

METHOD # 375.1 Approved for NPDES (Issued 1971)
TITLE: Sulfate (Colorimetric, Automated, Chloranilate)
ANALYTE: Sulfate, SO₄
INSTRUMENTATION: Autoanalyzer
STORET No. Total 00945

1.0 Scope and Application

1.1 This automated method is applicable to drinking and surface waters, domestic and industrial wastes, in the range of 10 to 400 mg SO₄/L. Approximately 15 samples per hour can be analyzed.

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 is proportional to the amount of sulfate present.

3.0 Sample Handling and Preservation

3.1 Refrigeration at 4°C.

4.0 Interferences

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

5.0 Apparatus

5.1 Technicon AutoAnalyzer consisting of:

5.1.1 Sampler I.

5.1.2 Continuous filter.

5.1.3 Manifold.

5.1.4 Proportioning pump.

5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 nm filters.

5.1.6 Recorder.

5.1.7 Heating bath, 45°C.

5.2 Magnetic stirrer.

6.0 Reagents

6.1 Barium chloranilate: Add 9 g of barium chloranilate (BaC₆Cl₂O₄) to 333 mL of

- ethyl alcohol and dilute to 1 liter with distilled water.
- 6.2 Acetate buffer, pH 4.63: Dissolve 13.6 g of sodium acetate in distilled water. Add 6.4 mL of acetic acid and dilute to 1 liter with distilled water. Make fresh weekly.
- 6.3 NaOH-EDTA solution: Dissolve 65 g of NaOH and 6 g of EDTA in distilled water and dilute to 1 liter.
NOTE 1: This solution is also used to clean out manifold system at end of sampling run.
- 6.4 Ion exchange resin: Dowex-50 W-X8, ionic form-H+.
NOTE 2: Column is prepared by sucking a slurry of the resin into 12 inches of 3/16-inch OD sleeving. This may be conveniently done by using a pipette and a loose-fitting glass wool plug in the sleeve. The column, upon exhaustion, turns red.
- 6.5 Stock solution: Dissolve 1.4790 g of oven-dried (105°C) Na₂SO₄ in distilled water and dilute to 1 liter in a volumetric flask. 1.0 mL = 1.0 mg.
- 6.5.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 mL with distilled water. The following dilutions are suggested:

ml of Stock Solution	Conc., mg/L
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

7.0 Procedure

- 7.1 Set up manifold as shown in Figure 1. (Note that any precipitated Ba SO₄ and the unused barium chloranilate are removed by filtration. If any Ba SO₄ 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 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain suitable baseline.
- 7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.
- 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 distilled water to sampler and begin analysis.

8.0 Calculation

- 8.1 Prepare standard curve by plotting peak heights of processed standards

against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.

9.0 Precision and Accuracy

- 9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 39, 111, 188 and 294 mg SO₄/L, the standard deviations were ± 0.6, ± 1.0, ± 2.2 and ± 0.8, respectively.
- 9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 82 and 295 mg SO₄/L, recoveries were 99% and 102%, respectively.

Bibliography

1. Barney, J. E., and Bertolocini, R. J., *Anal. Chem.*, 29, 283 (1957).
2. Gales, M. E., Jr., Kaylor, W. H. and Longbottom, J. E., "Determination of Sulphate by Automatic Colorimetric Analysis", *Analyst*, 93, 97 (1968).

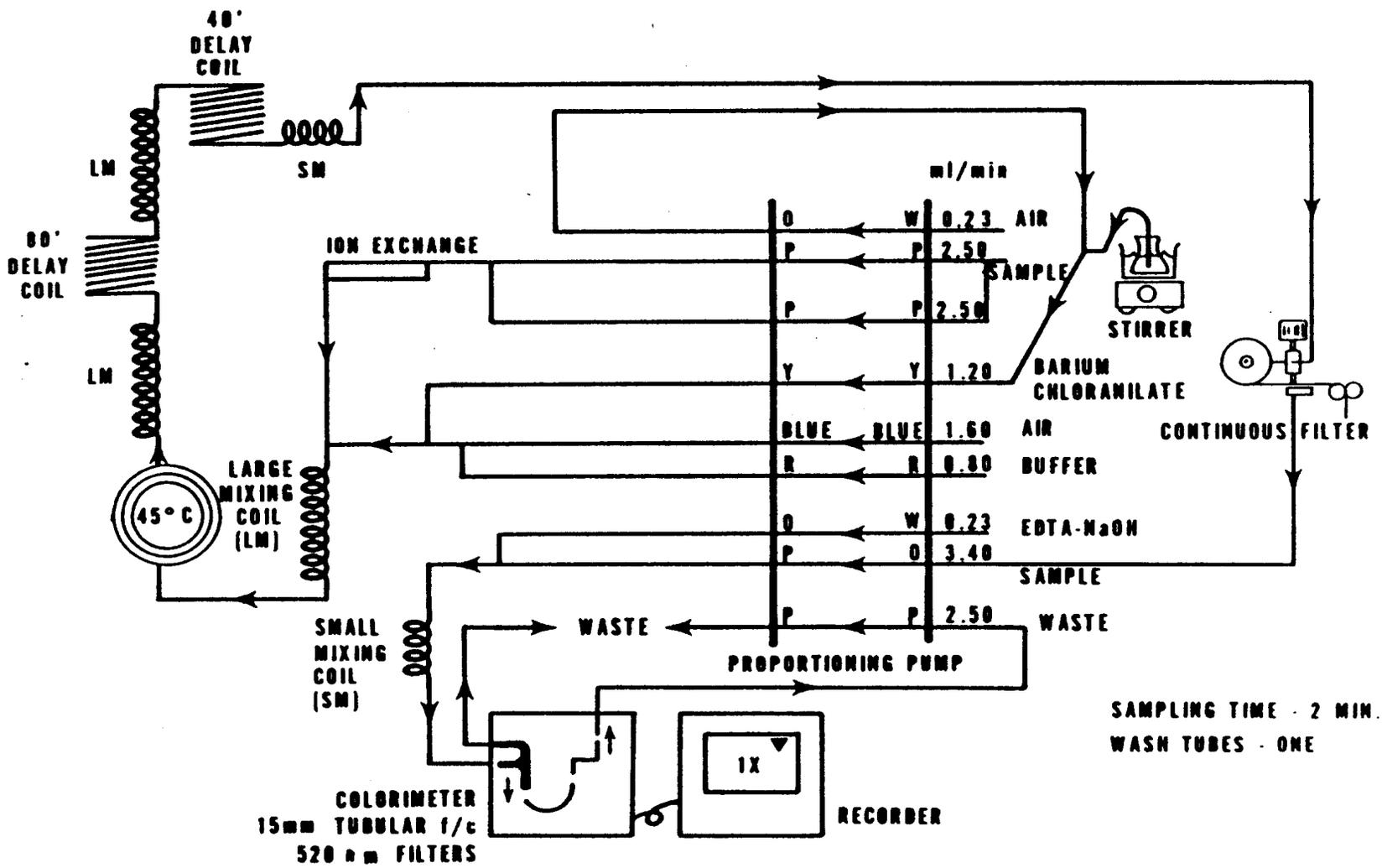


FIGURE 1 - SULFATE MANIFOLD AA-1