

## METHOD 9035

### SULFATE (COLORIMETRIC, AUTOMATED, CHLORANILATE)

#### 1.0 SCOPE AND APPLICATION

1.1 This automated method is applicable to ground water, drinking and surface waters, and domestic and industrial wastes containing 10 to 400 mg  $\text{SO}_4^{2-}$ /liter.

#### 2.0 SUMMARY OF METHOD

2.1 When solid barium chloranilate is added to a solution containing sulfate, barium sulfate is precipitated, releasing the highly colored acid chloranilate ion. The color intensity in the resulting chloranilic acid solution is proportional to the amount of sulfate present.

#### 3.0 INTERFERENCES

3.1 Cations such as calcium, aluminum, and iron interfere by precipitating the chloranilate. These ions are removed by passage through an ion-exchange column.

3.2 Samples should be centrifuged or filtered before analysis.

#### 4.0 APPARATUS AND MATERIALS

4.1 Automated continuous-flow analytical instrument, with:

4.1.1 Sampler I.

4.1.2 Continuous filter.

4.1.3 Manifold.

4.1.4 Proportioning pump.

4.1.5 Colorimeter: Equipped with 15 mm tubular flowcell and 520 nm filters.

4.1.6 Recorder.

4.1.7 Heating bath, 45°C.

4.2 Magnetic stirrer.

## 5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Barium chloranilate: Add 9 g of barium chloranilate ( $\text{BaC}_6\text{Cl}_2\text{O}_4$ ) to 333 mL of spectrophotometric grade ethyl alcohol and dilute to 1 liter with Type II water.

5.3 Acetate buffer, pH 4.63: Dissolve 13.6 g of sodium acetate in Type II water. Add 6.4 mL of acetic acid and dilute to 1 liter with Type II water. Make fresh weekly.

5.4 NaOH-EDTA solution: Dissolve 65 g of NaOH and 6 g EDTA in Type II water and dilute to 1 liter. This solution is also used to clean out the manifold system at end of sampling run.

5.5 Ion exchange resin: Dowex-50 W-X8, ionic form- $\text{H}^+$ . The column is prepared by sucking a slurry of the resin into 12 in. of 3/16-in O.D. tubing. This may be conveniently done by using a pipet and a loose-fitting glass wool plug in the tube. The column, upon exhaustion, turns red. Ensure that air does not enter the column.

5.6 Stock solution: Dissolve 1.4790 g of oven-dried ( $105^\circ\text{C}$ )  $\text{Na}_2\text{SO}_4$  in Type II water and dilute to 1 liter in a volumetric flask (1.0 mL = 1.0 mg).

5.7 Standards: Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 mL with Type II water. The following dilutions are suggested.

<u>Stock Solution (mL)</u>	<u>Concentration (mg/L)</u>
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
15.0	150
20.0	200
30.0	300
40.0	400

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Refrigerate at  $4^\circ\text{C}$ .

## 7.0 PROCEDURE

7.1 Set up manifold as shown in Figure 1. (Note that any precipitated  $\text{BaSO}_4$  and the unused barium chloranilate are removed by filtration. If any  $\text{BaSO}_4$  should come through the filter, it is complexed by the NaOH-EDTA reagent.)

7.2 Allow both colorimeter and recorder to warm up for 30 min. Run a baseline with all reagents, feeding Type II water through the sample line. Adjust dark current and operative opening on colorimeter to obtain suitable baseline.

7.3 Place Type II water wash tubes in alternate openings in sampler and set sample timing at 2.0 min.

7.4 Place working standards in sampler in order of decreasing concentration. Complete filling of sampler tray with unknown samples.

7.5 Switch sample line from Type II water to sampler and begin analysis.

7.6 Calculation:

7.6.1 Prepare a standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

## 8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A linear calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A spike duplicate sample is a sample brought through the whole sample preparation and analytical process.



## 9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 375.1 of Methods for Chemical Analysis of Water and Wastes.

## 10.0 REFERENCES

1. Bertolacini, R.J., and J.E. Barney, II, Colorimetric Determination of Sulfate with Barium Chloranilate, Anal. Chem., 29(2), pp. 281-283 (1957).
2. Gales, M.E., Jr., W.H. Kaylor, and J.E. Longbottom, Determination of Sulphate by Automatic Colorimetric Analysis, Analyst, 93, 97 (1968).

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