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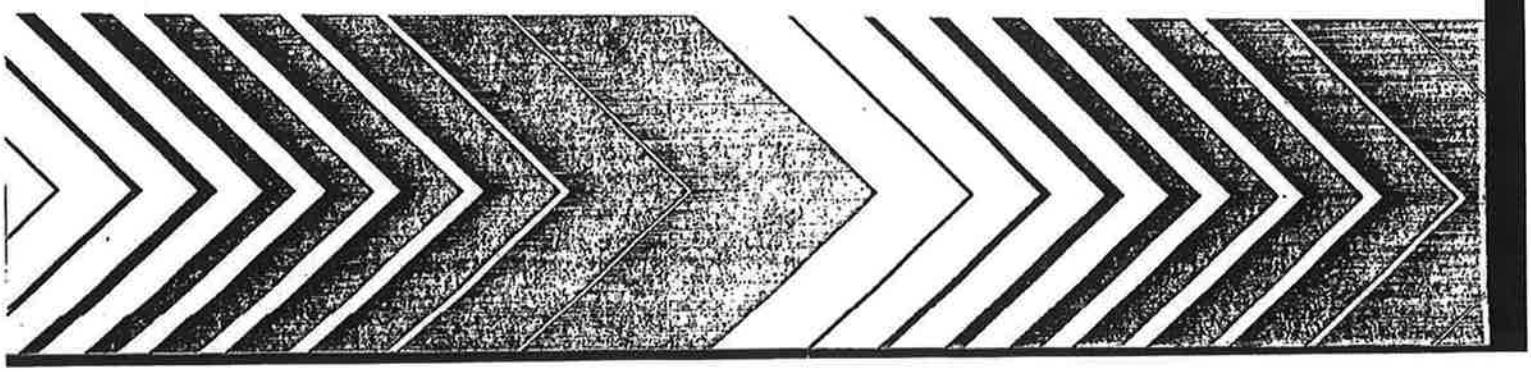
Methods for Chemical Analysis of Water and Wastes



SULFIDE

Method 376.2 (Colorimetric, Methylene Blue)

STORET NO. Total 00745
Dissolved 00746

1. Scope and Application
   1.1 This method is applicable to the measurement of total and dissolved sulfides in drinking, surface and saline waters, domestic and industrial wastes.
   1.2 Acid insoluble sulfides are not measured by this method. Copper sulfide is the only common sulfide in this class.
   1.3 The method is suitable for the measurement of sulfide in concentrations up to 20 mg/1.
2. Summary of Method
   2.1 Sulfide reacts with dimethyl-p-phenylenediamine (p-aminodimethyl aniline) in the presence of ferric chloride to produce methylene blue, a dye which is measured at a wavelength maximum of 625 nm.
3. Comments
   3.1 Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form. Dissolved oxygen should not be present in any water used to dilute standards.
   3.2 The analysis must be started immediately.
   3.3 Color and turbidity may interfere with observations of color or with photometric readings.
4. Apparatus
   4.1 Matched test tubes, approximately 125 mm long and 15 mm O.D.
   4.2 Droppers, delivering 20 drops/ml. To obtain uniform drops, hold dropper in vertical position and allow drops to form slowly.
   4.3 Photometer, use either 4.3.1 or 4.3.2.
      4.3.1 Spectrophotometer, for use at 625 nm with cells of 1 cm and 10 cm light path.
      4.3.2 Filter photometer, with filter providing transmittance near 625 nm.
5. Reagents
   5.1 Amino-sulfuric acid stock solution: Dissolve 27 g N,N-dimethyl-p-phenylenediamine oxalate (p-aminodimethylaniline) in a cold mixture of 50 ml conc. H_2SO_4 and 20 ml distilled water in a 100 ml volumetric flask. Cool and dilute to the mark. If dark discard and purchase fresh reagent. Store in dark glass bottle.
   5.2 Amino-sulfuric acid reagent: Dissolve 25 ml amino-sulfuric acid stock solution (5.1) with 975 ml of 1 + 1 H_2SO_4 (5.4). Store in a dark glass bottle. This solution should be clear.
   5.3 Ferric chloride solution: Dissolve 100 g $FeCl_3 \cdot 6H_2O$ in 40 ml distilled water.

