



A Honeywell Company

Sulfate and Thiosulfate in Caustic Aqueous Solutions by Ion Chromatography

UOP Method 953-13

Scope

This method is for determining levels of sulfate and thiosulfate in aqueous, spent caustic, process streams by ion chromatography (IC). The range of quantitation for sulfate and thiosulfate is 0.004 to 5 mass-%.

Outline of Method

For analysis, the sample is diluted by mass in water to an analyte concentration between 0.0004 and 0.0180 mass-%. A repeatable volume of diluted sample is injected into an ion chromatograph equipped with an anion exchange column, conductivity suppressor device and conductivity detector, see *Note 1*. 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.

Balance, readable to 0.0001 g

Chromatographic column, Dionex IonPac AS11-HC Analytical, 250-mm length by 4-mm ID, Thermo Scientific, Cat. No. 052960

Deionized water system, NANOpure II Water Purification System with Total Organic Carbon Analyzer, Thermo Scientific, VWR, Cat. No. 47729-610

Ion chromatograph, Dionex ICS-2100, equipped with a pump, injection valve/autosampler, eluent generator, continuously regenerated trap column, suppressor, conductivity detector, solvent bottles, computer, and Chromeleon software, Thermo Scientific

Pipet bulb, 1-mL, Fisher Scientific, Cat. No. 13-678-9A

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

Vortex mixer, digital, 120V, 50/60Hz, 75W, VWR, Cat. No. 14005-824

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Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean deionized and distilled water that is subsequently treated with a Thermo Scientific NANOpure II water purification system to produce ionically pure, 18.2 megohm-cm, organic-free (<1 ppm) water.

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

Potassium hydroxide cartridge, RFIC EluGen, EGC II KOH, Dionex, Thermo Fisher, Cat. No. 058900

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

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

Vials, autosampler, 2-mL, polypropylene, for use with Dionex Thermo Scientific AS Autosampler, Fisher Scientific, Cat. No. 10-800-167

Vial caps, for autosampler vials, blue, with pre-slit PTFE/silicone septum, Fisher Scientific, Cat. No. 03-376-482

Vials, sample, 40-mL, clear VOA vials with closed cap, borosilicate glass, with white PP cap with PTFE-faced silicone liner, Fisher Scientific, Cat. No. C336-0040

Water, deionized and distilled, subsequently treated with a Thermo Scientific NANOpure II Water Purification System with Total Organic Carbon Analyzer to produce ionically pure, 18.2 megaohm-cm, organic-free (<1 ppm) water

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of ion chromatography, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

Preparation of Instrument

1. Assemble and test all ion chromatographic system components per the manufacturer's specifications.
2. Install the analytical column and suppressor (configured in recycle mode).
3. Turn on the IC and establish the recommended chromatographic conditions listed in Table 1.

Table 1	
<u>Recommended Chromatographic Conditions</u>	
Analytical column	Dionex IonPac AS11-HC
Suppressor current	81 mA
Mobile phase	27mM KOH
Mobile phase flow rate	1.2 mL/min
Column temperature	35°C
Detector cell temperature	35°C
Background conductivity	<1µS
Analysis time	18 minutes
Injection loop	25µL

4. Allow the IC to equilibrate. Typical background conductivity should be at or below $1\mu\text{S}$. Change the source of deionized water or check the functionality of the suppressor if the background conductivity is above $1\mu\text{S}$.

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 separation equivalent to that shown in the Typical Chromatogram, see Figure.

Preparation of Calibration Standards

Calibration factors are required for both sulfate and thiosulfate that relate the varying instrument response for each analyte, see *Note 2*. Calibrate with freshly prepared calibration standards each day samples are to be analyzed.

