Sulfide

DOC316.53.01320

Methylene Blue Method[1]

Method 10254

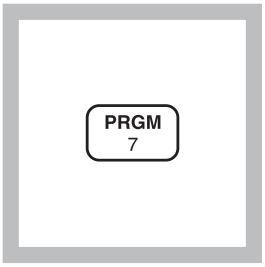
(0–0.70, 0–7.00 and 0–70.00 mg/L)

Scope and Application: For oil and gas field waters.

[1] Adapted from *Standard Methods for the Examination of Water and Wastewater*.

USEPA accepted for wastewater analysis. Procedure is equivalent to USEPA method 376.2 or Standard Method 4500-S2- D for wastewater.

Test procedure

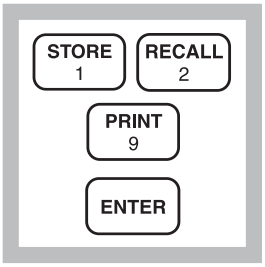


1. Push **PRGM.**

The display shows

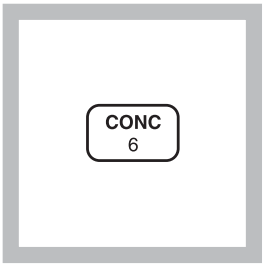
PRGM ?

Initial setup: go to Instrument setup on page 95 to add the program to the instrument.



2. Push **129 ENTER**.

The display shows mg/L, S LR, S MR or S HR and the ZERO icon**.**

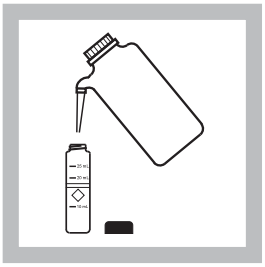


3. Push **CONC** to select the test range.

S LR: 0–0.70 mg/L

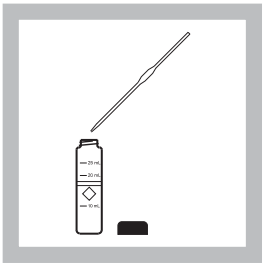
S MR: 0–7.00 mg/L

S HR: 0–70.00 mg/L



4. Blank preparation: Add 25 mL of deionized water to a sample cell.

A 25-mL graduated mixing cylinder can be used in steps 4 and 5.



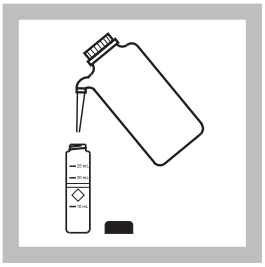
5. Sample preparation: Add the sample volume that is specified for the test range to a clean sample cell.

S LR: 25 mL

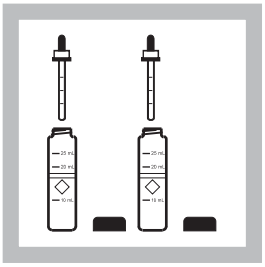
S MR: 2.5 mL

S HR: 0.25 mL

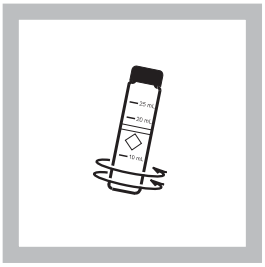
Use a pipet to measure 0.25 mL or 2.5 mL.



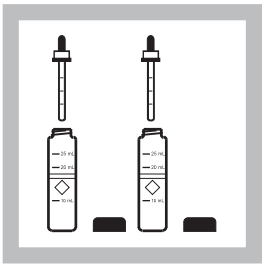
6. If the sample volume is less than 25 mL, add deionized water to the 25-mL line.



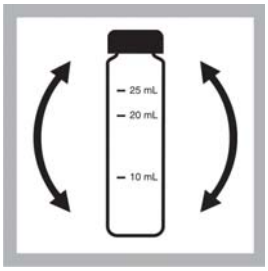
7. Use the dropper to add 1.0 mL of Sulfide 1 Reagent to each sample cell.



8. Swirl to mix.

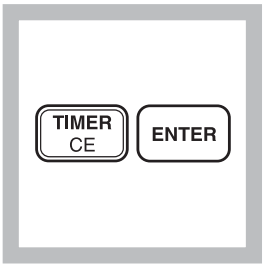


9. Use the dropper to add 1.0 mL of Sulfide 2 Reagent to each sample cell.



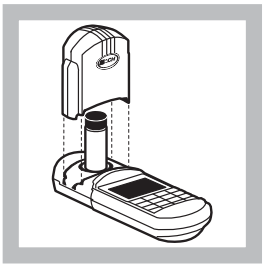
10. Immediately tighten the cap on each sample cell and mix.

The solution becomes pink and then blue if sulfide is in the sample.

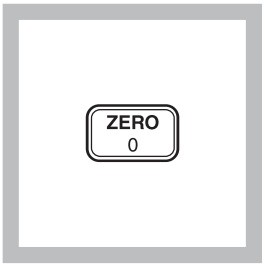


11. Push **TIMER,** then **ENTER**.

A 5-minute reaction period starts.



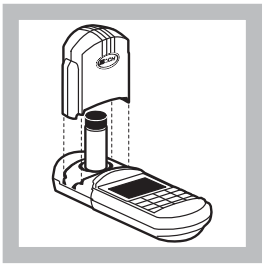
12. Put the blank in the instrument. Put the instrument cap over the sample cell.



