Sulfide in Water by Colourimetric Analysis - PBM

Parameter Sulfide, Total or Dissolved

Analytical Method Methylene Blue Colourimetry

Introduction

This method is applicable to the quantitative determination of sulfide in water. Sulfide, commonly found in ground water, is often formed by bacterial reduction of sulfate in rocks and ores and from decomposition of organic matter. Gaseous hydrogen sulfide has an unpleasant smell and is highly toxic to humans, acting as a chemical asphyxiant. Dissolved sulfide is toxic to fish and other aquatic organisms. Sulfide attacks metals directly, forming metal sulfides. Highly corrosive sulfuric acid may be formed from biological oxidation of sulfide, and will attack concrete sewer pipes.

Aqueous sulfide concentrations may be expressed in different forms and units. Schedule 3.2 BC CSR Generic Numerical Water Standards exist for “Sulfide (as H_2S)”.

Sulfide may be measured as Total Sulfide or Dissolved Sulfide. Dissolved Sulfide includes H_2S and HS- species, which exist at equilibrium as a function of pH, temperature, and ionic strength. Total Sulfide includes the Dissolved Sulfide species plus any acid-volatile metallic sulfides present in particulate matter. Total and Dissolved Sulfide measurements may be expressed in units of “as S”, or “as H_2S” (multiply Sulfide “as S” results by 34/32 to convert to “as H_2S” results, based on molecular weight ratios).

The truest and most direct measure of “Sulfide (as H_2S)” is “Unionized Sulfide (as H_2S)”, calculated from Dissolved Sulfide, field pH, field temperature, and ionic strength. Measurement of Dissolved Sulfide requires field flocculation using an aluminum hydroxide floc, because filtration may cause oxidation of sulfide.

“Unionized Sulfide (as H_2S)” can also be estimated from Total Sulfide, but may be high-biased if acid volatile sulfides are present in particulate matter.

Due to the complexity of measurement of Dissolved Sulfide, Total Sulfide (as H_2S) is commonly utilized as a screening measure to confirm compliance with Schedule 3.2 standards. Where screening measures indicate possible non-compliance, measurement of Dissolved Sulfide and/or computation of Unionized Sulfide are recommended.

Method Summary

Sulfide (as either H_2S or HS-) in waters is stabilized in the field by preservation with zinc acetate and sodium hydroxide, causing precipitation of zinc sulfide. ZnS precipitate in samples is measured colourimetrically as methylene blue, after reaction of zinc sulfide under acidic conditions with N,N-dimethyl-p-phenylenediamine and ferric chloride. The intensity of the methylene blue is read colourimetrically at 664 ± 10 nm. The test method is applicable to manual or automated analysis procedures.

Methods incorporating matrix isolation techniques are recommended for complex matrix samples or highly coloured samples to prevent interference due to sample colour or chemical matrix effects. Suitable matrix isolation techniques include membrane dialysis, distillation, or manual sample pre-treatment as per APHA 4500 S2- Method C. The Method C pre-concentration procedure can also be used to reduce the detection limit of the manual colourimetric method.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

Analyte	CAS No.	Approx. MDL	EMS Analyte Code**
Sulfide, Total (as S)	18496-25-8	1-20 µg/L	0125
Sulfide, Total (as H_2S)	7783-06-4 (est.)	1-20 µg/L	
Sulfide, Dissolved (as S)	18496-25-8	1-20 µg/L	1125
Sulfide, Dissolved (as H_2S)	7783-06-4 (est.)	1-20 µg/L	
Sulfide, Unionized, from total (as H_2S)	7783-06-4 (est.)	1-20 µg/L	
Sulfide, Unionized (as H_2S)	7783-06-4	1-20 µg/L	

MDLs vary based on test method options.

EMS Method Code(s)

Colourimetric, standard method: X257

**Refer to EMS Parameter Dictionary on the ministry website for all current EMS codes.

Matrix

Groundwater, Wastewater

Interferences and Precautions

Preserved samples must have pH ≥ 9 to ensure stabilization of sulfide. The pKa of H_2S is 7.0. Therefore, above pH 9, > 99% of H_2S exists as the anionic HS- species, which is highly water soluble.

Extremely high sulfide concentrations may completely inhibit the methylene blue colourimetric reaction, causing the solution to turn pink instead of the expected blue. Such samples require dilution before the addition of reagents.

