

SULFATE AND THIOSULFATE IN CAUSTIC AQUEOUS SOLUTIONS BY ION CHROMATOGRAPHY

UOP Method 953-97

SCOPE

This method is for determining levels of sulfate and thiosulfate in aqueous, spent caustic, process streams by Ion Chromatography (IC). The method yields quantitative results in the range of 0.0045 to 6 mass-% for each analyte.

OUTLINE OF METHOD

For analysis, the sample is diluted by mass in water to an analyte concentration between 0.0004 and 0.0050 mass-%. A reproducible volume of diluted sample is injected into an ion chromatograph equipped with an anion exchange column, conductivity suppressor device and conductivity detector. The analytes are separated by anion exchange with bicarbonate and carbonate ions supplied by the chromatographic system mobile phase. The column effluent enters a conductivity suppressor device, where the background conductivity of the column effluent is reduced and the analytes are simultaneously converted into a more conductive form. This is accomplished by exchange of sodium ions in the column effluent with protons supplied by electrolysis of the mobile phase. The analyte effluent from the conductivity suppressor device finally flows to a conductivity detector where solution conductance is continuously measured. The solution conductance at any given time is proportional to ionic concentration and the inherent mobility of each type of ion present in the detector flow cell. The method is calibrated by an external standard procedure using calibration standards prepared from pure sodium sulfate and sodium thiosulfate.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Anion Self-Regenerating Suppressor, conductivity suppressor device, Model ASRS (4-mm), Dionex, Cat. No. 46081

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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Balance, readability 0.1-mg

Chromatographic column, Model IonPac AS3 Analytical, dimensions: 250-mm length by 4-mm ID, Dionex, Cat. No. 43181

Filter apparatus, all glass filter, 47-mm diameter, 300-mL capacity, one-liter flask, Millipore, Cat. No. XX1504700

Flask, Erlenmeyer, filtering, 4-L Pyrex glass with tubulation, Fisher Scientific, Cat. No. 10-180N

Integrator, electronic, for obtaining peak areas

Ion chromatograph, equipped with an isocratic pump, injection valve and digital conductivity detector, Dionex, Model DX120

Magnetic stirrer, 4.3- x 10.5- x 13.5-inch, VWR Scientific Products, Cat. No. 33920-232

Magnetic stir bar, 2- x 5/16-inch, VWR Scientific Products, Cat. No. 58948-025

Mobile phase reservoir, 4-L reservoir and plastic tubing, Dionex, Cat. No. 38018

Recorder, 10-mV full scale

Refrigerator, laboratory, explosion proof, Fisher Scientific, Cat. No. 97-950

Syringe, HPLC, 250- μ L, Fisher Scientific, Cat. No. 14-815-291

Tubing, vacuum, 0.25-inch ID (6.4-mm), Fisher Scientific, Cat. No. 14-173C

Vacuum pump, house vacuum can be substituted

Water purification system, Barnstead NANOpure II, 3 module, equipped with Pretreatment (D0835), Ultrapure (D0809) and Organic Free (D0820) replacement cartridges, Fisher Scientific

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized and distilled water that is subsequently treated with a Barnstead NANOpure II water purification system to produce ionically pure, 18 megohm-cm, organic-free, water.

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Filters, Nylon-66, 47-mm diameter, 0.45- μ m pore size, Rainin Instrument, Cat. No. 38-114

Pasteur pipet, disposable, borosilicate glass, 146-mm length, Fisher Scientific, Cat. No. 13-678-20A

Sample vials, 6-dram, Kimble Scientific, Cat. No. 60957-1, with Qorpack black phenolic caps and polyseal liners, Cat. No. 02-883-5G, all available from Fisher Scientific

Sodium carbonate, granular, 99.5+% pure, Aldrich Chemical, Cat. No. 22,232-1

Sodium hydrogen carbonate (bicarbonate), 99% pure, Aldrich Chemical, Cat. No. 34,094-4

4.8 mM sodium carbonate, 6.0 mM sodium bicarbonate solution. Prepare four liters by adding 2.04 ± 0.01 g of sodium carbonate and 2.02 ± 0.01 g of sodium hydrogen carbonate to four liters of water in a 4-L Erlenmeyer vacuum flask containing a magnetic stir bar. Cap the flask with a rubber stopper. Evacuate the headspace of the flask with a vacuum pump and simultaneously stir the solution thoroughly with a magnetic stir bar for 20 minutes. Transfer the solution to a 4-L mobile phase reservoir.

