who cannot see it.

Part II—Proxy climate data—past 600 years

A recent study by Dr. Mann and coworkers⁴ inferred the mean Northern Hemisphere temperature in the recent past from "proxy measurements": chemical evidence of climatic change contained in tiny marine fossils, corals and ancient ice, along with fossilized pollen in lake sediments and annual growth rings in trees. In this part of the lab, you will analyze his data to see whether there is any evidence of global climate change on the millennial time scale.

1) You will need a graphing program called KaliedaGraph (this program will be used later in the term to model population growth). First, login to a Mac, then select "Chooser" from the apple menu. In the top left box of the chooser, click on "AppleShare", and then in the bottom left box, scroll down until you see "OIT Services" then make sure that "OIT Services" is highlighted. Once you have done this, the right box should say "Select a file server" above it. Double click on "ND Mac Server", and when the dialog box pops up, log in as a "guest". At the next dialog box, double-click on "ND Mac Applications". At this point, an icon should appear on the desktop, labeled "ND Mac Applications". Open this drive and scroll down until you see "KaliedaGraph 3.0", copy this folder to the local hard drive by dragging it onto the "Macintosh HD" icon. Now, when you open "Macintosh HD" you should see the KaliedaGraph folder and you can start getting to work.

2) Now you need Dr. Mann's data. Go to **NDAccess** and open the Chem191.01 folder. Drag the file marked "nhtemp.dat" onto the icon for your hard drive. Double click on the file, and Kaliedagraph should start running.

3) The data is organized in rows and columns. The first column (C0) lists the year, the second column (C1) gives the reconstructed temperature anomaly. The temperature anomaly in each year is the deviation of the temperature inferred from tree rings, corals, marine fossils etc. from the mean temperature measured in 1902-1980. A positive value means the year was warmer than the 1902-1980 average, a negative value means the year was cooler. The third column (C2) lists observed northern hemisphere temperature anomalies—note that these records don't start until 1902. The fourth column (C3) gives the standard deviation, which is a measure of the uncertainty of the data.

4) To see the overall trends in this data, make a plot of reconstructed temperature anomaly vs. year. Go to the "Gallery" menu and select "Scatter plot". Pick C0 as the x axis of the plot and C1 as the y-axis. Click "OK" to plot the data on the screen. Double-click on one of the axes to optimize the x or y range, and double-click on the legend to change the data symbol (a 5-pt dot or square will look nice). When it looks good, save this plot as Mean_Temps and print it out (black and white is fine).

⁴ Michael E. Mann, Raymond S. Bradley, and Malcolm K. Hughes, 1998, Global Six Century Temperature Patterns, IGBP PAGES/World Data Center-A for Paleoclimatology Data Contribution Series # 1998-016. NOAA/NGDC Paleoclimatology Program, Boulder CO, USA. ORIGINAL REFERENCE: Michael E. Mann, Raymond S. Bradley, and Malcolm K. Hughes, 1998, Global-Scale Temperature Patterns and Climate Forcing over the past Six Centuries, *Nature* **392**, 23 April 1998, pp.779-787.

- In your notebook, write a description of the observed trends in global mean temperature over the past 600 years. Be as precise as you can—imagine you're describing the graph to someone who cannot see it.

- The historical record contains several extreme climatic events that may show up in the reconstructed temperature anomaly data. These include the Little Ice Age, mid-14th century, the eruption of Mt. Krakatua in 1883—called "the year without a summer," the Dust Bowl 1930-40, and the eruption of Mt. Pinotubo in 1991. You may need to change the x-axis scale on your plot to study these years clearly. Describe in your notebook what temperature anomalies, if any, the data show happening around the times of these events.

5) Do reconstructed temperature anomalies agree with measured temperature anomalies?

- Think of a way to analyze the data in nhtemp.dat that will shed some light on this question. Write it down in your notebook. Check with a TA, then carry out your analysis and record your conclusions.

6) Uncertainties: Click on the window containing your first graph, Mean_Temps. This graph uses data points that were inferred from over 70 proxy measurements—coral growth rates, tree rings, isotope ratios in ice cores, etc. These proxy measurements do not all agree with each other, so the data carries a level of uncertainty, expressed by the standard deviation. The standard deviation can be used to calculate 95% confidence limits for the data—that is, for each temperature measurement that Mann et al. reconstructed from proxy measurements, we can calculate a range of values that has a 95% chance of including the real temperature value. The 95% confidence limits are given by $X_m \pm 1.96\sigma$, where X_m represents the mean value of the data point (eg the mean global temperature for 1432) and σ represents the standard deviation for X_m .

From the "data" menu choose "append column". This will create a new column in which the 95% confidence limits can be stored. Go to the "@@" menu and select "Formula entry". In the window which pops up, type the following: **C5=1.96*C4** The new column (C4) should fill up with numbers, which are the 95% confidence limits for each year's data point. Go to the "@@" menu and select "Error Bars." For the error in the y direction, pull down the menu and select "use a column of data". Pick C4. Click "OK" and replot the data.

- Does this graph convince you that global warming is occurring? In your notebook, explain why or why not.

Part III:--general circulation models (GCMs) Background reading:

<http://www.ipcc.ch/pub/sarsum1.htm>

1) Jump back to http://ipcc-ddc.cru.uea.ac.uk/cru_data/visualisation/visual_index.html and scroll down to the **Global Mean Time Series**. This will take you to a page which plots calculated outcomes of several state-of-the-art GCMs. All the GCMs use a scenario similar to sresa2 (you'll learn more about this later), with a 1% annual growth in CO₂ emissions. Each model was run both with (GSa) and without (GGa) including the cooling effects of aerosols from industrial pollution. Each model was used to predict precipitation and mean temperature for the world, and the results are available as graphs.

- The temperature data are given as temperature anomalies, that is, as deviations from some "baseline" temperature. What is the baseline?
- How much will the world warm by the year 2050, according to these models?
- What do the models predict about precipitation? Is this a) scientifically reasonable and b) desirable?

2) Go to <http://www.mri-jma.go.jp/Proj/goin/GOIN.html>. This web site has a Quicktime movie showing the spatial and temporal outcome of a 70-year simulation of global warming, assuming a 1% annual increase in the amount of CO₂ released (based on the SRESa2 scenario—you'll learn more about that later).

- Describe the regional patterns of climate change this model predicts over the next 70 years.
- Speculate about the economic/political consequences these climate changes might have.

3) The outcome of any GCM depends on the scenario it uses as input. The scenario describes how much CO₂ and other greenhouse gases are emitted per year, and the level of sulfate aerosols from industrial pollution. A scenario has a lot of assumptions about population growth, economic growth, technology, etc. Four basic global warming scenarios are described in the web site http://ipcc-ddc.cru.uea.ac.uk/cru_data/examine/emissions/SRES98.html. Go to this site and bookmark it. Follow the links to the Non-Climate Scenarios for the sresa2 and sresb1 scenarios.

