Silver

DOC316.53.01134

Colorimetric Method **Method 8120**

0.02 to 0.70 mg/L Ag **Powder Pillows**

Scope and application: For 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 specific instruments.

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.	

Before starting

Make sure that the mixing cylinder is completely dry before the test is started. If the Silver 1 Reagent Powder Pillow becomes wet, it will not fully dissolve and the color will not fully develop.
The sample pH must be 9–10 for accurate results. Do not use a pH meter to adjust the sample pH because the pH probe can contaminate the sample. For instruction on pH adjustment refer to Digest the sample on page 5.
If the sample contains an interference, digest the sample with heat and acid. Refer to Interferences on page 4 and Digest the sample on page 5. Set up the digestion apparatus in a fume hood to prevent exposure to hazardous gas.
For the best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to determine the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option.
Do not use the Pour-Thru Cell or sipper module (for applicable instruments) with this test.
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
Silver 1 Reagent Powder Pillow	1
Silver 2 Reagent Solution Pillow	1
Sodium Thiosulfate Powder Pillow	1

Items to collect (continued)

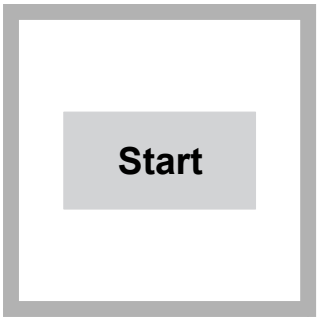
Description	Quantity
Mixing cylinder, graduated, 50 mL, with stopper	1
Cylinder, graduated, 50 mL	1
Clippers for plastic pillows	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

Refer to Consumables and replacement items on page 7 for order information.

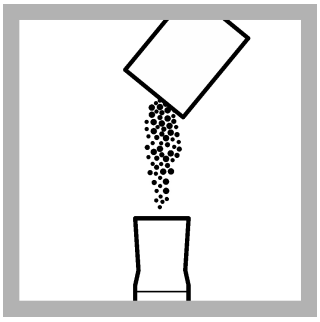
Sample collection and storage

- Collect samples in clean glass or plastic bottles that have been cleaned with 6 N (1:1) hydrochloric acid and rinsed with deionized water.
- To preserve samples for later analysis, adjust the sample pH to less than 2 with concentrated nitric acid (approximately 2 mL per liter. If the sample contains particulates, or for a dissolved metal analysis, filter the sample through a 0.45 µm filter during sample collection. After filtration, add the acid. No acid addition is necessary if the sample is tested immediately.
- Keep the preserved samples at room temperature for a maximum of 6 months.
- Before analysis, adjust the pH to 9–10 with 5 N sodium hydroxide solution. Do not use a pH meter to adjust the sample pH because the pH probe can contaminate the sample. Refer to Digest the sample on page 5.
- Correct the test result for the dilution caused by the volume additions.

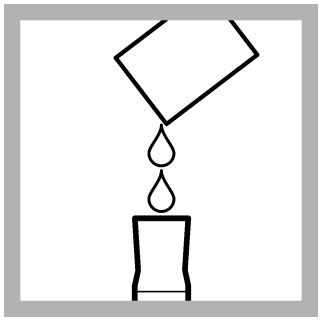
Test procedure



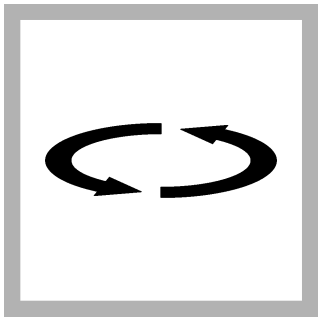
1. Start program **660 Silver**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



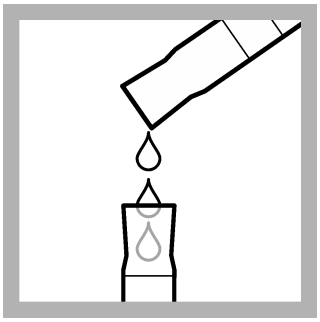
2. Add the contents of one Silver 1 Powder Pillow to a **dry** 50-mL mixing cylinder. If the powder becomes wet, it will not fully dissolve and the color will not fully develop.



