



Sulfate by Flow Injection Analysis (FIA)

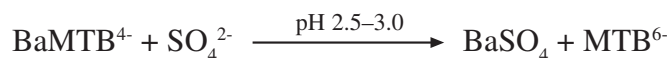
(Cartridge Part #A001569)

1.0 Scope and Application

- 1.1 This method is used for the determination of sulfate in drinking water, surface water, saline water, and domestic and industrial waste (References 15.4 and 15.5).
- 1.2 The Method Detection Limit (MDL) of this method is 1.61 mg/L sulfate. The applicable range of the method is 2.0–200 mg/L sulfate. The range may be extended to analyze higher concentrations by sample dilution.

2.0 Summary of Method

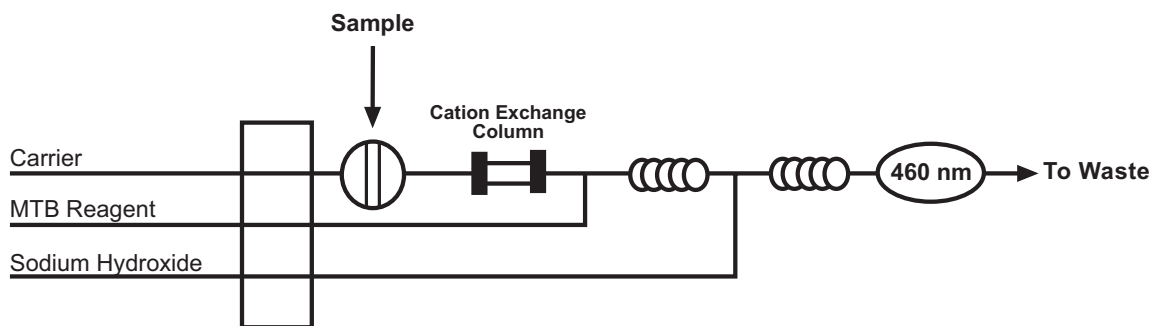
- 2.1 Within the pH range of 2.5–3.0, sulfate ions react with a barium-methylthymol blue (BaMTB) complex to form barium sulfate (BaSO_4) and free methylthymol blue (MTB). The analytical stream is then made highly basic (pH 12.5–13.0). At this pH, the absorbance maximum for the BaMTB complex is 610 nm while that of free MTB is 460 nm. Given that the molar concentrations of barium and MTB are approximately equal and that the maximum sulfate concentration to be measured does not exceed the concentration of the BaMTB complex, the sulfate concentration is directly proportional to the free MTB concentration measured at 460 nm.



The sulfate calibration curve is nonlinear. Colovos et al. (Reference 15.1) have attributed this to the formation of a binuclear BaMTB complex and to impurities in commercially available MTB dye.

- 2.2 The quality of the analysis is assured through reproducible calibration and testing of the Flow Injection Analysis (FIA) system.

- 2.3 A general flow diagram of the FIA system is shown below (see Section 17.0 for a detailed flow diagram).



3.0 Definitions

Definitions for terms used in this method are provided in Section 16.0, "Glossary of Definitions and Purposes."

4.0 Interferences

- 4.1 Multivalent cations such as calcium, magnesium, and aluminum are removed with a cation exchange column. Neutralize samples with pH values less than 2 to prevent the elution of cations from the ion exchange resin.
- 4.2 Filter or centrifuge turbid samples prior to analysis.

5.0 Safety

- 5.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been fully established. Each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level.
- 5.2 For reference purposes, a file of Material Safety Data Sheets (MSDS) for each chemical used in this method should be available to all personnel involved in this chemical analysis. The preparation of a formal safety plan is also advisable.
- 5.3 The following chemicals used in this method may be highly toxic or hazardous and should be handled with extreme caution at all times. Consult the appropriate MSDS before handling.
- 5.3.1 Ammonium Chloride, NH_4Cl (FW 53.49)
- 5.3.2 Ammonium Hydroxide, NH_4OH (FW 35.05)
- 5.3.3 Barium Chloride Dihydrate, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (FW 244.28)
- 5.3.4 Chloroform, CHCl_3 (FW 119.38)

- 5.3.5 Ethanol, 95%, C_2H_5OH (FW 46.07)
- 5.3.6 Ethylenediaminetetraacetic Acid Disodium Salt Dihydrate (EDTA), $C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$ (FW 372.24)
- 5.3.7 Hydrochloric Acid, concentrated, HCl (FW 36.46)
- 5.3.8 Methylthymol Blue Sodium Salt, $C_{37}H_{43}N_2O_{13}NaS$ (FW 778.82)
- 5.3.9 Sodium Hydroxide, $NaOH$ (FW 40.00)
- 5.3.10 Sodium Sulfate, Na_2SO_4 (FW 142.04)
- 5.4 Unknown samples may be potentially hazardous and should be handled with extreme caution at all times.
- 5.5 Proper personal protective equipment (PPE) should be used when handling or working in the presence of chemicals.
- 5.6 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.