- Briefly summarize the future world described in each model (a few sentences).
- Use Kaleidagraph to graph population growth in each scenario (on the same set of axes). Print out the graph and stick it in your notebook.
- Which of these scenarios do you regard as the most likely to occur?

4) Go back to http://ipcc-ddc.cru.uea.ac.uk/cru_data/examine/emissions/SRES98.html and click on the **Emissions scenario page**. Follow the links and scroll down until you find a chart of data for the emissions of various greenhouse gases for the sresa2 and sresb1 scenarios, then print them out. These two charts list some of the assumptions that would be fed into the GCM: emissions of a zillion greenhouse gases, rates of forestation or deforestation. You will also find graphs showing CO₂ level in the atmosphere, total CO₂ emissions, global mean temperature, and sea level for the sres2a and sresb1 scenarios—print them out too.

- What GCM was used for these calculations?
- Compare/contrast the emissions scenarios for the sresa2 and sresb1 scenarios.
- Compare/contrast the predicted fate of the world for the sresa2 and sresb1 scenarios, according to this GCM.
- A policy question: what policies would most effectively produce a world like the one in sresb1 instead of sresa2?

Part V. What impact, if any, did these computer "experiments" have on your beliefs about the issue of climate change?

- Is global warming occurring?
- Can humans "fix" global warming?

Lead Analysis (3 periods)

LOCATION: 857 Forest Avenue, South Bend, IN 46616

WORK ORDER: Identify sources of lead in and around the home.

DATE OF FIELD WORK: Homeowners have agreed to allow access to the home on Friday, October 8, 1999, from 2-3:30 pm.

SAMPLES: paint chips, household dust, soil, water

OUTLINE OF ACTIVITIES:

Friday October 8, 9:30 am: Meet with Prof. Lieberman to discuss sampling & analysis. Form a **sampling** team and an **analytical** team. The four job managers will head up these teams and later testify as expert witnesses at the trial.

Friday Oct. 8, 2:00 pm SHARP: Sampling team meets at the Library Circle for transportation to work site. Analytical team has a day off.

Job managers are responsible for deciding what types of sample to analyze, choosing the locations to sample, and ensuring that the samples are properly collected and labeled. The sampling team is responsible for the actual sample collection and for any other tasks set by the managers (such as preparing a map of the home to show where samples were taken). After obtaining the samples, sampling team returns to lab (ETA 4:00) and prepares the samples for analysis. The preparation of most samples will take less than 15 minutes.

Friday, October 15: Analytical team carries out analysis of samples by ICP-AES. Sampling team has a day off.

Job managers are responsible for allocating the work of sample analysis, including quality assurance, for posting the raw data on the web, and for converting the raw data into useful information about lead concentrations in the home. (help will be available).

Friday October 29: Presentation & discussion of methodology by sampling and analytical teams at the Evidence Discovery session. (< 1 hour)

Job managers will report results of analysis. (<1/2 hr)

Medical witnesses give brief presentation (<1/2 hr)

Time for prosecution and defense teams to question their expert witnesses (~1 hr)

Monday, Nov. 1—Opening arguments, cross examine plaintiff and defendant

Wed, Nov 3— medical testimony and cross

Friday, Nov 5-- analytical testimony and cross in morning, summing up in afternoon, jury deliberation <1 hour, followed by debriefing, discussion, and dinner.

Lab Flowchart:**A. Sampling—General background****A 1** Paint chips**A 2** Lead dust**A 3** Soil**A 4** Water**B. Analysis****B 1** General directions**B 2** Sample preparation**B 2a** Quality assurance**B 2b** Sampling team: Paint chips, lead dust, and soil (**A 1**, **A 2**, and **A 3**)**B 2c** Sampling team: Water (**A 4**)**B 2d** Analytical team: final prep for paint chips, lead dust, soil, and water**B 3** Sample analysis**B 3a** Quality assurance**B 3b** Analysis by ICP/AES**C** Data Interpretation (for the job managers)**A** General background on common sources of lead exposure for children:

The main source of lead exposure for urban children is leaded paint. Paint consists of pigments which give the paint its color and opacity in an oil or latex base. Most paints used before 1973 contained large amounts of lead oxides and carbonates—even colored paint. Paint from before 1950 could contain up to 500,000 ppm (50% by weight) lead. The amount of lead in paint was reduced in 1950 and again in 1973 (to its current level of <600 ppm), but any home built before 1973 will probably have some leaded paint, perhaps buried under more recent layers of unleaded paint.

Paint that is in bad condition—flaking, peeling, crumbling, or "powdering" at the surface—is potentially hazardous. Small children eat weird things; they chew on furniture and windowsills, eat chips of paint, or suck on dirty toys, clothes, hands, etc. Studies show that toddlers eat 20–40 mg of dirt every day.⁵ Particles of lead paint contaminate household dust; the particles may even be formed outside from exterior paint and be tracked into the home. This is why decrepit interior or exterior lead paint is a special hazard to children.

The permissible amount of lead in dust remaining on each of the following surfaces following lead paint abatement is as follows:⁶ (These are not legally binding standards, just guidelines for HUD contractors)

100 $\mu\text{g}/\text{ft}^2$ on floors.500 $\mu\text{g}/\text{ft}^2$ on interior window sills.800 $\mu\text{g}/\text{ft}^2$ on window troughs (the area where the window sash sits when closed).800 $\mu\text{g}/\text{ft}^2$ on exterior concrete.

Lead enters the soil mainly from lead paint or automobile exhaust (only a problem next to busy roads/freeways). Soil naturally may have as much as 50 ppm of lead. If there is >200 ppm

⁵ Ramon Barnes, U. Mass, talk at meeting of St. Joseph Valley section of ACS, Feb. 1997.

⁶ Indiana HUD cleaning directions

lead in soil, the homeowner is advised to take preventative action such as controlling nearby paint chips, planting thick ground cover, paving the area, or removing the soil. 200-500 ppm of lead is common in urban soil. If there is >1000 ppm lead in the soil, it may be considered hazardous waste.⁷

Old plumbing may use lead pipes or lead solder in joints. If the local water is acidic and/or "soft" the lead can leach out into the water. The highest levels of lead are found in the water that has stood in the pipes all night. The permissible level of lead in drinking water is 20 ppb (parts per billion).

Other sources: Ceramics, such as lead-glazed pottery or lead-glass crystal, can cause acute lead poisoning through leaching of lead into acidic foods like coffee, wine, or tomato sauce. Other sources of lead include hobbies such as shooting, gunsmithing, stained glass, electronics, some artist's pigments, fishing, and local industries like auto shops, car battery recyclers, or metal smelters. Garden vegetables are not a major exposure route for most urban dwellers.