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5.4 Sulfuric acid solution, H_2SO_4, 1+1

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

5.6 Methylene blue solution I: Dissolve 1.0 g of methylene blue in distilled water in a 1 liter volumetric flask and dilute to the mark. Use U.S.P. grade or one certified by the Biological Stain Commission. The dye content reported on the label should be 84% or more. Standardize (5.8) against sulfide solutions of known strength and adjust concentration so that 0.05 ml (1 drop) equals 1.0 mg/1 sulfide.

5.7 Methylene blue solution II: Dilute 10.00 ml of adjusted methylene blue solution I (5.6) to 100 ml with distilled water in a volumetric flask.

5.8 Standardization of methylene blue I solution:

5.8.1 Place several grams of clean, washed crystals of sodium sulfide $Na_2S{\cdot}9H_2O$ in a small beaker.

5.8.2 Add somewhat less than enough water to cover the crystals.

5.8.3 Stir occasionally for a few minutes. Pour the solution into another vessel. This reacts slowly with oxygen but the change is insignificnat over a few hours. Make the solution daily.

5.8.4 To 1 liter of distilled water add 1 drop of solution and mix.

5.8.5 Immediately determine the sulfide concentration by the methylene blue procedure (6) and by the titrimetric iodide procedure (Method 376.1, this manual).

5.8.6 Repeat using more than one drop of sulfide solution or less water until at least five tests have been made in the range of 1 to 8 mg/1 sulfide.

5.8.7 Calculate the average percent error of the methylene blue procedure (6) as compared to the titrimetric iodide procedure (Method 376.1).

5.8.8 Adjust by dilution or by adding more dye to methylene blue solution I (5.6).

6. Procedure

6.1 Color development

6.1.1 Transfer 7.5 ml of sample to each of two matched test tubes using a special wide tipped pipet or filling to a mark on the test tubes.

6.1.2 To tube A add 0.5 ml amine-sulfuric acid reagent (5.2) and 0.15 ml (3 drops) $FeCl_3$ solution (5.3).

6.1.3 Mix immediately by inverting the tube only once.

6.1.4 To tube B add 0.5 ml 1+1 H_2SO_4 (5.4) and 0.15 ml (3 drops) $FeCl_3$ solution (5.3) and mix.

6.1.5 Color will develop in tube A in the presence of sulfide. Color development is usually complete in about 1 minute, but a longer time is often required for the fading of the initial pink color.

6.1.6 Wait 3 to 5 minutes.

6.1.7 Add 1.6 ml $(NH_4)_2HPO_4$ solution (5.5) to each tube.

6.1.8 Wait 3 to 5 minutes and make color comparisons. If zinc acetate was used wait at least 10 minutes before making comparison.

6.2 Color comparison

6.2.1 Visual

6.2.1.1 Add methylene blue solution I (5.6) and/or II (5.7) (depending on sulfide concentration and accuracy desired) dropwise to tube B (6.1.4) until the color matches that developed in the first tube.

6.2.1.2 If the concentration exceeds 20 mg/1, repeat 6.2.1.1 using a portion of the sample diluted to one tenth.

6.2.2 Photometric

6.2.2.1 Use a 1 cm cell for 0.1 to 2.0 mg/1. Use a 10 cm cell for up to 20 mg/1.

6.2.2.2 Zero instrument with portion of sample from tube B (6.1.4).

6.2.2.3 Prepare calibration curve from data obtained in methylene blue standardization (5.8), plotting concentraton obtained from titrimetric iodide procedure (Method 376.1) versus absorbance. A straight line relationship can be assumed from 0 to 1.0 mg/1.

6.2.2.4 Read the sulfide concentration from the calibration curve.

7. Calculations

7.1 Visual comparison: With methylene blue solution I (5.6), adjusted so that 0.05 ml (1 drop) = 1.0 mg/1 sulfide and a 7.5 ml sample

mg/1 sulfide = number drops methylene blue solution I (5.6) + 0.1 x [number of drops methylene blue solution II (5.7)].

7.2 Photometric: see 6.2.2.4

8. Precision and Accuracy:

8.1 The precision has not been determined. The accuracy is about ±10%.

Bibliography

1. Standard Methods for he Examination of Water and Wastewater, 14th edition, p. 503, Method 428C (1975).

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 ¶ *c* above. Calculate sulfide concentration (¶ *c* above).

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:

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

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 (4500-S^{2-}.G.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.