6.0 Apparatus, Equipment, and Supplies

- 6.1 Flow Injection Analysis (FIA) System (OI Analytical Flow Solution® 3000) consisting of the following:
 - 6.1.1 120-Place Autosampler
 - 6.1.2 Expanded Range (ER) Photometric Detector with 5-mm path length flowcell and 460-nm optical filter
 - 6.1.3 Data Acquisition System (PC or Notebook PC) with WinFLOW™ software
 - 6.1.4 Sulfate Cartridge (Part #A001569)
- 6.2 Sampling equipment—Sample bottle, amber glass, with polytetrafluoroethylene (PTFE)-lined cap. Clean by washing with detergent and water, rinsing with two aliquots of reagent water, and drying by baking at 110°–150°C for a minimum of one hour.
- 6.3 Standard laboratory equipment including volumetric flasks, pipettes, syringes, etc. should all be cleaned, rinsed, and dried per bottle cleaning procedure in Section 6.2.

7.0 Reagents and Calibrants

7.1 Raw Materials

- 7.1.1 Ammonium Chloride, NH_4Cl (FW 53.49)
- 7.1.2 Ammonium Hydroxide, NH_4OH (FW 35.05)
- 7.1.3 Barium Chloride Dihydrate, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (FW 244.28)
- 7.1.4 Bio-Rex[®] 70 Resin, 50–100 dry mesh size, sodium form
- 7.1.5 Brij[®]-35, 30% w/v (Part #A21-0110-33)
- 7.1.6 Chloroform, CHCl_3 (FW 119.38)
- 7.1.7 Deionized Water (ASTM Type I or II)
- 7.1.8 Ethanol, 95%, $\text{C}_2\text{H}_5\text{OH}$ (FW 46.07)
- 7.1.9 Ethylenediaminetetraacetic Acid Disodium Salt Dihydrate (EDTA), $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8\text{Na}_2 \cdot 2\text{H}_2\text{O}$ (FW 372.24)
- 7.1.10 Hydrochloric Acid, concentrated, HCl (FW 36.46)
- 7.1.11 Methylthymol Blue Sodium Salt, $\text{C}_{37}\text{H}_{43}\text{N}_2\text{O}_{13}\text{NaS}$ (FW 778.82)
- 7.1.12 Sodium Hydroxide, NaOH (FW 40.00)
- 7.1.13 Sodium Sulfate, Na_2SO_4 (FW 142.04)

7.2 Reagent Preparation

Note: For best results, filter and degas all reagents prior to use.

7.2.1 Reagent Water

- 7.2.1.1 Degassed and deionized reagent water can be prepared in one of the following manners:

- 7.2.1.1.1 Place distilled/deionized water under a strong vacuum for 15–20 minutes. Magnetic stirring or sonification will aid in the degassing process.
- 7.2.1.1.2 Purge distilled/deionized water with a stream of nitrogen gas (or other inert gas) through a glass frit for approximately 5 minutes.
- 7.2.1.1.3 Boil distilled/deionized water in an Erlenmeyer flask for 15–20 minutes. Remove the flask from the heat source, cover it with an inverted beaker, and allow it to cool to room temperature.

7.2.1.2 After preparing the degassed reagent water, store the reagent water in a tightly sealed container to protect it from reabsorption of atmospheric gases. For best results, store degassed reagent water under a slight vacuum when not in use.

7.2.2 Start-up Solution (1 L)

7.2.2.1 Add 1 mL of Brij-35 to approximately 900 mL of reagent water (Section 7.2.1) in a 1-L volumetric flask.

7.2.2.2 Dilute to 1,000 mL with reagent water and mix gently.

7.2.3 Stock Barium Chloride (1 L)

7.2.3.1 Dissolve 1.526 g of barium chloride dihydrate in approximately 800 mL of reagent water in a 1-L volumetric flask.

7.2.3.2 Dilute to 1,000 mL with reagent water and mix well.

7.2.4 Stock 10 N Sodium Hydroxide (100 mL)

7.2.4.1 While stirring, carefully add 40 g of sodium hydroxide to approximately 70 mL of reagent water in a 100-mL volumetric flask.

7.2.4.2 Cool the solution to room temperature. Dilute to 100 mL with reagent water and mix well.

Warning: Mixing sodium hydroxide with water releases a great amount of heat. Take appropriate precautions.

Note: Store in a tightly capped polyethylene bottle. Prepare this solution monthly.

7.2.5 0.18 N Sodium Hydroxide (500 mL)

7.2.5.1 Add 9.0 mL of stock 10 N sodium hydroxide (Section 7.2.4) to approximately 400 mL of reagent water in a 500-mL volumetric flask.

7.2.5.2 Dilute to 500 mL with reagent water and mix well.

Note: Prepare this solution weekly.

7.2.6 1 N Hydrochloric Acid (1 L)

7.2.6.1 While stirring, carefully add 83.3 mL of concentrated hydrochloric acid to approximately 800 mL of reagent water in a 1-L volumetric flask.