Sampling procedures: Several tasks will need to get done at the job site: evaluation of the home to decide the likely hazards and sampling plan, drawing an artistic map of the house and its surroundings (this will be useful in court...), collecting a total of 15-20 samples of different types, and ensuring that they are properly labeled and processed. The job managers primary task is to divide up the work and check that it is done properly.

A 1 Paint chips: Windowsills, porches, garages, and exterior walls are good places to look for peeling paint. Lead content in paint is expressed in terms of ppm by weight; this is the same thing as the number of mg of lead in each kg of paint.

0) Materials needed: Zip-loc baggies, labels, pen, notebook

1) Survey the general condition of the paint in the areas you are assigned to sample; keep notes in your lab notebook. Include information such as the location of decrepit paint (is it at child height?), whether there are many layers of paint visible, and whether it appears that remodeling or repainting has been done recently (potential sources of paint dust). One group should look at interior paint and one group at exterior paint. Don't forget painted garages, sheds, or fences. Decide where each group will sample and describe the locations in your notebook.

2) For each sample, open a baggie, turn it inside out, and pick up some paint flakes. Don't touch the sample with your hand. Chemical analysis will require a piece of paint about the size of a quarter (or several smaller paint chips). Paint flakes that have fallen off of their own accord are best, or you can gently pull off some peeling paint. Please, do not destroy otherwise intact paintwork in order to get a sample!

3) Label the bag with your name, the location where you collected the paint chips, and the words "paint chips".

A 2 Lead dust: Surface lead loading is defined as the amount of lead present as dust in each square foot of floor area (the units are micrograms per square foot, $\mu\text{g}/\text{ft}^2$). The sampling procedure will work best on a smooth floor (no carpeting). If there is a small

⁷ Childhood Lead Poisoning Prevention Program brochure, California Dept. of Health Services.

child in the house, pick an area where he or she plays. You can sample dust on floors, window sills, inside window wells, even on ornamental molding or bookshelves. An accurate test will require an area at least 50 square inches in size. It is crucial to note down in your notebook the location and the actual area that you sample (eg 4"x18").

0) Materials needed: Roll of masking tape, ruler, gloves, wet wipe, Zip-loc baggie, labels, pen, notebook.

1) Survey the home to find areas where children play, eat, etc. Decide where your group should sample and describe the locations in your notebook.

2) Measure out a 12 inch by 12 inch square on the floor. Put tape down around all the edges of the square; the idea is to mask off all but one square foot of floor area. (you will obviously have to modify this if you are measuring a window sill or shelf) Note the area you actually sampled in your notebook.	3) Put on the gloves. Unfold the wipe and wipe the whole square foot of floor from side to side. You are trying to collect all the dust and paint chips in the area.	4) Fold the wipe so the dusty part is inside. Use the clean outside to wipe the whole square of floor from top to bottom.
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5) Place the wipe into the baggie. Remove the tape. Label the sample with your name, the location within the home, the area sampled (in square inches) and the words, "wipe sample."

A 3 Soil: The main concern here is the lead content of the soil, expressed in ppm. One ppm equals 1 mg of lead per kg of dry soil. Areas where children play are the most important locations to check, followed by bare soil near the home.

0) Materials needed: Zip-loc baggie, tongue depressor, ruler, labels, pen, notebook

1) Survey the area near the home to locate potential danger spots— areas of bare soil located near the home's entrances or near areas that children play. Note these down in your lab notebook and decide where your group should sample. Another location you may wish to sample is house dust collected from the household vacuum cleaner.

2) For each sample, mark out an area about 6" square. Describe the location and condition of the sampling site (how close is it to the house, is it wet or frozen, bare soil or covered with vegetation) in your notebook.

3) Scrape the dirt from the top 1/2" into a zip-loc baggie. Remove bugs, leaves, or grass, but leave the roots in the dirt. You will need about a cup of dirt.

4) Label the sample with your name and the location sampled.

A 4 Water: Trace concentrations of lead in water are expressed as ppm, parts per million. One ppm is equivalent to 1 mg of lead per liter of water.

0) Materials needed: two 50 ml plastic centrifuge tube (with blue cap), labels, pen, notebook.

1) Survey the home to find out if it is on city water or uses a well (homeowners may know, or you may have to poke around in the basement). Examine the plumbing to see what kind of pipes are used. Lead pipes are dark and soft enough to dent with the tip of a pencil;

copper pipes are reddish, plastic pipes may be black or white and will feel warmer to the touch than metal pipes. Note down your findings in your lab notebook.

2) Collect about 50 ml of water right out of the tap (a "first draw" sample). In your notebook, describe which tap you picked and why. Let the water run for 3 minutes, then collect another 50 ml sample ("post-3-min" sample). Label each sample with your name, location sampled, and whether it was a first draw or a post-3-min sample.

B. Analysis

B 1 General directions: After the field trip, the sampling team will return to lab and prepare the samples for analysis. Preparation will take under 15 minutes for most samples.

Each sample consists of a matrix—soil, paint, water, etc—with an unknown amount of lead hidden inside. The sample must be digested in nitric and hydrochloric acid to free the lead atoms from the matrix.

The job managers are responsible for preparing a list of all the samples to be analyzed and for ensuring that each sample is prepared properly and labeled so that the analytical team can do its job the following week. The sample list must include the sample ID, the location sampled, the weight of paint or soil samples, the area for dust wipe samples, and the volume for water samples.

B 2 Sample preparation

B 2a Quality assurance: In addition to the actual samples gathered at the job site, several control samples must be analyzed to meet EPA quality control requirements. These include a method blank for water analysis and spiked matrix samples for the paint, soil, and dust analyses. These control samples will be parceled out by the job managers for preparation.

B 2b Preparation of paint chips, lead dust, and soil (A 1, A 2, and A 3)

Reference: EPA SW-846 Method 3050B, section 7.5 (pdf file available at course website)

0) This analytical procedure requires a fairly fierce acid to dissolve the lead atoms from the matrix. A mixture of nitric and hydrochloric acids commonly known as *aqua regia* is used. Aqua regia will dissolve any metal, including gold. It will also dissolve notebooks, clothes, and skin. Treat the concentrated acids with respect, and you will be able to safely work with them—fool around, and you or someone else could be injured.

1) Measure out a known amount of the matrix.

- Paint chips: Grind the paint sample into powder in a mortar and pestle. Weigh out 0.5-1 grams of sample and record the actual weight in your lab notebook. Place the paint into a 250 ml conical flask, and label the flask with your initials, page number, and sample ID (for example, ML14 0.673 g paint from kid's N window)

- Lead dust: Transfer the entire wipe, dust and all, from its baggie to a 250 ml conical flask. Label the flask with your initials, page number, and sample ID (for example, ML14 70 in² wiped from kid's N windowsill)

- Soil: a) Preparing soil for lead analysis: Dump the sample into a large beaker and stir it with a spatula until it is homogeneous. Weigh out about 1.0 g of the damp soil and record the actual weight in your lab notebook. Place this sample in a 250 ml conical flask, and label the flask with your initials, page number, and sample ID (for example, ML14 1.037 g dirt from front walkway).

