Sulfide

DOC316.53.01136

USEPA[1] Methylene Blue Method[2] **Method 8131**

5 to 800 µg/L S^{2-} (spectrophotometers) **Reagent Solution**

0.01 to 0.70 mg/L (colorimeters)

Scope and application: For testing total sulfides, H_2S, HS^-, and certain metal sulfides in groundwater, wastewater, brines and seawater.

[1] USEPA approved for reporting wastewater analysis. Procedure is equivalent to Standard Method 4500-S2– D.
[2] Adapted from Standard Methods for the Examination of Water and Wastewater.

Test preparation

Instrument specific information

The table in this section shows all of the instruments that have the program for this test. Table 1 shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests.

To use the table, select an instrument, then read across to find the corresponding information for this test.

Table 1 Instrument-specific information for reagent addition

Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700	The fill line is to the right.	2495402
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The orientation mark is toward the user.	2401906

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
Some sulfide loss can occur if dilution is necessary.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used and use any recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Use the Safety Data Sheets for disposal information for unused reagents. Consult the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

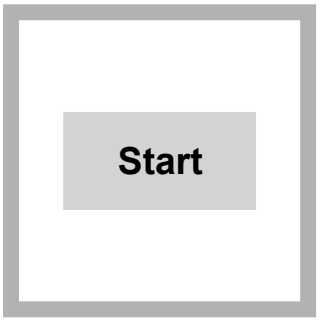
Description	Quantity
Sulfide 1 Reagent	1–2 mL
Sulfide 2 Reagent	1–2 mL
Water, deionized	10–25 mL
Pipet, serological, 10-mL	1
Pipet Filler, safety bulb	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument specific information on page 1.)	2
Stoppers	2

Refer to Consumables and replacement items on page 5 for reorder information.

Sample collection

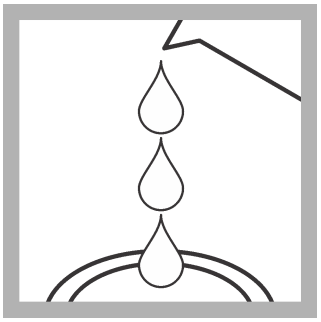
- Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
- Collect samples in clean glass or plastic bottles with tight-fitting caps. Fill the bottle completely and immediately tighten the cap.
- Prevent agitation of the sample or exposure to air.

Methylene Blue Method

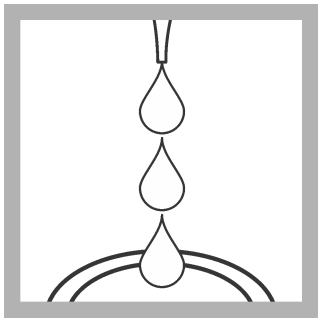


1. Start program **690 Sulfide**. For information about sample cells, adapters or light shields, refer to Instrument specific information on page 1.

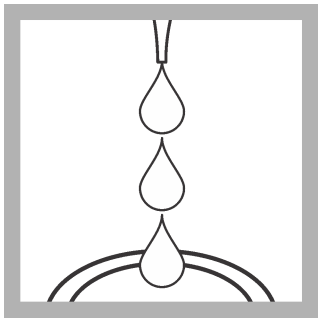
Note: *Although the program name may vary between instruments, the program number does not change.*



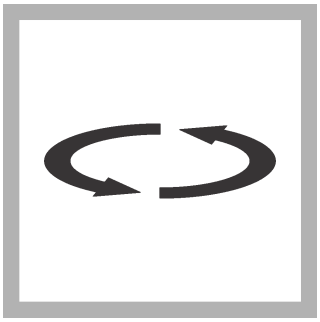
2. Prepare the blank: Fill a sample cell with deionized water. Use 10 mL for spectrophotometers and 25 mL for colorimeters.



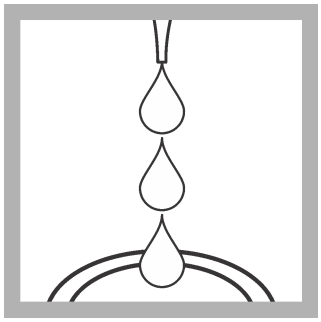
3. Prepare the sample: Use a pipet to add sample to a second sample cell. Use 10 mL for spectrophotometers and 25 mL for colorimeters. Do not mix the sample more than necessary to prevent sulfide loss.



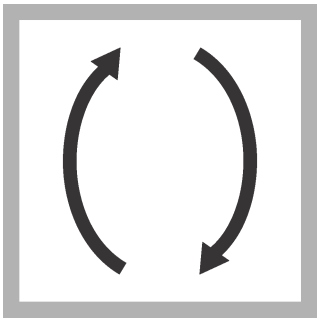
4. Use a dropper to add 0.5 mL Sulfide 1 Reagent to each cell.