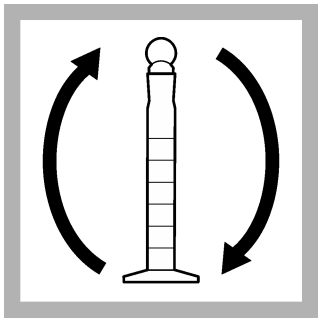
3. Add the contents of one Silver 2 Reagent Solution Pillow to the mixing cylinder.



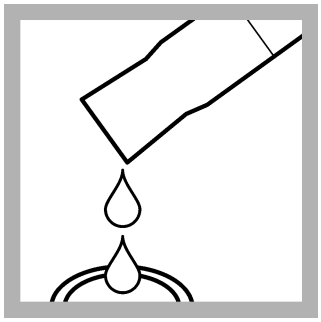
4. Swirl to mix.
If there are clumps of dry powder when the sample is poured in, the powder will not fully dissolve and the color will not fully develop.



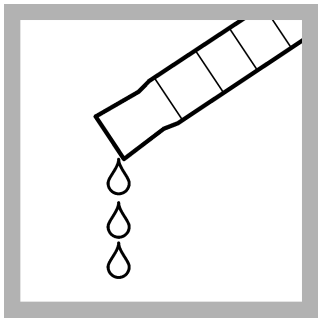
5. If the sample was preserved with acid, make sure that the sample pH is 9–10. Use a graduated cylinder to add 50 mL of sample to the mixing cylinder.



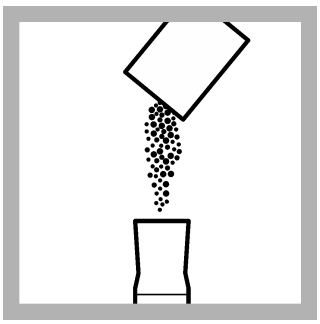
6. Put the stopper on the mixing cylinder. Continuously invert the mixing cylinder for 1 minute.



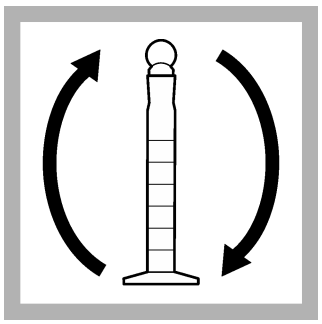
7. Prepare the sample: Pour 10 mL of the solution from the mixing cylinder into a sample cell.



8. Prepare the blank: Discard all but 25 mL of the sample from the mixing cylinder.



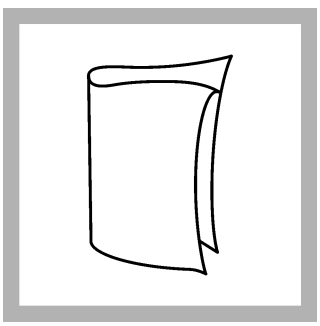
9. Add the contents of one Sodium Thiosulfate Reagent Powder Pillow to the remaining solution in the mixing cylinder. Make sure to prepare a blank for each sample.



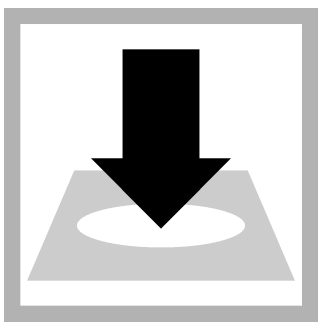
10. Put the stopper on the mixing cylinder. Invert the mixing cylinder several times to mix.

11. Start the instrument timer. A 2-minute reaction time starts.

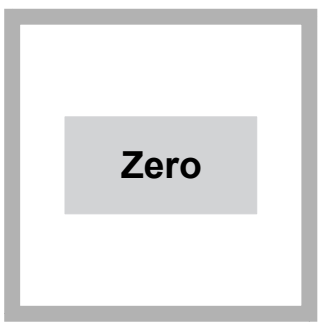
12. Pour 10-mL of the solution from the mixing cylinder into a second sample cell.



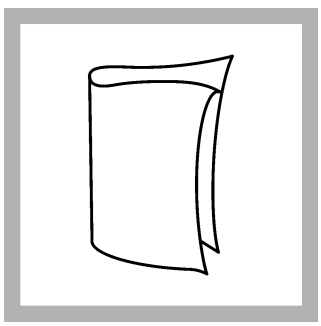
13. When the timer expires, clean the blank sample cell.