Soil: b) Determination of dry weight of soil: Get a clean, dry beaker and label it with your initials, page number, and sample ID. Tape the label on. Weigh the labeled beaker, and record its weight in your notebook and also on the label. Add about 10 g of soil and reweigh the beaker, recording the new weight in your notebook and on the label. The label should now read something like this: ML14, dirt from front walkway, beaker 56.902 g, beaker + soil 67.202 g. Place the beaker in the 120° oven and leave it there for the analytical team next week.

After the soil is dried, an analytical team member will cool the beaker and reweigh it to determine the dry weight of the soil.

2) Take the conical flask which contains your sample over to Reagent Central and add 2.5 ml concentrated nitric acid (CAUTION—this will burn your skin or clothes—wear goggles & gloves). Then add 10.0 ml of concentrated HCl (CAUTION—corrosive). Swirl to mix. You have now made aqua regia in the flask with your sample. At this point, stop, cap the flask with parafilm, and store it in the labeled tray in Reagent Central for the analytical team next week.

B 2c Water (A 4) Water samples will be analyzed for dissolved lead using the procedure described in EPA SW-846 Method 3005a (pdf file available at course web site). This procedure consists of filtering the water to remove suspended particles and acidifying it with nitric acid.

1) Get a clean 0.5 micron filter (it will look like a disk about 1" across) and a 10 ml syringe. Suck up 10 ml of sample, then attach the 0.5 micron filter firmly to the tip of the syringe. Gently push down the plunger to filter the water sample into a clean 250 ml conical flask. Add 2 drops of concentrated nitric acid and swirl to mix.

2) Label the conical flask with your initials, notebook page number, and sample ID (for example, ML 9 hose first draw). Cap the flask well with parafilm and leave it in the tray at Reagent Central for the analytical team. The analytical team does not need to process these samples any further—they go directly into the ICP/AES.

--Members of the analytical team will continue the analysis from this point on.--

B 2d Final sample preparation: Paint chips, dust wipes, and soil

1) Get a hotplate and set it to about 4-5. Remove parafilm from the flasks. Heat the samples until the aqua regia starts to boil; adjust the heat to maintain a gentle simmer for 15 minutes.

2) Set up a gravity filtration. A sample filtration apparatus will be set up at Reagent Central. You will need a ring stand, a ring, a glass funnel, a piece of filter paper, and a clean 250 ml conical flask to collect the filtrate. Fold a large circle of filter paper into quarters, open out to make a cone, and place the cone into the funnel. Moisten the filter paper with a few drops of concentrated HCl (CAUTION—corrosive). Pour the sample through and let it drip slowly. Do not poke at the filter paper, or it may break. While you are waiting, make a nice new label for the new conical flask (initials, page number, and sample ID) and tape it on.

3) Rinse out the original 250 ml flask with 5 ml of warm concentrated HCl, and filter it into the filtration flask (where it can join the sample extract)

4) Rinse out the original 250 ml flask with 5 ml of warm deionized water, and filter it into the filtration flask (where it can join the sample extract). The acid in the flask will heat up when the water is added—this can cause it to boil or sputter. If addition of the water causes the filtrate to turn cloudy, you may have a very high lead concentration. Try adding another 10 ml of HCl; if the solution clears up, go on with the lab; if not, check with the TA.

5) Carefully add about 40 g of ice to the filtrate in the filtration flask. Swirl to mix. Pour the solution into a 100 ml graduated cylinder and use a pipet or syringe to add more deionized water, up to a volume of 100 ml. Pour the solution back into the filtration flask and swirl for at least 1 minute to mix everything well.

6) Cap the flask well with parafilm and leave it in the tray at Reagent Central for analysis by ICP/AES.

The analytical team should be sure to take the beakers containing soil samples out of the oven, let them cool, and weigh them. The percent by weight of water in the soil will be needed for calculation of the concentration of lead in the soil. The analytical team does not have to do anything more to the water samples—they're ready for analysis.

B 3 Sample analysis—Atoms emit light when they are in a flame. This is the basis for the beautiful colors of fireworks. Because each element gives off specific wavelengths of light, atomic emission spectroscopy is a useful analytical tool. The lead atoms dissolved in the samples will be squirted into a special flame—a plasma created by radio-frequency discharge—and the lead emission wavelengths will be monitored by a sensitive light detector.

Job managers: Once most of the samples are ready for analysis, the whole analytical team should sit down with the TAs and make a list of all the samples that must be analyzed. In addition to the unknowns prepared by the sampling group, you must consider quality assurance.

B 3a Quality assurance:

Calibration: A range of standard lead solutions will be available. These standards contain lead in known concentrations. The standards are squirted into the ICP flame and the intensity of the detector signal is monitored. The more lead in the standard, the higher the detector signal.

Known samples: At least one of the standards should be re-run during the analysis, and a control sample consisting of deionized water should also be run. These measurements are useful for determining the precision of the method.

Replicate measurements: About 1 in 10 samples should be analyzed multiple times, preferably interleaved with other samples. These measurements are useful for statistical analysis of the accuracy of the method, and they can show whether the instrument readings are drifting with time.

B 3b Analysis by ICP/AES

Samples for analysis are taken to 230 NSH (instrument room on 2nd floor of Neiuwland). The TA will show you how to run the samples. Each analysis takes less than two minutes, so if you can start analyzing samples by 3:30 the lab should be done by 5. Raw data (sample identity and detector signal) should be recorded carefully and transferred to a Kaliedagraph file; this will be posted on the class web site.

C. Data Interpretation. This part of the lab is the responsibility of the four job managers in consultation with Ms. Canalas and Prof. Lieberman. Others are certainly welcome to get the raw data and work the calculations through in preparation for arguments at the trial.

1) If multiple measurements are available for a sample, they should be statistically analyzed. At very least, calculate the mean value. If three or more data points are available, calculate both the mean, the standard deviation, and the standard deviation as a percentage of the mean value.

2) Construct a calibration curve from the standard data by making a plot of the lead concentrations of the standards (x-axis) vs. mean detector signal (y-axis). The calibration curve should a) look linear and b) go through zero. If this is not the case, consult with Ms. Canalas or Prof. Lieberman. If the data look basically linear, it is appropriate to fit them to a straight line. Many calculators will do this, or we can show you a way to use Kaleidagraph to do it.

3) The linear curve fitting will yield an equation of the form $y = mx + b$, where y is the detector signal, x is the lead concentration, and m and b are constants. From this, derive an equation for lead concentration (the x-variable) in terms of detector signal (the y-variable), m , and b .

4) Calculate the raw concentration of each unknown, in ppm (parts per million, by weight—this is equivalent to mg of lead per kilogram of solution; for aqueous solutions, 1 ppm = 1 mg/liter).

