

GRAVIMETRIC DETERMINATION OF SULFATE IN AN UNKNOWN SOLUTION

AIM

The main objective of this experiment is to determine the concentration of sulfate ion in an unknown solution by using gravimetry.

INTRODUCTION

Gravimetric analysis is based on the measurement of the mass of a substance of known composition that is chemically related to the analyte. Gravimetric analysis includes precipitation, volatilization and electrodeposition methods.

In precipitation gravimetry of the analyte is carried out by the use of inorganic or organic precipitating agents. The two common inorganic precipitating agents are silver nitrate, which is used to precipitate halide ions such as chloride, and barium chloride for precipitating sulfate ion. Additionally, potassium, ammonium, rubidium, and cesium ions can be precipitated by sodium tetraphenylborate.

Sulfate is quite common in nature and may be present in natural water in concentrations ranging from a few to several thousand milligrams/liter. Sulfates are of considerable concern because they are indirectly responsible for two serious problems associated with the handling and treatment of wastewater. Odor and sewer corrosion problems result from the reduction of sulfates to hydrogen sulfide under anaerobic conditions.

In an aqueous solution, sulfate ion undergoes the following reaction with barium:



Barium sulfate which forms as a crystalline precipitate, is collected on a suitable filter, washed with water, then ignited and weighed. From the mass of BaSO_4 , the amount of sulfate present in the original sample is calculated.

Interferences

Although this method appears to be rather straightforward, it is subjected to numerous interferences due to the tendency of barium sulfate precipitate to occlude foreign anions and cations present in the matrix. Table below summarizes the common interferences affecting the sulfate analysis.

Note: It is necessary to eliminate the main interferences by preliminary treatment of the sample first and then to precipitate BaSO_4 from hot and dilute acid solutions as there is no practical solvent to dissolve BaSO_4 after its precipitation.

Effect on analysis	Nature of interference
Low Results	Excess amounts of mineral acid present.
	Coprecipitation of sulfuric acid. Note that this is a source of error in a gravimetric determination of sulfate but not of barium, since this H_2SO_4 is driven off during ignition.
	Coprecipitation of alkali metal and various divalent ions. Sulfates of these ions usually weigh less than the equivalent amount of BaSO_4 , which have formed.
	Coprecipitation of ammonium ion, $(\text{NH}_4)_2\text{SO}_4$, which is volatilized upon ignition of the precipitate.
	Coprecipitation of iron as a basic iron (III) sulfate.
	Partial reduction of BaSO_4 to BaS when filter paper charred too rapidly.
	In the presence of trivalent chromium, complete precipitation of BaSO_4 may not be achieved owing to formation of soluble sulfates of chromium (III).
High Results	Absence of mineral acid. Slightly soluble carbonate or phosphate of barium may precipitate.
	Coprecipitation of barium chloride.
	Coprecipitation of anions, particularly nitrate and chlorate, in the form of barium salts.

REAGENTS AND APPARATUS

- Unknown sulfate solution, Na_2SO_4 (2 replicates for each student)
- 25.0 mL of 6.0 M HCl for 2 students
- 100.0 mL of 0.10 M BaCl_2
- Iron nitrate (ready)
- 2 pieces ashless filter paper
- 2 porcelain crucibles
- 2 beakers of 400 mL
- 2 watch glasses
- Muffle furnace
- Desiccator
- 2 glass stirring rods
- Wash bottle

PROCEDURE

A. Preparation of Crucibles

- 1) Each crucible should be cleaned and rinsed thoroughly with distilled water.

- 2) Make sure that the crucibles are **marked properly** so they can be distinguished **from one another**. Use a permanent marker, not a paper or tape label. You can mark the sides of crucibles with a solution of iron nitrate.
- 3) For drying, place the cleaned crucibles in the furnace. Remove the crucibles with tongs (never touch crucibles with your hands or with paper for the duration of the experiment) and allow them to cool for 5 minutes before placing them in a desiccator for cooling to room temperature. Cooling will take about 10 min in the desiccator.
- 4) Weigh crucibles to the nearest 0.0001 g. Return them to the oven for 1 hour and repeat the weighing process which should be carried out until two consecutive masses agree to within ± 0.0010 g. It is extremely important that the crucibles should be treated exactly in the same way during this process and later on when they contain the precipitate.

