Standard Methods for the Examination of Water and Wastewater

4500-S^{2-} SULFIDE*#(1)

4500-S^{2-} A. Introduction

1. Occurrence and Significance

Sulfide often is present in groundwater, especially in hot springs. Its common presence in wastewaters comes partly from the decomposition of organic matter, sometimes from industrial wastes, but mostly from the bacterial reduction of sulfate. Hydrogen sulfide escaping into the air from sulfide-containing wastewater causes odor nuisances. The threshold odor concentration of H_2S in clean water is between 0.025 and 0.25 µg/L. Gaseous H_2S is very toxic and has claimed the lives of numerous workers in sewers. At levels toxic to humans it interferes with the olfactory system, giving a false sense of the safe absence of H_2S. It attacks metals directly and indirectly has caused serious corrosion of concrete sewers because it is oxidized biologically to H_2SO_4 on the pipe wall. Dissolved H_2S is toxic to fish and other aquatic organisms.

2. Categories of Sulfides

From an analytical standpoint, three categories of sulfide in water and wastewater are distinguished.

a. Total sulfide includes dissolved H_2S and HS^-, as well as acid-soluble metallic sulfides present in suspended matter. The S^{2-} is negligible, amounting to less than 0.5% of the dissolved sulfide at pH 12, less than 0.05% at pH 11, etc. Copper and silver sulfides are so insoluble that they do not respond in ordinary sulfide determinations; they can be ignored for practical purposes.

b. Dissolved sulfide is that remaining after suspended solids have been removed by flocculation and settling.

c. Un-ionized hydrogen sulfide may be calculated from the concentration of dissolved sulfide, the sample pH, and the practical ionization constant of H_2S.

Figure 4500-S^{2-}:1 shows analytical flow paths for sulfide determinations under various conditions and options.

3. Sampling and Storage

Take samples with minimum aeration. Either analyze samples immediately after collection or preserve for later analysis with zinc acetate solution. To preserve a sample for a total sulfide determination put zinc acetate and sodium hydroxide solutions into bottle before filling it with sample. Use 4 drops of 2*N* zinc acetate soution per 100 mL sample. Increase volume of zinc acetate solution if the sulfide concentration is expected to be greater than 64 mg/L. The final pH should be at least 9. Add more NaOH if necessary. Fill bottle completely

and stopper.

4. Qualitative Tests

A qualitative test for sulfide often is useful. It is advisable in the examination of industrial wastes containing interfering substances that may give a false negative result in the methylene blue method (D).

a. Antimony test: To about 200 mL sample, add 0.5 mL saturated solution of potassium antimony tartrate and 0.5 mL 6*N* HCl in excess of phenolphthalein alkalinity.

Yellow antimony sulfide (Sb_2S_3) is discernible at a sulfide concentration of 0.5 mg/L. Comparisons with samples of known sulfide concentration make the technique roughly quantitative. The only known interferences are metallic ions such as lead, which hold the sulfide so firmly that it does not produce Sb_2S_3, and dithionite, which decomposes in acid solution to produce sulfide.

b. Silver-silver sulfide electrode test: Dilute sample 1:1 with alkaline antioxidant reagent (see ¶ G.3*a* below). Measure electrode potential relative to a double-junction reference electrode and estimate the sulfide concentration from an old calibration curve or the example calibration curve in the electrode manual. This gives a reasonable estimate of sulfide concentration if the electrode is in good condition.

c. Lead acetate paper and silver foil tests: Confirm odors attributed to H_2S with lead acetate paper. On exposure to the vapor of a slightly acidified sample, the paper becomes blackened by formation of PbS. A strip of silver foil is more sensitive than lead acetate paper. Clean the silver by dipping in NaCN solution and rinse. CAUTION: *NaCN is toxic, handle with care.* Silver is suitable particularly for long-time exposure in the vicinity of possible H_2S sources because black Ag_2S is permanent whereas PbS slowly oxidizes.

5. Selection of Quantitative Methods

Iodine oxidizes sulfide in acid solution. A titration based on this reaction is an accurate method for determining sulfide at concentrations above 1 mg/L if interferences are absent and if loss of H_2S is avoided. The iodometric method (F) is useful for standardizing the methylene blue colorimetric methods (D, E, and I) and is suitable for analyzing samples freshly taken from wells or springs. The method can be used for wastewater and partly oxidized water from sulfur springs if interfering substances are removed first. The automated methylene blue method with distillation (I) is useful for a variety of samples containing more than 1 mg S^{-}/L.

The methylene blue method (D) is based on the reaction of sulfide, ferric chloride, and dimethyl-*p*-phenylenediamine to produce methylene blue. Ammonium phosphate is added after color development to remove ferric chloride color. The procedure is applicable at sulfide concentrations between 0.1 and 20.0 mg/L. The automated methlylene blue method (E) is similar to Method D. A gas dialysis technique separates the sulfide from the sample matrix. Gas dialysis eliminates most interferences, including turbidity and color. The addition of the antioxidant ascorbic acid improves sulfide recoveries. The method is applicable at sulfide concentrations between 0.002 and 0.100 mg/L.

Potentiometric methods utilizing a silver electrode (G) may be suitable. From the potential of the electrode relative to a reference electrode an estimate can be made of the sulfide concentration, but careful attention to details of procedures and frequent standardizations are needed to secure good results. The electrode is useful particularly as an end-point indicator for titration of dissolved sulfide with silver nitrate. The ion-selective electrode method is unaffected by sample color or turbidity and is applicable for concentrations greater than 0.03 mg/L.