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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 fraction of sulfide present as un-ionized 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. For both fresh water and seawater, it is convenient to define "conditional" dissociation constants, which are valid for the temperature and ionic strength of the water of interest. In the following mass-action equation for fresh water, K'_{FW} is a mixed equilibrium constant that relates the hydrogen ion activity (calculated from the pH) and the concentrations of H_2S and HS^-:

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

The square brackets indicate concentrations and the braces indicate activity. The value of pK'_{FW} for H_2S is approximately 7.0 ± 0.3 for the ionic strengths and temperatures likely to be encountered in water-quality monitoring. For seawater, it is convenient to use a stoichiometric equilibrium constant (K'_{SW}), which relates the concentrations of H^+, HS^-, and H_2S:

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

The mass-action equations can be rearranged to give:

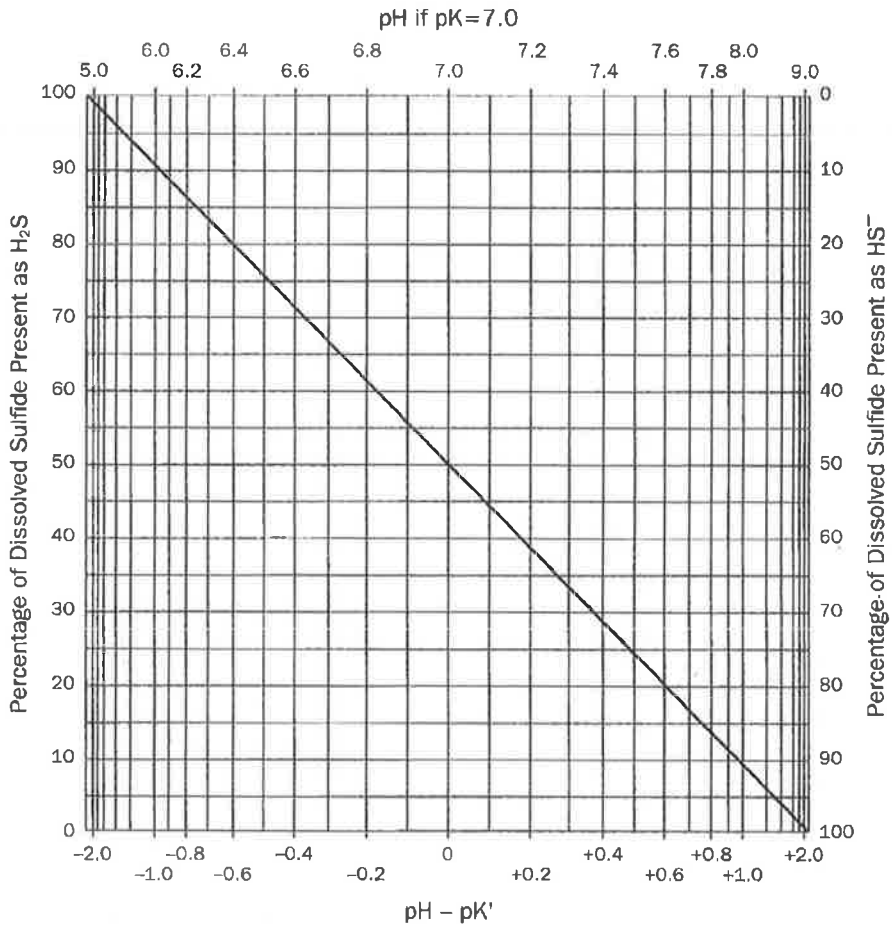

Figure 4500-S^{2-}:3. Proportion of H_2S and HS^- in dissolved sulfide.

$$pH - pK' = \log \frac{[HS^-]}{[H_2S]}$$

In this equation, pK' can be either pK'_{FW} or pK'_{SW}. The fraction of un-ionized H_2S can either be read from Figure 4500-S^{2-}:3 or calculated with the following equation:

$$\alpha_{H_2S} = \frac{[H_2S]}{S_T} = \frac{1}{10^{pH - pK'} + 1}$$

where:

S_T = total dissolved sulfide concentration.

1. Calculation for Fresh Water ($I \leq 0.01M$)

Calculate ionic strength I as in Table 2330:I. Read value of pK'_{FW} from Table 4500-S^{2-}:II.