5) Calculate the concentrations of lead in each sample.

- Paint samples: Lead content in paint is expressed in terms of ppm by weight; this is the same thing as the number of mg of lead in each kg of paint. Divide the raw concentration by 10. This gives the number of mg of lead that was extracted from the paint sample. Divide this number by the weight of the paint sample **in kilograms** (1 gram = 0.001 kg) to get concentration of lead in ppm in the paint. This value should be around a hundred times bigger than the concentration of lead in the solution.

- Dust wipe samples: Surface lead loading is defined as the amount of lead present as dust in each square foot of floor area (the units are micrograms per square foot, $\mu\text{g}/\text{ft}^2$). Divide the raw concentration by 10. This gives the number of mg of lead that was extracted from the dust on the wipe. Multiply this number by 1000 to get the number of micrograms of lead in the dust. Take the area that was wiped and divide by 144 to get the area in square feet. Now calculate surface lead loading by dividing the micrograms of lead found by the area in square feet.

- Soil: The lead content of soil is expressed in ppm. One ppm equals 1 mg of lead per kg of dry soil. Divide the raw concentration by 10. This gives the number of mg of lead that was extracted from the soil sample.

For each sample, calculate the percent by weight of dry soil. To do this, divide the weight of the dried soil sample by the weight of the damp soil sample. Now multiply the weight of the sample that was analyzed for lead content (it will be about 1 gram) by the percent by weight of dry soil. This gives you the number of grams of dry soil.

Divide the number of mg of lead in the soil by the weight of the dry soil, **in kilograms**, (1 gram = 0.001 kg), to get the concentration of lead by ppm in the soil.

- Water: The lead content of water is expressed in ppm. One ppm is equivalent to 1 mg of lead per liter of water. Use the raw concentration.

A Model for World Population (1 lab period)

In this lab, you will examine data about the population of the world and develop a mathematical model for human population from antiquity into the future. The technique used is called curve fitting. We will compare actual data--in this case, world population as a function of time--with mathematical models for how population changes with time. This kind of modeling is very common in the quantitative sciences, and this computer lab will help you understand the basic approach, its strengths, and its limitations.

Overview of lab:

- A Prelab exercises
- B Linear least-squares fitting with KaliedaGraph
- C Exponential fitting with KaliedaGraph
- D How good is a fit? Correlation coefficients
- E Post hoc, ergo proctor hoc
- F Modeling World Population as Exponential Growth
- G A more sophisticated model for world population
 - G.1 Specific growth rate and human population
 - G.2 Finding specific growth rates during different historical periods
 - G.3 Modeling the World population from antiquity into the future

A Prelab exercises:

The most common type of numerical data is two dimensional, that is, it involves two experimental variables and hence can be expressed as x,y pairs. One experimental variable, by convention x , is called the independent variable, and it is usually the variable whose value the researcher can choose. In our population examples, the independent variable is time. The other variable, y , called the dependent variable, is what the researcher measures (e.g., number of people). In order to do curve fitting, we need a model that makes predictions about how the value of y changes for different values of x . These models take the form of mathematical functions which can be graphed in two dimensions

1) Your first task is to make thumbnail sketches of how the following functions look on the interval $x=0$ to 5. Hint: calculate the value of each function for several values of x .

Linear:

$$y=mx+b, \quad m=2, \quad b=-1$$

Exponential:

$$y=y_0e^{(x-x_0)} + b, \quad y_0=0.8, \quad x_0=1, \quad b=0$$

Note that these functions all have a functional form with some parameters-- m , b , x_0 . For any given curve, the parameters have a constant value; you need to know this value in order to draw the curve. Changing the parameters changes the curve.

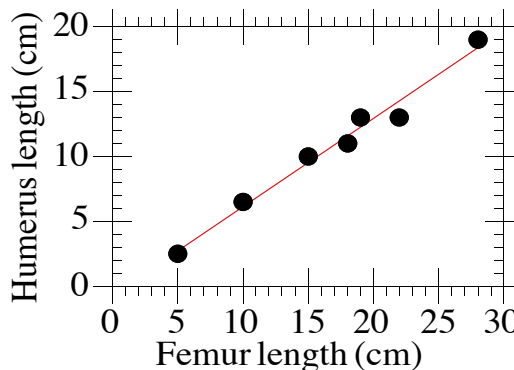
2) In the case of the linear example, to what features of the curve do the parameters 'm' and 'b' refer? Which parameter could you change, and how, to make the curve pass through the origin?

3) For the exponential curve, what happens to the value of y at very large and very small values of x ? Can you change the shape of the curve by changing y_0 ?

If a set of experimental data points are relatively close to the predictions of a mathematical model, we say the model "fits" the data, and that the data are related by the type of equation in the model. For example, if one measures the length of femurs (thigh bones) and humeruses (humeri? upper arm bones), one might get the following data:

<u>Femur length</u>	<u>Humerus length</u>
18.000	11.000
19.000	13.000
28.000	19.000
10.000	6.500
22.000	13.000
15.000	10.000
5.0000	2.500

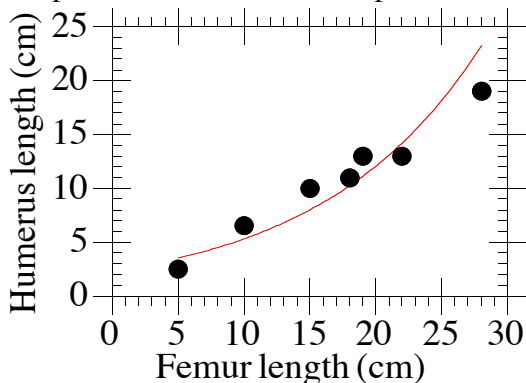
Plotting femur vs humerus length (black dots) shows that the longer the femur, the longer the humerus.



The line in the graph was generated by a computer program called Kaleidagraph. I told the program to fit this data as a line, with equation $y=mx + b$. The computer tried many values of the parameters 'm' and 'b' until it generated a line that was as close to all of the data points as possible. This process is called "curve fitting." Just by your eye, you can see that most of the data lies very close to the theoretical line (later we will learn more quantitative measures of how good a fit is).

Why is curve fitting important? First, the numerical parameters can be used to make predictions. An anthropologist can predict how tall a Neanderthal woman was from a single leg bone. More importantly, the fact that there is a linear relationship between these two bone sizes suggests some underlying rules about how bodies grow. One can then think of many measurements to test these rules, so curve fitting can give us ideas for new experiments.

Now, it is all well and good that the computer can juggle parameters and find the best curve, but one must always consider the GIGO principle (garbage in, garbage out). For example, what if I tell the computer to fit the same data using an exponential function?



