

USEPA¹ SulfaVer 4 Method²

2 to 70 mg/L SO₄²⁻

Method 8051

Powder Pillows or AccuVac[®] Ampuls

Scope and application: For water, wastewater and seawater.

¹ USEPA accepted for reporting wastewater analyses. Procedure is equivalent to USEPA method 375.4 for wastewater.

² Adapted from Standard Methods for the Examination of Water and Wastewater.



Test preparation

Instrument-specific information

The tables in this section show 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. [Table 2](#) shows sample cell and adapter requirements for AccuVac Ampul tests.

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

Table 1 Instrument-specific information for powder pillow





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.	2401906 
DR 900	The orientation mark is toward the user.	

Table 2 Instrument-specific information for AccuVac Ampuls

Instrument	Adapter	Sample cell
DR 6000 DR 5000 DR 900	—	2427606 
DR 3900	LZV846 (A)	2122800 
DR 3800 DR 2800 DR 2700	LZV584 (C)	

Before starting

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.

Use the Standard Adjust option with each new lot of reagent for the best results.

For best results, calibrate the instrument with each new lot of reagent. Refer to [Calibration](#) on page 6.

For best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to get the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option.

Filter samples that are turbid with filter paper and a funnel.

Do not use the Pour-Thru Cell or sipper module (for applicable instruments) with this test.

The reagents that are used in this test contain barium chloride. Collect the reacted samples for proper disposal.

An AccuVac Ampule for Blanks can be used to zero the instrument in the AccuVac test procedure.

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

Powder pillows

Description	Quantity
SulfaVer [®] 4 Reagent Powder Pillows, 10-mL	1
Sample Cells (Refer to Instrument-specific information on page 1.)	2

Refer to [Consumables and replacement items](#) on page 7 for reorder information.

AccuVac Ampuls

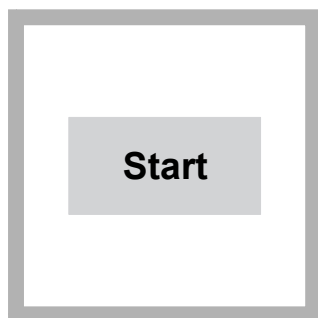
Description	Quantity
SulfaVer [®] 4 Reagent AccuVac [®] ampuls	1
Beaker, 50-mL	1
Sample Cells (Refer to Instrument-specific information on page 1.)	1
Stopper	1

Refer to [Consumables and replacement items](#) on page 7 for reorder information.

Sample collection and storage

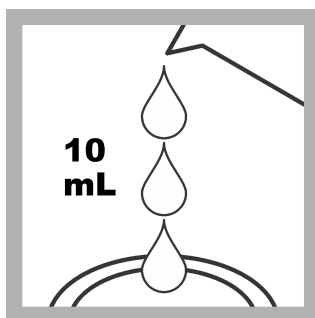
- Collect samples in clean glass or plastic bottles.
- To preserve samples for later analysis, keep the samples at or below 6 °C (43 °F) for up to 28 days.
- Let the sample temperature increase to room temperature before analysis.

SulfaVer 4 powder pillow procedure

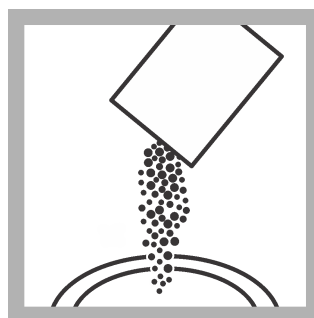


1. Start program **680 Sulfate**. For information about sample cells, adapters or light shields, refer to [Instrument-specific information](#) on page 1.

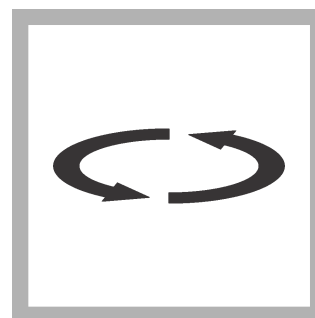
Note: Although the program name may vary between instruments, the program number does not change.



2. **Prepare the sample:** Fill a sample cell with 10 mL of sample.



3. Add the contents of one powder pillow to the sample cell.

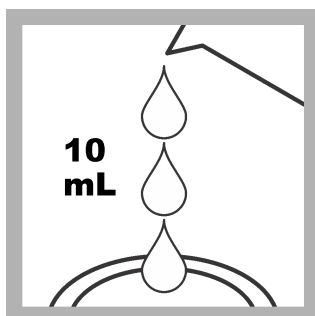


4. Swirl the sample cell to mix. Undissolved powder will not affect accuracy. White turbidity will form if sulfate is present.