Sodium sulfate, 99.99+% pure, Aldrich Chemical, Cat. No. 20,444-7

Sodium thiosulfate, 99% pure, Aldrich Chemical, Cat. No. 21,726-3

Stopper, one-hole, rubber, No. 12, Fisher Scientific, Cat No. 14-135R

PROCEDURE

It is imperative that all glassware used in this method be scrupulously clean, and stored in such a way to avoid contamination.

Chromatographic Technique

1. Assemble and test all ion chromatographic system components as per the manufacturer's specifications.
2. Install the analytical column and suppressor device (configured in the auto-suppression recycle mode).
3. Fill the mobile phase reservoir with four liters of 4.8 mM sodium carbonate, 6.0 mM sodium hydrogen carbonate solution, and pump mobile phase through the chromatographic system at a flow rate of 2.8 mL/min. Immediately turn on power to the Anion Self-Regenerating Suppressor.
4. Set the conductivity detector sensitivity to 30 μ SFS. The detector baseline should level off to a steady flat baseline within 20 minutes.
 - When the system is fully equilibrated, the background conductivity should be at a steady level of approximately 34 μ S.

Operating Conditions

Table 1 summarizes the recommended chromatographic operating conditions for the convenience of the method user. Other conditions may be used, provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram (see Figure).

Table 1
Recommended Chromatographic Conditions

Analytical column	Dionex HPIC AS3
Suppressor	Dionex ASRS (4-mm) configured in auto-suppression recycle mode
Mobile phase	4.8 mM sodium carbonate, 6.0 mM sodium hydrogen carbonate
Mobile phase flow rate	2.8 mL/min
Injection volume	50 μL
Column temperature	ambient
Detector	conductivity
Detector Sensitivity	30 μSFS

Calibration

Calibration factors are required for both sulfate and thiosulfate that relate the varying instrument response for each analyte. Detector response is measured in μ S units of conductivity. It is proportional to the ionic concentration and the inherent mobility of each analyte ion type present when measured by the conductivity detector. Calibrate with freshly prepared calibration standards each day samples are to be analyzed.

1. In one, 6-dram sample vial, weigh approximately 0.1 g each, of sodium sulfate and sodium thiosulfate, and record the weight of each compound to the nearest 0.1 mg.
2. Dissolve the salts with approximately 19.8 g of water and record the total weight to the nearest 0.1 mg. Cap the solution and shake vigorously until all of the solid is totally dissolved. Label the mixture: Standard Stock Solution. Calculate the analyte concentrations in this solution using Eq. 1 in *CALCULATIONS*.
3. Transfer approximately 0.1 g of the Standard Stock Solution, with a Pasteur pipet, to a separate 6-dram vial. Weigh and record the weight of the Standard Stock Solution aliquot to the nearest 0.1 mg.
4. Dilute the aliquot with approximately 19.9 g of water and record the total weight to the nearest 0.1 mg. Label the mixture: Standard Calibration Solution. Cap the vial and shake the solution vigorously for approximately 15 seconds.
 - The Standard Calibration Solution should contain approximately 0.0017 mass-% sulfate and 0.0018 mass-% thiosulfate. Calculate the actual concentrations using Eq. 2 in *CALCULATIONS*.
5. Using a syringe, inject 50 μ L of the Standard Calibration Solution into the ion chromatograph and immediately start the recorder and integrator. The chromatographic analysis should run for 20 minutes.
6. Identify and integrate the peak areas of sulfate and thiosulfate by comparing the chromatogram obtained with the Typical Chromatogram (see Figure).
7. Repeat steps 5 and 6 to obtain a duplicate analysis of the Standard Calibration Solution.

- If the area counts from the duplicates are within 5% of each other, proceed with the analysis. If not, repeat the injection until the desired repeatability is attained, or repair the instrument, as necessary.

8. Calculate the mean response factor for each analyte using Eq. 3 in *CALCULATIONS*.

Sample Analysis

Caustic solutions that contain sulfur compounds are quite susceptible to oxidation in air. The samples, therefore, should be protected by blanketing with an inert gas such as nitrogen. Samples should be stored in a refrigerator prior to analysis and analyzed within 24 hours.

