

POTENTIOMETRIC DETERMINATION OF SULFIDE
IN AQUEOUS SAMPLES AND DISTILLATES WITH ION-SELECTIVE ELECTRODE

1.0 SCOPE AND APPLICATION

1.1 This method can be used for measuring total sulfide in a distilled sample. The method is meant to be used as an alternate determinative step following the distillation in either SW-846 Methods 9030 or 9031.

1.2 This method must not be used for undistilled samples because of possible mercury and silver ion interferences. Also, the ISE only responds to free sulfide dianion and will not detect sulfide in complexes. Therefore, this method would provide low recoveries for undistilled samples.

1.3 The method detection limit is 1.0 mg/L. Sulfide concentrations from 0.1 to 12,000 mg/L may be measured. However, when a linear calibration is used, results less than 1 mg/L may be biased up to approximately 90 percent low.

2.0 SUMMARY OF METHOD

2.1 The distillations in Methods 9030 and/or 9031 are performed, except that the scrubber solution is sulfide anti-oxidant buffer (SAOB), with ascorbic and salicylic acids added as oxygen scavengers. The distillates are then analyzed potentiometrically using a sulfide ion-selective electrode (ISE) in conjunction with a double-junction reference electrode and a pH meter with an expanded millivolt scale or an ISE meter capable of being calibrated directly in terms of sulfide concentration.

2.2 This method is an alternative to the iodometric titration procedure, where a solution of thiosulfate is standardized against the thiosulfate solution, and the sulfide standard is standardized against the iodine solution/thiosulfate solution (which requires daily calibration itself). This method allows for standardizing the sulfide calibration standards by a potentiometric titration with standardized silver nitrate using the sulfide ISE as the working electrode. Silver nitrate solutions are stable when stored properly and are easily standardized against sodium chloride.

2.3 The key to acceptable recoveries is the use of the proper apparatus and careful assembly of the distillation apparatus prior to distillation. If these steps are not taken, low recoveries will result.

3.0 INTERFERENCES

3.1 Since this method may only be used for distillates, which will have a pH greater than 12, there are no expected interferences. As shown in Table 1, the data indicate that neither silver, mercury, nor humic acid interfere with the electrode. (An interference would be indicated by a positive response.)

3.2 The effect of sulfur(+4) compounds (which interfere with the titrimetric method) in the absorbing solution on the sulfide ISE was tested (*e.g.*, sulfite or thiosulfate). The electrode did not respond to either compound. A 110 mg/L sulfide solution was spiked with 100 mg/L sulfide and 100 mg/L thiosulfate. The measured concentrations for the unspiked and spiked samples were identical (114 mg/L).

3.3 Temperature changes affect electrode potentials. Standards and samples must be equilibrated at the same temperature ($\pm 1^\circ\text{C}$).

3.4 The user should be aware of the potential of interferences from colloidal substances and that, if necessary, the samples may be filtered.

4.0 APPARATUS AND MATERIALS

4.1 pH/mV meter capable of reading to 0.1 mV or an ISE meter.

4.2 Sulfide ISE (Orion 9416 or equivalent) and double-junction reference electrode (Orion 902000 or equivalent).

4.3 Thermally isolated magnetic stirrer, polytetrafluoroethylene(PTFE)-coated stir bar, and stopwatch.

4.4 Volumetric flask, 125 mL.

5.0 REAGENTS

5.1 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, where such specifications are available. 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.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sulfide anti-oxidant buffer (SAOB). Dissolve 80 g NaOH, 320 g sodium salicylate and 72 g ascorbic acid in 1 L reagent water. Prepare fresh weekly.

5.4 Standard sodium chloride solution (0.100N). Dissolve 5.84 g NaCl (dried for 2 hours at 140°C) in water and dilute to 1.00 L with reagent water.

5.5 Sodium hydroxide (6N), NaOH. Dissolve 240 g of NaOH in 1 L of reagent water. Keep tightly closed.

5.6 Potassium chromate indicator solution. Dissolve 50 g K_2CrO_4 in a little reagent water. Add AgNO_3 solution until a definite red precipitate is formed. Let stand 12 hrs, filter, and dilute to 1 L.

5.7 Standard silver nitrate solution (0.10N). Dissolve 16.99 g of AgNO_3 (dried for 2 hours at 150°C) in reagent water and dilute to 1.00 L. Store in a brown bottle. Standardize weekly against standard sodium chloride solution.

5.8 Sodium sulfide nonahydrate, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. For the preparation of sulfide standard solutions to be used for calibration curves. Standards must be prepared between pH 9 and pH 11. Protect standards from exposure to oxygen by preparing them without headspace. These standards are unstable and should be prepared daily.

5.9 Sodium sulfide (2% and 10%), Na_2S .

5.10 Ammonia, NH₃: concentrated.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All original, undistilled samples should be handled as described in Section 6 of Methods 9030 and/or 9031. Samples should be stored at 4°C prior to analysis.

