

Based on 4500-SO₃²⁻ B in Standard Methods for the Examination of Water and Wastewater

Amperometric Back Titration
0.00 – 20.00 mg/L as SO₃²⁻

1. Introduction

The scope of this application is to determine the sulfite concentration in water, (treated) wastewater and seawater for a range of concentrations from 0 to 20 mg/L as SO₃²⁻.

Sulfite is most commonly found in boilers and boiler feedwater, where it is used to inhibit corrosion by reducing dissolved oxygen. It may also be found in industrial wastes such as paper mill effluents. Sulfite is not normally present in natural waters because it readily oxidizes to sulfate.

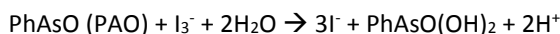
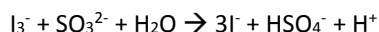
This procedure follows method number 4500-SO₃²⁻ B in *Standard Methods for the Examination of Water and Wastewater*.

2. Principle

The measurement is based on an amperometric back titration. In such a titration, a measured volume of oxidant (iodine, I₂) is added directly to a measured volume of the sample at collection time. This “fixes” the sulfite concentration and decreases the amount of sample loss throughout the titration. The method is performed at neutral pH to minimize interference from dissolved oxygen and organic chloramines.

At the time of analysis, the sample is adjusted to pH 7 with phosphate buffer, and excess potassium iodide (KI) is added. In this condition, potassium iodide (KI) and iodine (I₂) form the triiodide (I₃⁻) in situ. When all the sulfite has been converted to sulfate (SO₄²⁻), the unreacted oxidant (I₃⁻) is titrated. The sulfite concentration is derived from the difference in the amount of oxidant originally added to the sample and the amount remaining prior to titration.

The chemical equations for the titration are:



3. Electrode and reagents

Electrodes: Pt-electrode with temperature sensor, Intellical MTC695

Description	Qty. required per test
Required reagents	
Iodine Standard Solution, 0.0282 N	varies
Phenylarsine Oxide (PAO) Titrant, 0.00564 N	varies
Phosphate Buffer, pH 7	1 mL
Potassium Iodide	0.1 g
Required apparatus	
Beaker, Glass, 250-mL	1
Cylinder, Graduated, 250 mL	1
Magnetic Stir Bar, Teflon® coated	1
Optional reagents	
Dilution Water, organic-free	varies
Phenylarsine Oxide (PAO) Titrant, 0.00564 N, cartridge	varies
Acetate buffer solution, pH 4 (for calibration of the PAO)	1 mL
Optional apparatus	
Pipet, Volumetric, Class A, 1-mL	
Pipet, Volumetric, Class A, 2-mL	
Pipet, Volumetric, Class A, 3-mL	
Pipet, Volumetric, Class A, 4-mL	
Pipet, Volumetric, Class A, 5-mL	

4. Ranges and settings

4.1. Default parameters

Using the application note settings described below with the following parameters:

- Sample volume = 200 mL
- Syringe volume = 5 mL
- Titrant concentration: Phenylarsine Oxide (PAO) Titrant, 0.00564 N
- Oxidant: Iodine Standard Solution, 0.0282 N
- Continuous imposed voltage 450mV

The default syringe volume for the AT1000 is set to 10 mL. These applications need a 5 ml syringe. When loading an application, if the message **syringe to replace** is displayed, change the syringe volume in the **Syringe management** option of the **Maintenance** menu.

4.2. Working ranges

This titration has a range of concentration from 0.00 to 20.00 mg/L as SO_3^{2-} .

4.3. Titration settings (default parameters)

4.3.1. Application

	Setting
Application name	Sulfite
Advisable syringe	5mL (Hamilton)

4.3.2. Sample

	Setting	Unit
Name	Water ? ¹	
Amount	200	mL

4.3.3. Titrant settings used for the calculation

	Setting	Unit
Name	PAO	
Real concentration	0.00564	eq/L

4.3.4. Manual addition 1 settings

	Setting	Unit
Active	Yes	
Message	Add 0.1g KI and press OK	
Stirring speed	0	%

4.3.5. Automatic addition 2 settings

	Setting	Unit
Active	Yes	
Time	0.3	seconds
Reagent name	Buffer pH 7	
Pump ID	Pump 1	
Stirring speed	0	%

4.3.6. Back Titration and detection settings

	Setting	Unit
Stirring speed	1	%
Measured parameter	μA	
Pre-dose volume	0	mL

¹ "?" in the name, indicates that the sample name will be automatically incremented with a number for each analysis

Delay	30	seconds
Max. vol. stop point	15	mL
Stop on last EQP	Yes	
Stop on flat signal	Yes	
EQP min. ordinate	0	[μ A]
EQP max. ordinate	3	[μ A]

4.3.7. Excess reductant settings used for the calculation

	Setting	Unit
Back titration mode	Manual	
Excess volume	2.500	mL
Excess titrant name	Iodine	
Real conc. of excess titrant	0.0282	eq/L

4.3.8. Results settings:

R _x	R1	R2	R3
Result (R _x) name	Sulfite	Sulfur dioxide	Bisulfite
R _x min	0 mg/L	0 mg/L	0 mg/L
R _x max	21 mg/L	20 mg/L	22 mg/L
R _x QC min	0 mg/L	0 mg/L	0 mg/L
R _x QC max	21 mg/L	20 mg/L	22 mg/L
R _x unit	mg/L	mg/L	mg/L
R _x Molar weight	80.066	64.066	81.066

4.4. Recommendations for modifications of settings

4.4.1. Modification of the parameters

The predose feature allows the adjustment of titrant addition before starting the titration. Ensure the predose does not overshoot the end point by completely titrating the sample.

It is possible to add the pH 7 buffer manually. In this case, activate the buffer manual addition and deactivate the automatic addition in the application edit window.

4.4.2. Oxidant volume adjustment

Deviations can occur in the sulfite method due to loss of iodine through the iodine demand of the sample. Optimizing the total amount of free iodine to be titrated in the solution can reduce this phenomenon.

By increasing the oxidant volume to slightly more than is needed to react with the sulfite, the amount of free titratable iodine can be optimized to 2.5 mL of PAO titrant (0.00564 N) for a 5-mL burette. Data acquisition will be optimized and error due to iodine loss will be minimized.

Default parameters have been optimized for these conditions. Calculations can be done using the information given in section 6.2 Results calculation of sulfite in mg/L.

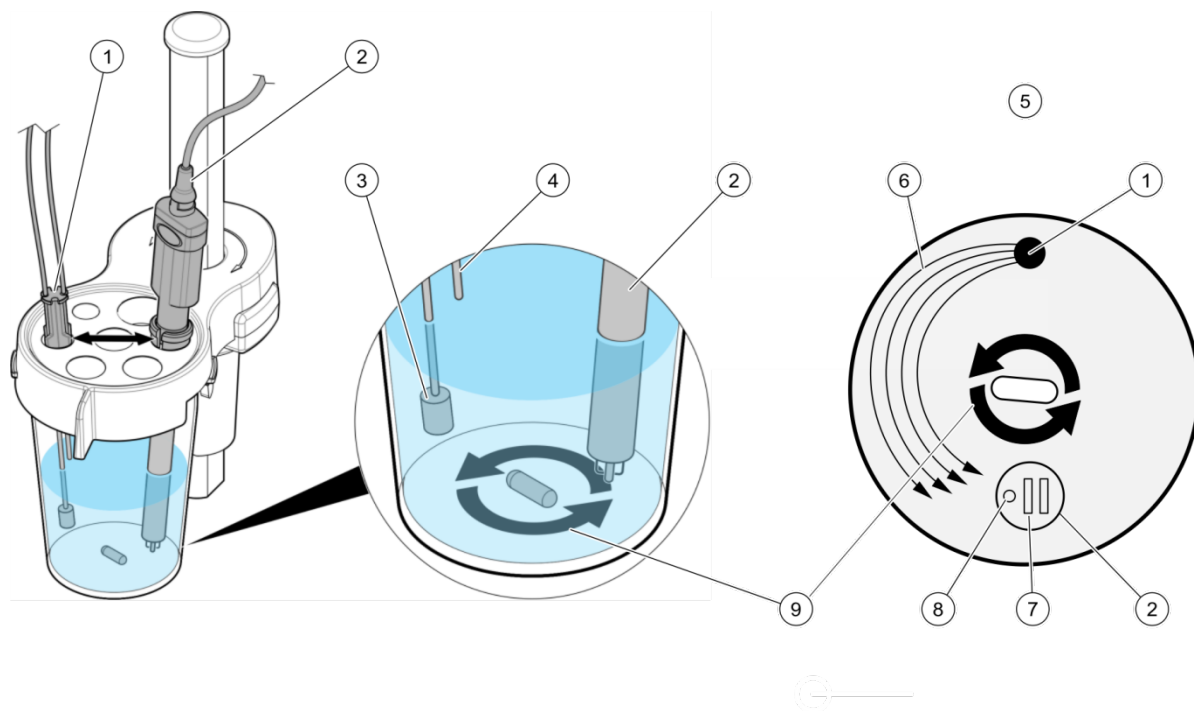
Estimated Sulfite conc. (mg/L as SO ₃ ²⁻)	Volume of 0.0282 N Iodine (mL)
0 – 2	0.5
2 – 4	1
4 – 7	1.5
7 – 10	2
10 – 12	2.5
12 – 15	3
15 – 18	3.5
18 – 21	4
21 – 24	4.5
24 – 26	5