Sample calculation: Total sulfide concentration, 1.5 mg S^{2-}/L; pH, 6.87; temperature, 10°C; ionic strength, 0.04. From Table 4500-S^{2-}:II, $pK'_{FW} = 7.11$.

$$pH - pK'_{FW} = -0.24$$

$$10^{pH - pK'_{FW}} = 10^{-0.24} = 0.575$$

$$\alpha_{H_2S} = \frac{1}{1 + 0.575} = 0.63$$

$$0.63 \times 1.5 = 0.95$$

The concentration of un-ionized H_2S is 0.95 mg S^{2-}/L.

2. Calculation for Seawater, Estuarine Water, and Brackish Water

This procedure is the same as that for fresh water. A potential source of error is the determination of the hydrogen ion concen-

TABLE 4500-S^{2-}:II. CONDITIONAL FIRST DISSOCIATION CONSTANT OF HYDROGEN SULFIDE, FRESH WATER*

Temperature °C	pK'_{FW} at Given Ionic Strength						
	0.00 mol/L	0.005 mol/L	0.01 mol/L	0.02 mol/L	0.03 mol/L	0.05 mol/L	0.10 mol/L
0	7.36	7.33	7.32	7.30	7.29	7.27	7.24
5	7.28	7.25	7.23	7.22	7.21	7.19	7.16
10	7.20	7.16	7.15	7.13	7.12	7.10	7.07
15	7.12	7.09	7.08	7.06	7.05	7.03	7.00
20	7.05	7.02	7.00	6.99	6.97	6.96	6.92
25	6.98	6.95	6.94	6.92	6.91	6.89	6.86
30	6.92	6.89	6.87	6.86	6.84	6.83	6.79

* Values calculated according to Millero[1].

TABLE 4500-S^{2-}:III. CONDITIONAL FIRST DISSOCIATION CONSTANT OF HYDROGEN SULFIDE, SEAWATER*

Temperature °C	pK'_{SW} at Given Salinity						
	5‰	10‰	15‰	20‰	25‰	30‰	35‰
0	7.17	7.12	7.09	7.07	7.06	7.06	7.06
5	7.08	7.02	6.99	6.97	6.96	6.96	6.96
10	6.99	6.93	6.90	6.88	6.87	6.86	6.86
15	6.91	6.85	6.82	6.80	6.78	6.78	6.77
20	6.83	6.77	6.74	6.72	6.70	6.69	6.69
25	6.76	6.70	6.66	6.64	6.63	6.62	6.61
30	6.70	6.63	6.60	6.57	6.56	6.55	6.54

* Values calculated according to Millero[1].

tration. If the pH electrode is calibrated using NIST buffers as in Section 4500-H^+, then a correction factor[2] must be determined. Add acid (HNO_3, HCl, or $HClO_4$, not H_2SO_4) to artificial seawater diluted to the salinity of interest and at the temperature of interest to give an acid concentration of 0.001*N*. (Prepare artificial seawater as in Table 8010:III, substituting NaCl for Na_2SO_4 on an equimolar basis and omitting NaF, $SrCl_2 \cdot 6H_2O$, H_3BO_3, KBr, $Na_2SiO_3 \cdot 9H_2O$, Na_4EDTA, and $NaHCO_3$.) Measure the pH. The difference between the negative logarithm of the known acid concentration and the measured pH is the correction factor. For example, if the acid concentration is 0.001*N* and the measured pH is 3.15, the correction factor is 0.15. Subtract 0.15 from measured pH values to get p°H, the negative logarithm of the hydrogen ion *concentration*. (The pH in fresh water corresponds to the negative logarithm of the hydrogen ion *activity*.) Alternatively, calibrate the pH electrode with Tris* buffer in artificial seawater diluted to the salinity of interest and at the temperature of interest.[3] Read pK'_{SW} from Table 4500-S^{2-}:III. Calculate the fraction of un-ionized H_2S as for fresh water.

Sample calculation: Total sulfide concentration, 1.5 mg S^{2-}/L; temperature 10°C; pH, 7.15; salinity 25‰. From Table 4500-S^{2-}: III, $pK'_{SW} = 6.87$.

$$pH - pK'_{SW} = 0.28$$

$$10^{pH-pK'_{SW}} = 10^{0.28} = 1.91$$

$$\alpha_{H_2S} = \frac{1}{1 + 1.91} = 0.34$$

$$0.34 \times 1.5 = 0.51$$

The concentration of un-ionized H_2S is 0.51 mg S^{2-}/L.

* Trishydroxymethylaminomethane.

3. References

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