

Standard Methods for the Examination of Water and Wastewater**4500-SO₃²⁻ SULFITE*#(1)****4500-SO₃²⁻ A. Introduction****1. Occurrence**

Sulfite ions (SO₃²⁻) may occur in boilers and boiler feedwaters treated with sulfite for dissolved oxygen control, in natural waters or wastewaters as a result of industrial pollution, and in treatment plant effluents dechlorinated with sulfur dioxide (SO₂). Excess sulfite ion in boiler waters is deleterious because it lowers the pH and promotes corrosion. Control of sulfite ion in wastewater treatment and discharge may be important environmentally, principally because of its toxicity to fish and other aquatic life and its rapid oxygen demand.

2. Selection of Method

The iodometric titration method is suitable for relatively clean waters with concentrations above 2 mg SO₃²⁻/L. The phenanthroline colorimetric determination, following evolution of sulfite from the sample matrix as SO₂, is preferred for low levels of sulfite.

4500-SO₃²⁻ B. Iodometric Method**1. General Discussion**

a. Principle: An acidified sample containing sulfite (SO₃²⁻) is titrated with a standardized potassium iodide-iodate titrant. Free iodine, liberated by the iodide-iodate reagent, reacts with SO₃²⁻. The titration endpoint is signalled by the blue color resulting from the first excess of iodine reacting with a starch indicator.

b. Interferences: The presence of other oxidizable materials, such as sulfide, thiosulfate, and Fe²⁺ ions, can cause apparently high results for sulfite. Some metal ions, such as Cu²⁺, may catalyze the oxidation of SO₃²⁻ to SO₄²⁻ when the sample is exposed to air, thus leading to low results. NO₂⁻ will react with SO₃²⁻ in the acidic reaction medium and lead to low sulfite results unless sulfamic acid is added to destroy nitrite. Addition of EDTA as a complexing agent at the time of sample collection inhibits Cu²⁺ catalysis and promotes oxidation of ferrous to ferric iron before analysis. Sulfide and thiosulfate ions normally would be expected only in samples containing certain industrial discharges, but must be accounted for if present. Sulfide may be removed by adding about 0.5 g zinc acetate and analyzing the supernatant of the settled sample. However, thiosulfate may have to be determined by an independent method (e.g., the formaldehyde/iodometric method¹), and then

Standard Methods for the Examination of Water and Wastewater

the sulfite determined by difference.

c. Minimum detectable concentration: 2 mg SO₃²⁻/L.

2. Reagents

a. Sulfuric acid: H₂SO₄, 1 + 1.

b. Standard potassium iodide-iodate titrant, 0.002083M: Dissolve 0.4458 g primary-grade anhydrous KIO₃ (dried for 4 h at 120°C), 4.35 g KI, and 310 mg sodium bicarbonate (NaHCO₃) in distilled water and dilute to 1000 mL; 1.00 mL = 500 µg SO₃²⁻.

c. Sulfamic acid, NH₂SO₃H, crystalline.

d. EDTA reagent: Dissolve 2.5 g disodium EDTA in 100 mL distilled water.

e. Starch indicator: To 5 g starch (potato, arrowroot, or soluble) in a mortar, add a little cold distilled water and grind to a paste. Add mixture to 1 L boiling distilled water, stir, and let settle overnight. Use clear supernatant. Preserve by adding either 1.3 g salicylic acid, 4 g ZnCl₂, or a combination of 4 g sodium propionate and 2 g sodium azide to 1 L starch solution.

3. Procedure

a. Sample collection: Collect a fresh sample, taking care to minimize contact with air. Fix cooled samples (<50°C) immediately by adding 1 mL EDTA solution/100 mL sample. Cool hot samples to 50°C or below. Do not filter.

b. Titration: Add 1 mL H₂SO₄ and 0.1 g NH₂SO₃H crystals to a 250-mL erlenmeyer flask or other suitable titration vessel. Accurately measure 50 to 100 mL EDTA-stabilized sample into flask, keeping pipet tip below liquid surface. Add 1 mL starch indicator solution. Titrate immediately with standard KI-KIO₃ titrant, while swirling flask, until a faint permanent blue color develops. Analyze a reagent blank using distilled water instead of sample.

4. Calculation

$$\text{mg SO}_3^{2-}/\text{L} = \frac{(A - B) \times M \times 6 \times 40\,000}{\text{mL sample}}$$

where:

- A* = mL titrant for sample,
- B* = mL titrant for blank, and
- M* = molarity of KI-KIO₃ titrant.

