Water Hardness and Nitrate Content

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PRE-LAB INSTRUCTIONS

In the Textbook

Use the index of your textbook to locate readings on; hardness, EDTA, soaps, nitrate ion, nitrite ion, ppm.

On the Web

View the following GenChem Pages (http://genchem.chem.wisc.edu/labdocs/):

- Buret
- Titration
- Spectrophotmeter, Scanning UV/visible
- Flask, volumetric

Take the On-Line Quiz for this experiment.

In Your Notebook

- Prepare an outline of the procedures you will use to determine water hardness and nitrate content.

For Your Safety

- The Na_2MgY reagent contains cyanide ion. This reagent must not be treated with or added to acid because poisonous HCN gas will form. This gas has a characteristic smell which resembles burnt almonds. If you detect such an odor, move away from the area and notify your T.A. immediately.
- The pH 10 buffer is sufficiently basic to cause minor burns if it contacts your skin. A “slippery” or “soapy” sensation on your fingers is characteristic of such a base solution. If you should get base on your skin, wash the affected area with water for 5 minutes.
- In the case of skin contact with any other chemicals in this experiment, wash the area well with cold water.
- Eye protection must, of course, be worn at all times.

Disposal

- Solutions from the all stages of the experiment can go down the drain, provided that the drain and sink are flushed with plenty of water both **before** and **after** pouring away the chemicals.
- Solids from the nitrate determination should go in the trash if possible. If not, wash these solids down the drain.

Background

Lime Away™, Shower Shine™, CLR™ — you can probably name several others. All are products designed to remove the stains and deposits left by **Hard Water**. "Softening" hard water is also a big industry. Many of you already know the joy of hauling forty pound sacks of Morton System Saver™ pellets down to the basement to refill the water softener. The Culligan Company has built a nationwide company around soft water. So what *is* "hard water" and how did it get that way?

"Hard water" is water with a high content (>100 ppm) of +2 and +3 metal ions. The most common hardening ions are Ca^{2+}, Mg^{2+}, and Fe^{3+}. All of these generally get into water which has been in contact with rocks such as limestone (primarily $CaCO_3$), dolomite (primarily $MgCO_3$) or other rocks which contain iron minerals such as ilmenite ($FeTiO_3$), hæmatite (Fe_2O_3 – named for its blood red appearance) and magnetite (Fe_3O_4). The taconite ores of northern Minnesota which contain about 30% iron as the minerals hæmatite and magnetite are a good example of iron bearing rocks. When carbonate ions are also present, $CaCO_3$ and $MgCO_3$ can deposit out as "scale". When water containing Fe^{3+} becomes oxygenated upon contact with air, iron oxide (rust) precipitates.

The other way in which humans observe "hard water" is in the interaction of the hardening metal ions with soaps. The chemistry of this interaction is discussed in part 1 of the "Water Chemistry Project" in your lab manual.

Water which has been pumped from an underground well is very likely to be hard because the porous strata where aquifers lie are often composed of limestone rocks. Surface water (lakes and streams), by contrast is less likely to be hard, as it has spent less time in contact with rocks than groundwater has. Rainwater would not be expected to have any hardening ions at all.

Nitrate, by contrast, gets into the water not as a result of geology but as a result of biology. Human and animal feces, as well as run-off from fields and lawns treated with artificial fertilizer, contribute to nitrogen in surface water. The exact chemical form of the nitrogen depends on how far it has progressed through the nitrogen cycle. Complex nitrogen containing organic molecules (such as amines and proteins), urea and ammonia are broken down by bacteria into first nitrite ion (NO_2^-) and then nitrate ion (NO_3^-). The assay you will use actually measures nitrite ion, and includes a step where nitrate is reduced to nitrite, so you will be getting a value for nitrogen as nitrate *plus* nitrite. Since there is one nitrogen per mole of nitrate or nitrite, it doesn't really matter which one nitrogen content is reported as, as long as everyone uses the same one. The convention is that nitrogen is reported as ppm of nitrate, and because you will use standards made up on a ppm nitrate basis, that is how your experimental data will appear. Note that nitrogen present in the sample as protein or ammonia will not register in your analysis.

Theory and Units

The unit used to quantify both water hardness and nitrate content is the *part per million* or *ppm*. This is an engineering unit, not a chemical one, and as such it requires some explaining. As the name suggests, 1 ppm is one of something in among a million things. In the context in which we use it here, ppm refers to *milligrams* of solute per 1000g of *solution*. If the solution is a dilute one in water, this works out to be mg per liter.