6. Preparation of Sulfide Standards

Take care in preparing reliable stock solutions of sulfide for calibration and quality control. Prepare sulfide standards from sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$) crystals. These crystals usually have excess water present on the surface, in addition to a layer of contamination from oxidation products (polysulfides, polythionates, and sulfate) of sulfide reacting with atmospheric oxygen. Further, solutions of sulfide are prone to ready oxidation by dissolved and atmospheric oxygen. Use reagent water to prepare sulfide standards and sample dilutions. Boil and degas with either argon or nitrogen while cooling. Purchase the smallest amount of solid standards possible and keep no longer than 1 year. Preferably handle and store solid sulfide standards and stock solutions in an inert atmosphere glove bag or glove box to reduce contamination due to oxidation.

Preferably remove single crystals of $Na_2S{\cdot}9H_2O$ from reagent bottle with nonmetallic tweezers; quickly rinse in degassed reagent water to remove surface contamination. Blot crystal dry with a tissue, then rapidly transfer to a tared, stoppered weighing bottle containing 5 to 10 mL degassed reagent water. Repeat procedure until desired amount of sodium sulfide is in weighing bottle. Determine amount of $Na_2S{\cdot}9H_2O$ in weighing bottle by difference, then multiply the weight by 0.133 to determine the amount of S^{2-}. Avoid excess agitation and mixing of the solution with atmospheric oxygen. Quantitatively transfer and dilute entire contents of weighing bottle to an appropriate size volumetric flask with degassed reagent water to prepare a known concentration sulfide stock solution (3.750 g $Na_2S{\cdot}9H_2O$ diluted to a final volume of 500 mL will give a stock solution of which 1.00 mL = 1.00 mg S^{2-}). Alternatively, purchase precertified stock solutions of sulfide. Verify concentration of stock solution daily using the iodometric method (F). Store stock solution with minimum headspace for no more than 1 week.

7. Bibliography

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4500-S^{2-} B. Separation of Soluble and Insoluble Sulfides

Unless the sample is entirely free from suspended solids (dissolved sulfide equals total sulfide), to measure dissolved sulfide first remove insoluble matter. This can be done by producing an aluminum hydroxide floc that is settled, leaving a clear supernatant for analysis.

1. Apparatus

Glass bottles with stoppers: Use 100 mL if sulfide will be determined by the methylene blue method and 500 to 1000 mL if by the iodometric method.

2. Reagents

a. Sodium hydroxide solution, NaOH, 6*N*.

b. Aluminum chloride solution: Because of the hygroscopic and caking tendencies of this chemical, purchase 100-g bottles of $AlCl_3 \cdot 6H_2O$. Dissolve contents of a previously unopened 100-g bottle in 144 mL distilled water.

3. Procedure

a. To a 100-mL glass bottle add 0.2 mL (nominally 4 drops) 6*N* NaOH. Fill bottle with sample and immediately add 0.2 mL (4 drops) $AlCl_3$ solution. Stopper bottle with no air under stopper. Rotate back and forth about a transverse axis vigorously for 1 min or longer to flocculate contents. Vary volumes of these added chemicals to get good clarification without using excessively large amounts and to produce a pH of 6 to 9. If a 500- or 1000-mL bottle is used, add proportionally larger amounts of reagents.

b. Let settle until reasonably clear supernatant can be drawn off. With proper flocculation, this may take 5 to 15 min. Do not wait longer than necessary.

c. Either analyze the supernatant immediately or preserve with 2*N* zinc acetate (see Section 4500-S^{2-}.C).

4500-S^{2-} C. Sample Pretreatment to Remove Interfering Substances or to Concentrate the Sulfide

The iodometric method suffers interference from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds, both solid and dissolved.

Strong reducing agents also interfere in the methylene blue method (D) by preventing formation of the blue color. Thiosulfate at concentrations about 10 mg/L may retard color formation or completely prevent it. Ferrocyanide produces a blue color. Sulfide itself prevents the reaction if its concentration is very high, in the range of several hundred milligrams per liter. To avoid the possibility of false negative results, use the antimony

method to obtain a qualitative result in industrial wastes likely to contain sulfide but showing no color by the methylene blue method. Iodide, which is likely to be present in oil-field wastewaters, may diminish color formation if its concentration exceeds 2 mg/L. Many metals (e.g., Hg, Cd, Cu) form insoluble sulfides and give low recoveries.

Eliminate interferences due to sulfite, thiosulfate, iodide, and many other soluble substances, but not ferrocyanide, by first precipitating ZnS, removing the supernatant, and replacing it with distilled water. Use the same procedure, even when not needed for removal of interferences, to concentrate sulfide. The automated methylene blue method (E) is relatively free from interferences because gas dialysis separates the sulfide from the sample matrix.

1. Apparatus

Glass bottles with stoppers: See Section 4500-S^{2-}.B.1.

2. Reagents

a. Zinc acetate solution: Dissolve 220 g $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in 870 mL water; this makes 1 L solution.

b. Sodium hydroxide solution, NaOH, 6*N*.

3. Procedure

a. Put 0.20 mL (4 drops) zinc acetate solution and 0.10 mL (2 drops) 6*N* NaOH into a 100-mL glass bottle, fill with sample, and add 0.10 mL (2 drops) 6*N* NaOH solution. Stopper with no air bubbles under stopper and mix by rotating back and forth vigorously about a transverse axis. For the iodometric procedure, use a 500-mL bottle or other convenient size, with proportionally larger volumes of reagents. Vary volume of reagents added according to sample so that the resulting precipitate is not excessively bulky and settles readily. Add enough NaOH to raise the pH above 9. Let precipitate settle for 30 min. The treated sample is relatively stable and can be held for several hours. However, if much iron is present, oxidation may be fairly rapid.

b. If the iodometric method is to be used, collect precipitate on a glass fiber filter and continue at once with titration according to the procedure of Method F. If the methylene blue method (D) is used, let precipitate settle for 30 min and decant as much supernatant as possible without loss of precipitate. Refill bottle with distilled water, shake to resuspend precipitate, and quickly withdraw a sample. If interfering substances are present in high concentration, settle, decant, and refill a second time. If sulfide concentration is known to be low, add only enough water to bring volume to one-half or one-fifth of original volume. Use this technique for analyzing samples of very low sulfide concentrations. After determining the sulfide concentration colorimetrically, multiply the result by the ratio of final to initial volume. No concentration or pretreatment steps to remove interferences are necessary for Method E.

