

# Chemistry of natural waters

## To instructors

This lab involves analysis of surface water by several field and lab methods, and an introduction to water modeling using an Internet-based version of the USGS program PHREEQ. Note that the [powerful PHREEQC program](#), now in a Windows version with interactive input features, is available for free. The instrumentation used here is specific to our lab, and the analyses can be adapted to any available chemical analysis capabilities.

## The exercise handout

In this lab you will collect and analyze water samples from the stream running through the Union College campus. This stream drains about 1 km<sup>2</sup> from a residential area of Schenectady to the east of Union College. We will analyze the water using several techniques, and then calculate analytical error, ionic speciation in the water, and the degree of saturation for several minerals.

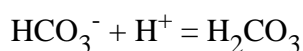
Most of the calculations will be done using one of two standard programs used in aqueous geochemistry, PHREEQ or WATEQ. For details on these programs, see the on-line program manuals. These programs are adaptations of a program developed by the U.S. Geological Survey to calculate chemical species in solution and the degree of saturation for various minerals.

Our chemical analyses will be based on the needs and limitations of the PCWATEQ program, the variables controlling speciation of components in water, and the limitations of our analytical facilities. Here is what we will analyze for:

Component	Ion chromatograph (cation, anion, silica modes)	ICP-MS (normal and DRC modes)	pH electrode in field	Oxygen electrode in field	Titration in field
F <sup>-</sup>	✓				
Cl <sup>-</sup>	✓				
Br <sup>-</sup>	✓				
NO <sub>2</sub> <sup>-</sup>	✓				
NO <sub>3</sub> <sup>-</sup>	✓				
PO <sub>4</sub> <sup>3-</sup>	✓				
SO <sub>4</sub> <sup>-2</sup>	✓				
Organic acids	✓				
Li <sup>+</sup>	✓				
Na <sup>+</sup>	✓				
NH <sub>4</sub> <sup>+</sup>	✓				
K <sup>+</sup>	✓				
Mg <sup>2+</sup>	✓				

Ca <sup>2+</sup>	✓				
SiO <sub>2</sub>	✓				
Many trace elements		✓			
pH			✓		
O <sub>2</sub>				✓	
HCO <sub>3</sub> <sup>-</sup>					✓

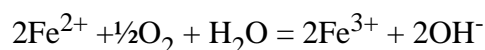
pH, dissolved oxygen, and alkalinity are three components that the must be analyzed in the field. Temperature must also be. pH is a measure of the acidity of a solution:  $-\log_{10}[\text{H}^+]$ , and is important for determining the speciation between weak acids and bases, such as:



Dissolved oxygen can be used as a crude measure of the environmental redox potential of the water, Eh. Eh principally affects the equilibria of redox reactions, such as:



or, as a more complete reaction:



Redox potential can also be expressed as pE, which is basically the electron activity in solution. Unfortunately, the actual redox potential is difficult to measure in most waters because of the lack of a concentrated, fast redox couple (reaction species in equilibrium). As a result, typical redox electrode readings are slow to equilibrate and have little meaning. Our surface waters are exposed to air and are quite oxidizing anyway.

Alkalinity is a measure of the acid neutralization capacity of water, which is caused by the presence of weak bases in solution. In most waters the alkalinity is mostly caused by HCO<sub>3</sub><sup>-</sup>. The carbonate species are among the most important anions in most natural fresh waters.

### In the field

1. Collect 2 samples of stream water, being careful to avoid sediment and visible solid particles. Collect a third water sample after filtering it through a 0.45 m m filter. Be sure all samples are appropriately labeled. If the temperature is below freezing, don't filter.
2. Measure the following with all available devices:
  - Water temperature.
  - Dissolved oxygen.
  - pH.
  - Alkalinity by titration. Collect 50 ml of water in a graduated cylinder and pour into a glass beaker. Add three drops of bromcresol green pH indicator dye to the beaker.

Using 0.1 N HCl and the 2 ml micrometer syringe, titrate the water to the end point. The blue alkaline solution turns green at the end point (pH = 4 to 4.5), and turns pale yellow in the acidic water beyond the end point.

**In the lab**

1. Prepare samples for normal [anion](#) and [cation](#) ion chromatograph analysis, and analyze them.
2. Prepare samples for [silica](#) ion chromatograph analysis, and analyze them.
3. Prepare samples for [ICP-MS analysis](#), and analyze them.
4. Samples not analyzed immediately should be frozen.

**The data set**

Each person will have produced data for their samples, so there will be several determinations of each analytical item from pH to silica.

1. Format the analytical data into an easily read table.
2. Using the water volume, acid concentration, and acid volume used for the alkalinity determination, calculate alkalinity, as ppm  $\text{HCO}_3^-$ , can be calculated using the [Alkalinity spreadsheet](#).
3. Recalculate phosphate to phosphorous.
4. Calculate the average value and analytical precision (2 standard deviations) for each of the determined water characteristics. Discard outlier values if you think it justified, but in each case comment on the discarded values.
5. Make a graph comparing the analytical precision of the standard for all measured components. Probably the relative deviation is the best measure of precision for this graph.
6. Several standards were also analyzed as unknowns in parallel with the water samples. Compare the analytical precision of the standards with the relative deviations of the water samples. Explain any systematic differences you see.

**Modeling**

Go to the [Web-PHREEQ web site](#). For our modeling choose the Advanced Speciation, Single Solution, and PHREEQ options.

