**Assay of SO3 by Gravimetric Analysis of Sulfate**

**Gravimetric analysis** is one of the oldest analytical techniques, and for this reason is referred to as a "classical method." Gravimetric procedures are usually very accurate, but more tedious than other methods. The only major equipment needed for gravimetric analysis is an accurate balance.

Sulfur in the form of the sulfate anion, that is, as sulfuric acid, sodium sulfate or some other soluble sulfate, may be determined by precipitation as barium sulfate.

**Procedure for the Determination of Sulfate**

Run three trials through this procedure at the same time.

Weigh out 0.4 - 0.6 g (0.1 mg) dried unknown sulfate sample into 200 mL or larger beakers. Add 50 mL distilled water to the beaker to dissolve the sample. Add concentrated HCl **drop wise** to adjust the pH to 3-4 (usually only 1-2 drops). Check the pH after each drop using pH paper. Heat the solution to 90°C with a watch glass on top of beaker. While stirring, slowly add the stoichiometric amount (this amount will be different for each sample) needed of **0.125 M BaCl2** over a 3-5 minute period with low heat. This is best accomplished by delivering the BaCl2 solution via burette. The goal is to minimize excess chloride which can get trapped within the precipitate. You must determine the stoichiometric amount (*the maximum to be added*) of 0.125 M BaCl2 to be added if the sample were **pure** (NH4)2SO4 (132.14 g/mole). Include 2 mL excess of the barium chloride solution.

**BaCl2 (aq) + SO4= (unknown) 🡺 BaSO4 (s) (Barium Sulfate Mixture)**

Keep the solution hot **(DIGEST)** for 1.5 hours. ***You must filter this the same day*.**

At this point heat the empty sintered glass crucibles (filter) to constant weight. This will be accomplished by placing the sintered glass crucible inside a 250 mL beaker and drying in the oven for at least for 15 minutes at 110oC to remove moisture.

Always keep track of each sintered glass crucible by some marking on the beaker and remember to handle them with clean crucible tongs. Following heating, let the sintered glass crucible cool for a few minutes within the beaker and keep covered with a watch glass to minimize moisture accumulation. Weigh the sintered glass crucible on the analytical balance after it has reached room temperature. Repeat the heating, cooling, and weighing until the weight difference between two measurements is within 0.3 to 0.4 mg (thus at LEAST three weighings).

*Notes: Remember to identify each filter with pen or pencil BEFORE drying to constant EMPTY weight! Also samples should be cooled to room temperature for approximately the SAME period since dried samples might begin to reabsorb moisture from air!*

After the above **BaSO4 mixture** has been heated for 1.5 hours, let it cool to room temperature. Assemble the sintered glass funnel filtration apparatus as shown in the figure below:

Now carefully pour the cooled BaSO4 mixture into the sintered glass crucible, making sure that the precipitate is completely transferred. Use only the tip of the rubber policeman to scrape precipitate off of the beaker. A wash bottle of MilliQ water can also be used to rinse precipitate from the beaker to insure that a quantitative transfer is obtained.

If any precipitate passes into the sidearm Erlenmeyer receiving flask, you will need to re-filter.

The sintered glass crucible containing the precipitate is now placed inside a 250 mL beaker and dried in the oven at least 25 minutes to remove moisture. Be careful not to touch and transfer any particulate on hands or gloves to the sintered glass crucibles. After heating, let the sintered glass crucible cool within the beaker until the beaker can be safely handled without hurting the hands; keep covered with a watch glass to minimize moisture accumulation. Weigh the sintered glass crucible on the analytical balance after it has reached room temperature. Repeat the heating, cooling, and weighing until the weight difference between two measurements is within 0.3 to 0.4 mg (thus at LEAST three weighings).

Using the weight of barium sulfate and the weight of the sample, calculate the percent of sulfur trioxide in the sample. The unknown percentages are 40-60% SO3.

**NOTE: Modifications are possible to this procedure. Your TA will inform you of any modifications which are going to be made. Be sure to note any deviations from the above procedure in your lab notebook.**

In this experiment, we will report the amount of sulfur present not as % S or % SO42- but as % SO3. This is known as an **assay**. In an assay, we measure one material and *infer* from that measurement the amount of another material. *An assay presumes a stoichiometric relation between what is measured and what is sought*. Here, BaSO4 is measured, but the weight percent [written as % (w/w) to indicate that this is a percentage by weight of the solid] of SO3 is sought. There is a 1:1 stoichiometric relationship between SO3 and BaSO4, so these two species are related by the gravimetric factor is FW SO3 / FW BaS04 for reporting **%** (w/w) SO3 when one measures BaSO4. A similar expression could be used to assay any other *sulfur-containing species* from measurements of the weight of BaSO4.



**Warning: Soluble barium salts are toxic! Handle BaCl2 carefully and wash your hands thoroughly when you complete this laboratory. Dispose of excess BaCl2 as instructed.**