4500-S^{2-} D. Methylene Blue Method

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1. Apparatus

a. Matched test tubes, approximately 125 mm long and 15 mm OD.

b. Droppers, delivering 20 drops/mL methylene blue solution. To obtain uniform drops hold dropper in a vertical position and let drops form slowly.

c. If photometric rather than visual color determination will be used, either:

1) *Spectrophotometer,* for use at a wavelength of 664 nm with cells providing light paths of 1 cm and 1 mm, or other path lengths, or

2) *Filter photometer,* with a filter providing maximum transmittance near 660 nm.

2. Reagents

a. Amine-sulfuric acid stock solution: Dissolve 27 g *N,N*-dimethyl-*p*-phenylenediamine oxalate*#(2) in an iced mixture of 50 mL conc H_2SO_4 and 20 mL distilled water. Cool and dilute to 100 mL with distilled water. Use fresh oxalate because an old supply may be oxidized and discolored to a degree that results in interfering colors in the test. Store in a dark glass bottle. When this stock solution is diluted and used in the procedure with a sulfide-free sample, it first will be pink but then should become colorless within 3 min.

b. Amine-sulfuric acid reagent: Dilute 25 mL amine-sulfuric acid stock solution with 975 mL 1 + 1 H_2SO_4. Store in a dark glass bottle.

c. Ferric chloride solution: Dissolve 100 g $FeCl_3 \cdot 6H_2O$ in 40 mL water.

d. Sulfuric acid solution, H_2SO_4, 1 + 1.

e. Diammonium hydrogen phosphate solution: Dissolve 400 g $(NH_4)_2HPO_4$ in 800 mL distilled water.

f. Methylene blue solution I: Use USP grade dye or one certified by the Biological Stain Commission. The dye content should be reported on the label and should be 84% or more. Dissolve 1.0 g in distilled water and make up to 1 L. This solution will be approximately the correct strength, but because of variation between different lots of dye, standardize against sulfide solutions of known strength and adjust its concentration so that 0.05 mL (1 drop) = 1.0 mg sulfide/L.

Standardization—Prepare five known-concentration sulfide standards ranging from 1 to 8 mg/L as described in 4500-S^{2-}.A.6, or proceed as follows: Put several grams of clean, washed crystals of $Na_2S \cdot 9H_2O$ into a small beaker. Add somewhat less than enough water to cover crystals. Stir occasionally for a few minutes, then pour solution into another vessel. This solution reacts slowly with oxygen but the change is insignificant if analysis is performed within a few hours. Prepare solution daily. To 1 L distilled water add 1 drop of Na_2S solution and mix. Immediately determine sulfide concentration by the methylene blue procedure and by the iodometric procedure. Repeat, using more than 1 drop Na_2S solution or smaller volumes of water, until at least five tests have been made, with a range of sulfide concentrations between 1 and 8 mg/L. Calculate average percent error of the methylene blue result as compared to the iodometric result. If the average error is negative, that is, methylene

blue results are lower than iodometric results, dilute methylene blue solution by the same percentage, so that a greater volume will be used in matching colors. If methylene blue results are high, increase solution strength by adding more dye.

g. Methylene blue solution II: Dilute 10.00 mL of adjusted methylene blue solution I to 100 mL with reagent water.

3. Procedure

a. Color development: Transfer 7.5 mL sample to each of two matched test tubes, using a special wide-tip pipet or filling to marks on test tubes. If sample has been preserved with zinc acetate, shake vigorously before taking subsample. Add to Tube A 0.5 mL amine-sulfuric acid reagent and 0.15 mL (3 drops) $FeCl_3$ solution. Mix immediately by inverting slowly, only once. (Excessive mixing causes low results by loss of H_2S as a gas before it has had time to react). To Tube B add 0.5 mL 1 + 1 H_2SO_4 and 0.15 mL (3 drops) $FeCl_3$ solution and mix. The presence of S^{2-} will be indicated by the appearance of blue color in Tube A. Color development usually is complete in about 1 min, but a longer time often is required for fading out of the initial pink color. Wait 3 to 5 min and add 1.6 mL $(NH_4)_2HPO_4$ solution to each tube. Wait 3 to 15 min and make color comparisons. If zinc acetate was used, wait at least 10 min before making a visual color comparison.

b. Color determination:

1) Visual color estimation—Add methylene blue solution I or II, depending on sulfide concentration and desired accuracy, dropwise, to the second tube, until color matches that developed in first tube. If the concentration exceeds 20 mg/L, repeat test with a portion of sample diluted tenfold.

With methylene blue solution I, adjusted so that 0.05 mL (1 drop) = 1.0 mg S^{2-}/L when 7.5 mL of sample are used:

$$\text{mg } S^{2-}/L = \text{no. drops solution I} + 0.1\ (\text{no. drops solution II})$$

2) Photometric color measurement—A cell with a light path of 1 cm is suitable for measuring sulfide concentrations from 0.1 to 2.0 mg/L. Use shorter or longer light paths for higher or lower concentrations. This method is suitable for sample concentrations up to 20 mg/L. Zero instrument with a portion of treated sample from Tube B. Prepare calibration curves on basis of colorimetric tests made on Na_2S solutions simultaneously analyzed by the iodometric method, plotting concentration vs. absorbance. A linear relationship between concentration and absorbance can be assumed from 0 to 1.0 mg/L.

Read sulfide concentration from calibration curve.

4. Precision and Bias

In a study by two chemists working in the same laboratory, the standard deviation estimated from 34 sets of duplicate sulfide measurements was 0.04 mg/L for concentrations between 0.2 and 1.5 mg/L. The average recoveries of known additions were 92% for 40 samples containing 0.5 to 1.5 mg/L and 89% for samples containing less than 0.1 mg/L.

