A. DETERMINATION OF SULPHATE

Aim
To determine the amount of sulphate present in the given samples.

Principle
Sulphate is widely distributed in nature and may be present in natural water in concentrations ranging from a few to several thousand milligrams/litre. Sulphates are of considerable concern because they are indirectly responsible for two serious problems often associated with the handling and treatment of wastewater. Odour and sewer corrosion problem result from the reduction of sulphates to hydrogen sulphide under anaerobic conditions.

Sulphates can be determined by
2. Gravimetric method with drying of residue.
3. Turbimetric method.

1. Gravimetric Method with Ignition of Residue

Principle
Sulphate is precipitated in hydrochloric acid medium as barium sulphates by the addition of barium chloride. The precipitation is carried out near the boiling temperature and after a period of digestion the precipitate is filtered; washed with water until free of chlorides, ignited and weighed as barium sulphates.

Apparatus
1. Drying oven
2. Desiccator
3. Steam bath
4. Analytical balance
5. Ashless filter paper (Whatman filter paper No. 42)
6. Muffle furnace
7. Glassware like funnel, flask and pipette

Reagents
1. Methyl red indicator solution
2. Hydrochloric acid
4. Silver nitrate–nitric acid reagent

Procedure
1. Take 250 mL of the sample in a conical flask.
2. Adjust the acidity with HCl to 4.5 to 5 using a pH meter or the orange colour of methyl red indicator.
3. Then add an additional 1 to 2 mL HCl.
4. Heat the solution to boiling and while stirring gently, add barium chloride solution slowly until precipitation appear to be completed. Then add about 2 mL in excess.
5. Digest the precipitate at 80°C to 90°C preferably overnight but for not less than 2 hours.
6. Filter the contents in the flask through an ashless filter paper.
7. Wash the precipitate with small portion of warm distilled water until the washing is free of chloride as indicated by testing with silver nitrate–nitric acid reagent.
8. Place the precipitate along with filter paper in a crucible after finding its empty weight and dry it.
9. Keep the crucible in a muffle furnace and ignite at 800°C for 1 hour.
10. Cool in a desiccator and weigh.
11. Find weight of the barium sulphate precipitate.

2. Gravimetric Method with Drying of Residue
If organic matter is not present in the sample, first method can be done without igniting and instead drying the residue and weighing.

3. Turbidimetric Method

Principle
The turbidimetric method of measuring sulphate is based upon the fact that barium sulphate tends to precipitate in a colloidal form and that this tendency is enhanced in presence of a sodium chloride—hydrochloric acid solution containing glycerol and other organic compounds. The absorbance of the barium sulphate solution is measured by a nephelometer or turbidimeter and the sulphate iron concentration, determined by comparison of the reading with a standard curve.

Apparatus
1. Nephelometer or Turbidimeter
2. Magnetic stirrer
3. Stopwatch
4. Measuring spoon 0.2 to 0.3 mL capacity.

Reagents
1. Conditioning agent
2. Barium chloride
3. Standard sulphate solution

Procedure
1. Measure 100 mL or suitable portion of the sample into a 250 mL Erlenmeyer flask.
2. Add 5 mL of conditioning reagent and mix it by placing on a magnetic stirrer.
3. Add a spoonful of barium chloride crystals and begin timing immediately.
4. Stir at constant speed exactly for one minute.
5. After stirring pour some of the solution into the absorption cell of the photometer, and measure the turbidity at 30 second intervals for four minutes.
6. Usually maximum turbidity occurs within two minutes and the reading remains constant thereafter for 3 to 10 minutes. So, take reading with maximum turbidity occurring in within four minutes.
7. Prepare a calibration curve. The standards are prepared at 5 mg/L increments in the 0–40 mg/L sulphate range and their turbidity or absorbance read.
8. Absorbance versus sulphate concentration is plotted and a curve is obtained.
9. Finding the absorbance for a given sample, the concentration of sulphates in the solution is determined with the help of calibration curve.

Observation

<table>
<thead>
<tr>
<th>Sample no. or description</th>
<th>Volume of the sample (mL)</th>
<th>Empty weight of the crucible + filter paper</th>
<th>Wt. of crucible + residue after ignition + filter paper</th>
<th>Wt. of BaSO₄ precipitated</th>
<th>mg/L SO₄</th>
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Weight of filter paper =..........
Calculation

\[ \text{SO}_4 \text{ in mg/L} = \frac{\text{mg of BaSO}_4}{\text{mL of sample}} \times 411.6 = \ldots \]

Results

<table>
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<tr>
<th>Sample no. or description</th>
<th>mg/L of SO(_4)</th>
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Discussion

B. DETERMINATION OF SULPHIDE

Aim
To determine the amount of sulphide present in the sample by titrimetric method.

Principle
Sulphides often occur in ground water especially in hot springs, in wastewater and polluted waters. Hydrogen sulphide escaping into the air from sulphide containing wastewater causes odour nuisance. It is highly toxic and cause corrosion of sewers and pipes. Sulphides include H\(_2\)S and HS\(^-\) and acid soluble metallic sulphides present in the suspended matter.

Iodine reacts with sulphide in acid solution, oxidising it to sulphur; a titration based on this reaction is an accurate method for determining sulphides at concentration above 1 mg/L if interferences are absent and if loss of H\(_2\)S is avoided.
Determination of Sulphate and Sulphide

Apparatus
1. Burette
2. Pipette
3. Erlenmeyer flask.

Reagents
1. Hydrochloric acid
2. Standard iodine solution (0.025N)
3. Standard sodium thiosulphate solution (0.025N)
4. Starch solution

Procedure
1. Measure from a burette 10mL of iodine into a 500 mL flask.
2. Add distilled water and bring the volume to 20 mL.
3. Add 2 mL of 6 N HCl.
4. Pipette 200 mL sample into the flask, discharging the sample under the surface of solution.
5. If the iodine colour disappears, add more iodine so that the colour remains.
6. Titrate with sodium thiosulphate solution, adding a few drops of starch solution, as the end point is approached and continuing until the blue colour disappears.

Observation

<table>
<thead>
<tr>
<th>Sample no. or description</th>
<th>Volume of iodine solution used (a mL)</th>
<th>Volume of sodium thiosulphate solution used (b mL)</th>
<th>Volume of sample used</th>
<th>mg/L sulphide</th>
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Calculation

\[
\text{mg/L sulphide} = \frac{400 (a - b)}{\text{mL of sample}}
\]

where, 
\[a = \text{mL 0.025 N iodine used}\]
\[b = \text{mL 0.025 N sodium thiosulphate solution used}\]
Results

<table>
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<tr>
<th>Sample no. or description</th>
<th>mg/L (Sulphide) in the sample</th>
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Discussion

Questions

1. What is the significance of high sulphate concentration in water supplies and in wastewater disposal?
2. What is the purpose of digestion of the sample in the gravimetric analysis for sulphates?
3. Explain the significance of the determination of sulphide concentration in environmental engineering.
4. The water to be used for the preparation of cement concrete products should be free from excess of sulphates and chlorides. Why?