7.2.6.2 Cool the solution to room temperature. Dilute to 1,000 mL with reagent water and mix well.

Warning: Mixing hydrochloric acid with water releases a great amount of heat. Take appropriate precautions.

7.2.7 Stock Methylthymol Blue Reagent (1 L)

Note: This reagent must be prepared at least 24–48 hours prior to use.

7.2.7.1 Dissolve 0.236 g of methylthymol blue sodium salt in 50 mL of stock barium chloride (Section 7.2.3) in a 1-L volumetric flask.

7.2.7.2 Add 142 mL of reagent water and 8 mL of 1 N hydrochloric acid (Section 7.2.6).

7.2.7.3 Dilute to 1 L with 95% ethanol.

7.2.7.4 Stir the solution vigorously on a magnetic stir plate for approximately 1 hour or until the solution is thoroughly degassed.

7.2.7.5 Add additional 95% ethanol to bring the solution back to a final volume of 1,000 mL. Filter through a 0.45- μ m filter.

Note: Store in an amber bottle at 4°C. If stored properly, this solution is stable for 1–2 weeks.

7.2.8 Working Methylthymol Blue Reagent (500 mL)

7.2.8.1 Add 2.5 mL of Brij-35 to 500 mL of stock methylthymol blue reagent (Section 7.2.7) and mix gently.

7.2.8.2 Adjust the pH of the reagent to 2.6–2.7 using 0.18 N sodium hydroxide (Section 7.2.5) or 1 N hydrochloric acid (Section 7.2.6).

Note: Prepare this solution fresh daily.

7.2.9 Buffer, pH 10.5 (1 L)

7.2.9.1 Dissolve 6.75 g of ammonium chloride in approximately 800 mL of reagent water in a 1-L volumetric flask.

7.2.9.2 Add 57 mL of ammonium hydroxide.

7.2.9.3 Dilute to 1,000 mL with reagent water and mix well.

Note: Prepare this solution fresh monthly.

7.2.10 Cleaning Solution, 4% Buffered EDTA (1 L)

7.2.10.1 Dissolve 40 g of EDTA in approximately 800 mL of pH 10.5 buffer (Section 7.2.9) in a 1-L volumetric flask.

7.2.10.2 Dilute to 1,000 mL with pH 10.5 buffer and mix well.

7.2.11 Sampler Wash—Reagent Water

7.2.12 Carrier—Reagent Water

7.3 Calibrant Preparation

7.3.1 Stock Calibrant 10,000 mg/L Sulfate (1 L)

7.3.1.1 Dissolve 14.787 g of sodium sulfate in approximately 800 mL of reagent water in a 1-L volumetric flask.

7.3.1.2 Dilute to 1,000 mL with reagent water and mix well. Preserve the solution with 2 drops of chloroform.

Note: Store at 4°C. If stored properly, this solution is stable for 3 months.

7.3.2 Intermediate Calibrant 1,000 mg/L Sulfate (100 mL)

7.3.2.1 Use a volumetric pipet to add 10 mL of stock calibrant (Section 7.3.1) to approximately 80 mL of reagent water in a 100-mL volumetric flask.

7.3.2.2 Dilute to 100 mL with reagent water and mix well.

Note: Prepare this solution fresh daily.

7.3.3 Working Calibrants (100 mL)

7.3.3.1 Add the designated volumes of stock or intermediate calibrant (see Equation 1) to the required number of 100-mL volumetric flasks that each contain approximately 80 mL of reagent water.

7.3.3.2 Dilute each solution to the mark with reagent water and mix well.

Note: Prepare working calibrants fresh daily.

EQUATION 1

$$C_1 V_1 = C_2 V_2$$

Where:

C_1 = Concentration (in mg/L) of stock solution (or calibrant)

V_1 = Volume (in L) of stock solution (or calibrant) to be used

C_2 = Desired concentration (in mg/L) of working calibrant to be prepared

V_2 = Final volume (in L) of working calibrant to be prepared

By solving this equation for the volume of stock solution to be used (V_1), the following equation is obtained:

$$V_1 = \frac{C_2 V_2}{C_1}$$

Since the desired concentration (C_2), the final volume (V_2), and the concentration of the stock solution (C_1) are all known for any given calibrant concentration in a defined volume, the volume of stock solution to be used (V_1) is easily calculated.

7.3.3.3 Calibrants covering the entire range of this analysis can be prepared from the following tables.

Final Concentration (mg/L)	Vol. of Inter. Cal. (μL)	Conc. of Inter. Cal. (mg/L)	Final Volume (mL)
2.0	200	1,000	100
5.0	500	1,000	100

Final Concentration (mg/L)	Vol. of Stock Cal. (μL)	Conc. of Stock Cal. (mg/L)	Final Volume (mL)
40	400	10,000	100
80	800	10,000	100
120	1,200	10,000	100
160	1,600	10,000	100
200	2,000	10,000	100

8.0 Sample Collection, Preservation, and Storage

- 8.1 Samples should be collected in plastic or glass bottles that have been thoroughly cleaned and rinsed with reagent water (Section 7.2.1).
- 8.2 The volume of sample collected should be sufficient to ensure that a representative sample is obtained, replicate analysis is possible, and waste disposal is minimized.
- 8.3 Preserve and store samples at 4°C. Sample analysis should be performed as soon as possible to eliminate loss of analyte.
- 8.4 The maximum holding time is 28 days from the time of collection (Reference 15.3).

9.0 Quality Control

Note: The following QC procedures are provided for reference purposes only and are not a substitute for any QC procedures that may be required for regulatory compliance.

- 9.1 It is recommended that each laboratory that uses this method operate a formal quality control program. The minimum requirements of such a program should consist of an initial demonstration of laboratory capability and the periodic analysis of Laboratory Control Samples (LCSs) and Matrix Spike/Matrix Spike Duplicates (MS/MSDs) as a continuing check on performance. Laboratory performance should be compared to established performance criteria to determine if the results of the analyses meet the performance characteristics of the method.
- 9.2 Method Detection Limit (MDL)—To establish the ability to detect sulfate at low levels, the analyst should determine the MDL using the apparatus, reagents, and calibrants that will be used in the practice of this method. An MDL less than or equal to the MDL listed in Section 1.2 should be achieved prior to practice of this method.
 - 9.2.1 An MDL is calculated by analyzing a matrix spike at a concentration of two to three times the expected detection limit of the analyzer. Seven consecutive replicate analyses of this matrix spike should be analyzed, and the MDL should be calculated using Equation 2.

EQUATION 2

$$MDL = (t) \times (S)$$

Where:

t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicates)

S = Standard deviation of the replicate analyses

- 9.2.2 It is recommended that the MDL be calculated after every six months of operation, when a new operator begins work, or whenever there is any significant change in the instrument response.
- 9.3 Analyses of MS/MSD samples are required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix).
 - 9.3.1 Matrix Spike/Matrix Spike Duplicate (MS/MSD)—The laboratory should spike, in duplicate, a minimum of 10% of all samples (one sample in duplicate in each batch of 10 samples) from a given sampling site.
 - 9.3.2 The concentration of the spike in the sample shall be determined as follows:
 - 9.3.2.1 If, as in compliance monitoring, the concentration of sulfate in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit.
 - 9.3.2.2 If the concentration of sulfate in a sample is not being checked against a limit, the spike shall be at the concentration of the LCS or at least four times greater than the MDL.
- 9.4 Analyses of Laboratory Reagent Blanks (LRBs) are required to demonstrate freedom from contamination and that the compounds of interest and interfering compounds have not been carried over from a previous analysis.
- 9.5 As part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records should be maintained.
 - 9.5.1 An LCS should be analyzed with every sample batch, and the mean (m) and the standard deviation (S) should be recorded. After multiple analyses, the mean should be plotted with limits of $m+2S$ and $m-2S$. The mean and the limits should be recalculated after every 5–10 new measurements.
 - 9.5.2 If the LCS measurement falls outside the range calculated in Section 9.5.1, then the problem should be addressed, and that sample batch should be reanalyzed if necessary.
- 9.6 Reference Sample—To demonstrate that the analytical system is in control, the laboratory may wish to periodically test an external reference sample, such as a Standard Reference Material (SRM) available from the National Institute of Standards and Technology (NIST). Corrective action should be taken if the measured concentration significantly differs from the stated concentration.

10.0 Configuration and Start-up

10.1 Instrument Configuration

- 10.1.1 Configure the OI Analytical Flow Solution 3000 Analyzer according to the Operator's Manual and verify that each module is properly powered on.

- 10.1.2 Verify that the Sulfate Cartridge (Part #A001569) is configured as illustrated in the flow diagram shown in Section 17.0.
- 10.1.3 Connect the appropriate pump tubes to the cartridge and to their appropriate reagent containers according to the flow diagram.

10.2 Instrument Stabilization

- 10.2.1 Connect the reagent pump tubes to a reagent bottle containing the start-up solution (Section 7.2.2). Connect the carrier pump tube to reagent water. Start the pump, allowing the solutions to flow through the entire system.
- 10.2.2 Verify that the flowcell of each detector is purged of all bubbles and that the flow is stable and free from surging before proceeding.

10.3 Baseline Verification

- 10.3.1 Create and save a Method in WinFLOW. Refer to the WinFLOW Operator's Manual (Reference 15.6) for help on creating a Method.
- 10.3.2 Create and save a Sample Table in WinFLOW that will be used to generate a calibration curve using at least three calibrants that cover the full range of expected concentrations in the samples to be analyzed. This Sample Table should also be used to analyze all necessary QC samples as well as the analytical batch of samples to be analyzed. For help on creating a Sample Table, refer to the WinFLOW Operator's Manual (Reference 15.6).
- 10.3.3 Select **Collect Data** in the WinFLOW main window, enter the user's identification, select the appropriate Method and Sample Table, and begin to collect baseline data. Very sharp fluctuations in the baseline and/or consistent drifting are typically signs of bubbles in the flowcell. The flowcell must be free of bubbles prior to beginning analysis.