5. Bibliography

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4500-S^{2-} E. Gas Dialysis, Automated Methylene Blue Method

1. Apparatus

a. Automated analytical equipment: An example of the continuous-flow analytical instrument consists of the interchangeable components shown in Figure 4500-S^{2-}:2.

The sampler is equipped with a mixer to stir samples before analysis and the gas dialysis membrane, which is maintained at room temperature, separates H_2S from the sample matrix.

2. Reagents

a. N,N-*dimethyl*-p-*phenylenediamine stock solution:* Dissolve 1 g *N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride in 500 mL 6*N* HCl. Prepare fresh monthly. Store in an amber bottle.

b. N,N-*dimethyl*-p-*phenylenediamine working solution:* Dilute 190 mL *N*,*N*-dimethyl-*p*-phenylenediamine stock solution to 1 L. Store in an amber bottle. Prepare weekly.

c. Ferric chloride stock solution: Dissolve 13.5 g $FeCl_3 \cdot 6H_2O$ in 500 mL 5*N* HCl. Store in an amber bottle. Prepare fresh monthly.

d. Working ferric chloride solution: Dilute 190 mL ferric chloride stock solution to 1 L. Store in an amber bottle. Prepare fresh weekly.

e. Hydrochloric acid, HCl, 6*N*:

f. Sodium hydroxide stock solution, NaOH, 1*N*.

g. Sodium hydroxide, NaOH, 0.01*N*: Dilute 10 mL NaOH stock solution to 1 L.

h. Sulfide stock solution, 1.00 mg S^{2-}/1.00 mL: See Section 4500-S^{2-}.A.6.

i. Sulfide intermediate standard solution: Dilute 10 mL sulfide stock solution to 1 L with water. Prepare fresh daily. Standardize by iodometric titration method, Section 4500-S^{2-}.F. 1 mL $\approx$ 0.01 mg S^{2-}.

j. Sulfide tertiary standard solution: Dilute 50 mL sulfide intermediate solution to 500 mL with 0.01*N* NaOH. Prepare fresh daily. Use standardization value from ¶ 2*i* to determine exact concentration. 1.00 mL $\approx$ 0.001 mg S^{2-}.

k. Working sulfide standard solutions: Prepare a suitable series of standards by diluting appropriate volumes of sulfide tertiary standing solutions with 0.01*N* NaOH. Prepare fresh daily.

l. Zinc acetate preservative solution: Dissolve 220 g $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in 870 mL

water (this makes 1 L solution).

3. Procedure

For unpreserved, freshly collected samples and sulfide working standards, add, in order, 4 drops 2*N* zinc acetate, 0.5 mL 6*N* NaOH, and 400 mg ascorbic acid/100 mL. For preserved samples, add 0.5 mL 6*N* NaOH and 400 mg ascorbic acid/100 mL. Shake well.

Let precipitate settle for at least 30 min. Pour a portion of well-mixed sample or working standard into a sample cup. Set up manifold as shown in Figure 4500-S^{2-}:2 and follow the general procedure described by the manufacturer. Determine absorbance at 660 nm.

4. Calculation

Prepare standard curves by plotting peak heights of standards processed through the manifold against S^{2-} concentration in the standards. Compute S^{2-} sample concentration by comparing sample response with standard curve.

5. Precision and Bias

In a single laboratory, samples with S^{2-} concentrations of 0.012, 0.015, 0.034, and 0.085 mg/L had standard deviations of 0.001, 0.001, 0.001, and 0.001 mg/L, respectively, with coefficients of variation of 8.3%, 6.3%, 2.9%, and 1.2%, respectively. In two environmental samples with added S^{2-}, recoveries were 104.2% and 97.6%.

6. Bibliography

FRANCOM, D., L.R. GOODWIN & F.P. DIEKEN. 1989. Determination of low level sulfides in environmental waters by automated gas dialysis/methylene blue colorimetry. *Anal. Lett.* 22:2587.

4500-S^{2-} F. Iodometric Method

1. Reagents

a. Hydrochloric acid, HCl, 6*N*.

b. Standard iodine solution, 0.0250*N*: Dissolve 20 to 25 g KI in a little water and add 3.2 g iodine. After iodine has dissolved, dilute to 1000 mL and standardize against 0.0250*N* $Na_2S_2O_3$, using starch solution as indicator.

c. Standard sodium thiosulfate solution, 0.0250*N*: See Section 4500-O.C.2*e*.

d. Starch solution: See Section 4500-O.C.2*d*.

2. Procedure

a. Measure from a buret into a 500-mL flask an amount of iodine solution estimated to be an excess over the amount of sulfide present. Add distilled water, if necessary, to bring volume to about 20 mL. Add 2 mL 6*N* HCl. Pipet 200 mL sample into flask, discharging sample under solution surface. If iodine color disappears, add more iodine until color remains. Back-titrate with $Na_2S_2O_3$ solution, adding a few drops of starch solution as end

point is approached, and continuing until blue color disappears.

b. If sulfide was precipitated with zinc and ZnS filtered out, return filter with precipitate to original bottle and add about 100 mL water. Add iodine solution and HCl and titrate as in ¶ 2*a* above.

3. Calculation

One milliliter 0.0250*N* iodine solution reacts with 0.4 mg S^{2-}:

$$\text{mg } S^{2-}/\text{L} = \frac{[(A \times B) - (C \times D)] \times 16\,000}{\text{mL sample}}$$

where:

A = mL iodine solution,
B = normality of iodine solution,
C = mL $Na_2S_2O_3$ solution, and
D = normality of $Na_2S_2O_3$ solution.

4. Precision

The precision of the end point varies with the sample. In clean waters it should be determinable within 1 drop, which is equivalent to 0.1 mg/L in a 200-mL sample.