5. Procedure for sample analysis

5.1. Position of the electrode and injection tips

Place the electrode in the opposite hole of the tubes in the sensor holder. If necessary, turn the electrode to place the platinum wires perpendicular to the sample flow and the temperature sensor before the

platinum wires. Place the tube from the pump above the sample surface and make sure that the tube with the anti-diffusion tip is fully into the sample. Refer to the figure that follows.



1. Tube holder	4. Tube from the pump	7. Platinum wires
2. Electrode	5. Top view	8. Temperature sensor
3. Anti-diffusion tip	6. Flow direction	9. Stirring direction

5.2. Sample tips and technique

Sample:

- *Standard Methods* recommends a default volume of 200 mL, and the parameters have been optimized with this volume for the whole range of concentration (0 to 20 mg/L as SO_3^{2-}). The final results are calculated based on the sample volume. Ensure that the sample volume is correct. However, as the TitraLab AT1000 Series can accommodate any sample size, the volume can be adjusted to expand the test range
- To avoid loss of sulfite, be careful not to agitate the sample when measuring or pouring
- Always use organic-free reagent water for sample dilution

Titrant:

- Download the “Certificate of Analysis” (CAO) to obtain the exact concentration of any unopened bottle of Hach titrant standard solution

Buffer:

- Hach buffer reagents are highly recommended for this analysis. Never substitute buffers designed for calibrating pH meters. They contain dyes that interfere with amperometric titration. Never use buffers contaminated with mold or bacteria

5.3. Reagent tips and technique

- Rinse the electrode and tip with deionized water before every titration
- Flush the burette each day before the first sample test or calibration is performed
- Flush the burette when changing titrants

5.4. Cleaning and storage of electrode MTC 695

- Clean the electrode daily or when necessary (e.g., after a titration when the equivalent point is not detected or before first use).
- Go to the maintenance menu and start the cleaning wizard. Use 10 to 20% Nitric Acid to clean the electrode. Fully rinse with deionized water before analysis, especially for sample analysis at very low concentrations.
- For short term storage or between titrations keep the electrode in tap water with approximately 1% Nitric Acid. Prepare the storage solution with 50 mL of tap water and add 5 mL of 10% Nitric Acid or 2.5 mL of 20% Nitric Acid.
- For long term storage (more than 3 days), rinse the electrode and carefully dry with a soft tissue. Store dry in the electrode protector.

5.5. Safety

Use good safety practices and laboratory techniques throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for specific reagent(s) information.

5.6. Analysis steps

Note: When samples are collected in the field, the sulfite can be “fixed” by adding pH 7.00 phosphate buffer, potassium iodide, and the exact amount of oxidant to exactly 200 mL of sample at the time of collection.

1. Turn the instrument on if necessary.
2. In the Main menu, highlight the desired method and press **Start**. Note that this method uses 0.00564 N PAO titrant.
3. Verify the Operator Name and the Sample Name. Modify them if necessary.
4. Measure 200 mL of sample solution with a 250-mL graduated cylinder and transfer to a 250-mL glass beaker with the specified magnetic stir bar.
5. Place the sample onto the TitraLab AT1000 Series stirrer platform. Press **Start**.
6. Add 0.1 g of potassium iodide (KI). Press **OK** to confirm. Note that KI is added in excess but the precise amount used is not crucial for the accuracy or precision of the analysis.
7. Addition of the buffer. Note that phosphate buffer is added to adjust the sample pH but the amount used is not crucial for the accuracy or precision of the analysis.
 - **Manual buffer addition:** Add 1 mL of pH 7.00 phosphate buffer as required. Press **OK** to confirm
 - **Automatic buffer addition:** The buffer addition starts automatically
8. Pipette the required volume of oxidant (0.0282 N iodine). For additional information refer to [4.4.2 Oxidant volume adjustment](#). Press **OK**.

