Analysis of Soil

Your team of chemists has been called out to a local farm. The farmer tells you that she is having problems with the crops in one of the fields. She seems to think that the soil has become contaminated after a road accident that occurred doing the winter. A truck jack knifed and spilled some of its contents on the field. She asked for your help. The farmer would like to know what the contaminant is and if there is anything she can do to alleviate the problem. The farmer did not know what the chemical spilled was. However, the truck was carrying bulk chemicals for a company that produced inorganic fertilizers, ice melting compounds for roads, inorganic industrial cleaners, and cement additives.

Goal of the project

1. Confirm the that observation that there is a problem with the soil.
2. Determine the identity of the soil of the contaminant.
3. Determine the amount of the contaminant present in the soil.
3. Suggest a possible remedy for the problem.

Resources available

1. A bucket of soil from the contaminated area of the farm.
2. A bucket of soil from a adjacent noncontaminated area of the farm.
3. Seeds from radishes, a very fast germinating plant.
4. Samples of the companies starting materials. Potassium chloride, sodium chloride, calcium chloride, sodium dihydrogen phosphate, Sodium monohydrogen phosphate, Trisodium phosphate, sodium carbonate, calcium hydroxide or oxide.
5. Some general guidelines for soil testing.

Useful Information

Plants require the presence of several different nutrients for proper growth. These essential foodstuffs must also be found in the proper proportions for the healthy sustainability of the plant. You may want to consider cultivating fast growing plants, like radishes, and monitor there growth in your soil samples.

Drying soil samples

Soils sampled from the field contain water, the amount depending on soil properties and the preceding weather conditions. Even when the soil is air-dried, some water remains. The water content of soils is determined by drying at about 105°C which gives oven-dry soil. Results of soil analyses are normally expressed relative to a mass of oven-dry soil. When an oven-dry soil is heated to 500°C, organic matter is burnt off and there is further loss of water. The mass lost between 105°C and 500°C is called the loss on ignition. For these tests, you will want to use 10g of the soil. The samples used for determining water content can be placed in glass dishes and the samples can be dried in a drying oven. Alternatively the samples can be place on a hot plate set fairly low for several hours. The test is complete when a constant weigh is achieved for each sample -- be patient because this might take time!

An ignition test requires the use of crucibles and Bunsen burners. The samples are heated to red heat until a constant weigh is achieved.

Qualitative analysis of Soil samples

For the qualitative analysis of the soil samples, you will want to test for the presence of various anions. Oftentimes, anions will complex with various reagents and then precipitate out of solution. Thus, the presence of a precipitate for an anion test will indicate the presence of that particular anion. These ion tests should be done with the soil in solution. A small amount on the end of a spatula of the soil sample mixed with approximately 1ml of water in a test tube will be sufficient for the tests.

pH of soil

The extent of a soil's basicity or acidity can be determined via a pH reading. pH values can be altered by some contaminates. Make a solution of your soil -- 10g of the soil sample mixed with 20ml of water. In this part of the experiment, you will want to use a pH meter. Remember to calibrate the probe before collection of values. (see supplement on how to use a pH meter)

Buffer capacity

A buffer helps resist change in pH. Some contaminants can affect the way a soil solution responds to the addition of acid. To test the buffer capacities of your soil samples, make a solution of your soil with KCl (0.1M) as the solvent. To make the solution, combine 5g of your soil sample with 10ml of the KCl solution. Why is KCl better than H_2O? Set up several runs with varying amounts of added HCl (0.1M). Allow to react for approximately 2 hours, stirring occasionally. Record pH values and plot the buffer curve. How could you replot the data and obtain a linear relationship in order to compare slopes?

Carbonate Analysis

To quantitatively determine the amount of carbonate in your soil samples, mix 10g of soil with 20ml of HCl (2M) and allow to react for approximately 15 minutes. What do you observe happening in the flask? Heat the solution on a hot plate and allow to react for another approximate 15 minutes. Filter with a Hirsch funnel and transfer filtrate to a 100ml volumetric flask and fill to mark. Use this soil solution with phenolphthalein indicator and titrate with 0.1 M NaOH. What is the carbonate content of your soil samples?

<u>Phosphate analysis</u>

NOTE 1: This analysis procedure is the most complicated one of those used in this project. All solutions must be carefully prepared using distilled or deionized water. You must keep track of all dilutions and make all volume measurements and dilution using volumetric glassware such as volumetric flasks, pipettes and burette. Sample selection must be made carefully.

