

## DETERMINATION OF SULFATE BY TURBIDIMETRY CHEM 365

### INTRODUCTION

Many natural waters and rain samples contain sulfate. Sulfate in natural waters can come from dissolved minerals, from pollutants (such as sulfuric acid), and from acid rain which has fallen or drained into the waters. Acid rain often contains sulfates. It is usually the result of combustion of fuels which contain sulfur, primarily coal and fuel oil.

During turbidimetry the decrease in radiation intensity passing through a sample as a result of scattered radiation from a suspended solid is measured. The measurements are similar to spectrophotometric measurements, however, the decrease in radiative intensity is caused by radiation scattering rather than by absorption. Although turbidimetric measurements are normally highly sensitive, they are often more difficult to perform than spectrophotometric measurements owing to the care which must be taken while preparing the suspension.

Radiation can be scattered by several mechanisms. When the dimensions of the particles that cause the scattering are equal to or greater than the wavelength of the incident radiation, Tyndall or Mie scattering occurs. When the particle dimensions are less than five percent of the wavelength, either Rayleigh or Raman scattering can occur. In this experiment scattering is caused by a barium sulfate suspension. Since the size of suspended particles is large compared to the 450 nm wavelength used for the assay, Tyndall scattering occurs. Tyndall scattering is caused by a combination of reflection of the incident radiation from the surface of the suspended particles, by internal reflection from within the particles, and by diffraction and refraction as the radiation passes through the particles. The intensity of the scattered radiation is a function of the frequency of the incident radiation. Theoretically the intensity of the scattered radiation increases with the fourth power of its frequency, however, for Tyndall scattering the intensity usually more nearly increases with the square of the frequency.

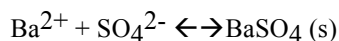
Quantitative analysis which utilizes scattered radiation can be performed in two ways. Either the intensity of the scattered radiation can be measured and related to particle concentration, or the decrease in intensity of the incident radiation owing to scattering can be measured after the radiation passes through the analyte. Measurements made by using the first method are similar to fluorescence measurements, and the method is nephelometry. Measurements made by using the second method are analogous to spectrophotometric absorbance measurements, and the method is turbidimetry. Turbidimetry is used for this experiment. In either case the working curve method has to be used for the assay owing to a typical lack of linearity in the measurements as a function of concentration.

When turbidimetry is used, the decrease in intensity of the incident radiation is measured after the radiation passes through the cell. Since turbidimetry is analogous to absorptimetry, a spectrophotometer can be used to make the measurement. The turbidance  $S$  of the analyte is defined for solutions containing suspensions in a manner identical to the way absorbance is defined for spectrophotometric measurements of solutions.

$$S = -\log \frac{I}{I_0} = \epsilon bc$$

Normally, nephelometry is the preferred method of measurement when  $S$  is less than 0.05, and turbidimetry is preferred at higher values.

In this experiment, a natural water or rain sample is assayed turbidimetrically. An excess of barium chloride is added to an acidic solution of the sample. The barium combines with sulfate in the sample to form a barium sulfate suspension.



In highly acidic solutions, the only common ion which forms a precipitate with sulfate is barium.

Since suspended material in the analyte can interfere with the assay, it is necessary to filter suspended material from the solution prior to reaction with barium. Any species which absorbs radiation at the wavelength (450 nm) of the study can also interfere. Because the size of the suspended barium sulfate particles affects the amount of scattered radiation, it is necessary to carefully control all experimental parameters (especially the rate of mixing and reaction time) which can alter the particle size.

## EXPERIMENTAL PROCEDURE

- A. Collection and Preparation of the Sample: Obtain an instructor-supplied unknown. Record the number of your unknown. Place 12-15 mg (weigh accurately) of your unknown in a **500 mL** volumetric flask and dilute to the mark with D.I. water. 2
- B. Preparation of Stock Sulfate Solution: Dry the potassium sulfate in a 110°C oven for at least one hour. Allow the salt to cool to room temperature. Weigh 0.18 g of the cooled salt to the nearest 0.1 mg, and add it to a 1-L volumetric flask. Dissolve the salt in deionized water and dilute the solution to the mark. The stock solution prepared in this step contains 100 mg/L sulfate.
- C. Preparation of Standard Sulfate Solutions: Respectively label 8, 50-mL volumetric flasks with the numbers 1-8. To each flask, use one or more pipets to add the volumes of sulfate stock solution indicated in the following table. Fill each flask with distilled water to the mark.

Table 1. Volumes of stock sulfate solution added to the 50-mL volumetric flasks.

<u>Flask number</u>	<u>Volume of stock solution, mL</u>
1	2.00
2	5.00
3	7.00
4	10.00
5	15.00
6	20.00
7	25.00

Respectively label 12, 125-mL erlenmeyers with B (for blank), 1, 2, 3, 4, 5, 6, 7, 8, S1, S2, and S3. Transfer the standard sulfate solutions to the erlenmeyers with the same number as the corresponding volumetric flask. Use a pipet to add 50 mL of deionized water to flask B. Use a pipet to add 50 mL of the unknown sample to each erlenmeyer S1, S2 and S3.

- D. Preparation of Sodium Chloride-Hydrochloric Acid Solution: Add 75 g of NaCl to 300 mL of distilled water. Then add 30 mL of concentrated HCl to this solution - **add the HCl carefully and under a hood**.
- E. Use of the Spectrophotometer: Your instructor will brief you on the operation of the SII CCD spectrophotometer. We will be looking at the "Absorbance" at 450 nm. Use distilled water as your blank.
- F. Suspension Preparation and Turbidity Measurements: **The time after preparation of each solution at which the turbidity is measured is critical. Perform the remainder of the procedure on individual samples serially rather than attempting to simultaneously prepare and measure all of the samples.** Use a pipet to add 5 mL of the sodium-chloride-hydrochloric acid solution to one of the solutions in an erlenmeyer. Place a stir bar in the solution and adjust the stirring rate so that a shallow vortex is formed. Note the position of the control knob on the stirrer. The same stirring rate must be used for all solutions. Add 0.3 g of barium chloride to the stirring solution and immediately start a timer. After 60 s stop the stirring, but allow the timer to keep running. Measure and record the absorbance (turbidance) of the solution at 5 minutes after the stirring was stopped (i.e. total time is 6 minutes). Similarly measure and record the absorbance of the remaining solutions in the erlenmeyers.
- G. Calculating Stock and Standard Solution Concentrations: Use the mass of potassium sulfate (MW = 174.27) to calculate the concentration (mg/L) of sulfate (MW = 96.06) in the stock solution. The sulfate concentration rather than the potassium sulfate concentration is calculated. Use the concentration of the stock solution and the volumes of the solution added to the volumetric flasks to calculate the concentration of sulfate in the volumetric flasks 1-8.
- H. Working Curve Preparation and Determination of Analyte Concentration: The SII CCD spectrophotometer will interpolate your standard samples for you! The software will also, based on the working curve, calculate the concentration of sulfate in the unknown solutions you measured.

## REPORT OF RESULTS

Your report/note card should include the following:

NAME OF EXPERIMENT

YOUR NAME

UNKNOWN NUMBER

mean weight percent of SULFATE IN YOUR UNKNOWN

RSD sulfate