Note: You need to use the same balance throughout the course of this experiment. Use of different balances, when weighing the crucibles, will introduce an error into your calculations (a common cause for not being able to bring the crucibles to constant mass).

B. Preparation and Precipitation of the Unknown Samples

Treat each unknown solution separately.

- 1) Obtain two replicate unknown sample solutions from your assistant. Add 100 mL of distilled water using a graduated cylinder to each solution in the beakers.
- 2) Add 4.0 mL of 6.0 M HCl, cover the beaker with watch glass and heat the solution nearly to boiling in a water bath.
 - *Solubility of $BaSO_4$ at room temperature is around 0.3-0.4 mg per 100 g of water. Its solubility increases when excessive amount of mineral acid is present. On the other hand, precipitation should be done in acidic medium. Because in neutral and basic solutions Ba^{2+} ions precipitate with PO_4^{3-} , CO_3^{2-} or OH^- ions which are present in the solution. Therefore, precipitation is carried out in weakly acidic medium and addition of excess acid is avoided. Precipitation in a weakly acidic medium provides precipitate to occur in the form of large particles.*
- 3) For each sample, heat 50.0 mL of 0.10 M $BaCl_2$ solution in a beaker nearly to boiling.
- 4) Add this solution quickly with vigorous stirring to the hot sample solution.
 - *Use a separate stirring rod for each sample and leave it in the solution throughout the experiment.*
- 5) Rinse the beaker walls with distilled water and then cover with a watch glass. Digest the precipitated $BaSO_4$ at just below the boiling point for 2 hours in the water bath.
- 6) Decant the hot supernatant through a fine ashless filter paper placed on a filtering funnel. Make sure the filter paper is well-seated as shown in Figs. 1 and 2 (*Prepare a piece of medium ashless paper by folding the paper in half and then in quarters. Tear off a corner of the outside fold as shown in Fig. 1, so it catches all of the precipitate.*) Initially, filter as much of the supernatant liquid as possible (solid accumulating on the filter paper drastically slows the rate of filtration). A glass rod over the top of the beaker and extending into the funnel will minimize spilling (ask your assistant for a demonstration). Rinse the glass rod and the beaker with distilled water to recover the final pieces of precipitate. Wash the precipitate twice by using about 10.0 mL portions of distilled water for each wash.

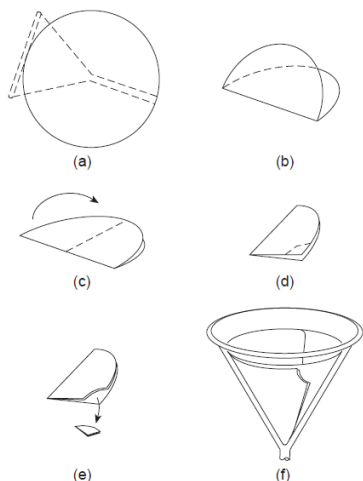


Figure 1. Folding filter paper

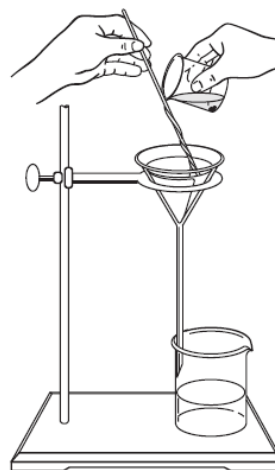


Figure 2. Proper filtering technique

7) Place paper and its contents into a porcelain crucible that has been brought to a constant mass previously. *Gently char off the paper* on a Bunsen burner:

- *Place the crucible vertically on a triangle supported by a ring stand and adjust the ring so that the bottom of the crucible is positioned 10 to 15 cm above a flame which is 1 to 2 cm in height as shown in Fig. 3. Place the lid on the crucible but displace it to one side so that steam can escape through a slit of ~2 mm in width. Apply heat slowly and gently so that violent boiling of the water and bursting of the package avoided.*
- *When drying is complete, fully cover the crucible and char the paper by increasing the heat applied to the crucible. Escaping gases should not burst into the flame. Occasionally lift the lid and check the progress of the charring operation, by observing the blackening of the paper and the disappearance of white areas.*