4500-S^{2-} G. Ion-Selective Electrode Method

1. General Discussion

a. Principle: The potential of a silver/sulfide ion-selective electrode (ISE) is related to the sulfide ion activity. An alkaline antioxidant reagent (AAR) is added to samples and standards to inhibit oxidation of sulfide by oxygen and to provide a constant ionic strength and pH. Use of the AAR allows calibration in terms of total dissolved sulfide concentration. All samples and standards must be at the same temperature. Sulfide concentrations between 0.032 mg/L ($1 \times 10^{-6}M$) and 100 mg/L can be measured without preconcentration. For lower concentrations, preconcentration is necessary.

b. Interferences: Humic substances may interfere with Ag/S-ISE measurements. For highly colored water (high concentration of humic substances), use the method of standard additions to check results. Sulfide is oxidized by dissolved oxygen. Sulfide oxidation may cause potential readings to drift in the direction of decreasing concentration, i.e., to more positive values. Flush surface of samples and standards with nitrogen to minimize contact with atmospheric oxygen for low-level measurements. Temperature changes may cause potentials to drift either upward or downward. Therefore, let standards and samples come to the same temperature. If samples cannot be analyzed immediately, preserve dissolved sulfide by precipitating with zinc acetate (Section 4500-S^{2-}.C).

2. Apparatus

*a. Silver/sulfide electrode:**#(3)

b. Double-junction reference electrode.

c. Electrode polishing strips.†#(4)

d. pH meter with millivolt scale, capable of 0.1-mV resolution. Meters that can be calibrated in concentration and that perform standard-additions calculations are available.

e. Electrochemical cell: Make suitable cell from a 150-mL beaker and a sheet of rigid plastic (PVC or acrylic) with holes drilled to allow insertion of the electrodes and a tube for flushing the headspace with nitrogen. Alternatively, purchase a polarographic cell with gas transfer tube.‡#(5)

f. Gas dispersion tube: Use to deaerate water for preparing reagents and standards.

g. Magnetic stirrer and stirring bar: Use a piece of styrofoam or cardboard to insulate the cell from the magnetic stirrer.

3. Reagents

a. Alkaline antioxidant reagent (AAR): To approximately 600 mL deaerated reagent water (DRW) in a 1-L volumetric flask, add 80 g NaOH, 35 g ascorbic acid, and 67 g Na_2H_2EDTA. Swirl to dissolve and dilute to 1 L. The color of freshly prepared AAR will range from colorless to yellow. Store in a tightly capped brown glass bottle. Discard when solution becomes brown.

b. Lead perchlorate, 0.1*M:* Dissolve 4.60 g $Pb(ClO_4)_2 \cdot 3H_2O$ in 100 mL reagent water. Standardize by titrating with Na_2H_2EDTA. Alternatively, use commercially available 0.1*M* $Pb(ClO_4)_2$ solutions.

c. Sulfide stock solution, 130 mg/L: See 4500-S^{2-}.A.6, and dilute 13.0 mL of 1.00 mg S^{2-}/mL stock to 100.0 mL with AAR. Alternatively, add 500 mL AAR and 10 g $Na_2S \cdot 9H_2O$ to a 1-L volumetric flask; dissolve. Dilute to 1 L with DRW. Use deaerated artificial seawater (DASW), Table 8010:III, or 0.7*M* NaCl if sulfide concentrations are to be determined in seawater. Standardize stock solution by titrating with 0.1*M* $Pb(ClO_4)_2$. Pipet 50 mL sulfide stock solution into the electrochemical cell. (Use 10 mL with a small-volume polarographic cell.) Insert Ag/S electrode and reference electrode and read initial potential. Titrate with 0.1*M* $Pb(ClO_4)_2$. Let electrode potential stabilize and record potential after each addition. Locate equivalence point as in Section 4500-Cl^-.D.4*a*. Alternatively, linearize the titration curve.[1] Calculate the function F_1 for points before the equivalence point.

$$F_1 = (V_o + V)10^{\frac{E}{m}}$$

where:

V_o = volume of stock solution, mL,

V = titrant volume, mL,
E = potential, mV, and
m = slope of calibration curve, mV/log unit.

Plot F_1 as a function of titrant volume. Extrapolate to find the intersection with the x-axis; that is, the equivalence point. Calculate sulfide concentration in the stock solution from:

$$C = \frac{V_{eq}[Pb]}{V_o}$$

where:

C = sulfide concentration, mg/L,
V_{eq} = equivalence volume, mL,
$[Pb]$ = concentration of Pb in titrant, mg/L, and
V_o = volume of stock solution, mL.

Store stock solution in a tightly capped bottle for 1 week or less. The stock solution also can be standardized iodometrically (see Section 4500-S^{2-}.E). CAUTION: *Store in a fume hood.*

d. Sulfide standards: Prepare sulfide standards daily by serial dilution of stock. Add AAR and $Zn(C_2H_3O_2)_2$ solutions to 100-mL volumetric flasks. Add sulfide solutions and dilute to volume with DRW (or DASW). Refer to Table 4500-S^{2-}:I for volumes. Prepare at least one standard with a concentration less than the lowest sample concentration.

4. Procedure

Check electrode performance and calibrate daily. Check electrode potential in a sulfide standard every 2 h. The procedure depends on the sulfide concentration and the time between sample collection and sulfide determination. If the total sulfide concentration is greater than 0.03 mg/L ($1 \times 10^{-6}M$) and the time delay is only a few minutes, sulfide can be determined directly. Otherwise, precipitate ZnS and filter as described in Section 4500-S^{2-}.C.

a. Check electrode performance: Pipet 50 mL AAR, 50 mL DWR, and 1 mL sulfide stock solution into the measurement cell. Place Ag/S and reference electrodes in the solution and read potential. Add 10 mL stock solution and read potential. The change in potential should be -28 ± 2 mV. If it is not, follow the troubleshooting procedure in the electrode manual.

b. Calibration: Place electrodes in the most dilute standard but use calibration standards that bracket the sulfide concentrations in the samples. Record potential when the rate of change is less than 0.3 mV/min. (This may take up to 30 min for very low sulfide

concentrations, i.e., less than 0.03 mg/L.) Rinse electrodes, blot dry with a tissue, and read potential of the next highest standard. For a meter that can be calibrated directly in concentration, follow manufacturer's directions. For other meters, plot potential as a function of the logarithm (base 10) of the sulfide concentration. For potentials in the linear range, calculate the slope and intercept of the linear portion of the calibration plot.

c. Sulfide determination by comparison with calibration curve, no ZnS precipitation: Add 40 mL AAR, 0.15 mL (3 drops) zinc acetate, and 50 mL sample to a 100-mL volumetric flask. Dilute to 100 mL with AAR. Pour into the electrochemical cell and insert the electrodes. Record potential when the rate of change is less than 0.3 mV/min. Read sulfide concentration from the calibration curve. Alternatively, for potentials in the linear range, calculate the sulfide concentration from:

$$S_{Tot} = 10^{\frac{E-b}{m}}$$

where:

E = electrode potential and

b and m are the intercept and slope of the calibration curve. For a meter that can be calibrated directly in concentration, follow the manufacturer's directions.

d. Sulfide determination by comparison with calibration curve, with ZnS precipitation: Place filter with ZnS precipitate in a 150-mL beaker containing a stir bar. Wash sample bottle with 50 mL AAR and 20 mL DRW and pour the washings into the beaker. Stir to dissolve precipitate. Remove filter with forceps while rinsing it into the beaker with a minimum amount of DRW. Quantitatively transfer to a 100-mL volumetric flask and dilute to mark with DRW. Pour into the electrochemical cell and place the electrodes in the solution. Measure potential as in ¶ 4*c* above. Calculate sulfide concentration (¶ 4*c*).

e. Sulfide determination by standard addition with or without ZnS precipitation: Measure the Ag/S-ISE electrode potential as in ¶ c or *d* above. Add sulfide stock solution and measure potential again. Calculate sulfide concentration as follows:

$$C_o = \frac{fC_s}{(1+f)10^{\frac{E_1-E_o}{m}} - 1}$$

where:

C_o and C_s = sulfide concentrations in sample and known addition,

E_o and E_s = potentials measured for sample and known addition,

m = slope of calibration curve (approximately 28 mV/log S^{2-}, and

f = ratio of known-addition volume to sample volume.

f. Sulfide determination by titration: Use the same procedure as for standardizing the

sulfide stock solution (¶ 3*c*). The minumum sulfide concentration for determination by titration is 0.3 mg/L ($10^{-5}M$).

5. Precision

For sulfide determination by comparison with the calibration curve, the relative standard deviation varies with the sulfide concentration. RSD values of 23% for 0.0091 mg/L and 5% for 0.182 mg/L have been reported.[2] (0.0091 µg/L was below the range for which the potential varied linearly with the logarithm of the sulfide concentration, i.e., the Nernstian range.) For sulfide determination by standard addition, the precision is greatest if the amount of sulfide added is as large as possible while staying within the linear range.[3]

6. References

1. GRAN, G. 1952. Determination of the equivalence point in potentiometric titrations. Part II. *Analyst* 77:661.
2. BAUMANN, E. 1974. Determination of parts per billion sulfide in water with the sulfide-selective electrode. *Anal. Chem.* 46:1345.
3. RATZLAFF, K.L. 1979. Optimizing precision in standard addition measurement. *Anal. Chem.* 51:232.

7. Bibliography

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VIVIT, D.V., J.W. BALL & E.A. JENNE. 1984. Specific-ion electrode determinations of sulfide preconcentrated from San Francisco Bay waters. *Environ. Geol. Water Sci.* 6:79.

4500-S^{2-} H. Calculation of Un-ionized Hydrogen Sulfide

Hydrogen sulfide (H_2S) and bisulfide ion (HS^-), which together constitute dissolved sulfide, are in equilibrium with hydrogen ions:

$$H_2S \rightleftharpoons H^+ + HS^-$$

The conditional ionization constant, which is valid for the temperature and ionic strength of the water of interest, relates the concentrations of H_2S and HS^-:

$$K_1' = \frac{[H^+]\,[HS^-]}{[H_2S]}$$

The conditional constant is used to calculate the distribution of dissolved sulfide between the two species. The conditional ionization constant of H_2S is approximately 7.0. It differs from 7.0 by less than 0.2 log units for the ionic strengths and temperatures likely to be

encountered in water-quality monitoring. The fraction of sulfide present as H_2S can be estimated with an error of less than 40% from Figure 4500-S^{2-}:3. If more accuracy is needed, use the methods given below.

1. Calculation for Fresh Water and Brackish Water (I < 0.1M)

Calculate the dissociation constant for zero ionic strength (pK_1) and the temperature of interest.[1] If the temperature is 25°C, then pK_1 is 6.98. Otherwise:

$$pK_1\,(T) = 32.55 + 1519.44/T - 15.672\log_{10}T + 0.02722T$$

where T is temperature (°K, i.e., T °C + 273.15). Next, calculate the ionic strength I as in Table 2330:I, the Debye-Huckel A parameter, and the negative logarithm of the monovalent ion activity coefficient (pf_m):

$$A = 0.7083 - 2.277 \times 10^{-3}T + 5.399 \times 10^{-6}T^2$$

$$A = 0.7083 - 2.277 \times 10^{-3}T + 5.399 \times 10^{-6}T^2$$

$$pf_m = A\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right)$$

Calculate the conditional ionization constant, K'_1, and the hydrogen ion concentration, $[H^+]$:

$$K'_1 = 10^{-pK_1+2\,pf_m}$$
$$[H^+] = 10^{-pH+\,pf_m}$$

Finally, calculate the un-ionized hydrogen sulfide concentration, $[H_2S]$, from the total sulfide concentration, S_T:

$$[H_2S] = \frac{S_T}{1 + \frac{K'_1}{[H^+]}}$$

Sample calculation: Total sulfide concentration 0.32 mg/L ($1.0 \times 10^{-5}M$), pH 6.75, ionic strength 0.02M, temperature 15.5°C.

$$pK_1 = 32.55 \times \frac{1519.44}{288.65} - 15.672 \times \log_{10}(288.65) + 0.02722 \times 288.65 = 7.11$$

$$A = 0.7083 - 2.277 \times 10^{-3} \times 288.65 + 5.399 \times 10^{-6} \times (288.65)^2 = 0.501$$

$$pf_m = 0.501 \times \left(\frac{\sqrt{0.02}}{1 + \sqrt{0.02}} - 0.3 \times 0.02\right) = 0.059$$

$$K_1' = 10^{-7.11 + 2 \times 0.059} = 1.014 \times 10^{-7}$$

$$[H^+] = 10^{-6.75 + 0.059} = 2.037 \times 10^{-7}$$

$$[H_2S] = \frac{1 \times 10^{-5}}{1 + \frac{1.014 \times 10^{-7}}{2.037 \times 10^{-7}}} = 6.68 \times 10^{-6} M = 0.21 \text{ mg/L (as S)}$$

2. Calculation for Seawater and Estuarine Water

This procedure differs only in calculating the conditional ionization constant, which can be calculated accurately.[1] The (potentially) largest source of error in calculating un-ionized hydrogen sulfide in seawater is the hydrogen ion concentration. Calibrate the pH electrode in artificial seawater at the temperature of the water of interest.[2] Alternatively, if the pH electrode is calibrated using NIST buffers (as in Section 4500-H), measure pH of dilute acid (10^{-4}–10^{-3}*N* HNO_3, HCl, or $HClO_4$) in artificial seawater diluted to the salinity of the water of interest and at the temperature of interest and calculate a correction factor.[3] (Prepare artificial seawater as in Table 8010:III, substituting NaCl for NaF, $NaHCO_3$, and $Na_2SiO_3 \cdot 9H_2O$ on an equimolar basis.)

Calculate pK'_1 as outlined in Section 4500-S^{2-}.H.1. Calculate the coefficients *A* and *B*[1] (*A* and *B* are not Debye-Huckel parameters):

$$A = -0.2391 + \frac{35.685}{T}$$

$$B = 0.0109 - \frac{0.3776}{T}$$

Calculate pK'_1:

$$pK'_1 = pK_1 + A\sqrt{S} + BS$$

where:

S = salinity, g/kg.

Calculate K'_1:

$$K'_1 = 10^{-pK'_1}$$

Sample calculation: Total sulfide concentration 0.32 mg/L ($1 \times 10^{-5}M$), pH 6.75, salinity 35 g/kg ($I = 0.7M$), temperature 15.5°C.

$$A = -0.2391 + \frac{35.685}{288.65}$$

$$= -0.115$$

$$B = 0.0109 - \frac{0.3776}{288.65}$$

$$= 0.009\,59$$

From 4500-S^{2-}.H.1, $pK_1 = 7.11$.

$$pK_1' = 7.11 - 0.115\sqrt{35} + 0.00959 \times 35$$
$$= 6.77$$

$$K_1' = 10^{-6.77}$$
$$= 1.70 \times 10^{-7}$$

$$pf_m = 0.501 \times \left(\frac{\sqrt{0.7}}{1 + \sqrt{0.7}} - 0.3 \times 0.7\right)$$
$$= 0.12$$

$$[H^+] = 10^{-6.75+0.12}$$
$$= 2.34 \times 10^{-7}$$

$$[H_2S] = \frac{1 \times 10^{-5}}{1 + \frac{1.7 \times 10^{-7}}{2.3 \times 10^{-7}}}$$
$$= 5.8 \times 10^{-6} M$$
$$= 0.19 \text{ mg/L (as S)}$$

3. References

1. MILLERO, F.J. 1986. The thermodynamics and kinetics of the hydrogen sulfide system in natural waters. *Mar. Chem.* 18:121.
2. MILLERO, F.J. 1986. The pH of estuarine waters. *Limnol. Oceanogr.* 31 :839.
3. SIGEL, H., A.D. ZUBERBUHLER & O. YAMAUCHI. 1991. Comments on potentiometric pH titrations and the relationship between pH-meter reading and hydrogen ion concentration. *Anal. Chim. Acta.* 255:63.

4. Bibliography

ARCHER, D.G. & P. WANG. 1990. The dielectric constant of water and Debye-Huckel Limiting Law Slopes. *J. Phys. Chem. Ref. Data* 12: 817.

4500-S^{2-} I. Distillation, Methylene Blue Flow Injection Analysis (PROPOSED)

1. General Discussion

a. Principle: Water and wastewater samples are distilled into a sodium hydroxide

trapping solution and the distillate is analyzed. Hydrogen sulfide (H_2S) reacts in acid media and in the presence of ferric chloride with two molecules of *N*, *N*-dimethyl-*p*-phenylenediamine to form methylene blue. The resulting color is read at 660 nm.

b. Sample preservation: Because H_2S oxidizes rapidly, analyze samples and standards without delay. To preserve samples, add 4 drops 2*M* zinc acetate to 100 mL sample and adjust pH to >9 with 6*M* NaOH, then cool to 4°C. Samples are distilled into a trapping solution resulting in 0.25*M* NaOH matrix.

Also see Section 4500-S^{2-}.A, Section 4500-S^{2-}.B, and Section 4500-S^{2-}.E, and Section 4130, Flow Injection Analysis (FIA).

c. Interferences: This method measures total sulfide, which is defined as the acid-soluble sulfide fraction of a sample. Total sulfide includes both acid-soluble sulfides such as H_2S, and acid-soluble metal sulfides present in suspended matter. This method does not measure acid-insoluble sulfides such as CuS.

