Objective

The concentration of sulfate ion in seawater will be determined gravimetrically by precipitation with barium chloride.

Text Reference:

Rubinson and Rubinson, *Contemporary Chemical Analysis*, Chapter 10.

Introduction

When a solution containing sulfate ion is mixed with one containing barium ion, sparingly soluble barium sulfate precipitates. The reaction may be written as

\[ \text{SO}_4^{2-} + \text{Ba}^{2+} \rightarrow \text{BaSO}_4 \]

This reaction can be used for the gravimetric determination of sulfate or, less commonly, for barium. Barium sulfate usually precipitates as very fine particles. The high surface area of the particles facilitates contamination by adsorption. Larger particles can be obtained by heating the precipitate in the presence of its mother liquor. During this digestion process, recrystallization takes place resulting in a precipitate of larger particle size. Since barium sulfate is stable in air and is nonhygroscopic, the weighing can be performed in an open crucible.

Recrystallized BaSO\(_4\) is collected on filter paper. The precipitate and filter paper are dried in a crucible. The filter paper is charred and ashed, leaving the dried sample in the crucible for ease in weighing. To reduce error, the paper ashing operation must be carried out with care. The paper should be charred carefully at low temperature with the crucible lid in place so that escaping gases do not burst into flame. When smoke formation has ceased, the temperature is slowly increased and air is allowed ample access to the interior of the crucible. If this practice is not followed, carbon will reduce sulfate ion to sulfide ion, forming carbon monoxide:

\[ \text{BaSO}_4 + 4C \rightarrow \text{BaS} + 4\text{CO} \]

Low mass determinations will result.

Apparatus Required (per student)

Desiccator
Two Bunsen burners
Two crucibles with lids
Ringstand
Wire gauze
Reagents (prepared by TA)

50% HCl solution
Barium chloride solution: Dissolve 100 g BaCl$_2$·2H$_2$O in 1 liter distilled water
Silver Nitrate solution: Dissolve 8.5 g AgNO$_3$ and 0.5 ml HNO$_3$ in 500 ml distilled water.

Procedure
1. Ignite two crucibles to constant weight while completing the following steps.
2. Obtain a 50 ml aliquot of seawater from the saltwater aquarium.

   NOTE: Prepare duplicate samples for analysis using the following procedure:

3. Pipet 20 ml of the seawater sample into a 600 ml beaker and dilute to 250 ml with distilled water.
4. Adjust the pH to 4.5 to 5 and then add 2 ml of 50% HCl.
5. Heat this solution to boiling while warming a 50 ml beaker containing 25 ml BaCl$_2$ solution.
6. While stirring the sample solution slowly add enough BaCl$_2$ solution until precipitation stops. Then add two ml more to confirm completeness of the precipitation.
7. Rinse the beaker walls with distilled water and then cover with a watch glass.
8. Digest the precipitate for about one hour.
9. Remove the beaker from the heat and let the precipitate settle.
10. Decant the clear supernatant through 9 or 11 cm ashless filter paper.
11. Wash the precipitation with hot distilled water. Decanting the solution through the filter paper.
12. Transfer the precipitate to the filter paper and rinse with hot distilled water until the filtrate tests negative for chloride.
13. Dry, char, and ash the filter paper in the crucible (weighed already to constant weight) as explained below.
14. Ignite for a full 15 minutes and then allow to cool in a desiccator.
15. Repeat the heating/cooling cycle until constant weight is reached.
16. Report the concentration of sulfate in the seawater sample in parts per thousand.

Directions for the Drying and Charring Process

- Drain the last washing as completely as possible, loosen the filter paper in the funnel and fold the edges over the precipitate so that the three-layer portion of the paper is uppermost.
- Place the resulting package in the crucible, taking care not to tear the paper.
- Place the crucible vertically on a triangle supported by a ring stand and adjust the ring so that the bottom of the crucible is positioned 10 to 15 cm above a flame 1 to 2 cm in
height. Place the lid on the crucible but displaced to one side so that steam can escape through a slit 1 to 2 mm in width. Apply heat slowly and gently so that violent boiling of the water and bursting of the package is avoided.

- When drying is complete, fully cover the crucible and char the paper by increasing the heat applied to the crucible. The escaping gases should not burst into flame. Occasionally lift the lid and note the progress of the charring operation, by observing the blackening of the paper and the disappearance of white areas.

- When the charring of the paper is complete, incline the crucible so that its bottom rests against one side of the triangle (see figure below).

- Place the lid against the crucible mouth so that the small openings allow a draft of air to pass through the crucible. Direct the flame of the burner toward the bottom of the crucible and gradually increase the flame size until the lower part of the crucible becomes dull red. Do not allow the flame to enter the crucible because the gas stream may carry away particles of the precipitate and in some cases may cause its chemical reduction. Do not allow the inner blue cone of the flame to touch the crucible because the carbon deposited would be difficult to burn off. Lift the lid occasionally and note the progress of the ashing operation. Rotate the crucible, as necessary, to speed the removal of any tar or carbon adhering to the walls.

- When the ashing of the paper is complete, bring the crucible upright (using tongs), adjust the flame so that the temperature, and continue heating for the specified time.

Questions

1. Why is the solubility of barium sulfate increased by the presence of acids?
2. Suppose that a small portion of the sulfate precipitated as sodium sulfate rather than as barium sulfate. How would this affect the result of the analysis?
3. From the following list, identify the interfering species for the sulfate determination method used in this experiment: $\text{Mg}^{2+}$, $\text{Pb}^{2+}$, $\text{Na}^+$, $\text{NO}_3^-$, $\text{Cl}^-$, $\text{PO}_4^{3-}$. 