Chem.243-Exp.-5 (2019)

Gravimetric determination of sulfate

Introduction:

Gravimetric analysis is a quantitative method for accurately determining the amount of an analyte by selective precipitation of the analyte from an aqueous solution. The precipitate is separated from the remaining aqueous solution by filtration and is then weighed. The process requires a container, usually a crucible to be weighed.

In this experiment an unknown sample that contains sulfate will be mixed with excess precipitating agent($BaCl_2$) to form a precipitate($BaSO_4$).

$$M_xSO_{4(aq)} + BaCl_{2(aq)} \rightarrow BaSO_{4(s)} + MCl_{x(aq)}$$

The precipitate formed should have the following properties:

- easily filtered and free from contaminant
- low solubility so losses can be avoided
- uncreative with atmosphere

One important factor during precipitation that should be considered during precipitation is the particle size. The precipitate should have a large size so that it does not easily pass through the filter paper. The formula that determines the particle size is the formula for relative supersaturation:

Relative supersaturation = $\frac{Q-S}{S}$

Where: Q = molar concentration of the mixed reagents before any precipitation occurs.

S = molar solubility ofthe precipitate.

The particle size is inversely proportional to the relative supersaturation of the solution during precipitation.

There are several ways that can control the solubility of the precipitate. The first is to elevate the temperature to increase the solubility of the precipitate (S), the second is to make diluted solution and the third is the slow addition of precipitating agent with constant stirring to keep (Q) small.

Reverse addition of sulfate solution to the precipitating agent reduce cation coprecipitation during precipitation which is very serious and gives a lower formula than does barium sulfate.

The precipitate along with the solution will be filtered using ashless filter paper. This type of filter paper is made of pure cellulose and decomposes into water and carbon dioxide upon ignition. The filter paper containing the precipitate should be washed with warm water to reduce the amount of unreacted $BaCl_2$ adsorbed on the surface of the precipitate formed.

The precipitate inside the crucible must be ignited with plenty of air to avoid partial reduction of the white precipitate of barium sulfate into the yellow barium sulfide precipitate.

$$BaSO_4 + 2\,C \rightarrow BaS + 2\,CO_2$$

The crucible containing the precipitate must be heated until constant mass is achieved.

Gravimetric factor for such analysis is: $G.F = \frac{\text{formula weight of substance sought}}{\text{formula weight of precipitae weighed}}$

The percentage of sulfate in the unknown sulfate sample can be easily calculated using the formula:

$$\%\ \text{sulfate} = \frac{\text{mass of precipitate X G.F}}{\text{mass of sulfate sample}} \text{X}100$$

Reagents and apparatus

- dried sample of the unknown sulfate
- concentrated HCl
- 0.25 M $BaCl_2$
- 3 M HNO_3
- 0.1 M $AgNO_3$
- 3 beakers of 150 mL ,3 beakers of 250 mL ,3 beakers of 400 mL
- 3 watch glasses
- 3 glass funnels
- 3 porcelain crucibles
- 3 ashless filter papers
- 3 glass stirring rods
- wash bottle
- desiccator

Procedure

The experiment will be completed within three laboratory meetings.

First meeting: preparation of clean and dry crucibles and preparation of diluted solutions of the analyte and the precipitating agent.

Preparation of clean and dry crucibles:

1. Mark each of the clean crucibles properly so they can be distinguished from the other, use HB or 2H pencils to mark the bottom of each crucible.
2. Use the Bunsen burner to heat the crucibles gently at first (for 2 min.) then strongly (for 15 min.) (Never touch the crucibles with your hands or with paper for the duration of the experiment).
3. Allow the crucibles to cool for 5 minutes before placing them in labeled 150mL beakers so as to be cooled to room temperature in a desiccator.
4. Weigh the crucibles to the nearest 0.0001 g.
5. Reheat the crucibles again for 10 minutes.
6. Cool again in the desiccator and reweigh to the nearest 0.0001 g.
7. Compare the two masses to check if you attained a constant mass. (Constant mass is attained if the second mass agrees with the first mass within ± 0.4 mg).
8. If the crucibles did not attain constant mass, they should be heated again to attain a constant mass.