The settling timer runs for 45 seconds, allowing the electrode to stabilize before data collection. During this time the reagents are stirred. After the electrode has stabilized, data acquisition begins and the titration curve is plotted.

6. Results

6.1. Displayed results

At the end of the titration, the results are automatically displayed:

On the first screen:

- Result expressed as Sulfite in mg/L
- Result expressed as Sulfur dioxide in mg/L
- Result expressed as Bisulfite in mg/L
- Temperature of the analysis and duration of the titration

On the second and third screens:

- Abscise of the equivalent point in mL
- Ordinate of the equivalent in μA
- Temperature of analysis and duration of the titration

If series of samples (with replicate), on the fourth screen:

Average of the series in mg/L and statistics on the series (Standard Deviation (SD) in mg/L, and Relative Standard Deviation (RD) in %) for each of the three results (Sulfite, Sulfur dioxide and Bisulfite)

6.2. Results calculation of sulfite in mg/L

The results are normally expressed in mg/L as Sulfite (SO_3^{2-}), Sulfur Dioxide (SO_2) and Bisulfite (HSO_3^-).

$$R = \frac{1}{2} * MW_x * 1000 * \frac{V(I_2) * C(I_2) - C(PAO) * V(PAO)}{V_{smp}}$$

- $C(I_2)$ = Concentration of the oxidant in eq/L: Iodine Solution, currently 0.0282 eq/L
- $V(I_2)$ = Added volume of the oxidant in mL
- $C(PAO)$ = Concentration of titrant: Phenylarsine Oxide (PAO) in eq/L, currently 0.00564 eq/L
- $V(PAO)$ = Volume of titrant: Phenylarsine Oxide (PAO) in mL added to reach the equivalent point
- $V(smp)$ = Volume of the sample in mL: currently 200 mL
- MW_x = Molar weight (with $x = 1, 2$ and 3):
 - $MW_1 = 80.066 \text{ g/mol}$ for R_1 expressed in mg/L as Sulfite (SO_3^{2-}),
 - $MW_2 = 64.066 \text{ g/mol}$ for R_2 expressed in mg/L as sulfur dioxide (SO_2)
 - $MW_3 = 81.066 \text{ g/mol}$ for R_3 expressed in mg/L as Bisulfite (HSO_3^-)

7. Examples of sulfite determination

The results described below are indicative and obtained for a given water type in optimized conditions respecting Good Laboratory Practices. These indicative values are sample-dependent, electrode-dependent and operating cell-dependent.

Experimental conditions:

- **Burette volume:** 5 mL;
- **Sample:** 200 mL of deionized water with 400 μL of standard solution of Sulfite Equivalent Standard (Na_2SO_3) at 5017.6 mg/L as SO_3^{2-}
- **Titratant:** PAO 0.00564 eq/L
- **Excess titrant:** 2.5 mL of commercial solution of iodine (I_2) 0.0282 eq/L which was calibrated at 0.0264 eq/L before use.

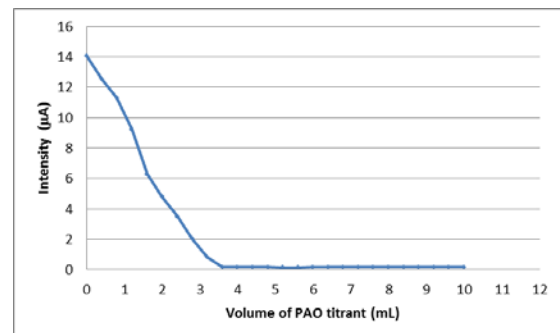
Settings:

- **Settings:** Refer to default values in [4.3 Titration settings \(default parameters\)](#)
- **Number of determinations:** 10 samples
- **Temperature of analysis:** Room temperature

Results:

Average concentration	9.97	mg/L as SO_3^{2-}
SD	0.13	mg/L as SO_3^{2-}
RSD	1.32	%

Titration curve: μA vs. volume of titrant:



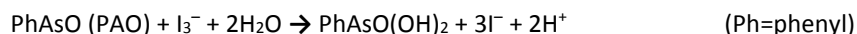
8. Bibliography

- *Standard Methods for the Examination of Water and Wastewater, Standard 4500-SO₃²⁻ B*

9. Appendix: Titrant Calibration

9.1. Principle

The PAO titrant can be calibrated against a standard solution of Iodine 0.0282 N.



The iodine solution can also be calibrated. The procedure is described in the **Total chlorine back titration** working procedure.

