

## Methylene Blue Method<sup>1</sup>

**Method 10254**
**0.01 to 0.70, 0.1 to 7.0, 1 to 70 mg/L S<sup>2-</sup>**
**Reagent Solution**
**Scope and application:** For oil and gas field waters.

<sup>1</sup> Adapted from Standard Methods for the Examination of Water and Wastewater.




### Test preparation

### Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also 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 applicable information for this test.

**Table 1 Instrument-specific information**

Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700 DR 1900	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. Use the recommended personal protective equipment.

Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to 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
Pipet or mechanical pipettor (appropriate sample and reagent size)	1

## Items to collect (continued)

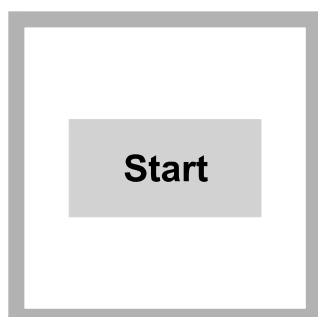
Description	Quantity
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2
Stoppers	2
Water, deionized	10 mL

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

## Sample collection

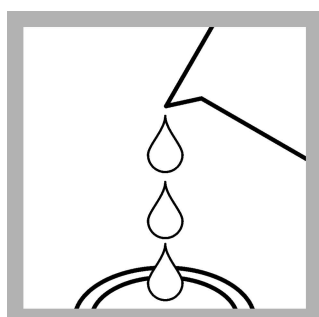
- Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
- Collect samples in clean glass or plastic bottles with tight-fitting caps. Completely fill the bottle and immediately tighten the cap.
- Prevent agitation of the sample or exposure to air.

## Methylene Blue method



**1. Start program 691 Sulfide HR.** For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

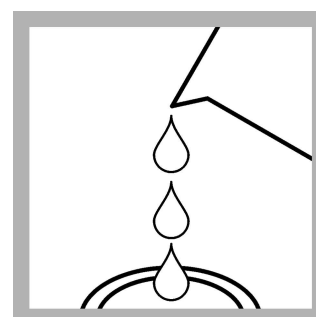
**Note:** Although the program name can be different between instruments, the program number does not change.



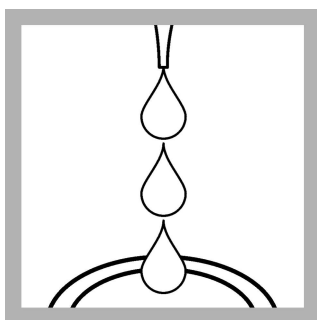
**2. Prepare the blank:** Fill a sample cell with deionized water. Use 10 mL for spectrophotometers and 25 mL for colorimeters.



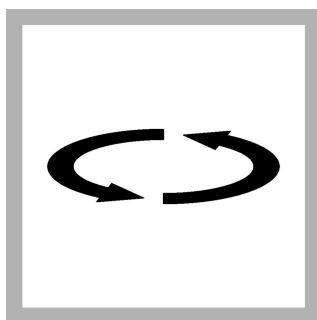
**3. Prepare the sample:** Add the sample volume that is specified for the test range to a clean sample cell. Refer to Table 2 on page 3. Use a pipet to measure small volumes.



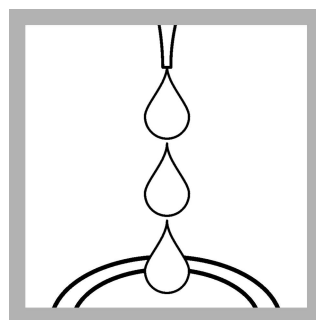
**4. Spectrophotometers:** Add deionized water to the 10-mL line. **Colorimeters:** Add deionized water to the 25-mL line. To prevent sulfide loss, do not mix the sample more than necessary.