Preparation of diluted solutions of the analyte and the precipitating agent:

1. Weigh three 0.3-0.5g samples of approximately equal size of your dry sulfate unknown into 250 mL beakers numbered to correspond with your crucibles.
2. Dilute each solution with 150 mL of deionized water and add 2 mL of concentrated HCl.(Addition of HCl is to increase the solubility of $BaSO_4$ and to prevent the formation of $Ba(OH)_2$ or $BaCO_3$ precipitates during precipitation)
3. Cover each of the beakers with Parafilm paper and store it in your locker for the next meeting.
4. Assume the largest sample of the unknown is pure lithium sulfate (Li_2SO_4, F.wt =109.94 g/mol) and calculate mmoles of barium chloride needed to precipitate it. From this value, calculate the number of mL of 0.25 M $BaCl_2$ solution needed to deliver this number of moles, and then increase the amount by 10% to determine the volume of $BaCl_2$ that will be added to each sulfate sample.
5. Measure the calculated volume of 0.25 M $BaCl_2$ with a graduated cylinder then pour it in 400 mL labeled beaker.
6. Dilute each solution with 50 mL of deionized water.
7. Cover each of the beakers with Para film paper and store it in your locker for the next meeting.

Second meeting: Precipitation and filtration of $BaSO_4$

1. Heat the beakers containing sulfate samples and barium chloride solutions on a hot plate and adjust the temperature to keep them slightly below boiling. (When you see bubbles forming on top of the beaker, it is generally a point when the solution is sufficiently hot).

2. Stirring vigorously, pour the hot sulfate sample solution slowly into the hot barium chloride solution.
3. Allow the precipitate to settle, and test for complete precipitation by adding few drops of 0.25 M $BaCl_2$.
4. After precipitation is complete , cover the beaker with a watch glass and digest below the boiling point for one hour.(Digestion is a step that allows the crystal size to become larger, thus creating a more easily and completely filterable sized solid.
5. Carefully decant the supernatant liquid through an ashless filter paper. (Review decantation techniques)
6. Use warm deionized water from a wash bottle to flush the precipitate to the filter paper.
7. Wash the precipitate in the filter paper with 3-5 mL portions of warm water until the wash water after acidification with 2 drops of diluted HNO_3 gives only a faint turbidity when tested with 2 drops of 0.1 M Ag NO_3 solution.
8. Fold the filter paper compactly around the precipitate and place it into a porcelain crucible that has been previously brought to constant mass.
9. Place each crucible in the labeled 150mL beaker and store it in your locker for the next meeting.

Third meeting: Ignition of the filter paper and weighing the $BaSO_4$ precipitate.

1. Cover the crucibles with lids, place them on a clay triangle on a ring stand. (Displace the cover to one side so that escaping gases and steam can escape through a slit of about 2 mm width)
2. Heat gradually with a Bunsen burner until the escaping gases burns.(If ignition is done at very high temperature $BaSO_4$ may decompose as follows : $BaSO_{4\,(s)} \rightarrow BaO_{(s)} + SO_{3\,(g)}$)
3. Continue heating until gases are no longer evolved.
4. Remove the lids, which may have brown organic deposits on them.
5. Heat strongly and position the burner so that the blue flame touches the bottom of the crucible. (The charred paper should burn with glow).
6. Continue heating until the crucible is white and no traces of black deposition can be seen.
7. Allow the crucibles to cool to room temperature in a desiccator, and then weigh them.
8. Repeat heating for 10 minutes ignition, cooling, etc., until constant mass is attained for the crucible and its contents.
9. Discard the $BaSO_4$ in a proper waste container.

Pre laboratory assignment

1. What will happen if the crucibles where cooled outside the desiccator?

2. What is the purpose of acidifying the samples before precipitation?

Report Sheet

Exp. 5 Gravimetric determination of sulfate

Student Name: ___________________________ Date performed: _________

Student I.D.:_________________________ Date submitted: _________

Data and Calculations

Code for the unknown: _______________

Sampling for the unknown			
	Sample 1	Sample 2	Sample 3
Mass of unknown sulfate, g			
Heating crucible to constant mass	crucible 1	crucible2	crucible3
Mass of empty crucible, g			
Constant mass of crucible (m1)			
Mass of crucible and precipitate, g			
Constant mass of crucible and precipitate,g (m2)			
Mass of barium sulfate,g (m2-m1)			

Calculations:

Sample calculation of % sulfate in sample 1:

Results of calculations:

Sample1:	Sample1:	Sample1:

Treatment of results of calculations(Mean, standard deviation, confidence limit, etc..):

Discussion and final results of analysis:

Post laboratory assignment:

1. How many mL of 0.25 M barium chloride is needed to precipitate 450 mg of sample? Assume that it is 100% sodium sulfate (Formula weight, 142 g/mol).
2. Why is the precipitate washed? Why silver nitrate is used to test for completeness of washing?
3. Suppose that a small portion of sulfate was precipitated as lead sulfate rather than as barium sulfate. How this would change the result of analysis?