Designation: D4658 – 15

Standard Test Method for Sulfide Ion in Water[1]

This standard is issued under the fixed designation D4658; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method uses an ion-selective electrode to determine sulfide ion in water. The test method is applicable in the range from 0.04 to 4000 mg/L of sulfide.

1.2 Precision data presented in this test method were obtained using reagent water only. It is the user's responsibility to ensure the validity of this test method for untested types of water.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Sulfide samples, when acidified, can release highly toxic hydrogen sulfide gas. For a specific precautionary statement, see 7.5.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D4127 Terminology Used with Ion-Selective Electrodes
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 For definitions of terms specific to this test method, refer to Terminology D4127.

4. Summary of Test Method

4.1 Sulfide ion is measured potentiometrically using a sulfide ion-selective electrode in conjunction with a double-junction sleeve type reference electrode. Potentials are read using a pH meter having an expanded millivolt scale capable of being read to the nearest 0.1 mV, or a specific ion meter having a direct concentration scale for sulfide ion.

4.2 Samples are treated prior to analysis with sulfide antioxidant buffer (SAOB). This buffer fixes the solution pH at a highly alkaline level and contains ascorbic acid to retard air oxidation of sulfide ion in solution. This ensures that the sulfide present occurs chiefly as S^{2-} ion rather than as complexed HS^{1-} or H_2S that are present at lower pH values.

5. Significance and Use

5.1 Sulfide ion is found in ground waters and wastewater, causing odor and corrosion problems. If acidified, these waters can release hydrogen sulfide, which is extremely toxic even at low levels. This test method provides a means for interference-free measurement of free sulfide ion.

NOTE 1—Sulfide forms complexes with hydrogen ions (HS^{1-} and H_2S). In addition, sulfide ion forms soluble complexes with elemental sulfur (S_2^{2-}, S_3^{2-}, S_4^{2-}, etc.), tin, antimony, and arsenic ions.

6. Apparatus

6.1 *pH Meter,* with expanded millivolt scale, or a specific ion meter having a direct concentration scale for sulfide ion.

6.2 *Sulfide Ion-Selective Electrode.*

6.3 *Reference Electrode,* double-junction sleeve type with 1.0 *M* potassium nitrate solution, pH adjusted to 13.5 with 1.0 *M* sodium hydroxide in the outer sleeve.

*A Summary of Changes section appears at the end of this standard

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D1193, Type I. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the test method. Type III water was specified at the time of round robin testing of this method.

7.3 *Cadmium Nitrate Solution* (0.1 *M*)—Place 12.84 g of cadmium oxide into a 125-mL beaker. Add 12 to 14 mL of concentrated nitric acid (sp gr 1.42), stir with a glass stirring rod, and add about 10 mL of water. Stir thoroughly, add an additional 40 to 50 mL of water, washing off the glass stirring rod with part of the water. Transfer to a 1-L volumetric flask and dilute to 1000 mL with water.

7.4 *Lead Perchlorate Solution* (0.1 *M*)—Commercially available. Alternatively, it can be prepared using lead perchlorate and water. Dissolve 46.02 g of the salt in water using a 1-L volumetric flask and dilute to 1000 mL with water.

7.5 *Sodium Sulfide Solution, Stock*—Prepare sodium sulfide stock solution from sodium sulfide hydrate ($Na_2S{\cdot}9H_2O$). Alternatively, certified sodium sulfide stock solutions of known purity are commercially available through chemical supply vendors and may be used. (**Warning—**All sulfide solution preparation and measurement must be performed in a hood to avoid breathing noxious fumes.)

7.5.1 Precise standards cannot be prepared by weighing the salt because of the large and variable water of hydration. Instead, prepare a saturated sodium sulfide solution by adding approximately 100 g of the $Na_2S{\cdot}9H_2O$ to approximately 100 mL of water, shake well, stopper securely, and allow it to stand, at least overnight.

7.5.2 To prepare the sodium sulfide stock solution, pipette 1 mL of the saturated solution described above into 50 mL of SAOB (7.6), and dilute to 100 mL with water.

