Gravimetric analysis of chloride and sulfate

Introduction

Chloride, Cl\(^–\) (aq), is the principal anion in seawater. In this laboratory you will determine the chloride concentration in seawater by a gravimetric procedure. In brief, the addition of excess silver ion, Ag\(^+\) (aq), to a solution containing Cl\(^–\) (aq) causes the precipitation of solid silver chloride, AgCl(s), which is then filtered, dried, and weighed. The presence of appreciable concentrations of sulfate ion, SO\(_4^{2–}\) (aq), in seawater presents a difficulty. Like Cl\(^–\) (aq), SO\(_4^{2–}\) (aq) will precipitate in the presence of Ag\(^+\) (aq). For this reason it is necessary to remove sulfate ion before carrying out the precipitation of AgCl(s). You will use two different methods to remove the sulfate ion, anion exchange and selective precipitation of BaSO\(_4\) (s).

Anion exchange - Through the action of a resin, the SO\(_4^{2–}\) (aq) in your sample will be replaced by NO\(_3^{–}\) (aq). Once the SO\(_4^{2–}\) (aq) is removed, you can precipitate AgCl(s) without interference.

Barium sulfate precipitation - Addition of a solution of barium nitrate to a solution containing SO\(_4^{2–}\) (aq) ion causes the precipitation of BaSO\(_4\) (s). By filtering, drying and weighing the barium sulfate precipitate you will also get an estimate of the sulfate concentration.

Before you begin work on this complex laboratory, it would probably be a good idea for you to read the procedures over carefully and to prepare a timeline indicating when you plan to carry out each of the steps.

Procedure

Reagents and special equipment

0.1 M NaCl  
0.5 M NaNO\(_3\)  
1.0 M NaNO\(_3\)  
0.2 M AgNO\(_3\) (in brown bottle)  
0.06 M Ba(NO\(_3\))\(_2\) in 0.01 M HNO\(_3\)  
0.01 M HNO\(_3\)

Why, in a class in quantitative analysis, do we report the concentrations of these solutions to only one significant figure?
Part 1 - Separation of chloride and sulfate by anion exchange

Sample

Clean, rinse with de-ionized water, and weigh a 50-mL beaker. Take a 1.5-mL sample of filtered seawater with an automatic pipette. Transfer the sample to the weighed beaker and weigh again.

Preparing the anion exchange column

Obtain an anion exchange column from your instructor. The column will have been packed with Dowex-1 X8 anion exchange resin conditioned so that the resin is in nitrate form.

The phrase "nitrate form" means that all the sites in the resin where ion exchange occurs are occupied by nitrate ions. By what simple laboratory process can one convert a column to "nitrate form?"

Place a beaker under the column to collect liquid that comes through. This beaker need not be clean. Familiarize yourself with the various parts of the column and with how flow through the column can be controlled. Remove the column cap. If necessary, drain the liquid in the column until it is 2-3 millimeters above the resin bed. Do not let the level of the liquid fall too low and expose the resin to air.

Why not? Think about what happens to the resin as it dries out.

To check that the column is free of chloride ion, introduce 5 mL of 0.5 M NaNO₃ solution. Allow the solution to run down the walls of the column; don't squirt it directly onto the resin. A plastic transfer pipette can make this process easier.

The object in adding the solution in this careful way is to disturb the resin bed as little as possible - why?

Adjust the stopcock so that the flow rate is about 1 mL/minute. Note 20 drops is roughly 1 mL. 20 drops in 60 seconds is equivalent to 1mL/minute

Why not faster?

Let the column drain until only about 1 mL of the 5 mL added remains above the resin. Close the stopcock. Replace the collection beaker with a clean test tube or 50-mL beaker. Collect the last ~1 mL (but don't let the resin go dry!) and close the
Fine point: To be a little more precise you will not be collecting the last mL of liquid in the column but rather the 1 mL of liquid that is displaced by the last mL above the resin.)