The computer is just as happy finding an exponential fit to the data, even though there is no rational reason why such a relationship should exist. As you can see, the exponential model is a worse fit to the data than the linear one. Fewer data points lie on the line, and the 28 cm femur is way off the line. That's because of a flaw in the model--it does not represent the underlying physical reality.

ALWAYS CONSIDER THE MODEL!!!

4) Why is the most obviously wrong data point the 28 cm femur? Hint--think about the difference between the two mathematical models for large values of x.

****The other sections of this lab will be distributed later in the term****

Cheap Fertilizer--or Toxic Waste? (1 lab period)

“Don’t look a gift horse in the mouth” --Anon.

“Beware of Greeks bearing gifts” --Cassandra

In June 1998, Washington State passed a law requiring analysis of commercial fertilizers for lead and cadmium. You may wonder why the law was necessary--neither lead nor cadmium is a plant nutrient, so why would commercial fertilizers have these metals in the first place? In the last ten years, as environmental regulations have required more pollution control equipment on smokestacks and chemical plants, certain waste products have acquired sales value. Today, fertilizers may include feedstocks that are essentially recycled from other chemical processes.

For example, $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 can be made by bubbling the waste gases from a coal-burning power plant through a tank of NH_4OH solution. The waste gases contain SO_2 and NO_x , which react with water and oxygen to form SO_4^{2-} and NO_3^- ions. When the scrubbing solution is concentrated enough, the NH_4^+ salts of these anions precipitate out and must be removed from the scrubber. Why not sell them as fertilizer?

Most coal contains small amounts of heavy metals, such as lead, cadmium, or arsenic. These metals can find their way into the scrubber and contaminate the NH_4NO_3 . It is an open question how much heavy metal contamination is tolerable in fertilizers, and whether the risks of the toxins outweigh the benefits of the fertilizer.

In this lab, your team will analyze a sample of NH_4NO_3 scrubber waste which is being offered to your country at a bargain price--just 50% the cost per kilogram of NH_4NO_3 fertilizer. Your task is to report back to your government on the following issues:

- 1) Just how much usable nitrogen is in the scrubber waste? There might be other NH_4 salts ($(\text{NH}_4)_2\text{SO}_4$ or NH_4Cl) in addition to the NH_4NO_3 , and there could also be “junk” such as NaOH , ash, or insoluble minerals. Are you really getting a bargain price?
- 2) How much lead and cadmium are in the scrubber waste, in ppm?
- 3) How sure are you of your analytical results? Include a statistical analysis (calculate the 95% confidence level) of the combined class data for NO_3^- , NH_4^+ , Pb , and Cd . Briefly discuss the assumptions, limitations, and possible pitfalls of the analytical methods.
- 4) Policy issues: How do the levels of lead and cadmium compare with regulatory requirements for your region of the world? If you use this material to fertilize fields at a normal rate of application (about 50 kg/acre), how much lead and cadmium would be deposited in the soil each year? What happens to lead and cadmium in the soil? Can they get into plants? What about groundwater? What are the potential risks and benefits to your country of using the cheap fertilizer? This is basically a library research question--be sure to properly cite your sources of information.
- 5) Recommendation: Should your country buy the cheap fertilizer? No waffling, take a clear stand and defend your opinion.

Lab Overview

This lab consists of several parts: analyzing how much NO_3^- and NH_4^+ is in the "fertilizer" sample, and analyzing trace amounts of lead and cadmium in the "fertilizer". Your team may split up the work in any way it likes. The NO_3^- and NH_4^+ analyses will require the whole lab period, and they are the least accurate analyses. Replicate measurements by several group members are strongly encouraged. Lead and cadmium analysis should take <1 hour—the main constraint is the availability of the ICP-AES instrument (see sign up sheet on blackboard).

Flowchart

- A.1** Preparation of NH_4^+ and NO_3^- standards
- A.2** Analysis of NH_4^+ concentration in "fertilizer"
 - A.2a** Preparation of samples of "fertilizer" for NH_4^+ analysis
 - A.2b** Development of color from NH_4^+ ion
 - A.2c** Measuring intensity of color with a spectrometer
 - A.2d** Calculating the concentration of NH_4^+ in the "fertilizer"
- A.3** Analysis of NO_3^- concentration in "fertilizer"
 - A.3a** Preparation of samples of "fertilizer" for NO_3^- analysis
 - A.3b** Development of color from NO_3^- ion
 - A.3c** Measuring intensity of color with a spectrometer
 - A.3d** Calculating the concentration of NO_3^- in the "fertilizer"
- A.4** Analysis of lead and cadmium concentrations in "fertilizer"
 - A.4a** Preparation of samples of "fertilizer"
 - A.4b** Analysis of lead and cadmium by ICP-AES
- A.5** Statistical treatment of data

A.1 Preparation of NH_4^+ and NO_3^- Standards

A standard solution is a solution of known concentration in a certain **analyte**. Several solutions with different concentrations of the analyte are prepared. The unknown sample and the standard samples are treated with some chemicals which react with the analyte and form colored compounds—lots of analyte gives an intense color, a small amount of analyte gives a weak color. The amount of analyte in the unknown sample can be deduced by comparing the color of the unknown sample to the color of the standard samples.

The two analytes in sections **A.2** and **A.3** are NO_3^- and NH_4^+ and so it is necessary to prepare standards for both these ions. It is easy to get both ions at the same time from NH_4NO_3 . It is very difficult to weigh small quantities of anything accurately, so the best method for making standards is to first make a very concentrated **primary standard**. Portions of the primary standard are then diluted to make less concentrated standard solutions.

In a dilution, a certain volume V_i of concentrated material (concentration C_i) is mixed with water to give a final volume V_f of dilute material (concentration C_f). The total amount of material present in a solution is given by CV (the concentration multiplied by the volume). Dilution does not change the total amount of material present, so it must be true that $C_iV_i = C_fV_f$. If you know the initial concentration, the initial volume, and the final volume, you can therefore calculate the final concentration.

1. Weigh about 1 g of pure NH_4NO_3 on the analytical balance. Record the actual weight to 3 decimal places in your lab notebook.
2. Transfer the NH_4NO_3 to a flask and dissolve it in 100 ml water (what will you use to measure the water accurately?) After all the solid dissolves, stir 1 minute to mix the solution thoroughly. The concentration of this primary standard is approximately 10,000 ppm in NH_4NO_3 .
3. Get seven clean flasks. The next step is to make a set of standards which are approximately 3000, 2000, 1000, 300, 200, 100, and 0 ppm in NH_4NO_3 (you will calculate the actual concentrations later). You will need at least 20 ml of each standard. Write down in your notebook a plan for how to make these dilutions, show it to the TA for approval, and carry out the dilutions.
4. The standard solutions may be kept in your lab bench from one lab period to the next if they are securely covered with parafilm to prevent evaporation of water.
5. Calculate the **actual concentrations of NO_3^- and NH_4^+** in each standard, in ppm. The easiest way to do this is to work out the actual concentration of NH_4NO_3 in the primary solution in ppm (recall that 1 ppm=1mg/L). From this, you can calculate the exact concentration of NH_4NO_3 in each of your diluted standards using the relationship $C_iV_i = C_fV_f$. The final step is to calculate what fraction of the mass of NH_4NO_3 comes from each ion and use this fraction to work out the actual concentration of NO_3^- and NH_4^+ in each standard, in ppm.