6.3 The distilled samples should be analyzed with the ISE immediately following distillation, distillates that are not analyzed immediately should be stored in a sealed flask at 4°C.

7.0 PROCEDURE

7.1 Replace the scrubber solution in Method 9030 or 9031 with 10.0 mL SAOB solution and 40.0 mL reagent water. Proceed to distill samples as described in those methods.

7.2 Standardization of silver nitrate

7.2.1 Add 10.00 mL of 0.100N NaCl and 40 mL reagent water to a 125 mL flask. Adjust pH to 7-10 with dilute NaOH solution. Add 1.0 mL potassium chromate indicator. Titrate with silver nitrate solution to a pinkish-yellow endpoint. Be consistent with endpoint recognition. Repeat with a reagent blank (water and indicator). Calculate the normality of the silver nitrate as follows:

$$N \text{ AgNO}_3 = \frac{(A - B) \times N(\text{NaCl})}{10.00 \text{ mL}}$$

A = mL titration for NaCl

B = mL titration for reagent blank

7.3 Standardization of sulfide standards

7.3.1 From the sodium sulfide salt, prepare standards with nominal concentrations of 10, 100, and 1,000 ppm sulfide in a matrix of 20% SAOB. Standardize each solution immediately prior to calibrating the ISE. The standards may be calibrated by iodometric titration or by potentiometric titration as described below.

7.3.2 Monitor the titration with the combination silver/sulfide electrode (silver-coated platinum ring sensing electrode with a silver/silver chloride reference electrode). Prior to use, condition the electrode by soaking it in 2% sodium sulfide for 5 minutes, soaking it in 10% sodium sulfide until the brownish layer becomes black, rinsing it with reagent water, and cleaning it with a soft cloth. After conditioning, connect the electrode to the pH/mV meter. Pipette 20 mL of a sulfide standard (or suitable quantity to get accurate titration) and 1 mL concentrated ammonia into a titration vessel. Insert the electrode and record the potential. Titrate the sample with the standardized silver nitrate until a potential of 100 mV is attained. Record the potential after each titrant addition. Determine the equivalence point from the first derivative of the titration curve. Then calculate the sulfide concentration as follows:

$$\text{sulfide (ppm)} = \frac{A \times B \times 16,000 \text{ mg/eq}}{C}$$

A = mL silver nitrate

B = normality of silver nitrate

C = mL of sulfide standard

7.4 Calibration of Sulfide ISE and Meter

7.4.1 Calibrate the sulfide ISE using the 10, 100, and 1,000 mg/L sulfide standards. The standards must be freshly standardized. Add 25.0 mL of standard into a 50 mL beaker. Add a PTFE-coated magnetic stir bar, place the beaker on a magnetic stir plate, and stir at slow speed (no visible vortex). Immerse the electrode tips to just above the rotating stir bar. If using an ISE meter, calibrate the meter in terms of sulfide concentration following the manufacturer's instructions. If using a pH/mV meter, record the meter reading (mV) as soon as the reading is stable, but in no case should the time exceed five minutes after immersing the electrode tips. Prepare a calibration curve by plotting measured potential (mV) as a function of the logarithm of sulfide concentration. The slope must be 54-60 mV per decade of sulfide concentration. If the slope is not acceptable, the ISE may not be working properly. For corrective action, consult the ISE operating manual.

7.5 Allow samples and standards to equilibrate to room temperature prior to analysis by ISE.

7.6 Prior to and between analyses, rinse the electrodes thoroughly with reagent water and gently shake off excess water. Low-level measurements are faster if the electrode tips are first immersed for five minutes in reagent water.

7.7 Measurement of Sulfide in Distilled Samples

7.7.1 Pour 25.0 mL of sample into a 50 mL beaker. Add a PTFE-coated magnetic stir bar. Place the beaker on a magnetic stir plate and stir at a slow speed (no visible vortex). Immerse the electrode tips to just above the rotating stir bar. Record the meter reading (mV or concentration) as soon as the reading is stable, but in no case should the time exceed five minutes after immersing the electrode tips. If reading mV, determine sulfide concentration from the calibration curve.

7.8 When analyses have been completed, rinse the electrodes thoroughly and store them in a 1.0 mg/L sulfide standard solution. If the electrodes will not be used more than one day, drain the reference electrode internal filling solutions, rinse with reagent water, and store dry.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and the distillation methods for specific quality control procedures.

8.2 Initial Calibration Verification standard (ICV): After performing the calibration step, verify calibration by analyzing an ICV. The ICV contains a known sulfide concentration at the mid-range of the calibration standards and is from an independent source. ICV recovery must be 90-110 percent. If not, the error source must be found and corrected. An acceptable ICV must be analyzed prior to sample analysis. The ICV also serves as a laboratory control sample.