1. In one 40-mL sample vial, weigh approximately 0.2 g each of sodium sulfate and sodium thiosulfate. Record the weight of each compound to the nearest 0.0001 g.
2. Dissolve the salts with approximately 39.6 g of water and record the total weight to the nearest 0.0001 g. Cap the solution and vortex until the entire solid is completely dissolved. Label the mixture: Standard Stock Solution. Calculate the analyte concentrations in this solution using Equation 1 in *Calculations*.
3. Using a Pasteur pipet, transfer approximately 0.2 g of the Standard Stock Solution to a separate 40-mL vial. Weigh and record the weight of the Standard Stock Solution aliquot to the nearest 0.0001 g.
4. Dilute the aliquot with approximately 39.8 g of water and record the total weight to the nearest 0.0001 g. Label the mixture: Standard Calibration Solution 1. Cap the vial and vortex for approximately 15 seconds. Calculate the analyte concentrations using Equation 2 in *Calculations*.
 - Standard Calibration Solution 1 should contain approximately 0.0017 mass-% sulfate and 0.0018 mass-% thiosulfate.
5. Using a Pasteur pipet, transfer approximately 0.2 g of the Standard Stock Solution to a separate 40-mL vial. Weigh and record the weight of the Standard Stock Solution aliquot to the nearest 0.0001 g.
6. Dilute the aliquot with approximately 19.8 g of water and record the total weight to the nearest 0.0001 g. Label the mixture: Standard Calibration Solution 2. Cap the vial and vortex for approximately 15 seconds. Calculate the analyte concentrations using Equation 2 in *Calculations*.
 - Standard Calibration Solution 2 should contain approximately 0.0034 mass-% sulfate and 0.0036 mass-% thiosulfate.
7. Using a Pasteur pipet, transfer approximately 0.5 g of the Standard Stock Solution to a separate 40-mL vial. Weigh and record the weight of the Standard Stock Solution aliquot to the nearest 0.0001 g.
8. Dilute the aliquot with approximately 19.5 g of water and record the total weight to the nearest 0.0001 g. Label the mixture: Standard Calibration Solution 3. Cap the vial and vortex for approximately 15 seconds. Calculate the analyte concentrations using Equation 2 in *Calculations*.
 - Standard Calibration Solution 3 should contain approximately 0.0085 mass-% sulfate and 0.0090 mass-% thiosulfate.

9. Using a Pasteur pipet, transfer approximately 1.0 g of the Standard Stock Solution to a separate 40-mL vial. Weigh and record the weight of the Standard Stock Solution aliquot to the nearest 0.0001 g.
10. Dilute the aliquot with approximately 19.0 g of water and record the total weight to the nearest 0.0001 g. Label the mixture: Standard Calibration Solution 4. Cap the vial and vortex for approximately 15 seconds.
 - Standard Calibration Solution 4 should contain approximately 0.0170 mass-% sulfate and 0.0180 mass-% thiosulfate. Calculate the actual concentrations using Equation 2 in *Calculations*.
11. Transfer each standard calibration solution to separate autosampler vials and place them in the autosampler. Set the software to inject 50 µL and initiate the sequence. The chromatographic analysis should run for 20 minutes.
12. Identify and integrate the peak areas of sulfate and thiosulfate by comparing the chromatogram obtained with the Typical Chromatogram, see Figure.

Sample Analysis

1. Weigh approximately 1 g of the sample into a 40-mL vial and record the weight to the nearest 0.0001 g.
2. Add approximately 9 g of water to the solution and record the total diluted sample weight to the nearest 0.0001 g. Cap the vial and vortex the diluted sample solution for approximately 15 seconds so that the sample is thoroughly mixed. Label the finished prepared solution to identify the sample.
 - Repeat step 1 and 2 if analyzing multiple samples
3. Transfer aliquot(s) into autosampler vial(s) and place in the autosampler. Set the software to inject 50 µL, enter the dilution factors, and initiate the sequence. The chromatographic analysis should run for 20 minutes per sample
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 0.0180 mass-%, prepare a quantitative serial dilution(s) of the diluted sample solution. This is done by diluting the diluted sample solution in water on a mass/mass basis until the resulting chromatographic analyte peak areas closely match the area between Standard Calibration Solution 1 and 4. Record the weights of each serial dilution.

Calculations

All calculations are performed by the instrument software, and results are displayed and printed in mass-%. It is recommended to include the origin in the calibration and have an r^2 value of at least 0.999. The calculations below are included for information, and for manual calculation, if desired.

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

$$A = \frac{BCX}{100 D} \quad (1)$$

where:

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

B = mass of analyte in pure solid, g; if the purity of the

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

D = total mass of Standard Stock Solution, g
X = purity of the pure solid, from the Certificate of Analysis, mass-%
100 = factor to convert purity from percent

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

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

where:

A = as defined in Equation 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 response factor for each analyte in each Standard Calibration Solution to three significant figures using Equation 3.

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

where:

E = as defined in Equation 2
H = analyte area response
M = response factor for each analyte

Calculate each analyte concentration in the original sample to two significant figures, but not exceeding three decimal places, using Equation 4.

$$R = \left(\frac{SMN}{L} \right) \left(\frac{Q}{P} \right) \quad (4)$$

where:

L = mass of sample weighed (Sample Analysis, Step 1), g
M = response factor (Equation 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 (*Sample Analysis*, Step 5), 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.

Notes

1. The analytes are separated by anion exchange with hydroxide 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 potassium ions in the column effluent with protons supplied by electrolysis of the mobile phase. The analyte effluent from the conductivity suppressor device then 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.