Procedure for preparation of a calibration curve

1. Switch on a Spec-20 spectrophotometer and allow to 'warm up' for 30 minutes, setting the wavelength to 630 nanometers (nm).
2. Prepare a solution of NaH_2PO_4 in DI water, which contains 30 ppm (i.e. weigh out 0.600 gram of NaH_2PO_4 in 2 liters of DI water in volumetric flask; dilute this solution 10-fold by pipetting 25 ml into a 250 ml volumetric flask and making up to the mark with DI water. This solution contains 30 ppm phosphate.)
3. Prepare a 'blank' solution consisting of 5.75 ml of 4% acetic acid, 0.25 ml of molybdate solution (0.1M in 12% acetic acid), and 1 ml of 5% ascorbic acid solution. With nothing in the Spec-20 sample beam, adjust the instrument to read 0% transmission. With a sample tube containing the blank solution in the beam, adjust the instrument to read 100% transmission.
4. Prepare five phosphate solutions for calibration purposes as follows.
   Step 1:
   In 5 separate clean test tubes prepare the following phosphate solutions, 15ppm, 7.5 ppm, 3.75 ppm and 1.875 ppm. by diluting the 30 ppm phosphate solution with DI water. Use a pipette. The easiest way to prepare the solutions is prepare 10ml of 15ppm first, then take 5.00 ml of it and dilute it with 5.00 ml of DI water to make 10 ml of 7.5 ppm. use the same procedure to make the other solutions.
   Step 2:
   Obtain 5 clean spec 20 tubes. Into each of five clean Spec-20 sample tubes pipette 2.75 ml of 4% acetic acid.
   Tube 1: add 3.0 ml of the 30 ppm phosphate solution previously prepared.
   Tube 2: add 3.0 ml of the previously prepared 15 ppm phosphate solution.
   Tube 3: add 3.0 ml of the previously prepared 7.5 ppm phosphate solution.
   Tube 4: add 3.0 ml of the previously prepared 3.75 ppm phosphate solution.
   Tube 5: add 3.0 ml of the previously prepared 1.875 ppm phosphate solution
5. Into each of the five Spec-20 tubes add 0.25 ml of molybdate solution followed by 1 ml of 5% ascorbic acid solution; mix well by inverting the tubes (insert a rubber stopper or cork in the 'open' end of the tube while doing this!).
6. Immerse each of these tubes in a beaker of water at 50^oC for 10 minutes in order to fully develop the blue color.
7. Insert each tube in turn into the Spec-20 and measure and record the absorbance of each of the five 'calibration' solutions. Note: transmission is related to absorbance by the expression Abs = $\log_{10}$(100/% transmission.

Soil sample preparation for analysis

1. Extract three separate 1.500 gram soil samples with 6 ml of 4% acetic acid solution for 5 minutes, and then filter into a small 50 ml beaker. Wash the solid with 2-3 rinses of 4% acetic acid collecting all rinses in the beaker. If the liquid has a dark color decolorize it with activated charcoal. if the solution is colorless or nearly so skip the decolorizing step.

Decolorizing sample

1. Add 1.0 gram of activated charcoal and boil for 15 minutes by placing the beakers on a hot-plate; this will remove the color of the untreated solution.
2. Filter when the solution is warm using fluted filter paper. Collect the liquid in a 50 ml volumetric flask. Collect all of the rinses in the flask and make up to the mark with 4% acetic acid. be careful not to loose any of the solution.

Spec 20 sample preparation

1. Pipette 3.0 ml of the soil extract into aSpec-20 tube along with 2.75 ml of 4% acetic acid, 0.25 ml of molybdate solution, and 1 ml of 5% ascorbic acid solution. Warm the solutions to 50°C for 10 minutes and then measure and record the absorbance of the sample soil solutions.

Data handling

Plot the absorbance of the calibration solutions against the calculated concentrations to produce a linear graph (confirming that Beer's Law is being obeyed). Then using the absorbance of the soil solution, read off from the graph the corresponding concentration. Finally calculate the ppm. phosphate in the 1.5 gram soil samples.

Determining the Amount of Soluble Chloride ion in Aqueous Solution

Note: the standard chloride analysis is much more accurate than the microscale analysis. However, the microscale is much faster than standard procedure and may be all that is necessary to determine if excess chloride ion is present in the soil sample. For the standard analysis procedure you will need to familiar with volumetric techniques and glassware. For the microscale analysis you will need to be familiar with well-plates and the use of transfer pipettes. The chemistry is the same for both procedures.

Standard Chloride Analysis

The chloride ion concentration of a solution is often determined by titrating the chloride ion with known concentration of silver ion to form an insoluble silver chloride precipitate. The end point in the titration is detected with chromate ion. When a mixture of chloride and chromate is titrated with silver nitrate, silver chloride precipitates first because it is less soluble then silver chromate. After the chloride in solution has precipitated as white silver chloride, the first excess of silver ion precipitates silver chromate which is a dark red. The appearance of the red precipitate signals the endpoint of the titration.

Equations

$$AgNO_3 + Cl^- \quad NO_3^- + AgCl_{(s)} \quad \text{white precipitate}$$

$$AgNO_3 + CrO4^{-2} \quad NO_3^- + Ag_2CrO_{4(s)} \quad \text{red precipitate}$$

Preparation of the $AgNO_3$ solution

In a small clean beaker weigh accurately enough silver nitrate to prepare 250 mL of 0.1 Molar solution. Dissolve $AgNO_3$ in a small amount of distilled water and then quantitatively transfer the solution to a 250 mL volumetric flask and dilute to the mark. Silver nitrate solution decompose on exposure to light so store the solution in the dark.
Caution: Silver nitrate solid is a corrosive material. Silver nitrate solutions turn black in strong light. If you spill silver nitrate on yourself and do not wash it off promptly and thoroughly it will temporarily stain your skin black.