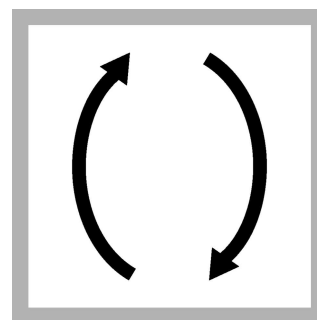
5. Add Sulfide 1 Reagent to each sample cell. Use 0.5 mL of reagent for spectrophotometers. Use 1.0 mL of reagent for colorimeters.



6. Swirl to mix.



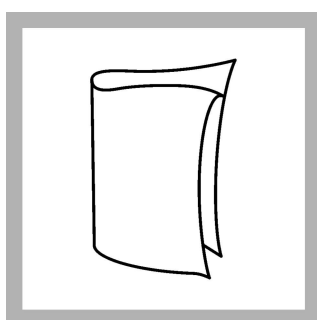
7. Add Sulfide 2 Reagent to each sample cell. Use 0.5 mL of reagent for spectrophotometers. Use 1.0 mL of reagent for colorimeters.



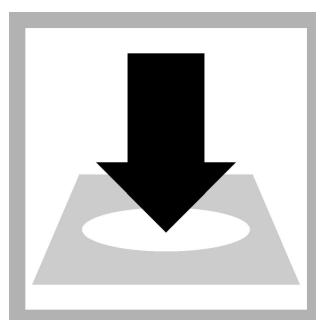
8. Put the stopper on both sample cells with a stopper. Invert to mix. The solution shows pink and then blue if sulfide is in the sample.



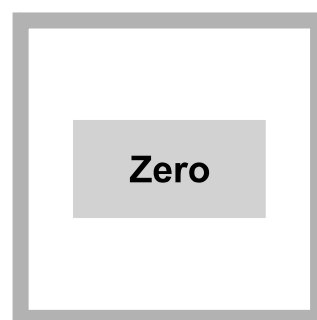
9. Start the instrument timer. A 5-minute reaction time starts.



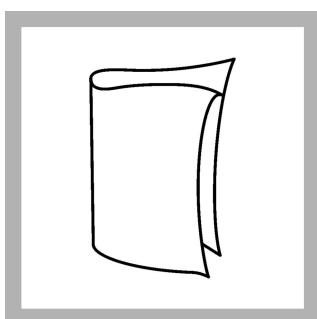
10. When the timer expires, clean the blank sample cell.



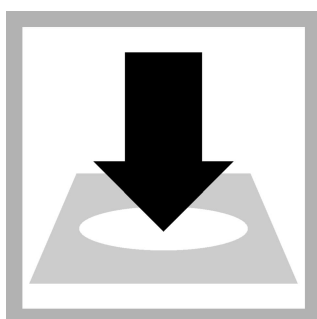
11. Insert the blank into the cell holder.



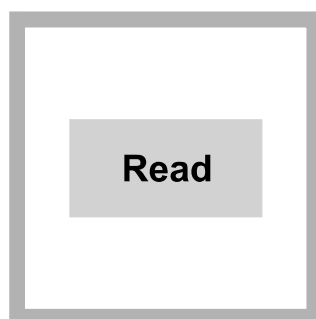
12. Push **ZERO**. The display shows 0 mg/L S<sup>2-</sup>.



13. Clean the prepared sample cell.



14. Insert the prepared sample into the cell holder.



15. Push **READ**. Results show in mg/L S<sup>2-</sup>.

## Select a sample volume

Table 2 Sample volumes and ranges

Range	Spectrophotometer volume	Colorimeter volume
0.01–0.70 mg/L (LR)	10 mL	25 mL
0.1–7.0 mg/L (MR)	1.0 mL	2.5 mL
1–70 mg/L (HR)	0.1 mL	0.25 mL

## Set the dilution factor

Instruments that have a dilution factor option can include the dilution factor in the result and show the concentration of the original, undiluted sample. For example, if the sample

is diluted by a factor of 10, the instrument multiplies the result by 10 and shows the calculated result in the instrument display.