A.2 Colorimetric analysis of NH_4^+ concentration in "fertilizer"

NH_4^+ ions react with phenol and bleach to form a blue compound. By measuring the intensity of color for a set of **standards** with known concentrations NH_4^+ ions you can make a calibration curve, which in turn can be used to find the concentration of NH_4^+ ions in an unknown solution prepared from the "fertilizer?"

A.2a Preparation of samples of "fertilizer" for NH_4^+ analysis

1. Weigh out about 0.5 g of unknown. Record the actual weight to 3 decimal places in your lab notebook.
2. Transfer to a flask and dissolve in 250 ml of distilled water. (how are you going to measure the water accurately?). Mix well for 1 minute.
3. Transfer 5 ml of the solution to each of two test tubes and label them "Unknown #1" and "Unknown #2"
4. You will need the 3000, 2000, 1000, and 0 ppm NH_4NO_3 standards from **A.1**. Get four clean test tubes and label them. Use a 10 ml syringe to measure 5 ml of each standard into the appropriate tube, rinsing out the syringe between samples with deionized water. Start with the most dilute standard and work up to the more concentrated standard, this helps prevent contamination.

A.2b Development of color from NH_4^+ ion

1. Get a 500 ml beaker, fill it halfway with DI water, add several boiling stones (available at Reagent Central) and place it on a hot plate set to about 4. Keep an eye on this water as it heats up—you want it to boil but not boil dry!
2. Go to Reagent Central and get 10 ml of bleach and 10 ml of phenol solution in two vials. Add 1 ml of bleach to each of the test tubes (standards and unknowns). Wash the syringe.
3. Add 1 ml of phenol solution to each of the test tubes. Wash the syringe.
4. Place the test tubes in the boiling water bath for two minutes. Record your observations.
5. Allow the tubes to cool for 5 minutes.
6. The next step (**A.2c**) must be done immediately.

A.2c Measuring intensity of color with a spectrometer

1. First, fill a cuvette with the solution from the 2000 ppm NH_4NO_3 standard. Then, take a complete spectrum (from 700 nm to 250 nm) of the sample. The TAs will help you do this.
2. Find the wavelength that corresponds to the highest peak, and set the spectrometer to that wavelength.
3. Record the absorbance of each of the samples at this wavelength.

A.2d Calculating the concentration of NH_4^+ in the "fertilizer"

1. Plot a calibration curve using your standards. You can either use a least-squares fit (your calculator will probably do this) or you can draw a best-fit line by eye. The calibration curve should look linear at low concentrations of NO_3^- , although it may not be linear for high concentrations.
2. Determine the concentration of NH_4^+ in your unknown.
3. Calculate the % **by mass of NH_4^+** in the fertilizer. Note that your original ~0.5 g sample in 100 ml water was diluted by a factor of 2.5 to make the solution that you analyzed.

Example: A concentration of 200 ppm NH_4^+ corresponds to 200 mg NH_4^+ per liter of water, which means that the original 100 ml of solution (remember, it was diluted by a factor of 2.5) would have to contain 500 mg/L, or 0.500 g NH_4^+ per liter. There would be 0.500g/10 or 0.050 g of NH_4^+ in 100 ml of this solution. If one had prepared the original solution by adding, say, 0.5400 g fertilizer to 100 ml water, the fertilizer is 0.050/0.5400 or 9.25 % by mass NH_4^+ .

4. Report your results on the blackboard.

A.3 Colorimetric determination of NO_3^- concentration in unknown

When NO_3^- ion reacts with resorcinol in sulfuric acid, it forms a red product. By carrying out the reaction and measuring the intensity of this color for a set of **standards** with known concentrations of NO_3^- ions, you can make a calibration curve, which in turn can be used to find the concentrations of NO_3^- ions in an unknown solution prepared from the “fertilizer”

A.3a Preparation of samples of "fertilizer" for NO_3^- analysis

1. Weigh out about 0.5 g of “fertilizer?” on the analytical balance. Record the exact weight used, to 3 decimal places, in your notebook.
2. Dissolve the fertilizer in 250 ml of distilled water in a large beaker. (How are you going to measure the water accurately?) After mixing this solution for at least 1 minute, take 10 ml with a 10 ml syringe, transfer to a 100 ml graduated cylinder, fill to the 100 ml mark with DI water, pour into a flask, and mix well.
3. Transfer 2.0 ml of the diluted solution into each of two test tubes. Label the test tubes “Unknown #1” and “Unknown #2”. The labels must withstand a boiling water bath, so use a pencil or a permanent marker to write on paper labels, then tape them down with clear tape.
4. Get four clean test tubes and label them. You will need one tube each for the 300, 200, 100, and 0 ppm NH_4NO_3 standards from A.1. The labels must withstand a boiling water bath, so use a pencil or a permanent marker to write on paper labels, then tape them down with clear tape. Use a graduated pipet to measure 2.0 ml of each standard into the appropriate tube. Start with the most dilute standard, and rinse out the pipet with deionized water after each standard.

A.3b Development of color from NO_3^- ion

1. Get a 500 ml beaker, fill it halfway with DI water, add several boiling stones (available at Reagent Central) and place it on a hot plate set to about 4. Keep an eye on this water as it heats up—you want it to boil but not boil dry!
2. You are wearing your goggles and gloves, aren't you? Go to Reagent Central and get about 10 ml of 1% resorcinol solution in a test tube. Use a graduated pipet to add 0.75 ml of the 1% resorcinol solution to each test tube you want to analyze.
3. At Reagent Central, collect about 10 ml of concentrated sulfuric acid in a small **dry** beaker. CAUTION: concentrated sulfuric acid is nasty stuff; it will burn skin and eat holes in clothes. Label the beaker, please. Also collect a large beaker of crushed ice.
4. Use a graduated pipet to add 3 drops of concentrated sulfuric acid to each of the test tubes. Swirl each tube gently to mix its contents. Add one boiling stone to each test tube.
5. Place the test tubes in the beaker filled with ice and slowly add 0.60 ml of concentrated sulfuric acid to each tube, using a 1 ml syringe. Wash out the syringe with deionized water. Pour

any remaining acid into the acid waste bottle (do not put it back into the sulfuric acid bottle!) and wash the beaker in plenty of deionized water. Dry the beaker.

