Reference Material:
- AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater

Methods: 4500-SO$_4^{2-}$ E. (Turbidimetric Method)

Objectives: Determine sulfate ion concentration in a water sample.

Background:
Sulfate are found in appreciable quantity in all natural waters, particularly high in arid and semi arid regions where natural waters in general have high salt content. Sulfate salts are mostly soluble in water and impart hardness. Water with high concentrations has a bitter test. Sulfate may cause intestinal disorders. These ions can produce hydrogen sulfides as per following equation (1):

\[
\text{SO}_4^{2-} + \text{organic matter} \rightarrow \text{S}^{2-} + \text{H}_2\text{O} + \text{CO}_2 \quad (1a) \quad \text{(in the presence of anaerobic bacteria)}
\]

\[
\text{S}^{2-} + \text{H}^+ \leftrightarrow \text{HS}^- \quad (1b)
\]

\[
\text{HS}^- + \text{H}^+ \leftrightarrow \text{H}_2\text{S} \quad (1c)
\]

The sulfate data is used in determining applicability of different water types for their public and industrial applications. It indirectly indicates extent of problems that can arise due to reduction of sulfates to hydrogen sulfides. In addition, sulfate content of organic matter fed to anaerobic digester is important information as it gives idea of generation of hydrogen sulfides, which needs to be removed.

Lab Procedure

Method:

The turbidimetric method depends on the fact that barium sulfate formed following barium chloride addition to a sample (Equation 2) tends to precipitate in a colloidal form and this tendency is enhanced in the presence of an acidic buffer (consists of magnesium chloride, potassium nitrate, sodium acetate, and acetic acid). These precipitates need to be separated through filtration (using a filter) before sample is analyzed for sulfate concentration. This is a very rapid method and can be used for samples with sulfate concentration greater than 10 mg/L (samples can be diluted and then it can be analyzed).

\[
\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4 \quad \text{(precipitate; poorly soluble)} \quad (2)
\]

Reagents:

1. **Buffer Solution A:** Dissolve 30 g magnesium chloride (MgCl$_2\cdot$6H$_2$O), 5 g sodium acetate ($\text{CH}_3\text{COONa}\cdot3\text{H}_2\text{O}$), 1.0 g potassium nitrate (KNO$_3$), and 20 mL acetic acid ($\text{CH}_3\text{COOH}; 99\%$) in 500 mL distilled water and make up to 1000 mL.
2. **Buffer Solution B** (required when the sample $SO_4^{2-} < 10$ mg/L): Dissolve 30 g magnesium chloride, 5 g sodium acetate, 0.111 g sodium sulfate, and 20 mL acetic acid (99%) in 500 mL distilled water and make up to 1000 mL.

3. **Dry Barium Chloride (BaCl$_2$) crystals**

4. **Standard Sulfate Solution**: Dissolve 0.1479 g of anhydrous sodium sulfate in distilled water to make the volume 1 L. This solution contains 100 mg sulfate/L (i.e., 1 mL=100µg $SO_4^{2-}$). Prepare standards of various strengths (preferably from 0.0 to 40.0mg/L at the intervals of 5 mg/L by diluting this stock solution). Above 40 mg/L accuracy decreases and BaSO$_4$ suspensions lose stability.

**Apparatus**: Whatman No. 1 filter paper; Spectrophotometer; Magnetic stirrer

**Steps**:

1. Filter the sample through filter paper (Whatman No. 1) and take 50 mL of filtrate in an Erlenmeyer flask.
2. Add 20 mL buffer solution and mix in stirring apparatus. While stirring, add 0.15 g of barium chloride to the sample and stir the sample with the help of magnetic stirrer for about an hour.
3. Measure the absorbance against a distilled water blank (DO NOT ADD BARIUM CHLORIDE TO IT.) at 420 nm using spectrophotometer. Absorbance for the blank sample is taken to correct for sample color and turbidity.

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<tr>
<th>Sample Name</th>
<th>Absorbance @420nm</th>
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<th>Absorbance @420nm</th>
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<tbody>
<tr>
<td>Distilled water blank</td>
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<td>Standard 1</td>
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<td>Sample 1</td>
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4. Process the standard solution of different strengths in similar way and record the absorbance for each solution. Plot a standard sulfate calibration curve on a graph paper from these absorbance values putting strengths (mg/L) on X-axis and absorbance @ 420 nm on Y-axis. Fit a best-fit linear model to the data. Express equation as:

$$\text{Absorbance value} = A + B \times \text{Sulfate concentration (in mg/L)} \quad (3)$$

5. Using the standard sulfate calibration curve (a linear-model; Equation 3), find out sulfate concentration in the given unknown sample in mg/L.

$$\text{Sulfate concentration (mg SO}_4^{2-}/\text{L}) = (1000 \times \text{mg SO}_4^{2-}/\text{mL sample}) \quad (4)$$

**Answer these questions also (for Submission with Lab report):**

Q1. Explain relevance of preparing standard sulfate solutions in determining sulfate concentration for unknown samples.