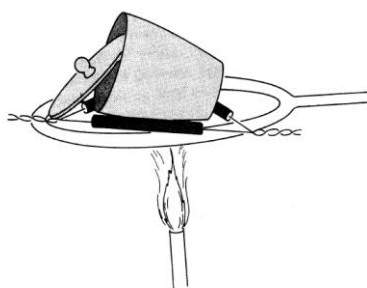
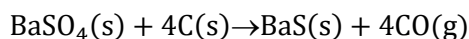


Figure 3. Igniting a precipitate

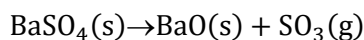
- *Because of difficulty of drying and weighing a precipitate on a filter paper, it is burned away, leaving behind only the precipitate.*
- *At high temperatures, BaSO₄ may be reduced to BaS by the reaction with C of the filter paper.*



This reaction can be prevented by burning the filter paper at rather low temperatures.

8) Ignite the crucible to a constant mass at 800 °C in an electric furnace, for 1 hour. Cool and weigh. Repeat heating, cooling and weighing until the mass of the crucible is constant within ± 0.0010 g. Once a constant mass is reached, discard the solid in the waste container provided.

- *The term ignition means “to heat to a high temperature” not “to set to fire to” If ignition is done at very high temperature BaSO_4 may decompose as follows.*



- *Clean the crucibles by rinsing each thoroughly with distilled water and return them to the technician.*

CALCULATIONS

- 1) On the basis of the two separate results, calculate and report:
 - i) mg sulfate in each unknown sample.
 - ii) mean mg sulfate value in the unknown sample.
 - iii) standard deviation and % relative standard deviation, %RSD.
- 2) Your assistant will send the true value of sulfate unknown to your e-mail address. Do not forget to write the true values to your data sheet.
- 3) Calculate percent relative error. If the experimental mean is larger or smaller than the true value, then write the possible sources of positive or negative error(s) in the discussion part.

PRE-LAB STUDIES

Read Gravimetry chapter from your text book.

- 1) Write the advantages and drawbacks of gravimetric analysis.
- 2) What are the properties of an ideal precipitating reagent?
- 3) What type of particles is preferred as precipitates? Why?
- 4) Write the experimental variables to control the size of the particle in a precipitation reaction.
- 5) What can be the types of impurities present in precipitates? Name at least three of them.
- 6) Describe the preparation of 25.0 mL of 6.0 M HCl from the concentrated HCl solution.*
- 7) Describe the preparation of 50.0 mL of 0.10 M BaCl_2 from solid $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

* Density and mass percent values for the concentrated HCl solution are written outside the bottle present in the hood. These values are also listed in the web page.

POST-LAB STUDIES

- 1) What is the importance of digestion step during precipitation?
- 2) What is the importance of making the sulfate solution slightly acidic before the addition of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ solution?
- 3) What is the importance of ignition at proper temperature?
- 4) Suppose that a small portion of the sulfate precipitated as lead sulfate rather than as barium sulfate. How this would change the result of the analysis?
- 5) From the following list, identify the interfering species in the sulfate determination method used in this experiment: Pb^{2+} , Na^+ , NO_3^- , CO_3^{2-} , PO_4^{3-} .

Name Surname: _____

Section: _____

Date: _____

REPORT SHEET
GRAVIMETRIC DETERMINATION OF SULFATE IN AN UNKNOWN SOLUTION

	Unknown solution	
	Replicate 1	Replicate 2
Mass of empty crucible, g		
Constant mass of crucible, g (m_1)		
Mass of crucible and precipitate, g		
Constant mass of crucible and precipitate, g (m_2)		
mass of barium sulfate, mg $(m_2 - m_1) * 1000$		
mg sulfate, $\bar{X} \pm s$ (% RSD)		

The following information (true values) will be sent to your e-mail address:

Concentration of Na ₂ SO ₄ unknown, M	
mL Na ₂ SO ₄	

TA's Name and Signature: