

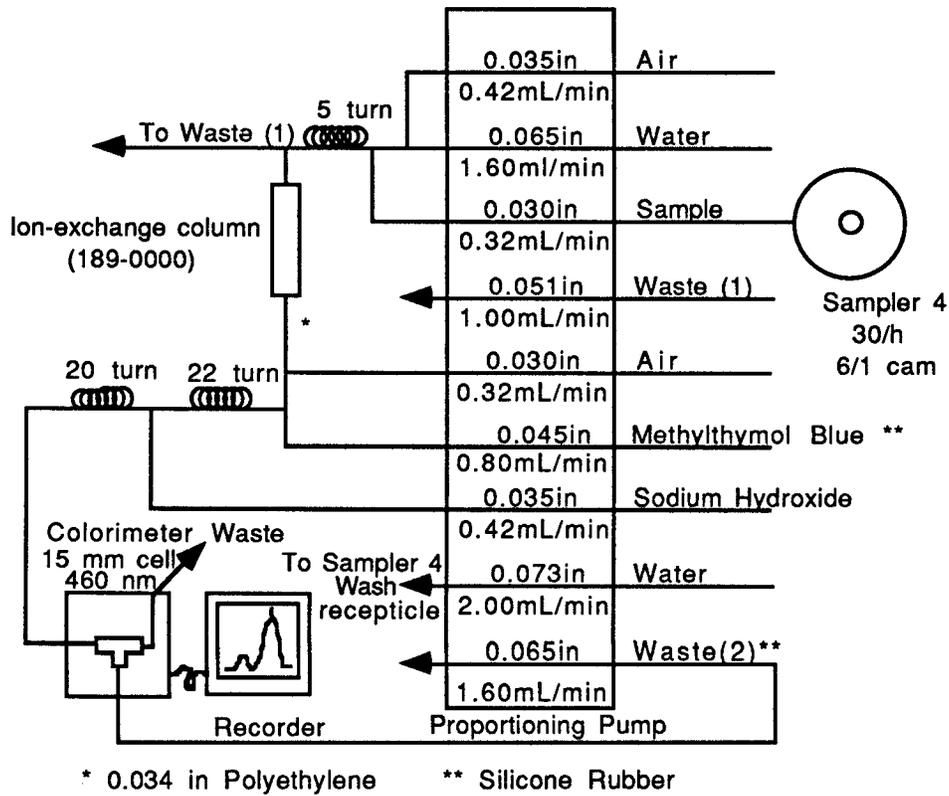
KANSAS GEOLOGICAL SURVEY Analytical Services Section L. R. Hathaway

A MODIFICATION OF THE SULFATE METHOD FOR THE TECHNICON AUTOANALYZER II SYSTEM

General Discussion:

The USGS 1-100 mg/l sulfate method for the Technicon AutoAnalyzer II system provides improved sensitivity and stability over the 3-100 mg/l Technicon method for analysis of natural waters. A modified version of the USGS 1-100 mg/l SO₄ method has been adopted for use in the Analytical Services Section of the Kansas Geological Survey.

Changes to the manifold include an increase in the size of the air pump tube used to inject air bubbles following the addition of the sample into the diluent flowstream from 0.32 ml/min (BLK/BLK) to 0.42 ml/min (ORN/ORN). This change serves to reduce unwanted mixing of the flowstream segments during debubbling and entry into the ion-exchange column. A cadmium reductor tube (189-0000) has also been substituted for the regular ion-exchange column (116-G006-01). This provides greater resin capacity, as well as the possibility of interchange of parts between manifolds. The modified system is presented in the following schematic drawing.



The pump tube configuration used in the USGS procedure results in about a 20% increase in the concentration of SO₄ in the solution being mixed with the color reagent, as compared to the Technicon method. Thus, the Technicon procedure for the preparation of the color reagent must be adjusted to compensate for this concentration increase. ***The procedure given in the USGS method for the optimization of the color reagent for the 1-100 mg/l SO₄ range, however, is in error because it adjusts the level of methylthymol blue (MTB) but not the level of barium chloride needed for the higher SO₄ concentrations present now in the flowstream.*** A 30 ml volume of barium chloride solution, instead of the 25 ml as listed, should be pipeted into the 500 ml volumetric flasks used in the preparation of the color reagent.