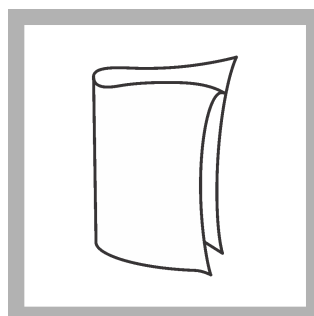


5. Start the instrument timer. A five-minute reaction time starts.

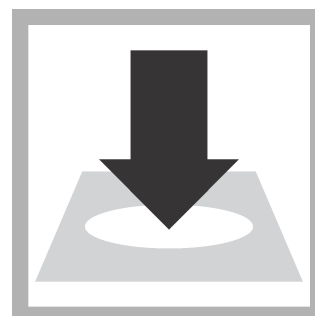
Do not disturb the cell during this time.



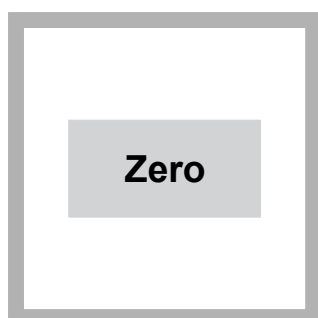
6. **Prepare the blank:** Fill a second sample cell with 10 mL of sample.



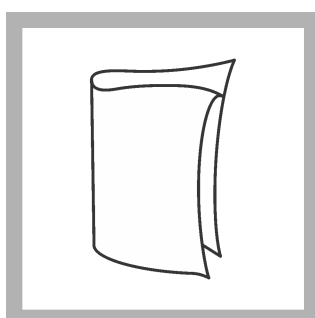
7. When the timer expires, clean the blank.



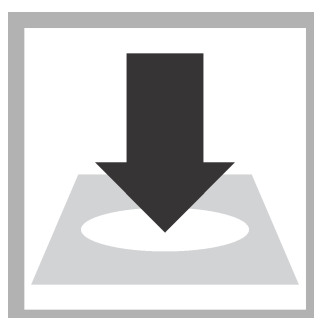
8. Insert the blank into the cell holder.



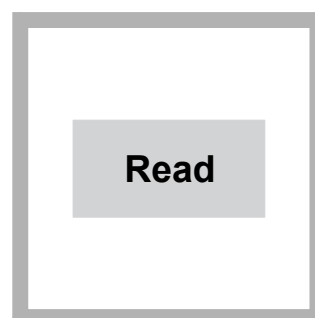
9. Push **ZERO**. The display shows 0 mg/L SO_4^{2-} .



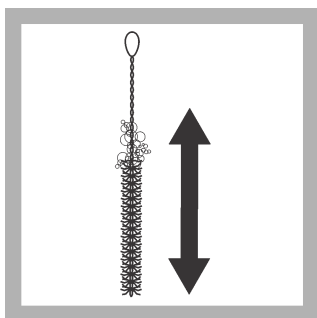
10. Clean the prepared sample.



11. Within five minutes after the timer expires, insert the prepared sample into the cell holder.

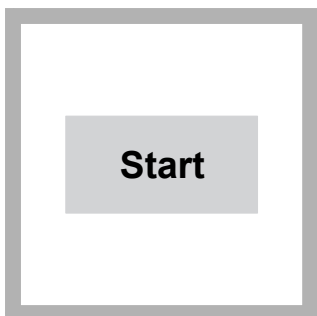


12. Push **READ**. Results show in mg/L SO_4^{2-} .



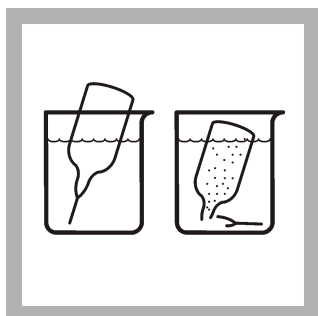
13. Clean the sample cells with soap and a brush.

SulfaVer 4 AccuVac[®] Ampuls procedure

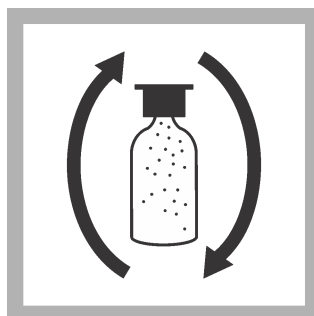


1. Start program **685 Sulfate AV**. For information about sample cells, adapters or light shields, refer to [Instrument-specific information](#) on page 1.

