SULFIDE

✔ Method 8131

Methylen Blue Method*  
(0 to 800 µg/L)

Scope and Application: For testing total sulfides, H₂S, HS⁻ and certain metal sulfides in groundwater, wastewater brines and seawater; USEPA accepted for reporting wastewater analysis**

* Adapted from Standard Methods for the Examination of Water and Wastewater.
** Procedure is equivalent to USEPA method 376.2 and Standard Method 4500-S²⁻ for wastewater.

1. Press the soft key under HACH PROGRAM.
   Select the stored program number for sulfide (S²⁻) by pressing 3500 with the numeric keys.
   Press: ENTER
   Note: The Flow Cell and Sipper Modules can be used with this procedure.
   Note: Samples must be analyzed immediately and cannot be preserved for later analysis. Avoid excessive agitation of samples.

2. The display will show:
   HACH PROGRAM: 3500 Sulfide
   The wavelength (λ), 665 nm, is automatically selected.

3. Measure 25 mL of sample into a sample cell. This will be the prepared sample.
   Note: For turbid samples, see Interferences (following these steps) for pretreatment instructions.
   Note: Excessive agitation will cause loss of sulfide. Use a pipet to minimize sulfide loss.

4. Measure 25 mL of deionized water into a second sample cell (the blank).

5. Add 1.0 mL of Sulfide 1 Reagent to each cell. Swirl to mix.
   Note: Use the calibrated 1-mL dropper.

6. Add 1.0 mL of Sulfide 2 Reagent to each cell. Immediately swirl to mix.
   Note: A pink color will develop, then the solution will turn blue if sulfide is present.

7. Press the soft key under START TIMER. A 5-minute reaction period will begin.

8. When the timer beeps, place the blank in the cell holder. Close the light shield.
Interferences

Table 1 Interfering Substances and Suggested Treatments

<table>
<thead>
<tr>
<th>Interfering Substance</th>
<th>Interference Levels and Treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong reducing substances (sulfite, thiosulfate and hydrosulfite)</td>
<td>Interfere by reducing the blue color or preventing its development</td>
</tr>
<tr>
<td>Sulfide, high levels</td>
<td>High concentrations of sulfide may inhibit full color development and require sample dilution. Some sulfide loss may occur when the sample is diluted.</td>
</tr>
<tr>
<td>Turbidity</td>
<td>For turbid samples, prepare a sulfide-free blank as follows. Use it in place of the deionized water blank in the procedure.</td>
</tr>
<tr>
<td></td>
<td>1. Measure 25 mL of sample into a 50-mL erlenmeyer flask.</td>
</tr>
<tr>
<td></td>
<td>2. Add Bromine Water dropwise with constant swirling until a permanent yellow color just appears.</td>
</tr>
<tr>
<td></td>
<td>3. Add Phenol Solution dropwise until the yellow color just disappears. Use this solution in place of deionized water in step 4.</td>
</tr>
</tbody>
</table>

Sample Collection, Storage and Preservation

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Analyze samples immediately.

9. Press the soft key under **ZERO**. The display will show:

   \[0 \text{ µg/L } S^{2-}\]

   **Note:** For alternate concentration units, press the soft key under **OPTIONS**. Then press the soft key under **UNITS** to scroll through the available options. Press **ENTER** to return to the read screen.

10. Place the prepared sample in the cell holder. Close the light shield. Results in µg/L sulfide (or chosen units) will be displayed.

   **Note:** Some sulfide loss may occur if dilution is necessary.
Method Performance

**Precision**
Standard: 400 µg/L $S^{2−}$

<table>
<thead>
<tr>
<th>Program</th>
<th>95% Confidence Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>3500</td>
<td>399–401 µg/L $S^{2−}$</td>
</tr>
</tbody>
</table>

For more information on determining precision data and method detection limits, refer to Section 1.5.

**Estimated Detection Limit**

<table>
<thead>
<tr>
<th>Program</th>
<th>EDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>3500</td>
<td>2 µg/L $S^{2−}$</td>
</tr>
</tbody>
</table>

For more information on derivation and use of Hach’s estimated detection limit, see Section 1.5.2. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, appendix B, see Section 1.5.1.

**Sensitivity**
Program Number: 3500

<table>
<thead>
<tr>
<th>Portion of Curve</th>
<th>∆Abs</th>
<th>∆Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entire Range</td>
<td>0.010</td>
<td>4.9 µg/L</td>
</tr>
</tbody>
</table>

See Section 1.5.3 Sensitivity Explained for more information.

**Determining Soluble Sulfides**

Determine soluble sulfides by centrifuging the sample in completely filled, capped tubes and analyzing the supernatant. Insoluble sulfides are then estimated by subtracting the soluble sulfide concentration from the total sulfide result.

**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.

**Safety**

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet for information specific to the reagents used. For additional information, refer to Section 1.

**Pollution Prevention and Waste Management**

Sulfide 2 reagent contains potassium dichromate. The final solution will contain hexavalent chromium (D007) at a concentration regulated as a hazardous waste by Federal RCRA. Please see Section 1 for further information on proper disposal of these materials.
REQUIRED REAGENTS AND STANDARDS

Cat. No.  
Sulfide Reagent Set (100 tests) ................................................................................................................. 22445-00  
Includes: (2) 1816-32, (2) 1817-32

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity Required</th>
<th>Unit</th>
<th>Cat. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfide 1 Reagent</td>
<td>2 mL</td>
<td>100 mL MDB</td>
<td>1816-32</td>
</tr>
<tr>
<td>Sulfide 2 Reagent</td>
<td>2 mL</td>
<td>100 mL MDB</td>
<td>1817-32</td>
</tr>
<tr>
<td>Water, deionized</td>
<td>25 mL</td>
<td>4 liters</td>
<td>272-56</td>
</tr>
</tbody>
</table>

REQUIRED EQUIPMENT AND SUPPLIES

Cylinder, graduated, 25-mL ............................................................................................................. 508-40

or

Pipet, volumetric, Class A, 25-mL ........................................................................................................ 14515-40

DR/4000 1-Inch Cell Adapter .............................................................................................................. 48190-00

Pipet Filler, safety bulb ..................................................................................................................... 14651-00

OPTIONAL REAGENTS AND STANDARDS

Bromine Water, 30-g/L ......................................................................................................................... 2211-20

Phenol Solution, 30-g/L ....................................................................................................................... 2112-20

OPTIONAL EQUIPMENT AND SUPPLIES

DR/4000 Carousel Module Kit ............................................................................................................... 48070-02

DR/4000 Flow Cell Module Kit, 1-inch ................................................................................................. 48070-04

DR/4000 Flow Cell Module Kit, 1-cm ................................................................................................. 48070-05

DR/4000 Sipper Module Kit, 1-inch ...................................................................................................... 48090-03

Dropper, for 1-oz. bottle ....................................................................................................................... 2258-00

Flask, Erlenmeyer, 50-mL ................................................................................................................... 505-41