Chem.243-Exp- 6 (2019)

Determination of sulfate using an adsorption indicator

Introduction

The determination of sulfate is very important, yet the gravimetric method is slow and tedious. A titration method with an adsorption indicator end point is quick and is reasonably accurate when preceded by ion-exchange removal of interfering cations.

In gravimetric analysis reverse addition of sulfate solution to the precipitating agent reduces cation coprecipitation during precipitation. In the adsorption indicator titration the normal addition of the precipitating agent to the sulfate solution which is expected to cause coprecipitation of cations as sulfate, causes underconsumption of titrant (the precipitating agent).

The titration is carried out at about pH 3.5 in a mixture of approximately 50:50 water and methanol. From this solvent mixture, barium sulfate precipitate is very different in appearance from the fine, crystalline precipitate obtained from aqueous solutions. A proper physical form of barium sulfate is needed for the adsorption indicator to function. (In water alone, no end point is obtained)

Alizarin red S is used as indicator. The indicator is yellow but forms a pink complex on the surface of the precipitate when the first excess of barium ion is added (At the end point there is a change in the primary adsorbed ion from sulfate ion to barium ion at the surface of the precipitate, causing electro static attraction of alizarin as a counter ion). The color change is sharp and distinct.

The mechanism of the end point can be shown in the following equations:

$$\underset{BaCl_2}{Ba^{2+}} + \underset{M_zSO_4}{SO4^{2-}} \rightarrow BaSO_4: SO4^{2-}..\ M^{z+} \qquad \text{Titration Reaction}$$

$$Ba^{2+} + BaSO_4: Ba^{2+}..\text{Indic}^{-} \qquad \text{End point Reaction}$$

As mentioned before cation coprecipitation causes underconsumption of the titrant:

$$BaSO_4: SO4^{2-}..\ M^{z+}$$

Since sulfate is calculated from the amount of titrant used, the results for sulfate determination are low. The error caused by the coprecipitation of sodium, potassium and ammonium is serious. A few metal cations also interfere by forming a colored complex with the indicator.

Ion exchange is used to remove cations that would interfere with the end point or cause error by coprecipitation. A column containing cation exchange resin in the hydrogen form is used. The cations in the sulfate solution are exchanged for hydrogen ions of the resin:

$$2M^{+}\ SO4^{2-} \quad + 2\ \text{Resin}-H^{+} \quad \rightarrow \quad 2\ \text{Resin}-M^{+} \quad + \quad 2H^{+}\ SO4^{2-}$$

The sulfuric acid is partially neutralized with magnesium acetate, and the sulfate is titrated with standard barium chloride.

$$MgAc_2 \quad + \quad 2H^{+}\ SO4^{2-} \rightarrow Mg^{2+}\ SO4^{2-} \quad + \quad 2HAc$$

Magnesium acetate is used to neutralize the excess acidity, because Mg^{2+} is one of the least coprecipitated cations in the sulfate titration.

Reagents and apparatus

Chemicals &Reagents	Glass ware
Dried sulfate sample	100mL volumetric flask
0.050M $BaCl_2$	10mL volumetric pipet
1:10 HCl	250 Erlenmeyer flask
Alizarin red S indicator	Burette
Methanol	150mL beaker
0.25 Magnesium acetate	Column of 1.1 cm inner diameter and 20 cm long
Dowex 50 or 50W (Hydrogen form,50-100mesh)	Wash bottle

Procedure

Preparation of sulfate solution

1. Use the results of gravimetric determination of sulfate to calculate the mass needed to prepare 100mL of sulfate ion solution having a concentration of 0.1M. (Use the same unknown sulfate).

2. Weigh on the analytical balance the calculated mass of sulfate and transfer it directly to a 150 mL beaker.
3. Dissolve the solid in about 40 mL deionized water.
4. Transfer quantitatively into 100mL volumetric flask, complete to the mark and shake well to make sure that the solution is homogenous.

Titration of sulfate without ion exchange

1. Pipet exactly 10.00 mL of 0.1M sulfate solution into 250 Erlenmeyer flask.
2. Add approximately 30mL of deionized water and 45mL of methanol.
3. Add 2 drops of alizarin red S indicator, and then add (1:10) hydrochloric acid dropwise until the indicator turns yellow.
4. Titrate rapidly with 0.050 M $BaCl_2$ until about 80% of the theoretical amount of titrant has been added, then add 3 more drops of alizarin red S indicator .
5. Continue titration in a dropwise manner while vigorously stirring the solution in the flask. When pink flashes appear, allow 3-5 seconds between addition of each increment of titrant.
6. Record the volume of titrant when the first permanent color changes to pale pink.
7. Repeat the titration with a second 10.00 mL sample to give duplicate analysis.

Titration of sulfate with ion exchange

1. Clean a column of about 1.1cm inner diameter and add a very small cotton plug to the bottom to hold the resin in place.
2. Pour some cation exchange resin (hydrogen form, 50-100 mesh) into a small beaker, add few mL of deionized water and stir to have slurry.
3. Pour the slurry into the column .Add enough resin to make a column 8-10 cm in height (Never pour dry ion exchange resin into column then add water, the rapid swelling of the resin may cause explosion)
4. Wash the resin with a little water, allow the liquid to drain almost to the top of the resin, and then shut off the flow using a rubber tube and a pinch-clamp attached to the tip of the column.
   (Never allow the liquid level to drop below the level of resin because this may form tunnels in the column resulting in an incomplete exchange of cations)
5. Place 250 Erlenmeyer flask under the column.
6. Pipet 10.00 mL of 0.1M sulfate solution directly into the ion exchange column.
7. Allow the solution to flow from the column at a low rate.

8. When the liquid level is almost down to the top of the resin ,wash the sample through the column with 30 mL of deionized water added in three or four separate portions.(Add the portion when the liquid level is about 1.0cm above the resin)

Note: The effluent contains all of the sulfate, now present as sulfuric acid.

9. Add 45 mL of methanol, 3.5 mL of 0.2M magnesium acetate solution to the flask containing the effluent.
10. Add 2 drops of alizarin red S indicator and titrate as directed in steps 4 to 6 of the procedure described previously to titrate the sulfate without ion exchange .
11. Repeat the ion exchange procedure (using the same column, because the resin will serve for 3-4 runs) and titrate to give duplicate results.

Pre laboratory assignment

1. What is the purpose of using the column and the cation exchange resin in this experiment?

2. What volume of $BaCl_2$ is expected to show a change in color at the end point? What volume of $BaCl_2$ is the 80% of the theoretical amount of titrant needed?

Report Sheet

Exp. 6 Determination of sulfate using an adsorption indicator

Student Name: ___________________________ Date performed: _________

Student I.D.:_________________________ Date submitted: _________

Data and Calculations

Code for the unknown: _________________________

Concentration of $BaCl_2$:_________________________

Mass of sulfate sample, g: ______________________

Total volume of sulfate solution: ________________

Volume of aliquot used in titration: ______________

Titration without ion exchange	Sample 1	Sample2
Final reading of burette (mL)		
Initial reading of burette (mL)		
Net volume of $BaCl_2$ (mL)		
Titration with ion exchange	Sample 1	Sample2
Final reading of burette (mL)		
Initial reading of burette (mL)		
Net volume of $BaCl_2$ (mL)		

	without ion exchange	**with ion exchange**
Average volume (mL)		
Average moles of $BaCl_2$ (mol)		
Average moles of sulfate (mol)		
Average mass of sulfate (g)		
Average mass of sulfate in the original weighed sample (g)		
Average %sulfate in the unknown		

% Deviation of sulfate =

Comparison of results of % of sulfate using the adsorption indicator analysis:

Without ion exchange and with ion exchange

Comparison of results of % of sulfate using two methods of analysis:

Gravimetric analysis and adsorption indicator analysis

Post laboratory assignment

1. Does the indicator color change throughout the solution or on the surface of the precipitate? Does this explain why the solution must be stirred to make the end point easily visible?

2. Why must the sulfuric acid in ion-exchange procedure be partially neutralized?