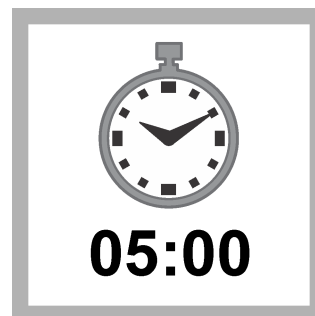
Note: Although the program name may vary between instruments, the program number does not change.



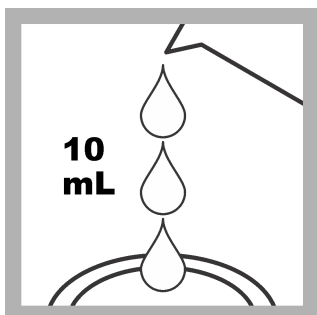
2. **Prepare the sample:** Collect at least 40 mL of sample in a 50-mL beaker. Fill the AccuVac Ampul with sample. Keep the tip immersed while the Ampul fills completely.



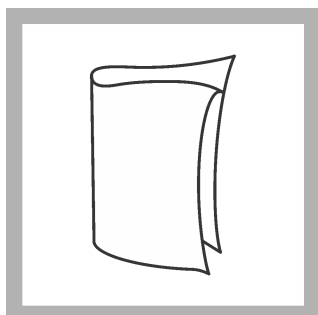
3. Close the Ampul and quickly invert the Ampul several times to mix. Undissolved powder will not affect accuracy. White turbidity will form if sulfate is present.



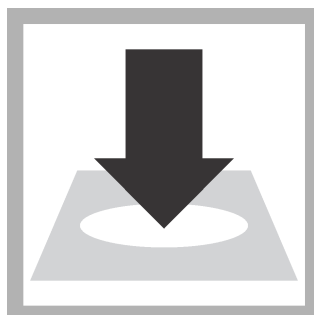
4. Start the instrument timer. A five-minute reaction time starts. Do not disturb the cell during this time.



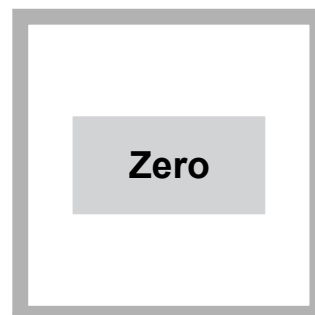
5. **Prepare the blank:** Fill the sample cell with 10 mL of sample.



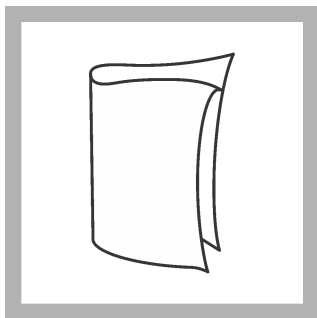
6. When the timer expires, clean the blank AccuVac Ampul.



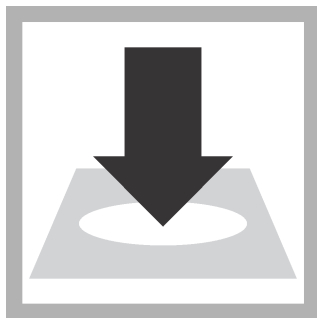
7. Insert the blank AccuVac Ampul into the cell holder.



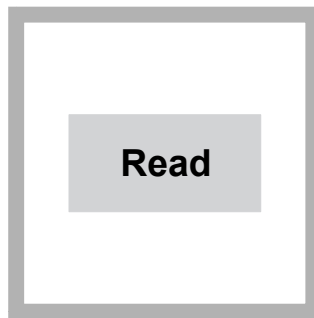
8. Push **ZERO**. The display shows 0 mg/L SO_4^{2-} .



9. Clean the AccuVac Ampul.



10. Within five minutes after the timer expires, insert the prepared sample AccuVac Ampul into the cell holder.



11. Push **READ**. Results show in mg/L SO_4^{2-} .

Interferences

Interfering substance	Interference level
Barium	Interferes at all levels. The higher the barium concentration when compared to the sulfate concentration, the higher the error. Samples with high barium concentrations will generally give a result that is 20% lower than the actual sulfate concentration.
Calcium	More than 20,000 mg/L as CaCO_3
Chloride	More than 40,000 mg/L as Cl^-
Magnesium	More than 10,000 mg/L as CaCO_3
Silica	More than 500 mg/L SiO_2

Accuracy check

Standard additions method (sample spike)

Use the standard additions method (for applicable instruments) to validate the test procedure, reagents and instrument and to find if there is an interference in the sample.