Test the eluate (what comes out of the column) in the test tube or beaker for the presence of Cl\textsuperscript{-} as follows. Add a few drops of 0.2 M AgNO\textsubscript{3} solution to the test tube or beaker and look for a white precipitate.

Caution! AgNO\textsubscript{3} solution will stain your skin. Avoid contact with it; wash exposed areas promptly with tap water.

If a precipitate forms, add 5 mL of 1.0 M NaNO\textsubscript{3} (the more concentrated solution) to the column, elute as described above, and repeat the test for chloride with the "last" mL of eluent. A faint cloudiness in the test solution is tolerable.

**Loading the sample**

Carefully clean a 250-mL Erlenmeyer flask and place it under the column. "Load" the sample of seawater that you weighed onto your column by using a plastic transfer pipette. Add a little at a time, allowing the sample to run down the walls of the column. To make sure that transfer of your sample to the column is complete, rinse the beaker (and the plastic transfer pipette) with 1 - 2 mL of 0.5 M NaNO\textsubscript{3} solution and transfer the rinse solution to the column. Open the stopcock on the column. Allow the liquid to drain through the column to the point where the resin is covered by 2-3 mm of liquid. Close the stopcock. The chloride ion and sulfate ion are caught on the column sites.

**Eluting chloride** (To learn to work efficiently, simultaneously work on Part 3 once you start the elution)

Attach a plastic funnel provided by the stockroom to the top of the column. The funnel will serve as a reservoir for eluent. To "elute" the chloride ion from the column, add ~ 60 mL of 0.5 M NaNO\textsubscript{3} solution (the "eluent") to the funnel - again, slowly, to minimize disturbance of the resin. Allow the solution to pass through the column, continuing to collect the eluate in the flask. The eluate in the flask contains the chloride ion; sulfate ion will remain on the column. (Why?)

The volume of eluent needed to wash down all the Cl\textsuperscript{-} will vary but should be in the range of 60 mL and should take about one hour to pass through the resin (around 1 mL/min).

For most of this period, you can proceed with part 3. **Continue,**
however, to check the column from time to time to make sure it does not run dry.

After all but about 1 mL of the eluent has passed through the column, stop the flow. Replace the Erlenmeyer flask with a clean test tube and collect a little less than 1 mL of the eluent remaining in the column.

See if the eluate in the test tube is free of Cl\(^{-}\) by adding a few drops of 0.2 M AgNO\(_3\) (brown bottle) solution. If a precipitate forms then it will be necessary to:

- save the AgCl(s) that you have just precipitated in the test tube. As AgCl(s) is light sensitive, wrap the test tube in Al foil (provided by the stockroom) and put it in your equipment drawer in an upright position.

What is the chemical reaction for the photodecomposition of AgCl(s)?

What color(s) would you expect the products of this reaction to be?

- put the Erlenmeyer flask back under the column
- add 15 mL more of 0.5 M NaNO\(_3\) (do not use 1 M NaNO\(_3\)) solution to the column
- continue eluting
- repeat the test for Cl\(^{-}\) in the eluate as previously described.

When no AgCl precipitate forms in the test sample of the eluate, elution is complete. Note approximately the final volume of eluate, including test samples. Transfer quantitatively any test samples (those in the test tubes if you have them) to the Erlenmeyer flask. If necessary, use de-ionized water to aid in transferring the AgCl precipitate(s) in the test tube(s). Precipitation of AgCl is described in Part 2.

Add about 10 mL of 0.5 M NaNO\(_3\) to the anion exchange column. Replace the column cap and return the set-up to the stockroom.
Part 2 - Quantitative gravimetric determination of chloride

Precipitating AgCl

To a sulfate-free sample (that is roughly the 50 mL of eluate), add 8.0 mL of 0.2 M AgNO₃ solution. Precipitation should be immediate. From this point on, try to shield the precipitate from light. Swirl the flask a few times. Place it in the oven (~105°C) for 20 minutes. Heating in the oven will cause the precipitate to coagulate and make it easier to filter.

Be sure to label your vessels with your name and a sample identifier so that you will know that they are yours and which sample is which.

While the precipitates are in the oven, continue to work on part 3.

After 20 minutes of heating (it is still a slurry), remove the sample from the oven and let it cool until you can handle it comfortably, remembering to shield it from light. Test for completeness of precipitation by adding a few drops of 0.2 M AgNO₃ solution to the flask. If additional AgCl precipitate forms, add 1 mL 0.2 M AgNO₃ solution.

Filtering, washing, and weighing AgCl

Set up a filtration apparatus with a trap. Make sure the collecting flask is clean. Using forceps, obtain a Fisher MCE membrane filter (Fisher catalog # 09-719-2E) from your instructor. (Do not use the blue separator). Weigh it before you put it in the filtration apparatus. Add ~1 mL of de-ionized water to the filter and make sure the filter is seated properly.

Leave the flask undisturbed for a few minutes for the precipitate to settle down. Transfer quantitatively the AgCl precipitate to the filter. Decant the supernatant liquid first. The filtration may go faster if by decanting carefully, you can arrange to transfer most of the liquid first. Use 0.01 M HNO₃ in a plastic transfer pipet to rinse the adhering precipitate from the Erlenmeyer flask and from the walls of the filter funnel.

Rinse the precipitate with two 5-mL portions of 0.01 M HNO₃. Refer to your textbook as to why the washing is performed in the presence of an electrolyte.

Why not simply use de-ionized water for the rinse?

Check for completeness of washing (i.e., for removal of excess Ag⁺ ion from excess AgNO₃ solution) as follows. Break the vacuum in the aspirator. With great care remove the filter assembly (do not separate the two parts or you may disturb the
precipitate!) and place it in an upright position in a beaker. Discard the solution in the filter flask, using the waste container for silver solutions that is provided in the lab. Rinse the filter flask with de-ionized water. Replace the funnel assembly in the filter flask. Rinse the precipitate with another 2 mL of 0.01 M HNO₃. Again break vacuum and carefully place the filter assembly in a beaker. Test the filtrate for completeness of washing (removal of excess Ag⁺) by adding a few drops of 0.1 M NaCl solution. If no appreciable amount of precipitate forms, then washing of the AgCl on the filter is complete. If appreciable precipitate forms, wash the precipitate with another 5-mL portion of 0.01 M HNO₃.

Allow the precipitate to dry on the filter for two or three minutes with aspiration on. Remove the filter and transfer it to a labeled watch glass. Place the sample in the 105°C oven for roughly 60 minutes. Gauge your time. Remove the sample, put in a desiccator, cool, and weigh. Note the color of your sample. Is there any decomposition?

If time allows, return the precipitate to the oven for further drying. Remove the sample, put it in a desiccator, cool and reweigh a second time to check for constant weight.

**Part 3 - Separation of chloride and sulfate by selective precipitation**

Prepare **two identical samples**. Directions for the preparation of one sample follow. Clean and weigh a 50-mL beaker. Take a 1.5-mL sample of filtered seawater ("filtered through Millipore APFF04700") with an automatic pipet. Transfer the seawater to the weighed vessel and weigh again. After weighing, for ease of handling add 4 - 5 mL of de-ionized water.

Add ~ 2 mL 0.06 M Ba(NO₃)₂ in 0.01 M HNO₃ to the beaker.

Seawater contains bicarbonate ion. What reaction would you expect between Ba²⁺ ion and HCO₃⁻(aq)? (Hint: which carbonates are insoluble?) What reaction would you expect between a solution of HNO₃ and HCO₃⁻(aq)? Do you see any fizzing? Based on your answers to these two questions, suggest a reason why we acidify the solution of Ba(NO₃)₂.

A faint precipitate of BaSO₄(s) should appear immediately. Swirl to mix and let the precipitate to stand for 15 to 20 minutes to allow complete precipitation.
Part 4 - Gravimetric determination of sulfate

Remember you will be performing part 4 in duplicate since you have two samples of seawater.