Data group	Initial values
<b>Environmental conditions</b>	pH: Set to fixed.
	Density: leave blank.
	Oxidation state: 4, select pE option.
	log P <sub>O2</sub> : leave blank
	T: actual value
	log P <sub>CO2</sub> : leave blank
<b>Concentration units</b>	ppm
<b>Major components</b>	K, Fe, Ca, Mg, Na, Cl: actual values
	Alkalinity, Fe(2), Fe(3): leave blank
	C: enter bicarbonate and select the bicarbonate option
	S: enter sulfate and select the sulfate option
	N: enter nitrate and select the nitrate option

	Si: enter silica and select the SiO <sub>2</sub> option
<b>Minor elements</b>	Al, Cd, Li, B, Cu, Mn, P, Ba, F, Pb, Zn, Br, Sr: actual values O(0), Mn(2), Mn(3), H(0): leave blank
<b>Equilibrium phases</b>	For Phase 1 type 'CO <sub>2</sub> '; for the Desired Saturation Index box type '-3.2' (0.00067 bars, in this case the saturation index refers to log <sub>10</sub> (partial pressure))
<b>Reaction temperature</b>	Leave all blank
<b>Selected output</b>	Leave all blank
<b>Output options</b>	Select Full Output option

Press the Continue button. This sends your data and options to the server at North Dakota State University, a computer there runs the [USGS PHREEQC](#) program with your data and options as the input file, and returns to you the calculated values for your water. Cut and paste this into the Notepad program window and save it as a text file.

1. The first half of this large mass of text (down to "Beginning of batch-reaction calculations") is just a restatement of the original solution, prior to equilibration with atmospheric CO<sub>2</sub>. This can all be deleted.
2. The last table has five columns. The first is the a list of phases or chemical components, the last is the chemical composition of the phase. logKT is the log<sub>10</sub> of the equilibrium constant for the dissolution reaction. IAP is the ion activity product for the dissolution reaction with the species concentrations actually in solution. The SI is the saturation index, which is the log<sub>10</sub> of the ratio of the IAP/KT. A SI value of 0.0 means the phase is exactly saturated (for gases it is the log<sub>10</sub> of the partial pressure). A SI value >0.0 means the phase is supersaturated (again, for gases it is the log<sub>10</sub> of the partial pressure). A SI value <0.0 means the phase is undersaturated.
3. Extract and make a table of SI values >0.1.
4. Compare the chemical composition of the stream from this exercise with other analyses done in the past several years. Does the chemical composition of the stream vary over time? Are there systematic changes in the composition of this water over time? Do any chemical components covary? Include two graphs to illustrate two of these time-dependent changes and/or two-element correlations. You will need to explain what you think the graphs show. The table ([Old Hans Grootkill analyses](#)) can be found on the Geochemistry web page.

Rerun your Web-PHREEQ dataset using several new constraints. Just press the back button to get back to the original web page *with your previous data still intact*. Recall that your first run had 'CO<sub>2</sub>', SI = -3.2 for Phase 1.

1. Add 'calcite' in the Equilibrium Phases area, Phase 2, SI value = 0.0. See how pH, bicarbonate, and Ca change in concentration in the output file, and see how the saturation indices for other Ca and carbonate-bearing minerals change. This would be a model of rainwater running down into a limestone aquifer.
2. In another run, keep 'calcite' as Phase 2, and change the Saturation Index value for Phase 1 (CO<sub>2</sub>) to -1.0 (log<sub>10</sub>(partial pressure) = 0.1 bar P<sub>CO<sub>2</sub></sub>). See how this increase of P<sub>CO<sub>2</sub></sub> dramatically lowers the pH, the amount of Ca and carbonate in solution, and the saturation indices for many minerals. This would be a model of CO<sub>2</sub>-rich soil water percolating down into a limestone aquifer. Soil waters typically have much higher P<sub>CO<sub>2</sub></sub> than rain because of active respiration in soils (roots,

fungi, bacteria, insects, etc.).

3. In a final run add 'siderite' as Phase 3 and use 0.0 as the Saturation Index value. This forces the equilibrated water to be in equilibrium with siderite, an  $\text{Fe}^{2+}$  carbonate. To do this the water is made much more reducing and as a result the calculated pE, and the saturation indexes of many oxidized species, are much lower. This is a model of water that has become reducing, perhaps by interaction with organic material and associated decomposition organisms.
4. For all three of these runs, compile a table comparing several pertinent phases and gas components these with the original run.

### **In your write up**

1. Include average water composition, analytical precision, detection limits, etc.
2. Graph comparing the relative uncertainty of the different analyzed components.
3. Comment on the precision of the analytical measurements, particularly with respect to measurements that have relatively large relative error. Comment on possible sources of the large errors.
4. Include the information from PHREEQ only as a well-formatted table or tables.
5. Comment on the degree of saturation of the minerals and of  $\text{CO}_2$ . Do any of these surprise you? Are any phases strongly supersaturated according to the program?
6. Comment on some time variations and/or some covariances shown in your two additional graphs.
7. Comment on the quality of the water as you have determined. What other things should be analyzed before this water could be considered drinkable?

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### **Things needed for this lab**

- It is very important that the minerals be quite pure, and in particular they should be free of phases that are more easily dissolved than the mineral of interest. Minor quartz in calcite, for example, is OK, but minor calcite in dolomite is not.
- One mineral sample for each student, ~12 g, crushed and sieved to 0.35-1 mm size before or during lab.
- One 125 ml plastic bottle for the dissolution experiments.
- Safety equipment (goggles, lab coats, aprons, rubber gloves).
- Plastic weighing boats.
- Autosampler test tubes (sets for ion chromatograph and ICP-MS).
- Ultrasonic cleaners.
- 2% acetic acid in a hood.
- 5% HCl in a hood.
- 5% HCl / 2% HF in a hood.
- Deionized water per student for washing.
- Syringe filter apparatus, 0.2 mm pore size, for filtering solutions prior to analysis.

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[Instrumentation lab exercises](#)  
[Pedagogy web page](#)

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