10.4 Calibration and Standardization

- 10.4.1 Prepare a series of at least three working calibrants using the stock solutions (Section 7.3) according to Equation 1, covering the desired analysis range.
- 10.4.2 Place the calibrants in the autosampler in order of increasing concentration. Each calibrant should be analyzed according to the analytical procedures in Section 11.0. A calibration curve will be calculated by the WinFLOW software.
- 10.4.3 Acceptance or control limits for the calibration results should be established using the difference between the measured value of each calibrant and the corresponding "true" concentration.
- 10.4.4 Each calibration curve should be verified by analysis of a Laboratory Control Sample (LCS, Section 9.5). Using WinFLOW software, calibration, verification, and sample analysis may be performed in one continuous analysis.

11.0 Procedure

11.1 Preparation of the Cation Exchange Column

- 11.1.1 Weigh 0.5 g of Bio-Rex 70 resin. Wash the resin several times with reagent water. Decant the resin fines with the supernatant.
- 11.1.2 Add enough reagent water to completely cover the resin plus an additional 100 mL. Degas the resin slurry by sonicating for 15–20 minutes.
- 11.1.3 Remove the 1/4–28 nut and union from the column inlet. Carefully remove the frit (see Figure 1).
- 11.1.4 Attach the 30-mL syringe onto the column using the union and the female Luer-Lok™ fitting. Hold the column vertically. The 0.034" PVC tubing should be parallel to the column. Pour reagent water into the syringe to fill the column.

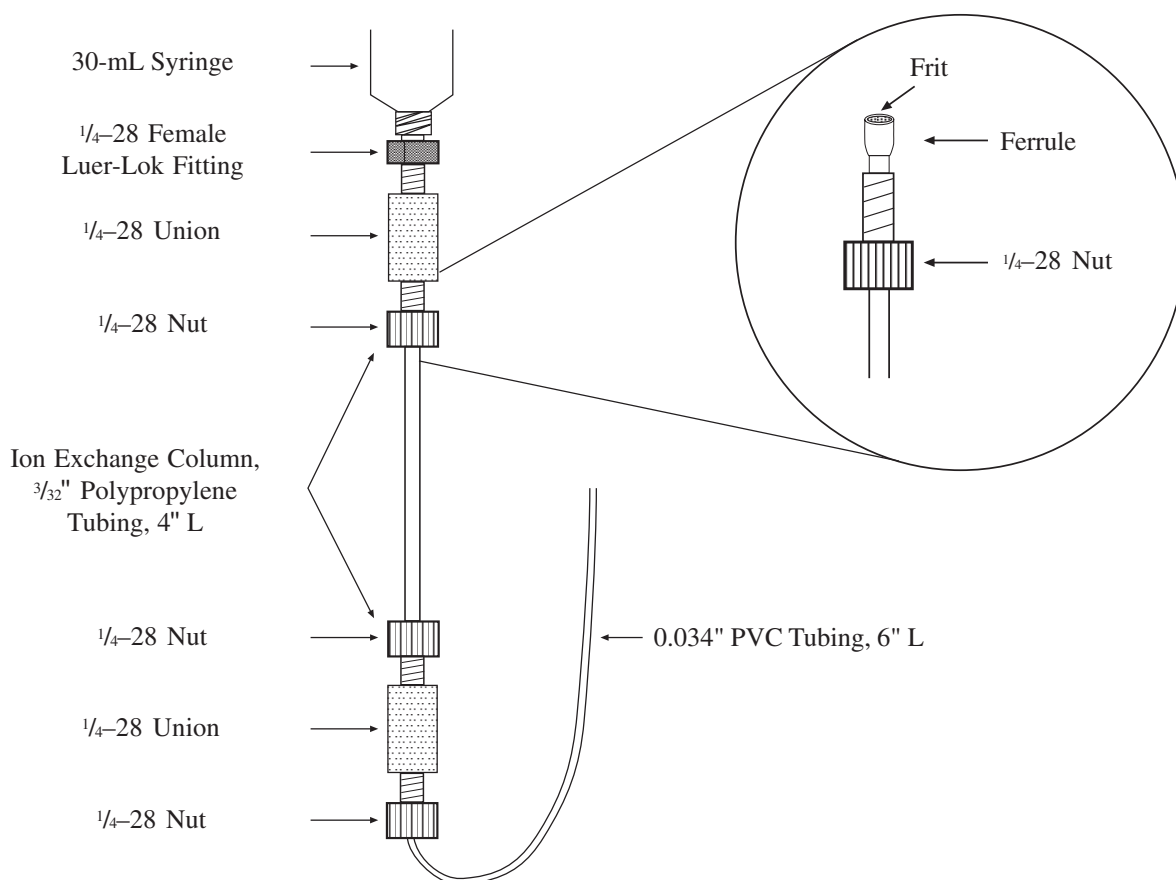


Figure 1. Preparation of the Cation Exchange Column

- 11.1.5 Agitate the slurry to resuspend the resin in the reagent water. Carefully add 2 mL of the resin slurry to the syringe. Allow the resin to settle into the column. Tap the column gently to facilitate packing and to avoid trapping air bubbles.
- 11.1.6 Repeat step 11.1.5 until the column is filled with resin.
- 11.1.7 Remove the syringe and the $\frac{1}{4}$ -28 female Luer-Lok fitting. Carefully replace the frit. Replace the union and the $\frac{1}{4}$ -28 nut onto the column inlet.