Sulfide is highly reactive, and is rapidly oxidized by dissolved oxygen (usually to thiosulfate or sulfate, sometimes to sulfur), especially when exposed to light or in the presence of heavy metals. Sulfide oxidation may be minimized through the use of nitrogen purged reagent water (for standards or dilutions), and by the use of ascorbic acid as an anti-oxidant.

Many metals such as Hg, Cd and Cu can form insoluble sulfides which may cause low recoveries.

Test method options that do not incorporate matrix isolation may be subject to the following interferences:

- Strong reducing agents such as sulfite and thiosulfate at concentrations above 10 mg/L may prevent colour formation.
- Iodide at concentrations greater than 2 mg/L may diminish colour formation.
- Ferrocyanide also produces a blue colour, which is removed by adding diammonium hydrogen phosphate.
- Highly coloured samples may experience colourimetric background interference that cannot be fully corrected by the Tube A / Tube B background colour correction procedure. Use of APHA 4500 S2- Method C is recommended in this case.

Sample Handling and Preservation

Container: Plastic or Glass.

Flocculation (for Dissolved Sulfide): Dissolved Sulfide requires field flocculation within 15 minutes of sampling using an aluminum hydroxide flocculant (aluminum chloride + sodium hydroxide, as per APHA 4500 S2-), prior to preservation.

Preservation: Field preservation is required within 15 minutes of sampling. Preserve with Zinc Acetate and Sodium Hydroxide to pH >9 (refer to APHA 4500 S2- for details).

Holding Time: 7 days (preserved), 15 minutes (unpreserved), as per APHA 1060.

Storage: Chill to ≤ 10°C immediately after sampling and during transit to the laboratory. In the laboratory, samples must be refrigerated at ≤ 6°C. Avoid freezing to prevent sample breakage.

Procedure

Detailed analytical procedures are not provided in this method. For detailed guidance, refer to APHA 4500-$S2^-$ Method D: Methylene Blue Method, Method C: Sample Pretreatment to Remove Interfering Substances or to Concentrate the Sulfide, Method E: Gas Dialysis, Automated Methylene Blue Method, or Method I: Distillation, Methylene Blue Flow Injection Analysis Method.

Samples for sulfide analysis must be preserved in the field within 15 minutes of sampling (or analyzed in the field). Samples that arrive unpreserved at the laboratory should be considered compromised. If analyzed at all, sulfide results for such samples must be qualified as unreliable.

If sample concentration of a preserved sample is required (as per APHA 4500 S2- Method C), either to achieve lower detection limits or to remove interferences, first check pH and add additional NaOH if necessary to increase pH to ≥ 9. Centrifuge or allow the zinc sulfide precipitate to settle, and replace the supernatant with an appropriate volume of deionized nitrogen-purged water.

Analysis of Dissolved Sulfide requires the use of an aluminum hydroxide flocculation procedure, which must be conducted within 15 minutes of sampling. Follow instructions from APHA 4500 $S2^-$ B, Separation of Soluble and Insoluble Sulfides. Allow sample to stand for 5 to 15 minutes, then decant clear supernatant to sampling container and preserve immediately with zinc acetate and NaOH.

Stock sulfide standards must be prepared and verified daily using the iodometric method outlined in APHA 4500-S2- Method F. Alternatively, commercially prepared single-use certified reference standards may be used.

Manual Colourimetric Analysis: Well-homogenized samples containing a Zinc Sulfide slurry (if sulfide is present) reacts directly with acid reagents, dimethyl-p-phenylenediamine and ferric chloride to liberate the sulfide from the zinc and to react to produce methylene blue colour. After colour formation, diammonium hydrogen phosphate is added to remove the colour associated with ferric chloride. Sulfide concentration is determined by quantifying methylene blue at 664 ± 10 nm against a linear calibration curve that brackets the working range of the method. A second sample aliquot goes through the same process but the active colour reagent (dimethyl-p-phenylenediamine) is replaced with H_2SO_4 to determine sample background correction.