Calibration Standards:

Mixed Cl-SO₄ standards are used which can provide calibration curves for both the Cl and the SO₄ analyses. These standards have values of 100, 80, 60, 40, 20, and 10 mg/l in both Cl and SO₄; and they are prepared from 1000 mg/l Cl and SO₄ stock solutions.

Color Reagent:

Only use MTB from Eastman Kodak (No. 8068) in preparation of the color reagent. MTB from other sources is of lower purity and gives poorer sensitivity and produces calibration curves with lower degrees of linearity, which is especially troublesome in the lower concentration range of the calibration curve.

The following amounts of materials are required for the preparation of 250 ml of color reagent:

Methylthymol Blue	0.0714 g
Barium Chloride Stock Solution	15 ml
1 N HCl Solution	2.0 ml
Distilled Water	33 ml
95% Ethanol	To Volume
Brij-35	0.5 ml

Weigh the MTB into a glass beaker. Pipet the barium chloride solution into the beaker and swirl to dissolve the MTB. Next pipet the HCl into the beaker and swirl to mix. Next pipet the distilled water into the beaker and swirl again to mix. Now transfer the solution into a 250 ml volumetric flask. Rinse the beaker several times with ethanol, adding the rinses to the volumetric flask. Mix the contents of the flask, and finally dilute to the mark with ethanol. Mix thoroughly to be sure the contents are diluted to the mark. Pipet 0.5 ml of the Brij-35 into the flask and mix again. This reagent can be used after standing for a few hours or can be prepared in the afternoon and allowed to stand over night before being used. If left overnight, the reagent should be placed in a cool, dark location. Any reagent not used within a 24 hour period should be discarded.

250 ml of the color reagent should provide about 312 minutes of run time.

Operating Notes:

1. A build up of bubbles in the silicon rubber wasteline pump tube near the exit side of proportioning pump seems to be related to noise observed on the strip chart record.

The tube should be cleared of bubbles by tapping the tube near the exit end before beginning the initial calibration process in order to minimize baseline drift and reduce noise in the sample and baseline signals. Occasional tapping of the tube during the course of the run may be necessary to hold this problem in check.

2. If the ion-exchange resin beads begin to degrade, the fine material produced may plug the ion-exchange column and reduce or halt flow within the column. The failure to inject air bubbles into the flowstream following injection of the sample into the diluent stream may be an indication that a flow related problem exists in the ion-exchange column. If this is the case, the column must be repacked with fresh resin.
3. It has been found to be desirable to run the system for about 30 minutes prior to beginning any analytical work in order to stabilize the baseline.
4. Samples for which the absorption signal drops below the baseline probably have too high a level of multivalent cations and their segments in the flowstream are not being stripped of these ions in an efficient manner by the ion-exchange column prior to injection of the color reagent. If large numbers of these samples have been run through the system, the ion-exchange column should be regenerated. All samples which exhibit a negative response should be diluted before being reanalyzed. If the SO₄ level is too low in the original sample to accommodate SO₄ measurement after dilution or if a negative response persists after dilution, then the SO₄ concentration should be determined by the turbidimetric SO₄ method.
5. Following the completion of the analytical run, the sample line is disconnected from the sampler probe and is placed into a 10% HCl solution. This solution is pumped through the ion-exchange column for a 10 minute period. During this period the color reagent line and the NaOH line should be placed in distilled water. After the 10 minute period, the sample line is also placed into distilled water and the ion-exchange column is rinsed for 10 minutes. This process serves to regenerate the column for future work. Next, an 8 inch length of heavy-walled tubing is connected to the exit-end of the ion-exchange column and is allowed to nearly fill with fluid. The column is then disconnected from the manifold and the other end of the tubing is slipped onto the entry end of the column. The column is stored in an up-right position with the tubing connection at the top. ***During the regeneration process and the preparation for storage care must be taken to avoid the introduction of air into the column.***
6. After the removal of the ion-exchange column, alkaline EDTA solution is run into the manifold system through the color reagent line. Final clean-up of the system is accomplished according to the instructions in the Technicon method.

References:

1. Technicon Industrial Systems, 1977, Sulfate in Water and Wastewater: Industrial Methods No. 118-71W/B, Technicon Instrument Corporation, Terrytown, N.Y.
2. US Geological Survey, 1989, Sulfate, Dissolved, Colorimetric, Complexometric, Methylthymol Blue, Automated-segment Flow: In Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, Book 5, Chapter A1, 3rd ed., US Government Printing Office, Washington, D.C., pp. 473-476.