7.6 *Sulfide Anti-Oxidant Buffer (SAOB)*—In a 1000-mL beaker containing approximately 600 mL of water, add 200 mL of 10 *M* sodium hydroxide (or 80 g pellets), 35 g of ascorbic acid, and 67 g of disodium EDTA. Stir until everything dissolves and transfer the solution to a 1000-mL volumetric flask. Dilute to the mark with water. The solution composition is as follows; 2 *M* NaOH; 0.2 *M* ascorbic acid, and 0.2 *M* disodium EDTA (dihydrate).

NOTE 2—Freshly prepared SAOB, when stored in a tightly stoppered bottle, has a shelf life of approximately two weeks, if opened frequently. When oxidized, the solution turns dark brown and should be discarded.

7.7 *Zinc Acetate Solution* (*2.0 M*)—Dissolve 43.90 g of zinc acetate [$Zn(C_2H_3O_2)_2{\cdot}2H_2O$] in water, using a 100 mL volumetric flask, and dilute to 100 mL with water.

8. Sampling and Storage

8.1 Collect samples in accordance with Practices D3370.

8.2 Samples should be taken with a minimum of aeration to avoid air oxidation of sulfide or loss of volatile hydrogen sulfide from the sample. Preserve samples by adding 0.2 mL (4 drops) of 2 *M* zinc acetate (equivalent to 128 mg/L $S^{=2-}$) and 0.05 mL (1 drop) of 6 *M* sodium hydroxide to a 100-mL bottle. Fill the bottle completely with the sample and stopper it. There should be no air bubbles trapped under the stopper. If the concentration of sulfide is greater than approximately 100 mg/L, the amounts of both reagents should be increased.

8.3 Sulfide in samples that have been "preserved" with zinc acetate can be determined without special treatment, since SAOB contains EDTA to redissolve the zinc and free the sulfide. The entire sample is used for analysis, and since the results will be given in milligrams sulfide per litre, the sample volume must be known.

8.4 The standards must be treated the same as the samples.

9. Calibration

9.1 Prepare four calibration standards each day using 100-mL volumetric flasks as follows:

9.1.1 *Standard A*—5.00 mL of sodium sulfide stock solution, 50 mL of SAOB (use a graduated cylinder), and dilute to a total volume of 100 mL with water.

9.1.2 *Standard B*—1.00 mL of sodium sulfide stock solution, 50 mL of SAOB (use a graduated cylinder), and dilute to a total volume of 100 mL with water.

9.1.3 *Standard C*—2.00 mL of calibration standard *A*, 50 mL of SAOB (use a graduated cylinder), and dilute to a total volume of 100 mL with water.

9.1.4 *Standard D*—1.00 mL of calibration standard *A*, 50 mL of SAOB (use a graduated cylinder), and dilute to a total volume of 100 mL with water.

9.2 The concentrations of the calibration standards, in milligrams per litre, are based on a 50 mL standard volume diluted 1:1 with SAOB and are calculated from the concentration, *S*, of the sodium sulfide stock solution as determined by titration:

$A = 0.1S$

$B = 0.02S$

$C = 0.002S$

$D = 0.001S$

9.3 Prepare a calibration curve by immersing the electrode pair in each of the calibration standards, beginning with the most dilute, and record the stable electrode potential millivolt reading developed in each. Construct a graph using this data,

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[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

using semilog paper. Record the sulfide ion concentrations on the logarithmic scale and the millivolt readings on the linear scale (Fig. 1). A specific ion meter having a direct concentration scale for sulfide ion may be used.

10. Standardization

10.1 The concentration of the sodium sulfide stock solution must be determined by potentiometric titration before proceeding with the calibration.

10.2 Take 50 mL of sodium sulfide stock solution, and add to it 25 mL of SAOB and 25 mL of water. Titrate using the sulfide and double-junction reference electrodes as the end-point indicator, and either the lead perchlorate or cadmium nitrate solution as the titrant.