Automated or Semi-Automated Analysis: Well-homogenized samples containing a Zinc Sulfide slurry (if sulfide is present) reacts with acid to liberate acid-dissociable sulfide into a basic trapping solution using either a membrane dialyzer or distillation as matrix isolation techniques. The trapping solution containing sulfide is free of most matrix interferences, and reacts with dimethyl-p-phenylenediamine and ferric chloride to produce methylene blue colour. The Sulfide concentration is determined by quantifying methylene blue at 664 ± 10 nm using a calibration curve that brackets the working range of the method.

Reporting and Conversion of Sulfide Test Results

Total or Dissolved Sulfide test results may be reported in µg/L (ppb) units “as S” or “as H_2S”. Multiply “as S” results by 34.1/32.1 (1.063, the molecular weight ratio of H_2S / S) to convert to “as H_2S” results. Regardless of the reporting units, Dissolved and Total Sulfide include both H_2S and HS- species. Total Sulfide also includes acid volatile sulfides associated with particulate matter, if present.

The most accurate measure of “Sulfide (as H_2S)” is “Unionized Sulfide (as H_2S)”, calculated from Dissolved Sulfide as per APHA 4500 S2- Method H. The calculation requires inputs of Dissolved Sulfide (as S), field pH, field temperature, and ionic strength. Ionic strength may be estimated either from a full mineral analysis (if available), or from Electrical Conductivity, or from Total Dissolved Solids (each of these approaches will require one or more additional analyses, with submission of an unpreserved sample).

“Unionized Sulfide (as H_2S)” may also be estimated from Total Sulfide, which may be utilized for demonstration of compliance with standards. However, estimates derived from Total Sulfide may potentially be high biased. Test reports should indicate whether calculated results for “Unionized Sulfide (as H_2S)” are derived from Total or Dissolved Sulfide measurements.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements, and apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 85-115% for Lab Control Samples or Certified Reference Materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision of ≤ 15% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives
Calibration Verification Standard (CVS) – 2nd source	1 per initial calibration	85 - 115%
Continuing Calibration Verification (CCV)	At least every 12 hours (max 20 samples), and at end of each batch.	80 - 120% for mid-level standards
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	75 – 125%
Lab Duplicate (DUP)	One per batch (max 20 samples)	20% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS)	One per batch (max 20 samples)	75 – 125%

If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.

Other QC Requirements

Method Blanks, Laboratory Control Samples, and Reference Materials must be prepared using zinc acetate / NaOH preservative so that they will be representative of test samples.

Control Standard / Initial Calibration Verification must be from a source that is independent from calibration standards. Control Standards may also be used as Continuing Calibration Verifications (CCV's).

Prescribed Elements

The following components of this method are mandatory:

a) Sample holding times and preservation requirements must be adhered to. Field preservation or field analysis is required. Samples analyzed beyond the stated holding time must be qualified.

b) All performance requirements and Quality Control requirements must be met.

c) Sulfide stock must be standardized daily to establish a known concentration of sulfide. Alternatively, commercially prepared single-use reference standards may be used. Working standards are prepared at nominal concentrations from standardized or commercial reference source stocks.

d) For the colourimetric method without matrix removal by either membrane dialysis, distillation, or the APHA 4500 S2- Method C concentration procedure, samples

without colour reagent must be used to establish background colour, as per the Tube A / Tube B procedure from APHA 4500 S2- Method D. B samples do not contain N,N-dimethyl-p-phenylenediamine oxalate and act as background colour correction when the B result is subtracted from the A result.

e) Automated test methods for sulfide must incorporate adequate stirring mechanisms to ensure homogeneous distribution of zinc sulfide precipitate during instrumental sub- sampling.

f) Samples to be analyzed for dissolved sulfide must be flocculated within 15 minutes of sampling using aluminum chloride and NaOH as per APHA Method 4500 S2- Method B, followed by field preservation with zinc acetate and NaOH to pH ≥ 9.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency

References

Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington DC, 2011, Method 4500-S^{2-} SULFIDE.

Revision History

Mar 8, 2021	Revision made to clarify different options for measuring Sulfide "as H_2S", including measures of Unionized Sulfide (as H_2S), for comparison with the Schedule 3.2 Generic Numerical Water Standards, and to expand analytical options to include distillation, membrane dialysis, and the APHA Method C concentration protocol as matrix isolation techniques. New requirement added for Matrix Spikes as routine QC samples. CAS numbers added.
July 26, 2013	First version of BC Lab Manual sulfide method in PBM format. Effective date for this method is October 1, 2013.