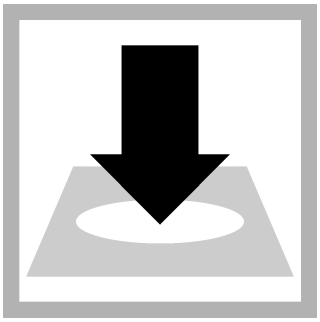
14. Insert the blank into the cell holder.



15. Push **ZERO**. The display shows 0.00 mg/L Ag.



16. Clean the prepared sample cell.



17. Insert the prepared sample into the cell holder.

18. Push **READ**. Results show in mg/L Ag. Immediately rinse the sample cells.

Interferences

Standard solutions of approximately 0.4 mg/L Ag with different concentrations of a potential interfering ion were prepared. The concentration of silver was measured. Table 2 shows the ions that caused a change in the silver concentration of more than ten percent (±10%).

Table 2 Interfering substances

Interfering substance	Interference level
Aluminum	Negative interference above 30 mg/L
Ammonia	Negative interference above 750 mg/L
Cadmium	Negative interference above 15 mg/L
Calcium	Positive interference above 600 mg/L
Chloride	Negative interference above 19 mg/L
$Chromium^{6+}$	Negative interference above 90 mg/L
Copper	Negative interference above 7 mg/L
Iron	Negative interference above 30 mg/L
Lead	Negative interference above 13 mg/L
Manganese	Negative interference above 19 mg/L
Magnesium	Positive interference above 2000 mg/L
Mercury	Positive interference above 2 mg/L
Nickel	Negative interference above 19 mg/L
Zinc	Negative interference above 70 mg/L

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:

- 1000-mg/L Silver Standard Solution
- 100-mL volumetric flask, Class A
- 5-mL volumetric pipet, Class A and pipet filler
- Deionized water
- Pipet, TenSette, 0.1–1.0 mL and tips

1. Prepare a 50.0-mg/L silver standard solution as follows:
   a. Use a pipet to add 5.00 mL of a 1000-mg/L Silver Standard Solution into a 100-mL 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 sample, then keep the (unspiked) sample in the instrument.
3. Go to the Standard Additions option in the instrument menu.
4. Select the values for standard concentration, sample volume and spike volumes.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the prepared standard solution, respectively, to three 50-mL portions of fresh sample. Mix well.
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, the reagents and the instrument.

Items to collect:

- 1000-mg/L Silver Standard Solution
- 1-L volumetric flask, Class A
- 0.5-mL volumetric pipet, Class A and pipet filler safety bulb
- Deionized water

1. Prepare a 0.5-mg/L silver standard solution as follows:
   a. Use a pipet to add 0.5 mL of a 1000-mg/L silver 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 small variations in the reagents or instruments.*

Digest the sample

⚠WARNING

Gas inhalation hazard. Operate the instrument in a fume hood to prevent exposure to hazardous gas.

⚠CAUTION

Chemical exposure hazard. Obey laboratory safety procedures and wear all of the personal protective equipment appropriate to the chemicals that are handled. Refer to the current safety data sheets (MSDS/SDS) for safety protocols.

If the sample contains organic matter, thiosulfate or cyanide, digest the sample before analysis. Possible sources for these compounds are wastewater, silver electroplating baths and silver strike solutions.

Use the Digesdahl Digestion Apparatus[1] for the digestion[2]. Refer to the documentation for the Digesdahl Digestion Apparatus for operation and safety information. Obey the safety precautions in the documentation.

1. Refer to the documentation for the Digesdahl Digestion Apparatus to digest the sample. Use the digestion procedure for aqueous liquids.

   Note: *Do not exceed the maximum sample volume of 25 mL. Several 25-mL aliquots can be digested in succession to concentrate a very dilute sample.*

   Note: *The digestion is complete when the digestate is colorless or the color of the digestate does not change after hydrogen peroxide is added. A completely digested sample does not cause foam.*

2. After the digested sample has cooled, adjust the pH of the digested sample as follows.

   a. Slowly add approximately 25 mL of deionized water to the digestion flask. Swirl to mix.
   b. Add 2 drops of 1 g/L phenolphthalein indicator solution.
   c. Add 2 drops of 1 g/L thymolphthalein indicator solution.
   d. Add sodium hydroxide to adjust the pH of the solution to 9–10. Start with 50% sodium hydroxide, then use 1 N sodium hydroxide as the color starts to change. The solution is pink in the 9–10 pH range.