Chromate Indicator

You will need 1 mL of 5% Potassium Chromate for each titration. Prepare only what you think you will need.
Caution: Potassium Chromate is a strong oxidizing agent and a suspected carcinogen. Discard the solid residue and dichromate solution in the designated disposal container.

Preparation of the sample

If you are going to determine the chloride concentration in an unknown solution. It is a good idea to run a quick trial titration. To do so add a 25 mL sample of the solution to a clean 125 mL Erlenmeyer flask then add about 0.5 grams of $NaHCO_3$ and 1 mL chromate indicator solution. Titrate with the silver nitrate solution with constant stirring until the first permanent appearance of red-orange in the yellow solution. If you are not sure what to look for as an end point you can run a blank by substituting 2 grams of $CaCO_3$ in 25 mL of distilled water plus some sodium chloride for the unknown solution. Titrating this with a few drops of silver nitrate will show you what the end point should look like. After this first trial titration adjust the amount of solution to be tested so that at least 20 mL of the silver nitrate solution is needed to reach the end point. Now titrate at least 3 samples to determine the sample chloride concentration.

<u>Microscale chloride analysis</u>

The microscale approach is less accurate but much faster and cheaper then a standard titration

Caution: good results requires counting drops very accurately.
To each of 3 wells in a well plate add exactly 25 drops of unknown chloride solution, 5 drops of 0.5 molar $NaHCO_3$ and two drops of chromate indicator solution. Titrate the individual sample with 0.050 molar $AgNO_3$ solution by adding the $AgNO_3$ solution drop wise with stirring after the addition of each drop. (Note: if stirring is not done after each drop the transient red precipitate tends to clump and does not readily disappear.) The titration is complete when the red orange precipitate no longer disappears when the mixture is stirred. The sample should require at least 20 drops of $AgNO_3$. If less is required adjust the amount of chloride unknown sample.

Soil Planning sheet 1 **Group name_____________**

To be completed before leaving the Laboratory

1. You have a bucket of soil since it is not possible analyze all of the soil how will you take a representative sample of the soil?

2. How will you need to prepare the soil for analysis?

3. Soil analysis usually begins with drying the soil. Why is this necessary ?

4. Because soil normally contains most of the ions that can be found in the compounds that the company makes, how will you determine what the contaminant is?

5. Which contaminants are likely to change the pH of the soil ?

6. Today you should sample and dry the soil it in preparation for next week. If you plan to test the viability of seeds in the soil samples plant them today.

7. Next week you will need to determine the pH of the soil and develop a procedure for separating the compounds from the insoluble components of the soil. Before you leave today outline what each member of the group will do next week.

Soil planning sheet 2 **Group name_____________**

1. Briefly discuss how you will determine the pH of the soil. What reagents or equipment will you need for this determination?
2. What procedure are you going to use to separate the soluble compounds in the soil.
3. If soil samples are extracted with aqueous solvents a dark colored solution is usually obtained. Since most acid base indicators and many spot tests depend on color, how will you deal with this problem? The dark color is most likely due to organic materials in the soil. Two simple approaches to removing the color involving adsorbing it on activated charcoal or heating the soil sample at red heat for 30-60 minutes to burn off all the organic materials

4. How will you determine which ions are present in excess in the contaminated soil sample. What reagents will you need to accomplish this?
5. By the end of today your group should have identified many of the ions in the soil. Next week your group will have to on determine the concentration of some of these ions in the soil. It will be necessary for your group to have decided on a standard method for extracting soluble ions from the soil sample and your group must decide on the analysis methods you will use. For phosphate analysis you will need to be familiar with pipeting, dilution techniques with volumetric glassware and the use of a spectrometer. For chloride analysis you will need to be familiar with microscale titrations. For carbonate analysis you will need to be familiar with pH meters and burettes.

Soil planning sheet 3 **Group name_____________**

1. Briefly discuss the analytical procedures you will use today to determine the concentration of ions in the soil. It is likely that you will want to analyze the soil sample for phosphate, carbonate and chloride ions .
2. How will decide how much soil sample to use? During the most analytical procedures there are usually several dilutions and transfers of solution it is important to keep track of these. Why?
3. Usually analytical procedures are on at least three samples of the materials to be analyzed. Why?
4. Before you leave to day decide what else has to be done and who will be responsible for doing it.

Soil planning sheet 4 **Group name**_____________

1. Discuss your teams results for the various analytical procedures the team used. Decide how to tabulate and interpret the results. Do any of the procedure need to be repeated. Based on your results suggest possible remedies for the farmers field. Carry out any procedure needed to test your suggested remedies.