11.2 Installation of the Cation Exchange Column

- 11.2.1 After all reagents have been placed on-line, the air bubbles are cleared from the system (Section 10.2), and with the pump still running, remove the jumper tubing that connects ports 4 and 8 of the cartridge (see Figure 2).
- 11.2.2 Remove the union connecting the 0.034" PVC tubing on the inlet and outlet of the cation exchange column. Install the column between ports 4 and 8 using the $\frac{1}{4}$ -28 nuts (see Figure 2). Attach the nut to port 8 first to avoid introduction of air into the column.

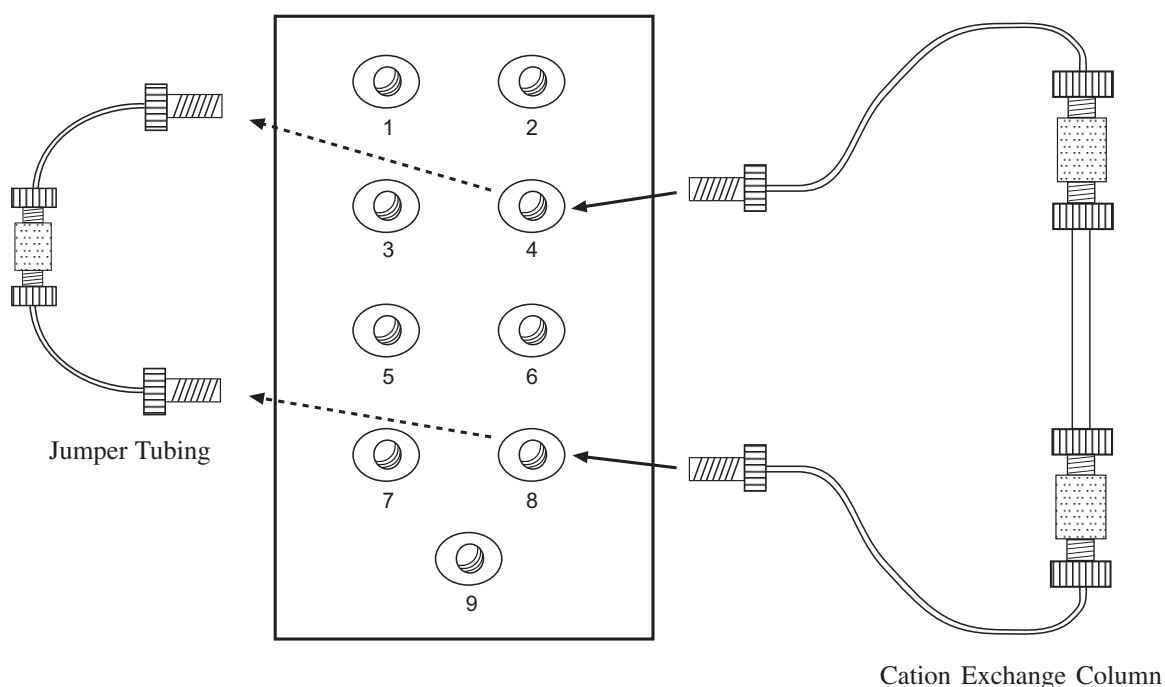


Figure 2. Installation of the Cation Exchange Column

- 11.2.3 Allow the baseline to restabilize before proceeding with the analysis (about 30 minutes).

11.3 Analysis

- 11.3.1 Begin pump flow with the start-up solution (Section 7.2.2) and reagent water as the carrier. Verify a stable baseline (Section 10.3).
- 11.3.2 After the baseline has been verified according to Section 10.3, place all reagents on-line and allow to pump at least 30 minutes and verify there are no bubbles in the flowcell. Install the cation exchange column (Section 11.2). Obtain a stable baseline at 460 nm and autozero the baseline before beginning analysis.
- 11.3.3 Load the sampler tray with calibrants, blanks, samples, and QC samples.

Note: The matrix of the working standards, blanks, and QC samples should match that of the samples being analyzed.
- 11.3.4 Using the Method and Sample Table created for the analytical batch to be analyzed and with the baseline verified to be stable, begin the analysis by selecting the “Fast Forward” button on the left side of the Data Analysis window in WinFLOW. This will initiate the sequential analysis of samples as defined in the Sample Table.
- 11.3.5 When analysis is complete, remove the cation exchange column and reinstall the jumper tubing between ports 4 and 8.
- 11.3.6 Pump reagent water through the system for at least 10–15 minutes. Pump cleaning solution (Section 7.2.10) through the working methylthymol blue and sodium hydroxide reagent lines for at least 5 minutes. Repeat the reagent wash for 10–15 minutes. Stop the pump, release the tension on all pump tubes, and power off the system.