1. Weigh approximately 1 g of the sample into a 6-dram vial and record the weight to the nearest 0.1 mg.
2. Add approximately 9 g of water to the solution and record the total diluted sample weight to the nearest 0.1 mg. Cap the vial and shake the diluted sample solution vigorously for approximately 15 seconds so that the sample is thoroughly mixed. Label this finished prepared solution: IC Sample Stock Solution.
3. Inject 50 μL of the IC Sample Stock Solution into the ion chromatograph and immediately start the recorder and integrator. The chromatographic analysis should run for 20 minutes.
4. Identify and integrate the peaks by comparing the chromatogram obtained with the Typical Chromatogram (see Figure).
5. If the values obtained for either of the analytes are above 0.0050 mass-%, prepare a quantitative serial dilution(s) of the IC Sample Stock Solution. This is done by diluting the IC Sample Stock Solution in water on a mass/mass basis until the resulting chromatographic analyte peak areas closely match that of the Standard Calibration Solution. Record the weights of each serial dilution.
 - Several serial dilutions may be required in order to obtain the appropriate peak area response. A final analyte peak area between $\pm 50\%$ of the Standard Calibration Solution is considered appropriate.

Analysis of Blank

A sample of the laboratory water is analyzed each day an analysis of a sample is to be performed. The water must contain less than 0.00005 mass-% each of sulfate or thiosulfate for a valid sample analysis. If not, check first for errors due to dirty glassware by rerunning the blank in a fresh set of glassware. If glassware is not the problem, replace the cartridges on the water purification unit.

1. Inject 50 μL of water into the ion chromatograph and immediately start the recorder and integrator. The chromatographic analysis should run for 20 minutes.
2. Identify and integrate the peak areas of sulfate and thiosulfate by comparing the chromatogram obtained with the Typical Chromatogram (see Figure).

CALCULATIONS

Calculate the concentration of sulfate and thiosulfate in the Standard Stock Solution to three significant figures using Eq. 1.

$$A = \frac{BC}{D} \quad (1)$$

where:

A = concentration of analyte (sulfate or thiosulfate) in Standard Stock Solution, mass-%

B = mass of analyte in pure solid, g

C = percent sulfate (67.62) or thiosulfate (70.92) in pure solid, mass-%

D = total mass of Standard Stock Solution, g

Calculate the concentration of each analyte in the Standard Calibration Solution to three significant figures using Eq. 2.

$$E = \frac{AF}{G} \quad (2)$$

where:

A = as defined in Eq. 1

E = concentration of analyte in Standard Calibration Solution, mass-%

F = mass of aliquot of Standard Stock Solution, g

G = total mass of Standard Calibration Solution, g

Calculate the mean response factor for each analyte in the Standard Calibration Solution to three significant figures using Eq. 3.

$$M = \frac{2E}{H} \quad (3)$$

where:

E = as defined in Eq. 2

H = sum of analyte area responses in duplicate injections

M = mean response factor for each analyte

2 = number of injections

Calculate each analyte concentration in the original sample to two significant figures using Eq. 4.

$$R = \frac{SMNQ}{LP} \quad (4)$$

where:

L = mass of sample weighed (Sample Analysis, Step 1), g

M = mean response factor (Eq. 3) for each analyte

N = total IC Sample Stock Solution mass, g

P = mass of IC Sample Stock Solution aliquot (Sample Analysis, Step 5), g

Q = final diluted sample mass, g
R = concentration of each analyte in sample, mass-%
S = analyte peak area of injected sample

Note: $Q/P = 1$ if no further dilution is required.

PRECISION

The following precision data were obtained from analysis of synthetic blends prepared in spent caustic as process samples were unavailable.

Repeatability

Based upon two tests performed by each of two analysts on each of two different days in the same laboratory, the within-laboratory estimated standard deviations (esd) were calculated for sulfate and thiosulfate at specific concentrations and are listed in Table 2. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences listed in Table 2 at the concentrations listed (95% probability).

Table 2
Repeatability

<u>Component</u>	<u>Concentration, mass-%</u>	<u>Within-Lab esd, mass-%</u>	<u>Allowable Difference, mass-%</u>
Sulfate	0.044	0.0008	0.003
Sulfate	4.3	0.06	0.2
Thiosulfate	0.024	0.0005	0.002
Thiosulfate	2.3	0.06	0.2

The data in Table 2 is a short-term estimate of the repeatability. When the test is run routinely in the field, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