Obtain a 0.45 μm membrane (mce 47 mm non-sterile; Fisher) and weigh it. Assemble a filtration apparatus with the filter paper. Make sure the receiving flask is clean. Transfer the BaSO₄ precipitate from part 3 to the filter with 4-5 mL of 0.01 M HNO₃. Filter with aspiration. Rinse the precipitate with 3-4 mL of 0.01 M HNO₃. Allow the filter to dry for 2 or 3 minutes with aspiration running. Carefully remove the filter and transfer to a labeled watch glass. Place in the oven at 105°C for a minimum of ~ 15-20 minutes. When dry, remove the sample from the oven, allow to cool, and weigh.

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Report

Your report should include:

- Abstract. Maximum 100 words. Include the concentrations of sulfate and chloride measured in different ways and your best estimate of their concentrations in seawater from this gravimetric experiment. Report the concentration in three different units, mg/L, mmol/L, and mass %.
- Introduction. Maximum 3 sentences. State the purpose of the experiment.
- Experimental methods. None.
- Results and discussion. About 1.5 pages. Include:
  - A calculation for one sample illustrating how to convert the mass of precipitate to the concentration of chloride in seawater.
  - A calculation for one sample illustrating how to convert the mass of precipitate to the concentration of sulfate in seawater.
  - Comment on the cross-comparison of the concentration of the sulfate ion determined by the turbidimetric analysis performed earlier and the gravimetric analysis;
  - An easy-to-read table showing
    - the masses of each sample, the volume of each sample taken, and the mass of each precipitate.
    - the calculated concentrations of chloride and sulfate in mg/L, mmol/L, and in mass %
    - a single best estimate of the chloride and sulfate concentrations
    - literature values for chloride ion in seawater.
• literature values for sulfate ion in seawater
• a cross-comparison of the concentration of the sulfate ion
determined by the turbidimetric analysis performed earlier and
the gravimetric analysis;

Grading of the Lab Report

Please type your lab report and submit a stapled hardcopy to your instructor at the
beginning of the next lab period. Include the date and your section no. Please write your
name on every page.

Your lab report will generally be graded based on the following:

Abstract: include best estimates for concentrations of Cl\(^-\) and SO\(_4^{2-}\).
Introduction: 3 sentences max.
Tables should be easy to read.
Tables should include: Mass of Sample in g, Sample volume, ppt mass, mg/L, mmol/L, % by mass
(include both Cl\(^-\) and SO\(_4^{2-}\))
Sample calculation for mg/L
Sample calculation for mmol/L
Sample calculation for mass%
Comparison with literature value of Cl\(^-\) concentration. Cite source.
Comparison with literature value of SO\(_4^{2-}\) concentration. Cite source.

Accuracy of Cl\(^-\) concentration;
Accuracy of SO\(_4^{2-}\) concentration

A cross-comparison of the concentration of the sulfate ion determined by
the turbidimetric analysis performed earlier and the gravimetric analysis
and your comments

Please make sure all the above information is included in your lab report. Prepare a
grading grid and include it in your cover page.
Grading Grid

Prepare a grading grid on the cover sheet of your report similar to the following table:

<table>
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<tr>
<th></th>
<th>Name</th>
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<td>2</td>
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<td>Sample Calculation for mg/L</td>
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<td>Sample Calculation for mmol/L</td>
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<td>7</td>
<td>Sample Calculation for mass %</td>
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<td>8</td>
<td>Comparison with literature value of Cl concentration. Cite source.</td>
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<td>9</td>
<td>Accuracy of Chloride Concentration</td>
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<td>Accuracy of Sulfate Concentration</td>
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Please make sure all the above is included in your lab report. Make sure your answers have the correct number of significant figures and the correct required units. Presentation, your understanding, discussion and explanation and accuracy are taken into account when reports are graded. You may receive bonus points or lose points when appropriate.