10.3 Calculate the concentration (S) of sodium sulfide stock solution in mg/L as follows:

$$S = (\text{mL of } 0.1\ M \text{ lead perchlorate or cadmium nitrate}) \times 64.12 \quad (1)$$

where:

64.12 = (0.1 mole/L titrant × 32.06 g/mole S × 1000 mg/g) / 50 mL sulfide stock.

11. Procedure

11.1 Pipette a sample into an equal volume of SAOB, stir thoroughly without vortex, and allow it to stand for 3 to 5 min. Place the electrodes in the solution, record the stable electrode potential, and determine the sulfide ion concentration of the sample from the calibration curve.

11.2 Between samples, rinse the electrodes with water, blot dry, and immerse in a "blank" solution of 50 mL SAOB plus 50 mL water.

11.3 To measure the next sample, blot the electrodes dry and repeat 11.1.

12. Precision and Bias[4]

12.1 The instability of sulfide ion in the presence of oxygen makes conventional round robin testing (the distribution of "unknowns" to a number of laboratories) an impossibility. For that reason, and with the concurrence and advice of the Results Advisor, this test method was tested as described here, so that users of this test method might have some guidance as to the validity of their results.

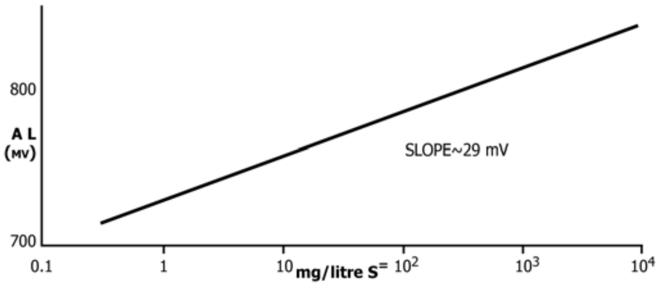

FIG. 1 Typical Electrode Response to Sulfide Ion

12.2 On each of three days, operators in each of six laboratories standardized a sodium sulfide stock solution as described in Section 10. Full calibration, using four standards prepared by dilution of the standardized stock solution, was carried out five times on each day by each operator, and the potential values were recorded.

12.3 The five replicates at each level were averaged and standard deviations were calculated. By averaging the standard deviation values in segments of the concentration range, Table 1 was developed. Since the sodium sulfide stock solutions varied from day to day, this approach was chosen to provide the most useful information. The data show the average standard deviation in millivolts (from which concentration variations may be calculated) that an average user may expect at the concentrations indicated.

12.4 An additional, rather unusual, treatment of the data is shown in Fig. 2. Each of the nominal concentration values is plotted against the average of five potential values obtained for it (72 points), as if all had been obtained by one laboratory. Letters are used to indicate which data came from which laboratory. The straight line combines data taken by six different operators using six different electrode pairs on three different days at 72 different concentrations, with all laboratories using the same procedure. It is intended only to provide a potential user of this test method with a practical, if not completely statistically valid, estimate of the kinds of results which can be expected.

12.5 The testing described was carried out using reagent water only. It is the user's responsibility to ensure the validity of this test method for untested types of water.

12.6 This precision statement has been reviewed and approved by the Results Advisor, with the concurrence of the Technical Operations Section of Executive Subcommittee D19.90 at their meeting on November 5, 1985 for conformance to Section 1.4 of Practice D2777 – 13.

13. Quality Control

13.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing sulfide ion.

13.2 *Calibration and Calibration Verification:*

13.2.1 Analyze at least three working standards containing concentrations of sulfide ion that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. The calibration correlation coefficient shall be equal to or greater than 0.990.

13.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration.

13.2.3 If calibration cannot be verified, recalibrate the instrument.

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1127. Contact ASTM Customer Service at service@astm.org.