1. Select **Options>More>Dilution** factor from the instrument menu.  
*Note: DR 1900: Select **Options>Advanced Options>Dilution Factors>On**.*  
*Note: Colorimeters include a dilution factor when the chemical form is set. Go to **Options>Advanced Options>Chemical Form** and select LR, MR or HR.*
2. Enter the dilution factor:
  - 1 mL sample diluted to 10 mL: dilution factor is 10.
  - 0.1 mL sample diluted to 10 mL: dilution factor is 100.
3. Push **OK** to confirm. Push **OK** again.
4. Push **RETURN** to go back to the measurement screen.

## 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 supernatant as the sample in the test procedure.

## Interferences

Interfering substance	Interference level
Barium	<p>Concentrations more than 20 mg/L barium react with the sulfuric acid in Sulfide 1 Reagent and form a BaSO<sub>4</sub> (barite) precipitate. To correct for this interference:</p> <ol style="list-style-type: none"> <li>1. Dilute the sample in the test procedure as follows:               <ul style="list-style-type: none"> <li>• Spectrophotometers: use a 0.1-mL or 1.0-mL sample volume and add deionized water to the 10-mL mark.</li> <li>• Colorimeters: use a 0.25-mL or 2.5-mL sample volume and add deionized water to the 25-mL mark.</li> </ul> </li> <li>2. Add both Sulfide 1 and Sulfide 2 reagents per the procedure steps.</li> <li>3. After the 5-minute reaction period, pour the sample into a 50-mL beaker.</li> <li>4. Pull the sample into a Luer-Lock syringe (10 cc for spectrophotometers or 60 cc for colorimeters).</li> <li>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.</li> <li>6. Set the instrument zero and read the result, per the procedure steps.</li> <li>7. Multiply by the appropriate dilution factor for the dilution used (10 or 100).</li> </ol>
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	<p>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:</p> <ol style="list-style-type: none"> <li>1. Measure 25 mL of sample into a 50-mL Erlenmeyer flask.</li> <li>2. Add 30-g/L Bromine Water by drops with constant swirling until a yellow color remains.</li> <li>3. Add 30-g/L Phenol Solution by drops with constant swirling until the yellow color is removed.</li> <li>4. Use this solution to replace the deionized water blank in the test procedure.</li> </ol>

## Accuracy check

### Standard solution method

Sulfide standard solutions are not stable and must be prepared by the user. Refer to Standard Methods, 4500S<sup>2-</sup> for preparation and standardization instructions.

### Method performance

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

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
691	0.52 mg/L S <sup>2-</sup>	0.50–0.54 µg/L S <sup>2-</sup>	0.005 mg/L S <sup>2-</sup>

### 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, TenSette <sup>®</sup> , 0.1–1.0 mL	1	each	1970001
Pipet Tips, for TenSette <sup>®</sup> Pipet, 0.1–1.0 mL	2	50/pkg	2185696
Pipet, TenSette <sup>®</sup> 1.0–10.0 mL	1	each	1970010
Pipet Tips, for TenSette <sup>®</sup> Pipet, 1.0–10.0 mL	varies	50/pkg	2199796
Pipet, adjustable volume, 0.2–1.0 mL	1	each	BBP078
Pipet tips, for 0.2–1.0 mL pipet	2	100/pkg	BBP079
Pipet, adjustable volume, 1.0–5.0 mL	1	each	BBP065
Pipet tips, for 1.0–5.0 mL pipet	1	75/pkg	BBP068

## Optional reagents and apparatus

Description	Unit	Item no.
Beaker, 50-mL	each	50041H
Bromine Water, 30-g/L	29 mL	221120
Mixing cylinder, graduated, 10-mL	each	2088638
Flask, Erlenmeyer, 50-mL	each	50541
Phenol Solution, 30-g/L	29 mL	211220
Pipet, serological, 10-mL	each	53238
Pipet filler, safety bulb	each	1465100
Syringe, 10-cc, Luer-Lock tip	each	2202400
Syringe, 60 cc, Luer-Lock tip	1	2258700
Syringe filter, 0.45- $\mu$ m, 33-mm PVDF	50/pkg	2513603



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