11.4 Operating Notes

- 11.4.1 Sulfate determination by the methylthymol blue method is an inherently noisy test. Use the following suggestions to diminish the baseline noise.
 - 11.4.1.1 Use reagent water (Section 7.2.1) to prepare all reagents, including the water for the sampler wash.
 - 11.4.1.2 High quality methylthymol blue is essential. Request a certificate of analysis when ordering this reagent since significant variation in water content occurs from lot to lot. Use only methylthymol blue with a water content of less than 10%.
 - 11.4.1.3 Use ACS reagent grade 95% ethanol.
- 11.4.2 The quantity of interfering cations will vary with the sample matrix. Samples with high cation concentrations may require more frequent replacement of the cation exchange resin or the installation of a longer cation exchange column.
- 11.3.3 Check the cation exchange capacity of the column by periodically running a mid-level calibrant that contains a calcium concentration similar to that of the samples being analyzed. Low recovery indicates that the cation exchange capacity is exhausted.

- 11.4.4 After a large number of high level samples have been analyzed, an increase in baseline drift may be observed. Clean the flowcell with cleaning solution (Section 7.2.10), followed by reagent water. If the baseline drift is not improved, treat the entire manifold with cleaning solution.
- 11.4.5 Prepare and filter the stock methylthymol blue reagent (Section 7.2.7) at least 24–48 hours prior to use. Store in an amber bottle at 4°C.
- 11.4.6 The pH of the working methylthymol blue reagent (Section 7.2.8) must be adjusted to between 2.6–2.7 prior to analysis. The pH of the final reagent stream as it leaves the flowcell should be ≥ 12.5 .
- 11.4.7 When installing the cation exchange column, always have the pump running. Back pressure prevents air from becoming trapped in the column. If the pump is not running during installation, air will enter the column when the pump is turned on.
- 11.4.8 After any changes are made to the manifold, allow enough time (at least 30 minutes) for the baseline to restabilize.
- 11.4.9 Clean the flowcell with 1 N sodium hydroxide and 1 N hydrochloric acid to help prevent bubbles from becoming trapped in the flowcell.
- 11.4.10 If an erratic baseline is observed, replace the working methylthymol blue reagent pump tube.

12.0 Data Analysis and Calculations

- 12.1 The calibration curve allows for accurate quantitation of the concentration in each sample.
- 12.2 WinFLOW software reports the concentration of each sample relative to the calibration curve.

13.0 Method Performance

Range:	2.0–200 mg/L
Throughput:	55 samples/hour
Precision:	
40 mg/L	<3% RSD
160 mg/L	<2% RSD
Method Detection Limit (MDL):	1.61 mg/L

14.0 Pollution Prevention and Waste Management

- 14.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land-disposal restrictions. In addition, it is the laboratory's responsibility to protect air, water, and land resources by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

- 14.2 For further information on waste management, consult Section 13.6 of *Less is Better: Laboratory Chemical Management for Waste Reduction* (Reference 15.2).

15.0 References

- 15.1 Colovos; Panesar; Perry. Linearizing the Calibration Curve in Determination of Sulfate by the Methylthymol Blue Method. *Analytical Chemistry* **1976**, 48 (No. 12), 1693–1696.
- 15.2 *Less is Better: Laboratory Chemical Management for Waste Reduction*. Available from the American Chemical Society, Department of Government Regulations and Science Policy, 1155 16th Street, NW, Washington, DC, 20036.
- 15.3 Sample Preservation. *Methods for Chemical Analysis of Water and Wastes*; EPA-600/4-79-020; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1984; xvii.
- 15.4 Sulfate (Automated Colorimetry). *Methods for the Determination of Inorganic Substances in Environmental Samples*; EPA-600/R-93/100; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1984; Method 375.2.
- 15.5 Sulfate. *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; American Public Health Association: Washington, D.C., 1998; Method 4500-Sulfate.
- 15.6 WinFLOW Software and Operator's Manual (Part #A002877). Available from OI Analytical, P.O. Box 9010, College Station, TX, 77842-9010.

16.0 Glossary of Definitions and Purposes

The definitions and purposes are specific to this method but have been conformed to common usage as much as possible.