Items to collect:

- Sulfate Ampule Standard Solution, 2500 mg/L sulfate
- Ampule breaker
- Pipet, TenSette®, 0.1–1.0 mL and tips
- Mixing cylinders (3), 25

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 25-mL portions of fresh sample. Mix well.

Note: For AccuVac® Ampuls, add 0.2 mL, 0.4 mL and 0.6 mL of the standard solution to three 50-mL portions of fresh sample.

6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

Note: If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and

sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.

Standard solution method

Use the standard solution method to validate the test procedure, reagents and instrument.

Items to collect:

- Sulfate standard solution, 1000 mg/L
- 100-mL volumetric flask, Class A
- 7-mL volumetric pipet, Class A and pipet filler
- Deionized water

1. Prepare a 70 mg/L sulfate standard solution as follows:
 - a. Use a pipet to add 7.0 mL of 1000 mg/L sulfate standard solution into the volumetric flask.
 - b. Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
2. Use the test procedure to measure the concentration of the prepared standard solution.
3. Compare the expected result to the actual result.

Note: The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are slight variations in the reagents or instruments.

Calibration

A calibration is recommended for the SulfaVer 4 method for the best accuracy. Complete the following steps to enter a new calibration curve in the instrument. Perform this procedure for each new lot of reagent.

Items to collect:

- Sulfate standard solution, 1000 mg/L
 - 100-mL volumetric flasks (7), Class A
 - 1–10 mL TenSette pipet and tips
 - Deionized water
1. Prepare seven calibration standard solutions (10, 20, 30, 40, 50, 60 and 70 mg/L SO_4^{2-}) as follows:
 - a. Use a pipet to add 1, 2, 3, 4, 5, 6 and 7 mL of the 1000-mg/L sulfate standard solution into seven different 100-mL volumetric flasks.
 - b. Dilute each flask to the mark with deionized water. Mix well.
 2. Use the test procedure to measure the concentration of each standard solution.
 3. Refer to the user manual for the instrument to enter the calibration into the instrument as a user program.

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
680	40 mg/L SO_4^{2-}	30–50 mg/L SO_4^{2-}	0.4 mg/L SO_4^{2-}
685	40 mg/L SO_4^{2-}	32–48 mg/L SO_4^{2-}	0.7 mg/L SO_4^{2-}

Summary of method

Sulfate ions in the sample react with barium in the SulfaVer 4 and form a precipitate of barium sulfate. The amount of turbidity formed is proportional to the sulfate concentration. The measurement wavelength is 450 nm for spectrophotometers or 520 nm for colorimeters.

Pollution prevention and waste management

Reacted samples contain barium 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.
SulfaVer [®] 4 Reagent Powder Pillows, 10-mL	1	100/pkg	2106769
OR			
SulfaVer [®] 4 Sulfate Reagent AccuVac [®] Ampuls	1	25/pkg	2509025

Required apparatus

Description	Quantity/test	Unit	Item no.
AccuVac Snapper	1	each	2405200
Beaker, 50-mL	1	each	50041H
Sample cell, 10 mL round, 25 x 54 mm	1	each	2122800
Sample cell, 10 mL round, 25 x 60 mm	1	6/pkg	2427606
Sample cell, 10 mL square, matched pair	2	2/pkg	2495402
Stoppers for 18-mm tubes and AccuVac Ampuls	2	6/pkg	173106

Recommended standards

Description	Unit	Item no.
Sulfate Standard Solution, 1000-mg/L as SO ₄	500 mL	2175749
Sulfate Standard Solution, 2500-mg/L, 10-mL Ampules as SO ₄	16/pkg	1425210
Drinking Water Standard, Mixed Parameter, Inorganic for F ⁻ , NO ₃ , PO ₄ , SO ₄	500 mL	2833049

Optional reagents and apparatus

Description	Unit	Item no.
Cylinder, mixing, 25-mL	each	189640
Cylinder, mixing, 50-mL	each	189641
Blank AccuVac Ampules	25/pkg	2677825
Ampule Breaker, Voluette [®] ampules	each	2196800
Pipet, TenSette [®] , 0.1–1.0 mL	each	1970001
Pipet tips for TenSette Pipet 1970001	50/pkg	2185696
Pipet, TenSette [®] , 1.0 to 10.0 mL	each	1970010
Pipet tips for TenSette Pipet 1970010	50/pkg	2199796
Flask, volumetric, Class A, 100-mL	each	1457442



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