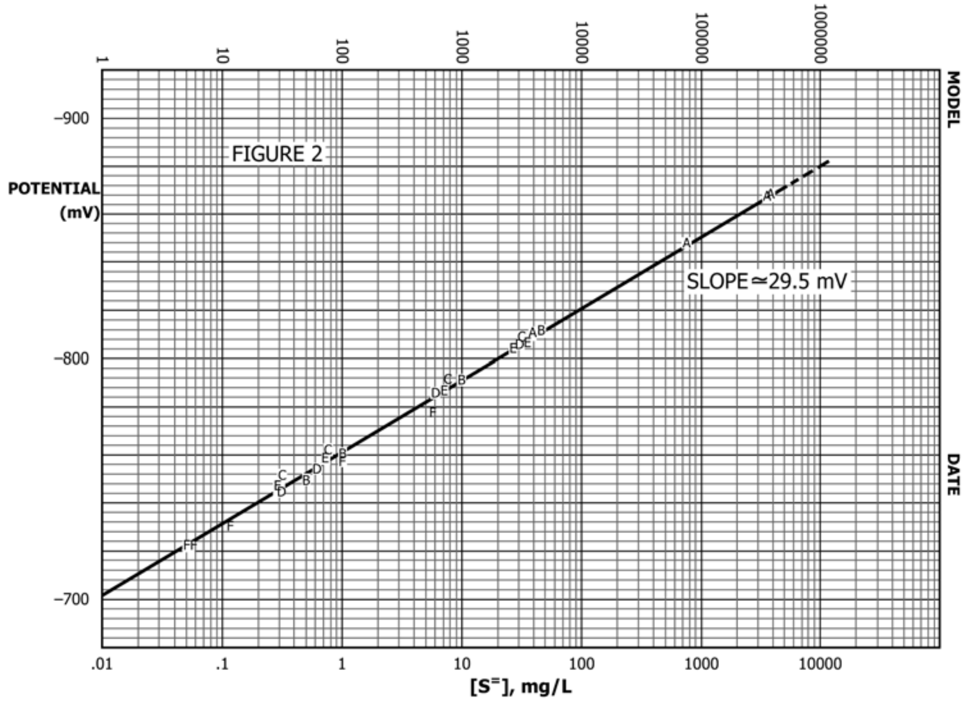

FIG. 2 Sulfide Data Plotted as if Obtained by Only One Laboratory

TABLE 1 Estimated Single Operator Precision for Sulfide (See 12.3)

Concentration Range, mg/L	Average Standard Deviation, ± mV	Concentration Variation, ± %
0.05–1.0 (33 pts.)	0.75	6.5
1.0–100 (39 pts.)	0.42	2.6
100–4000 (9 pts.)	0.33	2.0

13.2.4 It is recommended to analyze a blank and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15% of the known concentration.

13.3 *Initial Demonstration of Laboratory Capability:*

13.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

13.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of sulfide ion. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

13.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 1. This study should be repeated until the recoveries are within the limits given in Table 1. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the *F* test and *t* test in evaluating the acceptability of the mean and standard deviation.

13.4 *Laboratory Control Sample (LCS):*

13.4.1 To ensure that the test method is in control, prepare andanalyze a LCS containing a known concentration of sulfide ion with each batch (laboratory-defined or twenty samples). The laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within ±15 % of the known concentration.

13.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

13.5 *Method Blank:*

13.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of sulfide ion found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of sulfide ion is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

13.6 *Matrix Spike (MS):*

13.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each laboratory-defined batch by spiking an aliquot of the sample with a known concentration of sulfide ion and taking it through the analytical method. If a MS is not applicable, analyze more duplicate samples per batch.

13.6.2 The spike concentration plus the background concentration of sulfide ion must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

13.6.3 Calculate the percent recovery of the spike (P) using the following calculation:

$$P = 100\left[A\left(V_s + V\right) - B\, V_s\right]/C\, V \quad (2)$$

where:

A = analyte concentration (mg/L) in spiked sample,
B = analyte concentration (mg/L) in unspiked sample,
C = concentration (mg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

13.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 3—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

13.7 *Duplicate:*

13.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

13.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

13.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

13.8 *Independent Reference Material (IRM):*

13.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

14. Keywords

14.1 electrode; potentiometric; sulfide; water

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D4658 – 09) that may impact the use of this standard. (Approved March 15, 2015.)

(1) Modified 7.5 for the purity of commercial standards.

(2) Modified Section 13.