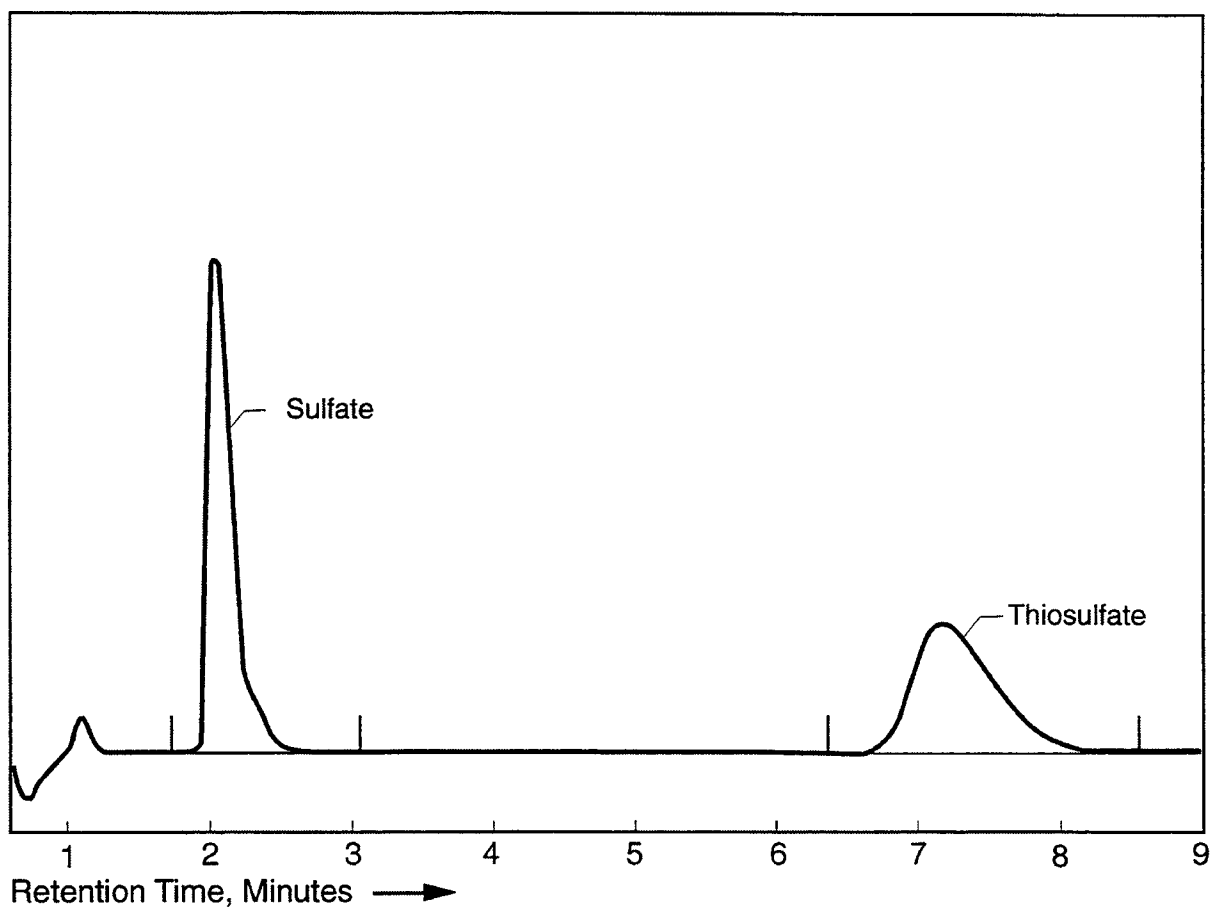
There is insufficient data to calculate the reproducibility of the test at this time.

TIME FOR ANALYSIS

The elapsed time for the preparation and analysis of one sample, including the analysis of a blank and calibration, is 2 hours. The labor requirement is 1 hour.

SUGGESTED SUPPLIERS

Aldrich Chemical Co., 1001 W. St. Paul Ave., Milwaukee, WI 53233 (414-273-3850)
Dionex Corp., 1228 Titan Way, P.O. Box 3603, Sunnyvale, CA 94088-3603 (408-737-0700)
Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-562-8300)
Millipore Corp., Waters Chromatography Div., 34 Maple St., Milford, MA 01757 (508-478-2000)
Rainin Instrument Co., 1715 64th St., Emeryville, CA 94608-1097 (415-654-9142)
VWR Scientific Products, 800 E. Fabyan Pkwy., Batavia, IL 60510 (847-879-0600)

**Figure**

Typical Chromatogram (Calibration Standard)