# Gravimetric Analysis: Determination of % Sulfur in Fertilizer

This is another "real world" sample experiment – in this case we will analyze a fertilizer sample for the sulfate content and express the result as %S. Fertilizers are often specified by their N, P, K content – referring to the three important nutrients nitrogen, phosphorous, and potassium as explained further below. Since we'll be analyzing a commercially available fertilizer (purchased at the Fred Meyer store in Newberg) that was labelled "Ammonium Sulfate" we can reasonably presume that the mole percent nitrogen would be twice that of sulfur and work our way around to a nitrogen mass percentage if we wanted. This is our first exposure in this class to a Gravimetric analysis – one of the oldest and best-established analytical methods we consider this term.

## Precipitation Gravimetry

Gravimetric analysis is a standard classical method for determining the amount of a given component present in a host of solid and solution sample types. The method used here involves precipitating the component of interest from the unknown by means of an added reagent. From the mass of the precipitate formed, the moles and thus mass percentage of the unknown component in the original sample can be calculated.

A complete gravimetric analysis includes a series of distinct steps. First, a precise, known amount of the original sample must be taken for the analysis. If the sample is a solid, an appropriately sized portion is precisely weighed typically to the nearest 1 mg or 0.1 mg. If the sample is liquid, an appropriately sized aliquot (a known fraction) is taken with a volumetric pipet. The sample of unknown taken for the analysis must be large enough that precision may be maintained at a high level during the analysis, but not so large that amount of precipitate generated cannot be handled easily.

Next the unknown sample must be brought into solution (if it is not already dissolved). The reagent that causes the precipitation is then added to the sample. The precipitation reagent is added slowly, and in fairly dilute concentration, to allow large, easily filterable crystals of precipitate to form. The precipitate is often allowed to stand in the *mother liquor* for an extended period, sometimes at an elevated temperature, to allow the crystals of precipitate to grow as large as possible. This process is called **digestion** of the precipitate.

The precipitate must then be filtered to remove it from the liquid. Although filtration could be accomplished with an ordinary gravity funnel and filter paper, this is often prohibitively slow. The precipitates produced in gravimetric analysis are often very finely divided and tend to clog the pores of the filter paper. Specialized *sintered glass filtering funnels* (a.k.a. crucible) and/or filter inserts have been produced for gravimetric analyses. These crucibles (as shown in Figure 1) have a frit plate constructed of several layers of very fine compressed glass fibers that act to hold back the particles of precipitate. These glass funnels can use suction to speed up the removal of liquid from a precipitate, can be cleaned easily before and after use, and are not affected by reagents in the solution.


Figure 1. Crucible (C represents the pore size of the crucible). During method development, the analyst will often need to choose an appropriate size for the filtrate and precipitation/digestion used.

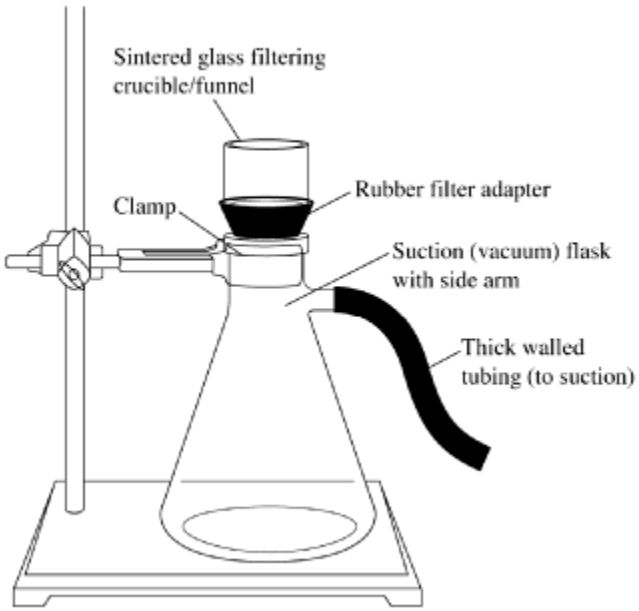


Figure 2. Set-up for suction filtration. The crucible is resting on a soft rubber filter adapter, which makes a tight seal between the crucible and the suction flask that prevents liquid from entering the vacuum line.

Once the precipitate has been transferred to the crucible, it must be washed to remove adsorbed contaminants. The liquid chosen for washing the precipitate solvates the contaminants, but can be removed quantitatively (usually during the drying step). The washing of the precipitate must be

performed carefully to prevent re-dissolution or *peptization* of the precipitate where the agglomerated crystals might be lost through the pores of the filter.