If the standard iodine concentration is given in the "Certificate of Analysis" (or obtained by calibration) is different from the default concentration: 0.0282 N, the real value has to be manually entered as the concentration of the standard.

9.2. Procedure

Accurately pipette 0.5 mL of iodine standard solution 0.0282 N and dilute it to 200 mL with deionized water.

Calibrate the titrant using the titrant calibration option instead of the sample analysis. Add KI powder and pH4 when required.

9.3. Results

The results described below are indicative and obtained respecting good laboratory practices. These indicative values are sample-dependent, electrode-dependent and operating cell-dependent.

The instrument calculates the titrant concentration directly in eq/L.

$$C_{(\text{PAO})} = \frac{V_{(\text{I}_2)} * C_{(\text{I}_2)}}{V_{(\text{PAO})}}$$

- $C_{(\text{PAO})}$ = Concentration of titrant: Phenylarsine Oxide (PAO) in eq/L
- $C_{(\text{I}_2)}$ = Concentration of standard: Iodine (I2) in eq/L, currently 0.0282 eq/L
- $V_{(\text{I}_2)}$ = Volume of standard: Iodine (I2) in mL, currently 0.5 mL
- $V_{(\text{PAO})}$ = Volume of the titrant: Phenylarsine Oxide (PAO) in mL added to reach the equivalent point

Experimental conditions:

- **Burette volume:** 5 mL
- **Sample:** 200 mL of deionized water with 0.5 mL of standard solution of iodine 0.0282 eq/L.
- **Addition of:** 0.1 g KI and 1 mL buffer pH 4
- **Titrant:** PAO 0.0564 eq/L

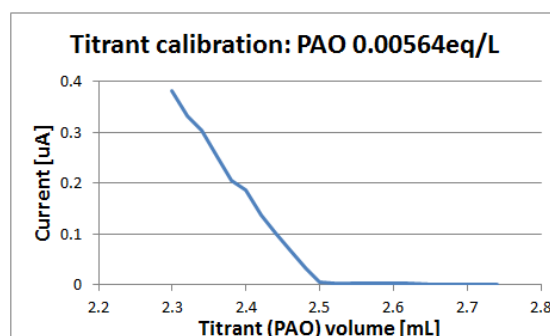
Settings:

- **Settings:** Refer to default values in [9.4 Titrant calibration settings \(default parameters\)](#)
- **Number of determinations:** 5 samples
- **Temperature of analysis:** Room temperature

Results:

Average concentration	0.00561	eq/L
SD	0.00002	eq/L
RSD	0.4	%

Titration curve: μA vs. volume of titrant:



9.4. Titrant calibration settings (default parameters)

	Setting	Unit
Titrant name	PAO	
Nominal concentration	0.00564	eq/L
Calibration frequency	0	days
Stirring speed (%)	1	%
Predose volume	2.1	mL
Delay	20	seconds
Stop on last EQP	Yes	
Min increment size	0.02	mL
Max increment size	0.05	mL
Stop on flat signal	Yes	
EQP min. ordinate	-0.1	µA
EQP max. ordinate	0.2	µA
Titrant calibration result		
Min. titrant concentration	0.0055	eq/L
Max. titrant concentration	0.0058	eq/L
Standard		
Name	Iodine	
Amount	0.500	mL
Min amount	0.490	mL
Max amount	0.510	mL
Concentration	0.0282	eq/L

9.5. Modification of the parameters

The titrant calibration application has been optimized for an amount of standard higher than 0.49mL, a standard concentration higher than 0.0270 eq/L and a titrant concentration between 0.0055 eq/L and 0.0058 eq/L.

Due to the greater concentration of the standard, the titrant volume needed for the equivalence will be affected by an amount or a concentration of the standard different to the default values. The predose volume has to be adjusted as a function of this amount, to ensure about 0.2 mL of titrant before the equivalence.

As an example, the table below shows the effect of the standard concentration on the equivalent volume and the optimum predose volume as a function of the equivalent volume expected.

Standard volume and concentration	Titrant concentration	Theoretical equivalent titrant volume	Number of addition points before equivalent point detection with default predose @2.1mL	Optimized predose volume
0.50 mL @ 0.0270 eq/L	0.0058 eq/L	2.33 mL	11	2.1 mL
0.50 mL @ 0.0270 eq/L	0.0055 eq/L	2.45 mL	18	2.2 mL
0.50 mL @ 0.0290 eq/L	0.0058 eq/L	2.50 mL	20	2.3 mL
0.50 mL @ 0.0290 eq/L	0.0055 eq/L	2.64 mL	27	2.4 mL

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