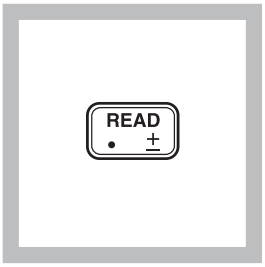
13. Push **ZERO.**

The cursor moves to the right, then the display shows

0.00 mg/L S and LR, MR or HR



14. At the end of the reaction period, put the prepared sample in the instrument. Put the instrument cap over the sample cell.



15. Push **READ.**

The cursor moves to the right, then the result in mg/L sulfide is shown.

Notice! Do not push the **CONC** key at the end of the test to change the range. The result is applicable only to the test range that was selected in step 3.

Note: *For best results use the Standard Adjust option. Refer to the instrument manual.*

Sampling and storage

Collect the samples in clean plastic or glass bottles. Fill the bottles completely, then put the caps on tightly. Keep any agitation or air exposure to a minimum. Analyze the samples immediately.

Soluble sulfides

Complete the steps that follow to measure the concentration of soluble sulfides in the sample.

1. Use a centrifuge to make a separation of the soluble and insoluble sample components. Make sure that the centrifuge tubes are filled completely and have a cap.
2. Use the liquid portion as the sample in the test procedure to measure the concentration of soluble sulfides.

To make an estimate of the insoluble sulfides, subtract the soluble sulfide concentration from the total sulfide concentration.

Pollution prevention and waste management

The Sulfide 2 Reagent contains potassium dichromate. Dispose of chemicals and wastes in accordance with local, regional and national regulations.

Interferences

The known interferences are shown in Table 1. The interference levels are applicable to an undiluted 10-mL sample. The interference levels increase proportionally as the sample is diluted.

Table 1 Interferences

Substance	Interference
Barium	Concentrations greater 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.** Use a 0.25-mL or 2.5-mL sample volume in the test procedure and add deionized water to the 25-mL line. **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 60 cc Luer-Lock syringe. **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 (sulfite, thiosulfate and hydrosulfite)	Can decrease the blue color or prevent the full color development.
Sulfide, high levels	Can prevent the full color development. Make a dilution if the sample has a high sulfide concentration. Some sulfide loss can occur when the sample is diluted.
Turbidity	Can be corrected with a prepared sulfide-free blank: **1.** Measure 25 mL of sample into a 50-mL Erlenmeyer flask. **2.** Swirl the flask and add bromine water by drops only until the solution has a permanent yellow color. **3.** Continue to swirl the flask and add phenol solution by drops only until the yellow color is gone. Replace the deionized water in step 4 of the procedure with this solution. This procedure removes the sulfide from the sample but does not remove the turbidity or background color. The interference from turbidity or color will be corrected when the instrument is set to zero with this solution.

Accuracy check

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

Method performance

Precision

In a single laboratory, with standard solutions of 0.73 mg/L sulfide and two representative lots of reagent, a single operator got a standard deviation of ±0.02 mg/L sulfide with the instrument.

Estimated detection limit (EDL)

The EDL for program 129 is 0.01 mg/L S^{2-}.

Summary of method

Hydrogen sulfide and acid-soluble metal sulfides react with N, N-dimethyl-p-phenylenediamine to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration.

Instrument setup

This procedure adds program 129 to a DR/850 or DR/890 instrument.

1. Push **SETUP**.
2. Push the **DOWN ARROW** until the display shows USER.
3. Push **ENTER**.
4. Push the numbers **8138**, then push **ENTER**. The display shows LINE 1?

5. Refer to Table 2. Find the 1 in the Line Number column, then read across to find the numbers in the Enter column. Push these numbers on the keypad, then push **ENTER**.

6. Continue to add the numbers that correspond to each line number on the display.

Note: *Use the arrow keys to scroll and review or change numbers at any time.*

Table 2 Instrument setup

Line number	Enter	Line number	Enter
1	129	29	0
2	42	30	83
3	74	31	32
4	0	32	72
5	0	33	82
6	0	34	0
7	0	35	65
8	0	36	32
9	0	37	0
10	0	38	0
11	0	39	66
12	63	40	200
13	129	41	0
14	202	42	0
15	184	43	0
16	0	44	80
17	0	45	1
18	0	46	244
19	0	47	20
20	83	48	1
21	32	49	44
22	76	50	0
23	82	51	0
24	0	52	0
25	83	53	0
26	32	54	167
27	77	55	0
28	82	56	255

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Sulfide reagent set, includes:	—	—	2244500
Sulfide 1 Reagent	1 mL	100 mL MDB	181632
Sulfide 2 Reagent	1 mL	100 mL MDB	181732
Water, deionized	10 mL	4 L	27256

Required apparatus

Description	Quantity/Test	Unit	Item no.
Pipet, variable volume, 0.2–1.0 mL	1	1	BBP078
Pipet tips, 0.2–1.0 mL for BBP078 pipet	2	100/pkg	BBP079
Pipet, variable volume, 1.0–5.0 mL	1	1	BBP065
Pipet tips, 1.0–5.0 mL for BBP065 pipet	2	75/pkg	BBP068
Pipets, variable volume, one BBP078 and one BBP065 with tips	1	1	LZP320
Sample cell, 10-20-25 mL, with cap	1	6/pkg	2401906

Optional reagents and apparatus

Description	Unit	Item no.
Beaker, 50 mL, low form	1	50041H
Bromine water, 30 g/L	29 mL	221120
Cylinder, graduated mixing, 25 mL	1	2088640
Flask, Erlenmeyer, 50 mL	1	50541
Phenol solution, 30 g/L	29 mL	211220
Pipet, volumetric, Class A, 25.00 mL	1	1451540
Pipet filler, safety bulb	1	1465100
Syringe, 60 cc, Luer-Lock tip	1	2258700
Syringe filter, 0.45 µm, 33 mm PVDF	50/pkg	2513603

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