

## Gravimetric Determination of Soluble Sulfate

The quantitative determination of sulfate ions in inorganic compounds can be accomplished by using the selective precipitation of the sulfate ion from a hot solution using  $\text{BaCl}_2$  (barium chloride), provided proper control over reaction conditions are exercised and good analytical techniques are practiced. In this experiment, the sulfate ion will be reacted with an excess of barium ion in a hot solution to drive the precipitation of barium sulfate. Following digestion of the precipitate, it will be filtered through ashless filter paper and then washed to remove ionic contaminants that are adsorbed on the surface of the crystallizing barium sulfate. The precipitate and filter paper will be transferred to a crucible and the contents will be ignited in a muffle furnace. The process of ignition oxidizes the filter paper, leaving barium sulfate salt in the crucible. Measurement of the mass of  $\text{BaSO}_4$  will allow the determination of sulfate in the original unknown sample using known stoichiometry.

### Materials Needed:

- 3 porcelain crucibles and lids
- Barium Chloride solution at (0.25 M)
- Aqueous silver nitrate solution (0.1 M)
- Concentrated HCl (hydrochloric acid)
- Ashless Filter Paper
- Sulfate Unknown Sample (provided by your instructor)

### Preparation for sulfate determination.

1. Obtain an unknown sample from your instructor. It should be of sufficient quantity for triplicate samples. Dry this unknown sample for at least 2 hours at  $110\text{-}120\text{ }^\circ\text{C}$ . Allow it to cool in your desiccator for a minimum of  $\frac{1}{2}$  hour prior to massing.
2. Clean each crucible and lid (3 each) thoroughly. Place them paired with the lids slightly ajar to allow air circulation into a convection oven at  $110\text{-}120\text{ }^\circ\text{C}$  for 1 hour. Remove from the oven, place in your desiccator and allow to cool. Accurately weigh each crucible and lid. Repeat the heating/cooling process until a constant mass for each crucible and lid pair is achieved.
3. Prepare a 100 mL of a 0.25 F solution of barium chloride and store this in a plastic bottle.

### Procedure:

1. Accurately weigh three samples of approximately 0.5000 g of your unknown material directly into clean 400 mL beakers. Dissolve each sample in approximately 200 mL of distilled, deionized water and add 0.5 mL of concentrated hydrochloric acid to each beaker. You should use a different stirring rod for each sample and leave that stirring rod in the beaker throughout.
2. To determine the quantity of barium chloride necessary, assume your sample is pure sodium sulfate (knowing it isn't) and calculate the number of moles of barium chloride needed to precipitate all of the sulfate in the largest sample. From this value, calculate the number of mL of 0.25 F  $\text{BaCl}_2$  solution needed to deliver this number of moles, then increase this amount by 10% to determine the volume of  $\text{BaCl}_2$  solution that will be added in step 4.
3. Heat the three solutions to nearly boiling on a hot plate and adjust the temperature to keep them slightly below boiling. (When you see bubbles forming on the bottom of the beaker is generally a point where the solution is sufficiently hot).

- Using a buret, slowly add the calculated volume of barium chloride solution determined in step 2 into each beaker, stirring vigorously throughout the addition. After the addition, let the precipitate settle and then test for complete precipitation by adding ~5 mL additional barium chloride solution. If a precipitate forms, stir and let the precipitate settle. Repeat this process until precipitation is complete. Leave the stirring rods in the beakers, cover each with a watch glass and digest the mixture on a hot plate until the supernatant is clear (DO NOT BOIL). Digestion is a step that allows the crystal size to become larger, thus creating a more easily and completely filterable sized solid. This will require at least an hour to complete. If the volume of your solution drops below 200 mL, you should add more distilled water.

***If there is insufficient time to complete the ensuing filtering steps, you may stop at this step and continue the procedure during the next lab period.***

- Prepare filter funnels to filter each solution. Each should be fitted with a piece of ashless filter paper provided you by your instructor. If you are unsure how to fold this paper for quantitative filtration activities consult with your instructor for the proper approach (fluted folding is not preferred for quantitative filtering activities). While preparing these, if your solutions have cooled, warm them on a hot plate until nearly boiling. Also prepare a beaker of hot distilled water for transferring and washing your precipitate.
- Filter the solutions while hot, being careful to not fill the paper too full. If you do not understand, look up the term “creeping” as pertaining to filtering operations. Quantitatively transfer the barium sulfate into the filter using hot distilled water, your stirring rod and a rubber policeman.
- Wash the filtered precipitate and the filter paper with hot distilled water until a few mL of filtrate show no turbidity when several drops of acidic silver nitrate are added. During the filtering and washing steps, do your best to rinse the precipitate down into the cone of the filter. Be sure to analyze the filtered liquid for any signs of cloudiness indicating that crystalline barium sulfate has passed through the filter paper. If none is apparent, you can proceed to the ignition operation. If not, you will need to isolate the filtrate, add an additional 5 mL barium chloride solution, and repeat the digestion and filtration steps to remove all of the barium sulfate precipitate.
- Loosen the filter paper from the funnels gently, allowing them to drain for a few minutes. Be careful not to tear them or lose crystalline material. Fold each filter paper into a packet enclosing the precipitate in the folded filter paper. Place the packet into a crucible with the cone side down and the folded paper on the top side, gently pressing it down into the crucible. Make sure all the precipitate has been removed from the funnel. If not, wipe it off with a small piece of ashless filter paper and add it to the crucible. Repeat with a new crucible for each sample.
- Transfer each crucible to a muffle furnace, setting the crucible lid to leave the contents of the crucible exposed to air with only a slight “crack”. Make sure the lid covers the contents with only a mm or two crack. Set the muffle furnace to approximately 100 °C for about ½ hour to dry the moisture from the crucible, precipitate and paper. After drying, raise the temperature of the muffle furnace to 800 °C and allow ignition to occur for 1 hour once the furnace reaches 800 degrees. After the one hour period, shut the furnace off and allow the crucibles to cool to nearly room temperature before removing them from the muffle furnace. The precipitate should be white with no black particles. If it has black particles, it means that your filter paper was not completely oxidized and your crucibles will need to be ignited further. If the precipitate is white, then the crucibles can be transferred to your desiccator to complete cooling and proceed with reaching constant mass.

10. After cooling, weigh the crucibles and lids. Heat them in a convection oven at 110-120 °C for ½ hour, cool in your desiccator and re-weigh. Continue this operation until you reach constant mass and successive mass measurements agree within  $\pm 0.4$  mg. If gaining constant mass proves difficult, moisten the precipitate with a little dilute sulfuric acid and heat it very gently.
11. After constant mass has been reached, calculate the percent sulfate in each of your samples. Report the mean, standard deviation and confidence limit of your results.