2. Detector response is measured in μS 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.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods." The following precision data were obtained from analysis of synthetic blends prepared in spent caustic as process samples were unavailable.

Repeatability and Site Precision

A nested design was carried out for determining sulfate and thiosulfate in caustic aqueous solutions. The sample was analyzed by two analysts, with each analyst performing analyses on two separate days, performing two analyses each day for a total of eight analyses. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated at the concentration means listed in Table 2. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 2 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 2 with 95% confidence.

Table 2
Repeatability and, Site Precision, mass-%

Component	Mean	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Sulfate	0.005	0.0001	0.001	0.0001	0.001
Sulfate	0.011	0.0001	0.001	0.0002	0.001
Thiosulfate	0.005	0.0001	0.001	0.0001	0.001
Thiosulfate	0.015	0.0001	0.001	0.0001	0.001

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

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, USA, 1-412-490-8300,
www.fishersci.com

Sigma-Aldrich, Milwaukee, WI 53201, USA, 1-414-438-3850, www.sigma-aldrich.com

Thermo Fisher Scientific Inc. 81 Wyman Street, Waltham, MA 02454, USA, 1-781-622-1000,
www.thermoscientific.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA, 1-610-431-1700,
www.vwr.com

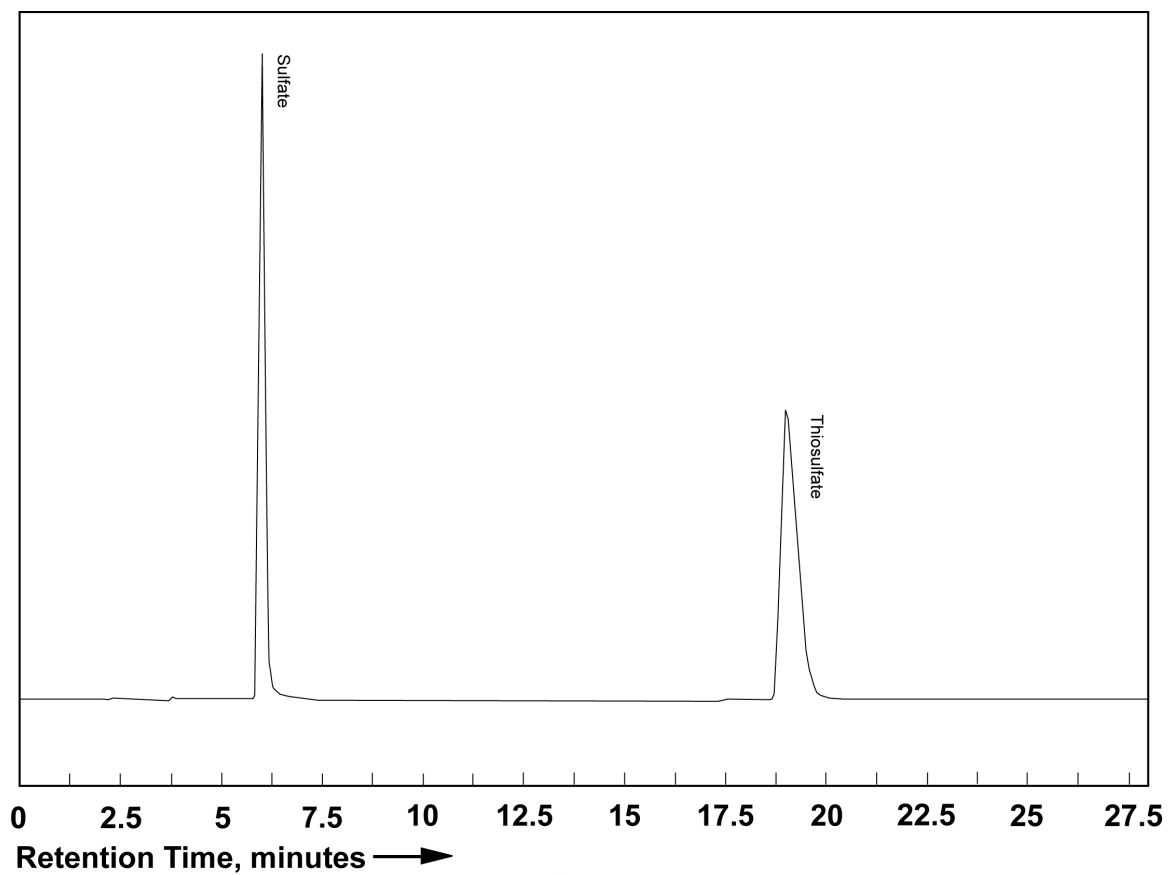


Figure
Typical Chromatogram (Calibration Standard)