      Note: *If the solution is purple, the pH is too high. Add 1 drop of sulfuric acid and 2 drops of each indicator. Do the pH adjustment again with the sodium hydroxide.*

3. Dilute to the mark with deionized water and mix.

   Note: *If the digestate is turbid, filter the digestate. Quantitatively transfer the filtrate to a clean 100-mL volumetric flask. Dilute to the mark with deionized water and mix. Correct the results for any dilution caused by the use of a sample volume other than 100 mL.*

4. Use the diluted digestate in the test procedure. If the original sample volume was less than 100 mL, correct the test result for the dilution.

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
660	0.50 mg/L Ag	0.49–0.51 mg/L Ag	0.005 mg/L Ag

Summary of Method

Silver ions in basic solution react with cadion 2B to form a green to brown to red-purple complex. The sodium thiosulfate acts as a decolorizing agent for the blank. The Silver 1 and Silver 2 reagents contain the buffer, indicator and masking agents. Organic extractions are not necessary and this method does not have as many interferences as the traditional dithizone method. The measurement wavelength is 560 nm.

[1] Sales of the Digesdahl Digestion Apparatus have stopped because of electrical compliance regulations.
[2] If a Digesdahl Digestion Apparatus is not available, use the EPA digestion procedure for total metals in Section 5 "Sample pretreatment by digestion" of the Water Analysis Handbook (http://hach.com/wah). As an alternative, use the EPA digestion procedure for total metals in the article "How should a sample intended for total metals analyzer be digested?" at Hach Support (http://support.hach.com).

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Silver Reagent Set (50 tests), includes:	—	—	2296600
Silver 1 Reagent Powder Pillows	1	50/pkg	2293566
Silver 2 Reagent Solution Pillows	1	50/pkg	2293666
Sodium Thiosulfate Powder Pillow	1	50/pkg	2293766

Required apparatus

Description	Quantity/test	Unit	Item no.
Clippers for plastic pillows	1	each	96800
Mixing cylinder, graduated, 50 mL, with glass stopper	1	each	189641
Cylinder, graduated, 50 mL, polycarbonate	1	each	2117941

Recommended standards

Description	Unit	Item no.
Silver Standard Solution, 1000 mg/L Ag	100 mL	1461342

Required digestion reagents and apparatus

Description	Quantity/Test	Unit	Item no.
Hydrogen Peroxide, 50%	20 mL	490 mL	2119649
Phenolphthalein Indicator Solution, 1 g/L		15 mL SCDB	189736
Sodium Hydroxide Solution, 50%		500 mL	218049
Sodium Hydroxide Solution, 1.00 N		100 mL MDB	104532
Sulfuric Acid, concentrated, ACS	75 mL	2.5 L	97909
Thymolphthalein Indicator Solution, 1 g/L		15 mL SCDB	2185336
Water, deionized	varies	4 L	27256
Boiling chips, silicon carbide	2–3	500 g	2055734
Digesdahl® Digestion Apparatus, 115 VAC	1	each	2313020
Digesdahl® Digestion Apparatus, 220 VAC	1	each	2313021
Safety shield	1	each	5003000

Optional reagents and apparatus

Description	Unit	Item no.
Filter holder, 25-mm, for Luer-type syringe	each	246800
Filter membrane, 0.45-micron, 25-mm	100/pkg	2514101
Flask, volumetric, Class A, 100 mL, glass	each	1457442
Flask, volumetric, Class A, 1000 mL glass	each	1457453
Nitric Acid, concentrated	500 mL	15249
Pipet, TenSette®, 0.1–1.0 mL	each	1970001

Optional reagents and apparatus (continued)

Description	Unit	Item no.
Pipet, volumetric, Class A, 0.5 mL	each	1451534
Pipet, volumetric 5.00-mL	each	1451537
Pipet filler, safety bulb	each	1465100
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	245032
Syringe, 10-cc, Luer-Lock tip	each	2202400
Water, deionized	4 L	27256

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