The hardness titration does not differentiate between calcium and magnesium (and iron if present). By convention, water hardness is reported as ppm of $CaCO_3$ (because this is the primary component of the "scale" deposited by hard water). This means that having found (by titration) the concentration (molarity) of Ca^{2+} *and* Mg^{2+} in solution, we assume that this is moles of $CaCO_3$ in order to get ppm. Confused? The example below should help.

e.g. Titrations with EDTA lead to a Ca^{2+}/Mg^{2+} ion concentration of $1.72x10^{-3}$ M Calculate the hardness in ppm.

$1.72x10^{-3}$ mol/L x 100.09g/mol = 0.172g/L x 1000 mg/g= 172 mg $CaCO_3$ per liter = 172 ppm

Data Collection

Each lab section will be divided into six groups of three or four students. Three of these groups (assigned by your T.A.) will study water hardness, the other three will study nitrate content. The experimental procedures for the tests are detailed in Sections 1 and 3 of the "Water Chemistry Project" in your Lab Manual.

Testing Water Hardness

Begin by testing the "known" solution provided in lab. The known solution has a total hardness in the range 50 - 200 ppm. This will permit you to practice your titration technique and to verify that you are performing the procedure correctly and obtaining accurate data. Every student in the group should perform at least one titration. Average the results of your three best titrations (ppm concentrations within 2% of each other).

Check Point

Show your data on the known solution to your instructor. You may only proceed to the next step if your technique is good enough to have brought you close to the correct answer. If you are too far off, your instructor will require you to perform more titrations with the known solution.

There is also an *unknown* sample for all the groups to test. Each group member should perform at least one titration of this unknown sample. To have a *conclusive* result for hardness, you should have at least three titrations which result in hardness values differing by less than 2%. Once you have determined the hardness of this sample to a sufficient level of accuracy, write your value up on the board. Copy down the data from the other two groups studying hardness and the groups studying nitrate content so that you can write your report.

All the data from your titrations should be neatly tabulated. One example of the calculation of hardness (as ppm $CaCO_3$) should be shown.

Testing Nitrate Content

Begin by preparing and testing the standard solutions called for in the lab manual. Go to the computer room and use Excel to make a valid Beer's Law plot. The r^2 value for the line of best fit on your plot should be at least 0.98. If it is worse than this, you will need to re-test (and possibly re-make some of your standards). Next, test the "known" solution provided in lab. Each member of the group should perform the test. Your results should agree within 2%. If they do not, continue to perform tests until you have three tests which agree to within 2%.

Check Point

Show your data on the known solution to your instructor. You may only proceed to the next step if your technique is good enough to have brought you close to the correct answer. If you are too far off, your instructor will require you to repeat your measurements with the known solution. This will permit you to verify that you are performing the procedure correctly and obtaining accurate data.

There is also an *unknown* sample for all the groups to test. Each group member should work up a sample of this unknown to determine its nitrate content. Your results should agree within 2%. If they do not, continue to perform tests until you have three tests which agree to within 2%.

Once you have determined the nitrate content of this sample to a sufficient level of accuracy, write your value up on the board. Copy down the data from the other two groups studying nitrate content and the groups studying hardness so that you can write your report.

All the data from your experiment should be neatly tabulated. Include a copy of your Beer's law plot with your report.

A Group Report

Attach all the duplicate copies of all lab manual pages used in this experiment. Copies from *every* member of the group are required.

(4 points) **1a. Complete the following table:**

Group	Expt'l hardness of known solution (ppm $CaCO_3$)	Expt'l hardness of *unknown* sample (ppm $CaCO_3$)	Expt'l nitrate content of known solution (ppm)	Expt'l nitrate content of *unknown* sample (ppm)
Our group				
Group 2 (same test)				
Group 3 (same test)				
average value				
Group 4				
Group 5				
Group 6				
average value				

1b. If you did hardness, give the notebook page number where an example calculation of the total hardness in the unknown sample can be found.

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(2 points) **2. Based on the table below, how would you classify the unknown sample's hardness?**

ppm $CaCO_3$	Classification
< 15 ppm	very soft water
15 – 50 ppm	soft water
50 – 100 ppm	medium hard water
100 – 200 ppm	hard water
>200 ppm	very hard water

(1 point) **3. Based on the hardness of the unknown sample, suggest where it might have come from (e.g. river, well, lake).**

(3 points) **5. Comment on the *precision* of the class data on hardness and nitrate content for the unknown samples.**

The rest of your grade for this experiment will be awarded as follows. Attach copies of all notebook pages used to record data or observation in this experiment.

(3 points) **WebCT Quiz** *(2 points)* **Pre-Lab Preparation**

(2 points) **Notebook skills** *(3 points)* **Performance Evaluation**