5. Precision and Bias

Three laboratories analyzed five replicate portions of a standard sulfite solution and of secondary treated wastewater effluent to which sulfite was added. The data are summarized

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Standard Methods for the Examination of Water and Wastewater

below. Individual analyst's precision ranged from 0.7 to 3.6% standard deviation ($N = 45$).

Sample	\bar{x} mg/L	Standard Deviation, σ mg/L	Relative Standard Deviation %
Standard, 6.3 mg SO_3^{2-} /L	4.5	0.25	5.5
Secondary effluent with 2.0 mg SO_3^{2-} /L	2.1	0.28	13.4
Secondary effluent with 4.0 mg SO_3^{2-} /L	3.6	0.17	4.8

6. Reference

1. KURTENACKER, A. 1924. The aldehyde-bisulfite reaction in mass analysis. *Z. Anal. Chem.* 64:56.

4500-SO₃²⁻ C. Phenanthroline Method

1. General Discussion

a. Principle: An acidified sample is purged with nitrogen gas and the liberated SO_2 is trapped in an absorbing solution containing ferric ion and 1,10-phenanthroline. Ferric iron is reduced to the ferrous state by SO_2 , producing the orange tris(1,10-phenanthroline) iron(II) complex. After excess ferric iron is removed with ammonium bifluoride, the phenanthroline complex is measured colorimetrically at 510 nm.¹

b. Interferences: See Section 4500-SO₃²⁻.B..

c. Minimum detectable concentration: 0.01 mg SO_3^{2-} /L.

2. Apparatus

a. Apparatus for evolution of SO_2 : Figure 4500-SO₃²⁻:1 shows the following components:

- 1) *Gas flow meter*, with a capacity to measure 2 L/min of pure nitrogen gas.
- 2) *Gas washing bottle*, 250-mL, with coarse-porosity, 12- mm-diam fritted cylinder gas dispersion tube.

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Standard Methods for the Examination of Water and Wastewater

3) *Tubing connectors*, quick-disconnect, polypropylene.

4) *Tubing*, flexible PVC, for use in all connections.

5) *Nessler tube*, 100-mL.

b. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer*, for use at 510 nm, providing a light path of 1 cm or longer.

2) *Filter photometer*, providing a light path of 1 cm or longer and equipped with a green filter having maximum transmittance near 510 nm.

3. Reagents

a. 1,10-phenanthroline solution, 0.03M: Dissolve 5.95 g 1,10-phenanthroline in 100 mL 95% ethanol. Dilute to 1 L with distilled water. Discard if solution becomes colored.

b. Ferric ammonium sulfate solution, 0.01M: Dissolve 4.82 g $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in 1 L distilled water to which has been added 1 mL conc H_2SO_4 to suppress ferric hydrolysis. Filter through a glass fiber filter if insoluble matter is visible. If necessary, adjust volume of acid so that a mixture of 10 parts of phenanthroline solution and one part of ferric ammonium sulfate solution will have a pH between 5 and 6.

c. Ammonium bifluoride, 5%: Dissolve 25 g NH_4HF_2 in 500 mL distilled water. Store in a polyethylene bottle and dispense with a plastic pipet.

d. Potassium tetrachloromercurate, (TCM), K_2HgCl_4 , 0.04M: Dissolve 10.86 g HgCl_2 , 5.96 g KCl, and 0.066 g disodium EDTA in distilled water and dilute to 1 L. Adjust pH to 5.2. This reagent normally is stable for 6 months, but discard if a precipitate forms.²

e. Dilute TCM-stabilized sulfite standard: Dissolve 0.5 g Na_2SO_3 in 500 mL distilled water. Standardize on the day of preparation, but wait at least 30 min to allow the rate of oxidation to slow. Determine molarity by titrating with standard 0.0125M potassium iodide-iodate titrant using starch indicator (see Section 4500- SO_3^{2-} .B). Calculate molarity of working standard as follows:

$$\text{Molarity of } \text{SO}_3^{2-} \text{ standard} = \frac{(A - B) \times M}{\text{mL sample}}$$

where:

A = titrant for sample, mL,

B = titrant for blank, mL,

M = molarity of potassium iodide-iodate titrant.