After the precipitate has been filtered and washed, it must be dried. This is usually accomplished in an oven whose temperature is rigorously controlled at 110 degrees C. The oven must be hot enough to boil off water adhering to the crystals but cannot be so hot that might decompose the crystals. Some precipitating reagents are organic in nature and cannot stand very strong heating. Finally, the dried precipitated is weighed and the mass of the presumably pure substance is converted to moles.

## Fertilizer

**Fertilizer products are prominently labeled with three numbers, usually on the front of the package. These numbers specify the relative content of the chemical elements Nitrogen, Phosphorus, and Potassium (N, P, K) in the fertilizer. This label is known as the fertilizer grade and is a national standard. A bag labeled 10-10-10 indicates that the fertilizer has 10% nitrogen, 10% phosphate and 10 % potassium by mass. You can also get fertilizers that contain only one of each of the primary nutrients. Common nitrogen sources include ammonium nitrate (33.5-0-0), urea nitrogen (46-0-0), sodium nitrate (16-0-0), liquid nitrogen (30-0-0) and ammonium sulfate (20-0-0).**

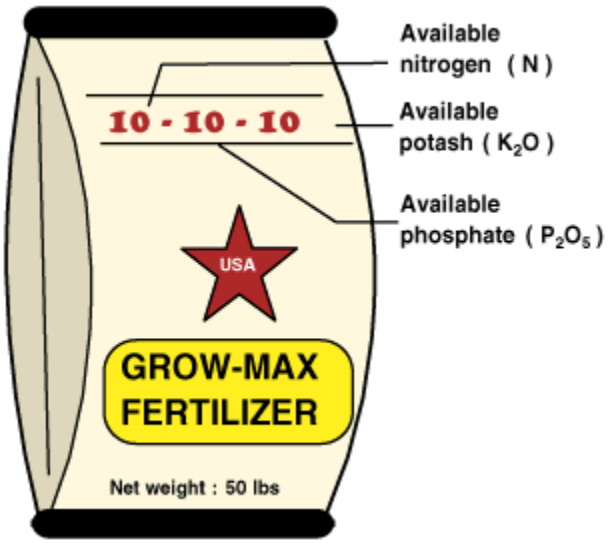


Figure 3. Labeling of Fertilizer

In this experiment you will conduct a gravimetric analysis of the sulfur (S) mass percentage in an unknown fertilizer. Nitrogen-sulfur materials are often used as the source of both nitrogen and sulfur in the fertilizer, including **ammonium sulfate** (21-0-0 +24S), **ammonium nitrate-sulfate** (30-0-0 +15S), **ammonium phosphate-sulfate** (13-39-0 +7S), and **ammonium phosphate-nitrate** (27-12-0 +4.5S). The label "+15S" means the fertilizer contains 15% sulfur by mass.

## Calculation

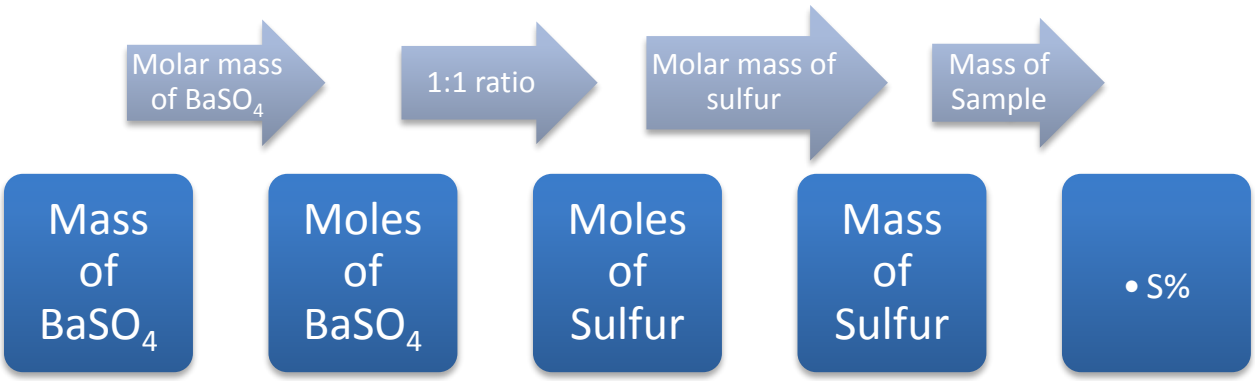


Figure 4 diagram of the calculation

The S% can be determined by forming $BaSO_4$ precipitates upon addition of excess $BaCl_2$ to a solution that contains $SO_4^{2-}$. Sulfate ion is removed from acidic solution by barium ion, producing a very finely divided crystalline precipitate of barium sulfate:

$$Ba^{2+} + SO4^{2-} \rightarrow BaSO_{4\,(s)}$$

The percent of sulfur in the unknown fertilizer is

$$\frac{Mass\ of\ S}{Mass\ of\ sample} \times 100\%$$

## Apparatus and Chemicals available

250 mL Erlenmeyer flask (x3), crucibles (x3), glass microfiber filters, vacuum suction flask and adapter, fertilizer, $BaCl_2$ solution (1 M), AgCl (in dropper bottle), HCl (1 M)