5. Swirl to mix.

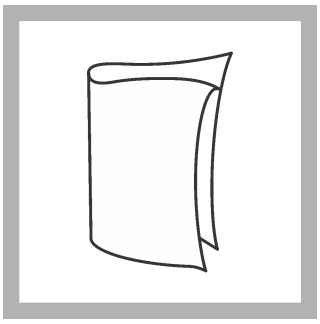


6. Use the dropper to add Sulfide 2 Reagent to each cell. Use 0.5 mL for spectrophotometers and 1.0 mL for colorimeters.



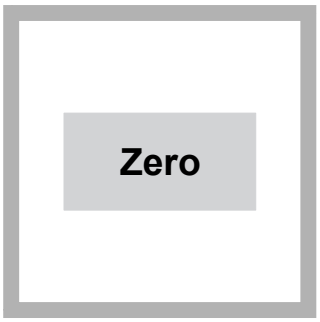
7. Close the sample cell. Invert the sample cell to mix. A pink color will develop initially. If sulfide is present, the solution becomes blue.

8. Start the instrument timer. A five-minute reaction time starts.

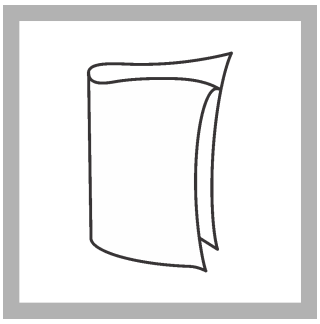


9. When the timer expires, clean the blank.

10. Insert the blank into the cell holder.



11. Push **ZERO**. The display shows 0 µg/L or 0.00 mg/L S^{2-}.



12. Clean the prepared sample.

13. Insert the prepared sample into the cell holder.

14. Push **READ**. Results show in µg/L or mg/L S^{2-}.

Soluble sulfides

To measure soluble sulfides, use a centrifuge to separate the solids. To make an estimate of the amount of insoluble sulfides in the sample, subtract the soluble sulfide concentration from the total (with solids) sulfide concentration.

1. Fill a centrifuge tube completely with sample and immediately cap the tube.
2. Put the tube in a centrifuge and run the centrifuge to separate the solids.
3. Use the supernatent as the sample in the test procedure.

Interferences

Interfering substance	Interference level
Barium	Concentrations more than 20 mg/L react with the sulfuric acid in Sulfide 1 Reagent and form a $BaSO_4$ (barite) precipitate. To correct for this interference: **1.** Dilute the sample in the test procedure as follows: • Spectrophotometers: use a 0.1-mL or 1.0-mL sample volume and add deionized water to the 10-mL mark. • Colorimeters: use a 0.25-mL or 2.5-mL sample volume and add deionized water to the 25-mL mark. **2.** Let the sample fully react with both reagents. **3.** After the 5 minute reaction period, pour the sample into a 50-mL beaker. **4.** Pull the sample into a Luer-Lock syringe (10 cc for spectrophotometers; 60 cc for colorimeters). **5.** Put a 0.45-µm filter disc on the Luer-Lock tip and filter the sample into a clean sample cell for measurement. Use deionized water to prepare the blank.
Strong reducing substances such as sulfite, thiosulfate and hydrosulfite	Prevent the full color development or reduce the blue color
Sulfide, high levels	High concentrations of sulfide can inhibit the full color development. Use a diluted sample in the test procedure. Some sulfide loss can occur when the sample is diluted.
Turbidity	Pre-treat the sample to remove sulfide, then use the pre-treated sample as the blank in the test procedure. Prepare a sulfide-free blank as follows: **1.** Measure 25 mL of sample into a 50-mL Erlenmeyer flask. **2.** Add 30-g/L Bromine Water by drops with constant swirling until a yellow color remains. **3.** Add 30-g/L Phenol Solution by drops with constant swirling until the yellow color is removed. **4.** Use this solution to replace the deionized water blank in the test procedure.

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users may get different results under different test conditions.

Program	Standard	Precision (95% Confidence Interval)	Sensitivity Concentration change per 0.010 Abs change
690	520 µg/L S^{2-}	504–536 µg/L S^{2-}	5 µg/L S^{2-}

Summary of method

Hydrogen sulfide and acid-soluble metal sulfides react with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration. High sulfide levels in oil field waters may be determined after proper dilution. The measurement wavelength is 665 nm for spectrophotometers or 610 nm for colorimeters.

Pollution prevention and waste management

Reacted samples contain hexavalent chromium and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Water, deionized	varies	4 L	27256
Sulfide Reagent Set	—	—	2244500
Includes:			
Sulfide 1 Reagent	1–2 mL	100 mL MDB	181632
Sulfide 2 Reagent	1 –2 mL	100 mL MDB	181732

Required apparatus

Description	Quantity/test	Unit	Item no.
Pipet, serological, graduated, 10-mL	1	each	53238
Pipet filler, safety bulb	1	each	1465100
Stoppers for 18-mm tubes and AccuVac Ampuls	2	6/pkg	173106

Optional reagents and apparatus

Description	Unit	Item no.
Bromine Water, 30-g/L	29 mL	221120
Phenol Solution, 30-g/L	29 mL	211220
Stoppers for 18-mm tube	25/pkg	173125
Flask, Erlenmeyer, 50 mL	each	50541

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