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

**Background**

*Gravimetric analysis* is one of the oldest analytical laboratory techniques. For this reason, it 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 analytical balance.

Sulfur (S) in the form of the sulfate anion (SO42-), as sulfuric acid, sodium sulfate, or some other soluble sulfate, may be determined through precipitation of a soluble sulfate via addition of a barium chloride (BaCl2) solution. The insoluble precipitate that forms as a result is barium sulfate (BaSO4).

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

In this experiment sintered glass crucibles (Gooch crucibles) will be used to quantitatively collect solid BaSO4, which can then be weighed in an analytical balance (weight = precipitate + crucible). This information, along with the weight of the sintered glass crucibles (empty), is used to determine the quantity of solid BaSO4 produced. Once that is calculated, the weight of solid BaSO4 along with the initial mass of the solid soluble unknown is used to complete the calculations. You will report the amount of sulfur in the unknown not as % SO4 but as an assay, reporting percent sulfur trioxide, % SO3.

**Treatment & Digestion of Unknowns**

Weigh out 0.4 - 0.6 g (0.1 mg) of dried unknown soluble sulfate sample: Three samples must be weighed out and transferred to 3 separate 400 mL beakers. All three unknown samples must run through the remaining procedure at the same time. Label each beaker to keep track of which unknown sulfate sample (weight) went into which beaker! Using a 100.0 mL graduated cylinder, add 50.0 mL of Nanopure H2O to each beaker to dissolve the unknown sample. Add concentrated (12 M) HCl **dropwise** to adjust the pH to 3-4. Check the pH after each drop using pH paper. Put beakers on a hot plate and cover each of them with a watch glass. Heat the solutions to 90°C. [Put a 4th beaker on the hotplate w/ Nanopure H2O, with a digital thermometer to monitor temperature]. Fill a buret with 0.125 M BaCl2. While stirring the beaker’s solution, slowly add the stoichiometric amount\* (different for each sample) of **0.125 M BaCl2** using the buret into each beaker over a 3-5 minute period with low heat. The goal is to minimize excess chloride, which can get trapped within the precipitate.

\*To determine the stoichiometric amount of 0.125 M BaCl2 to add, use the equation below. The equation assumes the unknown sample is **pure** ammonium sulfate, (NH4)2SO4 (*thus the maximum %*). The molecular mass of (NH4)2SO4 is 132.14 grams/mole.

Wt. of unkwn x x  x x  + 2 mL excess

After the BaCl2 has been added, keep the solution hot **(DIGESTION)** for 1.5 hours MINIMUM*.* Nucleation and particle growth are two phases of crystallization. The latter is desired to produce large enough product crystals, essential for quantitative collection. Digestion allows a precipitate (BaSO4) to remain in contact with the mother liquor (liquid from which the precipitate forms in). Digestion promotes 1) particle growth of crystals via recrystallization and 2) expels any impurities from the product crystal. After digestion is complete, turn the hotplate off and let solutions cool. An ice bath can be used to accelerate cooling. Parafilm beakers and store in lab locker until the next class period.

**Constant Weight of Sintered Glass Crucibles**

While the solutions are digesting, heat 3 empty ***fine*** *(F)* sintered glass crucibles to constant weight.

CRUCIBLES CANNOT BE HANDLED WITH BARE HANDS; OILS WILL DEPOSIT ON CRUCIBLES AND PREVIOUS WEIGHTS WILL BE IRRELEVANT. Only handle crucibles with gloved hands or crucible tongs.

*NOTES: Label each crucible with Industrial Sharpie marker BEFORE drying to a constant EMPTY weight! Crucibles should be cooled to room temperature for approximately the SAME time since dried crucibles begin to re-absorb moisture from air! Record heating and cooling time in notebook!*

Heating crucibles to a constant weight is accomplished by placing the 3 LABELED sintered glass crucibles in a 600 mL beaker [labeled with your name using a grease pencil] in the oven for at least 20 minutes at 110 oC to remove moisture. Keep a watch glass on the beaker when it is in the oven to prevent large debris or dust from getting into the crucibles. If crucibles are washed with soap/water first, they must remain in an oven for at least 24 hours to remove the water.