16.1 Units of weights and measures and their abbreviations

16.1.1 Symbols

°C	degrees Celsius
%	percent
±	plus or minus
≥	greater than or equal to
≤	less than or equal to

16.1.2 Alphabetical characters

g	gram
L	liter
mg	milligram

mg/L	milligram per liter
μg	microgram
μg/L	microgram per liter
mL	milliliter
ppm	parts per million
ppb	parts per billion
M	molar solution
N	normal solution

16.2 Definitions

- 16.2.1 **Laboratory Control Sample (LCS)**—An aliquot of LRB to which a quantity of the analyte of interest is added in the laboratory. The LCS is analyzed like a sample. Its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 16.2.2 **Laboratory Reagent Blank (LRB)**—An aliquot of reagent water and other blank matrix that is treated like a sample, including exposure to all glassware, equipment, and reagents that are used with other samples. The LRB is used to determine if the method analyte or other interferences are present in the laboratory environment, reagents, or apparatus.
- 16.2.3 **Matrix Spike/Matrix Spike Duplicate (MS/MSD)**—An aliquot of an environmental sample to which a quantity of the method analyte is added in the laboratory. The MS/MSD is analyzed like a sample. Its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot, and the measured values in the MS/MSD must be corrected for the background concentration.
- 16.2.4 **Method Detection Limit (MDL)**—The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.

17.0 Figures

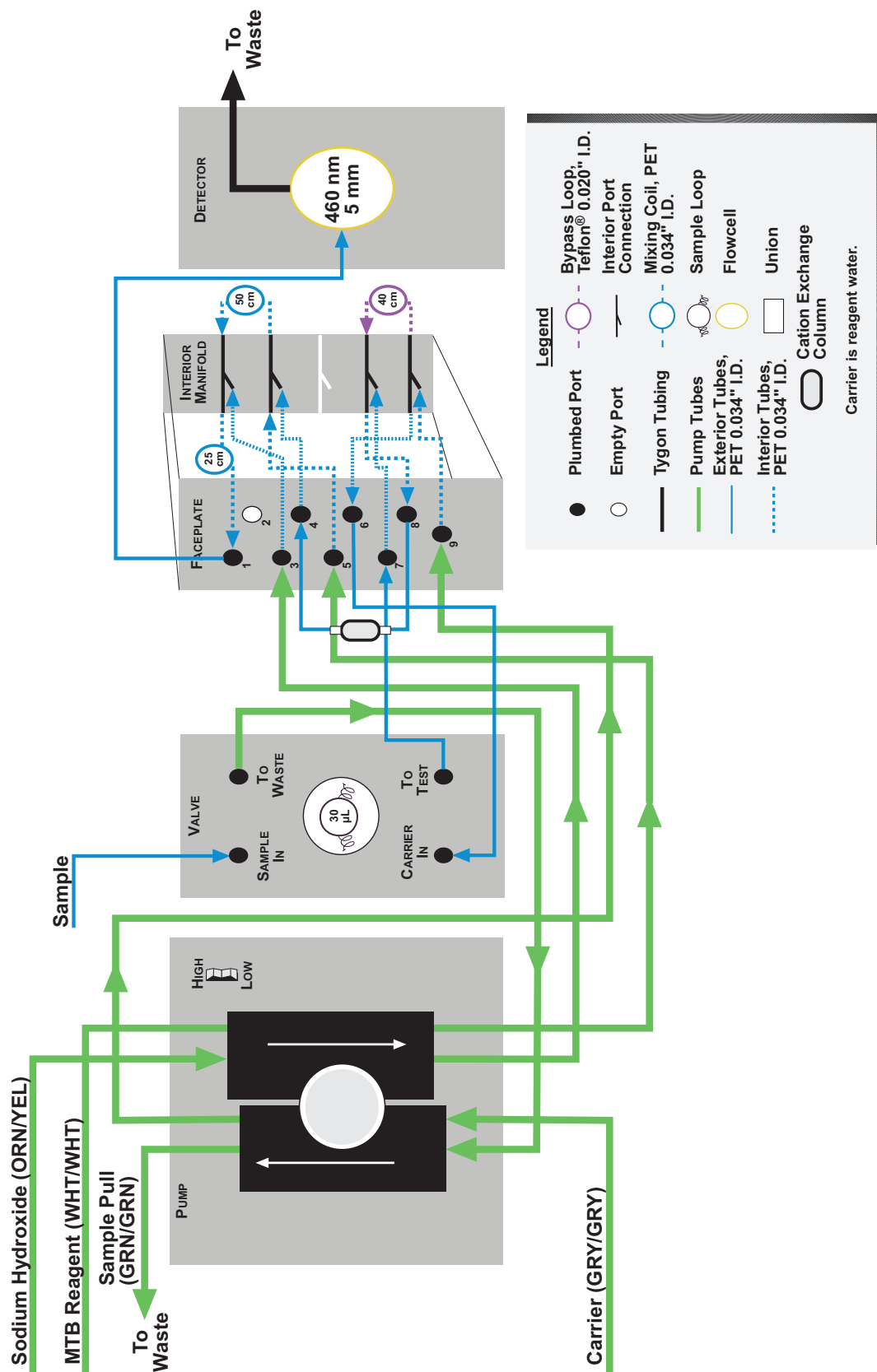


Figure 3. Detailed Flow Diagram for Sulfate by FIA on a Flow Solution 3000, Cartridge Part #A001569

Results were obtained under optimal operating conditions. Actual results may vary depending on sample introduction, cleanliness of sample containers, reagent purity, operator skill, and maintenance of instruments.

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