8.3 Continuing Calibration Verification standard (CCV): After every 10 samples, and after the final sample, a CCV must be analyzed. The CCV contains a known sulfide concentration at mid-calibration range. CCV recovery must be 90-110 percent. If not, the error source must be found and corrected. If the ISE calibration has changed, all samples analyzed since the last acceptable CCV must be re-analyzed.

8.4 Reagent blank: After the ICV and after every CCV, a reagent blank must be analyzed. A reagent blank is reagent water mixed 100:1 with SAOB. The indicated reagent blank concentration must be less than 0.05 mg/L sulfide. If not, the contamination source must be found and corrected. All samples analyzed since the last acceptable reagent blank must be re-analyzed.

8.5 Matrix spike: Follow the matrix spike protocols presented in Chapter One. The spike concentration must be 10 times the detection limit and the volume added must be negligible (less than or equal to one-thousandth the sample aliquot volume). Spike recovery must be 75-125 percent. If not, samples must be analyzed by the method of standard additions.

8.6 The sulfide calibration standards may degrade by more than 10% from day-to-day. The standards must be standardized daily before use (by titration) and checked throughout the day if used as QC samples.

9.0 METHOD PERFORMANCE

9.1 The sulfide ISE was calibrated with 100 and 1,000 mg/L standards, and a series of sulfide standards was analyzed as unknowns. The results are listed in Table 2. As shown, recoveries ranged from 76-124% over the range 0.25-12,000 mg/L sulfide. This indicates that there is no practical difference between the true and observed values for sulfide over this concentration range.

9.2 Three acid-soluble sulfide samples were prepared (low, medium, and high; 25, 100, and 1,000 mg/L). Triplicate measurements of each were performed in the following order: medium, low, high, high, low, medium. The data are provided in Table 3.

9.3 Precision estimates were calculated from the average percent RSD taken within each block of triplicate measurements in Table 3. The CV% was calculated as 2.0 to 10.

9.4 Accuracy estimates from average percent recovery reported in Table 3 were calculated to be 75-105%.

9.5 To test the efficiency of the SAOB as a scrubber solution, three standards (1, 10, and 40 mg/L) were distilled into SAOB scrubber and the resulting sulfide concentration measured. The results are listed in Table 4. As seen in the table, excellent recoveries are obtained using the SAOB scrubber solution. The one low recovery for the 40 mg/L standard is most likely due to incomplete sparging of oxygen from the system prior to distillation.

10.0 REFERENCES

1. Franson, Mary Ann H., Ed. Standard Methods for the Examination of Water and Wastewater, 18th Edition. American Public Health Association, Washington, DC, 1992.
2. Model 94-16 Silver/Sulfide Electrode Instruction Manual. Orion Research, Inc., Boston, MA, 1986.

3. Hillerman, D.C., Nowinski, P. "Modification of Methods 9030 and 9031 for the Analysis of Sulfide by Specific Ion Electrode". U.S. Environmental Protection Agency, EMSL-LV. EPA/600/4-90/024. September 1990.

TABLE 1
INTERFERENCE STUDY RESULTS

Interferant	Sulfide Concentration (mg/L)	
	DI matrix	Tap water matrix
Ag ⁺ (20 mg/L)	<1	<1
Ag ⁺ + NH ₄ ⁺ (20 mg/L each)	<1	<1
Hg ⁺ (20 mg/L)	<1	<1
Humic acid* (100 mg/L)	2.1	1.6
Humic acid* + sulfide (100 mg/L each)	114	87.8

* The humic acid contains 2-3 mg/L sulfide as determined by Method 9030.

TABLE 2
RESULTS FROM A SINGLE-LABORATORY ACCURACY
EVALUATION OF A SULFIDE ISE

Sulfide Concentration (mg/L)	Sulfide Detected (mg/L)	Sulfide Recovery (%)	Rel. Std. Deviation (%)
0.10	0.01	10	-
0.25	0.19	76	-
0.50	0.47	94	12.7
1.00	0.99	99	9.3
1.09	1.10	101	-
5.00	4.94	99	3.4
27.4	26.8	98	-
55.0	52.3	95	-
110	109	99	-
591	607	103	-
1,183	1,157	98	0.4
6,000	6,028	100	2.0
12,000	14,850	124	2.2

TABLE 3
PRECISION AND ACCURACY DATA FOR THE SULFIDE ISE

True (mg/L)	Measured (mg/L)	Std. Dev. (mg/L)	RSD (%)	Recovery (%)
23.6	19.2	0.81	4.2	82.5
118.1	114.8	2.2	1.9	97.2
1,503	1,455	26	1.8	96.8
n = 6 for all samples				

TABLE 4
RECOVERY OF HYDROGEN SULFIDE IN SAOB SOLUTION

Sulfide (mg/L)	Recovery (%)
1	91.0
	89.8
	86.7
10	96.6
	100
	96.0
40	69.3
	98.9
	89.2

METHOD 9215

POTENTIOMETRIC DETERMINATION OF SULFIDE
IN DISTILLED SAMPLES WITH ION-SELECTIVE ELECTRODE