Following heating, remove the 600 mL beaker with crucibles from the oven and set on an upside down beaker. Let the crucibles cool for 20-30 minutes inside the beaker, keeping the watch glass on in order to minimize moisture accumulation. Record the actual # of minutes the crucibles were cooled for! Then, weigh the sintered glass crucibles individually, on an analytical balance. Record weights in notebook. Repeat the heating, cooling, and weighing cycle until the weight difference between two measurements [of the *same* crucible] is within 0.3 to 0.4 mg (achieved through at LEAST three cycles).

**Filtering the Precipitate (BaSO4) after Digestion is Complete**

Reheat the digested unknown samples on the hotplate for 20 minutes. Then let cool, using an ice bath to accelerate the cooling process. Proceed with vacuum filtration via the following directions.

Assemble the sintered glass funnel filtration apparatus discussed in the pre-lab lecture presentation. Make sure to clean the side-arm Erlenmeyer flask and the walter crucible holder before use! Assign a crucible to each beaker, noting which crucible is filtering which beaker of precipitated BaSO4. Carefully pour the cooled BaSO4 mixture into the sintered glass crucible, making sure that the precipitate is completely transferred. Use proper quantitative transfer techniques! *You cannot lose a single drop of your digested sample; if you do, your results will reflect it!*

Use the tip of a rubber policeman (wash between beakers) to scrape any precipitate off of the beaker and into the crucible. Then use a wash bottle of Nanopure H2O to rinse remaining precipitate from the beaker into the crucible, to insure that a quantitative transfer is obtained. Do NOT rinse the beaker more than 5 times, as excess washing will negatively affect results. ALL MOTHER LIQUOR/RINSE MUST BE DISPOSED OF IN WASTE CONTAINERS.

\*If any precipitate passes into the sidearm Erlenmeyer flask [i.e. the mother liquor is cloudy], you will need to re-filter it through the crucible to ensure no product (BaSO4) has been lost!\*

**Heating Crucibles w/BaSO4 Product to a Constant Weight**

Once filtering is complete, place the sintered glass crucible containing the precipitate inside a 600 mL beaker. Proceed filtering the other two samples with their assigned sintered glass crucible. When all 3 samples have been filtered, put the 600 mL beaker [containing the crucibles] in the oven for at least 24 hours before taking the first weight measurement. Make sure a watch glass is placed atop the beaker.

After heating, wait the same time for crucibles to cool as was done when they were empty. Keep the 600 mL beaker covered with a watch glass while the crucibles are cooling. Weigh all crucibles individually on the *same* analytical balance. Be careful not to touch or transfer any particulate on hands or gloves to the sintered glass crucibles NOR accidently lose some of the white precipitate. Repeat the heating, cooling, and weighing cycles until the weight difference between two measurements [of the same crucible] is within 0.3 to 0.4 mg.

Using the weight of solid BaSO4 produced and the initial weight of the solid unknown soluble sulfate aliquots, calculate the percent sulfur trioxide (% SO3) in the unknown for each trial (beaker). Calculate average % SO3, standard deviation, and ppt. The range of sulfur trioxide the unknowns contain is 20.00 – 56.00 % SO3.

**Assay Calculations**

In this experiment, the amount of sulfur present is reported not as % S or % SO42- but as % SO3. This is referred to as an **assay**. For an assay, one material is measured and an *inference* of an amount of a different material is made from the initially measured material. *An assay presumes a stoichiometric relation between what is measured and what is sought*. BaSO4 is measured in this experiment, but the weight percent of SO3 [written as % (w/w) to indicate that this is a percentage by weight of the solid] is sought. There is a 1:1 stoichiometric relationship between SO3 and BaSO4. So these two species are related by the gravimetric factor, which is the ratio of the formula weights of sulfur trioxide and barium sulfate (FW SO3 / FW BaSO4) for reporting **%** (w/w) SO3. A similar expression may be used to assay any other *sulfur-containing species* using the measured weight of BaSO4 produced. The unknowns range from 20.00 – 56.00 % SO3.

F.W. SO3 = 80.06 grams/mole

F.W. of BaSO4 = 233.43 grams/mole

**Warning: Soluble barium salts are toxic to humans and the environment! Handle BaCl2 carefully. Wear gloves during lab and wash hands thoroughly before leaving. Dispose of excess BaCl2 in waste containers as instructed! Do not dispose of anything down the drain!**