Most nonvolatile interferences are eliminated by distillation. Strong reducing agents inhibit color formation at concentrations of several hundred milligrams per liter. Iodide interferes at concentrations greater than 2 mg I/L.

Also see Section 4500-S^{2-}.A and Section 4500-S^{2-}.B.

2. Apparatus

a. Distillation apparatus consisting of a glass or polypropylene micro-distillation device*#(6) capable of distilling 6 mL or more of sample into a 0.25*M* NaOH final concentration trapping solution.

b. Flow injection analysis equipment consisting of:

1) *FIA injection valve* with sample loop or equivalent.

2) *Multichannel proportioning pump.*

3) *FIA manifold* (Figure 4500-S^{2-}:4) with cation exchange column and flow cell.

Relative flow rates only are shown in Figure 4500-S^{2-}:4. Tubing volumes are given as an example only; they may be scaled down proportionally. Use manifold tubing of an inert material such as TFE.

4) *Absorbance detector,* 660 nm, 10-nm bandpass.

5) *Injection valve control and data acquisition system.*

3. Reagents

Use reagent water (>10 megohm) for all solutions. To prevent bubble formation, degas carrier and buffer with helium. Pass He at 140 kPa (20 psi) through a helium degassing tube. Bubble He through 1 L solution for 1 min.

a. Sodium hydroxide carrier and diluent, NaOH, 0.25*M*: In a 2-L volumetric flask, dissolve 20 g NaOH in approximately 1800 mL water. Dilute to mark and mix with a magnetic stirrer until dissolved. Store in a plastic container.

b. Hydrochloric acid, HCl, 3*M*: To a tared 1-L container, add 752 g water and then slowly add 295 g conc HCl. Invert to mix.

c. Hydrochloric acid, HCl, 0.20*M*: To a tared 1-L container, add 983.5 g water. Then add 19.7 g conc HCl. Invert to mix.

d. N,N-*dimethyl*-p-*phenylenediamine:* In a 1-L volumetric flask dissolve 1.0 g *N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride, $(CH_3)_2NC_6H_4NH_2 \cdot 2HCl$, in about 800 mL 3*M* HCl (¶ 3*b*). Dilute to mark and invert to mix. If solution appears dark, it is likely that the *N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride is decomposed; discard, and use fresh reagent.

e. Ferric chloride: In a 500-mL volumetric flask dissolve 6.65 g ferric chloride hexahydrate, $FeCl_3 \cdot 6H_2O$, in about 450 mL 0.20*M* HCl (¶ 3*c*). Dilute to mark with water and invert to mix.

f. Stock sulfide standard, 100 mg S^{2-}/L: In a 1-L volumetric flask dissolve 0.7491 g sodium sulfide nonahydrate, $Na_2S \cdot 9H_2O$, in approximately 900 mL NaOH diluent (¶ 3*a*). Dilute to mark and invert to mix.

g. Standard solutions: Prepare sulfide standards in desired concentration range, using stock standard (¶ 3 *f*), and diluting with NaOH diluent (¶ 3*a*).

h. Sulfuric acid distillation releasing solution, H_2SO_4, 9*M*: To a tared 500-mL container, add 150.0 g water, then add slowly while swirling, in increments of 40 g, 276 g conc H_2SO_4. CAUTION: *Solution will become very hot.* Allow to cool before using.

4. Procedure

a. Distillation: This procedure is designed for the determination of sulfides in aqueous solutions, solid waste materials, or effluents. To preserve and remove sulfide from interfering substances, distill samples immediately after collection.

Follow manufacturer's instructions for use of distillation apparatus. Add sufficient 9*M* H_2SO_4 (¶ 3*h*) to sample to dissolve ZnS (s), digest total sulfides, and release the sulfide as hydrogen sulfide gas. Immediately place sample on-line with the receiving vessel or collector tube and distill hydrogen sulfide and water in the sample into a 0.25*M* trapping solution.

b. Flow injection analysis: Set up a manifold equivalent to that in Figure 4500-S^{2-}:4 and follow method supplied by the manufacturer or laboratory standard operating procedure. The carrier concentration should be identical to the final concentration of NaOH in the trapping solution from the distillation procedure (¶ 4*a*). Follow quality control protocols outlined in Section 4020.

5. Calculations

Prepare standard curves by plotting absorbance of standards processed through the manifold versus sulfide concentration.

6. Precision and Bias

a. MDL: A 200-µL sample loop was used in the method described above. Using a

published method,[1] analysts ran 21 replicates of a 10.0-mg S^{2-}/L standard. These gave a mean of 9.0 mg S^{2-}/L, a standard deviation of 0.23 mg S^{2-}/L, and MDL of 0.58 mg S^{2-}/L. A higher MDL may be obtained by decreasing sample loop volume.

b. Precision: Ten injections of a distilled 50-mg S^{2-}/L standard gave a mean of 49.4 mg S^{2-}/L, a standard deviation of 0.27 mg S^{2-}/L, and percent relative standard deviation of 0.54.

7. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1984. Definition and procedure for the determination of method detection limits. Appendix B to 40 CFR 136 Rev. 1.11 amended June 30, 1986. 49 CFR 43430.

Standard Methods for the Examination of Water and Wastewater

Endnotes

1 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
2 (Popup - Footnote)
* Eastman catalog No. 5672 has been found satisfactory for this purpose.
3 (Popup - Footnote)
* Orion 941600 or equivalent.
4 (Popup - Footnote)
† Orion 948201 or equivalent.
5 (Popup - Footnote)
‡ EG&G Princeton Applied Research K0066, K0060, G0028, or equivalent.
6 (Popup - Footnote)
* Lachat Instruments MICRO DIST or equivalent.