6. Go to Reagent Central and collect about 5 ml of concentrated hydrochloric acid in a small **dry** beaker. Add 0.30 ml of hydrochloric acid to each of the test tubes sitting in the beaker of ice, using a 1 ml syringe. Pour any left-over hydrochloric acid into the acid waste bottle. Wash the syringe and beaker in lots of deionized water.
7. Place all of the test tubes in the boiling water bath and let them boil gently for half an hour. Record your observations.
8. Remove the test tubes from the water and let them cool down for 5 minutes.
9. The next step (**A.3c**) must be done immediately.

A.3c Measuring intensity of color with a spectrometer

0. THE SAMPLES ARE ACIDIC ENOUGH TO BURN SKIN OR EAT HOLES IN CLOTHES--use care in handling them, wear your goggles and gloves, and clean up spills immediately by rinsing with water.

2. First, fill a plastic cuvette with the solution from the 200 ppm NH_4NO_3 standard. Then, take a complete spectrum (from 700 nm to 250 nm) of the sample. The TA will help you do this. Label this spectrum (your initials, lab book page number, and sample identification) and include it in your lab book.
3. Find the wavelength that corresponds to the highest peak, and set the spectrometer to that wavelength.
4. Record the absorbance of each of the samples at this wavelength.

A. 3d Calculating the concentration of NO_3^- in the "fertilizer"

1. You need to know the concentration of NO_3^- in each of your standards (calculated in section **A.1**)
2. Make a plot of absorbance (on the y-axis) vs. NO_3^- concentration for the four standards. Find the equation of the best-fit line through the four data points and plot the line on the graph. Your calculator may be able to calculate the least-squares fit, or you may draw the best-fit line by eye—ask the TA if you need help with this. The line is your calibration curve for NO_3^- concentration.
3. Did your two unknowns have the same absorbance? If not, take the average of the two values, then use the calibration curve to determine the concentration of NO_3^- in your unknown.
4. Calculate the **% by mass of NO_3^-** in the fertilizer. Remember that your original ~0.5 g sample in 250 ml water was diluted by a factor of 10 to make the solution that you analyzed.

Example: A concentration of 137 ppm NO_3^- corresponds to 137 mg NO_3^- per liter of water, which means that the original 250 ml of solution (remember, it was diluted by a factor of 10) would have to contain 1370 mg/L, or 1.370 g NO_3^- per liter. There would be 1.370g/4 or 0.3425 g of NO_3^- in 250 ml of this solution. If one had prepared the original solution by adding, say, 0.5400 g fertilizer to 250 ml water, the fertilizer is 0.3425/0.5400 or 63.00 % by mass NO_3^- . That is pretty close to pure NH_4NO_3 , by the way.

5. Enter your results on the blackboard.

A.4 Analysis of lead and cadmium concentrations in "fertilizer"

Most atoms can be induced to absorb or emit light of very specific energy by putting the atoms in a very hot flame. The inductively coupled plasma atomic emission spectrometer (ICP-AES) is an instrument which does just that. Solutions with a known concentration of lead or cadmium (standards) are first analyzed to measure how much light is emitted at the "lead" and "cadmium" energies, and a calibration curve is constructed. Next, the unknown sample is analyzed and the **concentrations of lead and cadmium** are deduced by comparing the intensity of light at the lead and cadmium energies with the calibration curves.

A.4a Preparation of samples of "fertilizer"

1. Get three test tubes and label them Unknown 1, 2, and 3.
2. Weigh about 2.5 g of "fertilizer" on the analytical balance and record the weight in your lab notebook.
3. Dissolve the sample in 25 ml of deionized water (how can you measure this accurately?) in a small flask. After the sample has dissolved, stir for 1 minute to mix.
4. If the solution is cloudy or contains "junk" such as sand or floating garbage, filter it. You should end up with at least 15 ml of clear solution.
5. This solution may be stored in your lab drawer if it is capped with parafilm to prevent evaporation of the water.

A.4b Analysis of lead and cadmium by ICP-AES

1. Sign up for an analysis time slot on the whiteboard.
2. Take your three test tubes down to the room with the ICP. The instrument TA will help you run the samples. The standards needed for this part of the lab have been prepared and you will be provided with the calibration curves for lead and cadmium. Stick them into your notebook.
2. Use the calibration curves to determine the concentration of lead and cadmium in your unknown solutions.
4. Calculate the weight % of lead and cadmium in the solid fertilizer and report your results on the whiteboard.

Example: a solution that was found to be 43 ppm in lead would contain 43 mg lead per liter of water. Say that solution was made using 2.036 g (2036 mg) of fertilizer dissolved in 25 ml of water. Since the concentration is 43 ppm in lead, there would be $43 \text{ mg/L} \times 0.025 \text{ L}$ or 1.075 mg of lead in the water, and the lead must have come from the 2.036 g of fertilizer. Then there would be 1.075 mg lead/2036 mg fertilizer, or 0.00053 mg lead/mg fertilizer. This is equivalent to 530 ppm. Note that the level of lead in the solid is a lot higher than the level in the solution (why?)

A.5 Statistical treatment of the data

How sure are you that your results really represent the concentrations of NO_3^- , NH_4^+ , lead, and cadmium in the big bag of fertilizer? In this next section of the lab, you will analyze the combined data from the whole class to work out the 95% confidence intervals for the actual concentrations of the various analytes in the fertilizer.

For a group of replicate measurements, the mean value x_m is just the sum of the values divided by the number of measurements made—like the average score on a test. The standard deviation σ is a measure of how “spread out” the values are from this mean value. A large standard deviation means many data points varied a lot from the mean, a small standard deviation means most values were close to the mean value.

Most calculators have a function for determining σ , or σ^2 can be calculated using the following equation:

$$\sigma^2 = 1/(n-1) \times \sum (x_i - x_m)^2$$

- If five samples of paint were analyzed and gave lead levels of 29, 31, 33, 35, and 37 ppm, what would the mean and standard deviation be?

Ans: The mean value would be 33 ppm, and the standard deviation 3.2 ppm (some calculators give you a choice between finding $\sigma_{x(n-1)}$ and $\sigma_{x(n)}$. It is $\sigma_{x(n-1)}$ that is most valid for small sample size; if you got a standard deviation of 2.8 you're finding $\sigma_{x(n)}$.)

Statistical analysis is used to calculate what are called 95% confidence limits (95% CL) for results. The 95% CL are related to both x_m and σ by the following equation: $95\% \text{ CL} = x_m \pm 1.96\sigma$. In the lead paint example, the 95% CL is 33 ± 6.4 ppm. This means that there is a 95% chance that the actual level of lead lies somewhere between 26.6 and 39.4 ppm. Note that this assumes the actual chemical analysis worked as expected—if a reagent was bad, or an instrument wasn't working properly, the statistical calculations might be completely meaningless.

- 1) Analyze the class data to find the mean value x_m , the standard deviation σ , and the 95% CL of NO_3^- , NH_4^+ , lead, and cadmium in the fertilizer.