Because stock Na_2SO_3 solution is unstable, immediately after standardization, pipet 10 mL into a 500-mL volumetric flask partially filled with TCM and dilute to mark with TCM. Calculate the concentration of this dilute sulfite solution by multiplying the stock solution

Standard Methods for the Examination of Water and Wastewater

concentration by 0.02. This TCM-stabilized standard is stable for 30 d if stored at 5°C. Discard as soon as any precipitate is noticed at the bottom.

f. Standard potassium iodide-iodate titrant, 0.0125M: See Section 4500-SO₃²⁻.B..

g. Hydrochloric acid, 1 + 1.

h. Octyl alcohol, reagent-grade.

i. Sulfamic acid, 10%: Dissolve 10 g NH₂SO₃H in 100 mL distilled water. This reagent can be kept for a few days if protected from air.

j. EDTA reagent: See Section 4500-SO₃²⁻.B..

4. Procedure

a. Sample collection: Collect a fresh sample taking care to minimize contact with air. Fix cooled samples (<50°C) immediately by adding 1 mL EDTA solution for each 100 mL sample.

b. SO₂ evolution: Prepare the absorbing solution by adding 5 mL 1,10-phenanthroline solution, 0.5 mL ferric ammonium sulfate solution, 25 mL distilled water, and 5 drops octyl alcohol (to act as defoamer) to a 100-mL nessler tube; insert a gas dispersion tube. Add 1 mL sulfamic acid solution to the gas washing bottle and 100 mL of sample or a portion containing less than 100 µg SO₃²⁻ diluted to 100 mL. Add 10 mL 1 + 1 HCl and immediately connect the gas washing bottle to the gas train as shown in Figure 4500-SO₃²⁻:1. Place a spring or rubber band on the gas washing bottle to keep the top securely closed during gas flow. Adjust nitrogen flow to 2.0 L/min and purge for 60 min.

c. Colorimetric measurement: After exactly 60 min, turn off nitrogen flow, disconnect nessler tube, and immediately add 1 mL ammonium bifluoride solution. Remove gas dispersion tube after rinsing it with distilled water into the tube and forcing the rinse water into the nessler tube with a rubber bulb. Dilute to 50 mL in the nessler tube and mix by rapidly moving the tube in a circular motion. Do not let rubber stoppers or PVC tubing come in contact with the absorbing solution. After at least 5 min from the time of adding ammonium bifluoride, read the absorbance versus distilled water at 510 nm using either a 5-cm cell for a range of 0 to 30 µg SO₃²⁻ per portion or a 1-cm cell for a range of 0 to 100 µg SO₃²⁻. Avoid transferring octyl alcohol into the cell by letting it rise to the surface of the absorbing solution and transferring the clear lower solution to the cell with a pipet. Make a calibration curve by analyzing a procedure blank and at least three standards. Run at least one standard with each set of samples. For maximum accuracy hold samples and standards at the same temperature and keep the time interval from start of purging to the addition of ammonium bifluoride constant. This is easier to do if several gas trains are used simultaneously in parallel. If ambient temperatures are subject to frequent fluctuation, a water bath may be used to control color development at a fixed temperature.

5. Calculation

Standard Methods for the Examination of Water and Wastewater

$$\text{mg SO}_3^{2-}/\text{L} = \frac{\mu\text{g SO}_3^{2-} \text{ from calibration curve}}{\text{mL sample}}$$

6. Precision and Bias

Three laboratories analyzed five replicate portions of a standard sulfite solution and of secondary treated wastewater effluent to which sulfite was added. The data are summarized below. Individual analyst's precision ranged from 4.1 to 10.5% standard deviation ($N = 45$).

Sample	\bar{x} mg/L	Standard Deviation, σ mg/L	Relative Standard Deviation %
Standard, 4.7 mg SO ₃ ²⁻ /L	3.7	0.78	21
Secondary effluent with 0.12 mg SO ₃ ²⁻ /L	0.12	0.03	25
Secondary effluent with 4.0 mg SO ₃ ²⁻ /L	3.7	0.30	8.0

7. References

1. STEPHENS, B.G. & F. LINDSTROM. 1964. Spectrophotometric determination of sulfur dioxide suitable for atmospheric analysis. *Anal. Chem.* 36:1308.
2. WEST, P. W. & G.C. GAEKE. 1956. Fixation of sulfur dioxide as sulfitomercurate and subsequent colorimetric determination. *Anal. Chem.* 28:1816.

Standard Methods for the Examination of Water and Wastewater

Endnotes

1 (Popup - Footnote)

* APPROVED BY STANDARD METHODS COMMITTEE, 1996.