## Experimental Procedure

Accurately weigh three 0.1 g portions of fertilizer (to 0.1 mg) and dissolve each with 25 mL DI water in the 250 mL Erlenmeyer flasks. Add 5 drops of 1 M HCl to the solution and swirl to mix; then add extra DI if needed until all of the solid fertilizer dissolves. The solution from which the sulfate is precipitated must be acidic for two reasons: 1) the presence of acid helps larger crystals of $BaSO_4$ to form, 2) atmospheric $CO_2$ can dissolve in the solution to form carbonate ion which would also be precipitated by barium ion but this is strongly suppressed at low pH.

Obtain 10ml of 1 M $BaCl_2$ in a graduated cylinder and slowly add the $BaCl_2$ into the Erlenmeyer flask containing the sample solution while stirring. You should be able to see the precipitate forming immediately. (Try not to add more $BaCl_2$ than is needed, the sulfate in the fertilizer is the limiting

reagent and you will need to wash the extra $Ba^{2+}$ from the precipitate later in the experiment.) Bring the solution to almost boiling (this takes about 15 mins on a hot plate so do the replicate trials in parallel) then let it cool. Try not to disturb (don't swirl) the solution/precipitate during the heating and cooling (digestion) steps. Once a clear layer of liquid is visible on top of the solution add one more drop of 1 M $BaCl_2$ to confirm the precipitation (if no precipitate forms, which would be indicated by milky white liquid, the precipitation process is complete).

Obtain three crucibles and three glass microfiber filters from your TA. Place one filter into each crucible (This experiment requires *pore size 4 crucibles* designed for trapping very fine particles, but the crucibles we have are for medium size particles, so the glass microfiber filter is used to supplement the frit of the crucible.) Make sure the crucible and filter are dry before the assembly – using a clean stir rod, push the filter into the bottom of the crucible (from here on, we will refer to the assembled filter and crucible as the crucible). Mark your crucibles before weighing them (you have to find your product among your peers and distinguish between your three replicates). Record the weight of the dry crucible to 0.1 mg.

After confirming the precipitation as described above, assemble the filtration system as shown in Figure 2. Turn on the vacuum and wet your filter with DI water to secure the glass microfiber filter to the bottom of the crucible (keep the vacuum running). Decant the liquid from the flask to the crucible, trying to concentrate the stream near the center of the filter (don't allow the crucible to fill with liquid during the transfer). (Note 1) Try to be quantitative in the transfer of the solid precipitate. You can use a small amount of DI water to wash the solid from the flask (less than 10 mL). Test the liquid in your vacuum flask with 1 drop of $AgNO_3$ - the formation of a milky/cloudy precipitate (of insoluble silver chloride) in your wash liquid indicates that the wash, and thus the $BaSO_4$ precipitate, contains unreacted $BaCl_2$. Transfer the liquid to a waste container and rinse your vacuum flask before reassembling the suction filtration set-up. Wash the $BaSO_4$ precipitate again with minimal (less than 10 mL) of DI water. Test the wash and repeat the procedure until there is no indication of precipitation in the vacuum flask upon addition of silver nitrate.

After washing the precipitate, place the crucible in a 250 °C oven for 30 minutes. Remove the crucible from the oven and let it cool to room temperature in your desiccator before obtaining the mass to 0.1 mg. If time remains, an additional cycle of heating and cooling can be used to make sure no water remains in the filter/precipitate (bringing to constant mass).

After the experiment, you will be responsible for cleaning the crucibles. Take the glass microfiber filter out of the crucible and dispose of the used filter as directed by your TA. Place the crucible in the filtration system, turn on the vacuum, and fill the crucible with 1 M HCl. Pull three aliquots of HCl through the crucible, then rinse with DI water. Return the cleaned crucible to your TA.

## Required measurements

You will present the individual results and mean and RSD for the mass % S in your solid unknown to your lab TA at the end of the lab as usual (if you run out of time, ask your TA if you can present the final results during the next lab period). You should expect the precision to be very good (ppth level) in this experiment.

**Sample Results Table**

| Unknown # | %S | StDev | RSD (‰) |
|---|---|---|---|
| | | | |

## NOTES

**1.** Use a separate stirring rod/rubber policeman for each sample and leave it in its beaker throughout the determination.

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