Cadmium

DOC316.53.01012

Dithizone Method[1]

Method 8017

0.7 to 80.0 µg/L Cd

Powder Pillows

Scope and application: For water and wastewater; digestion is necessary to measure total cadmium.

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

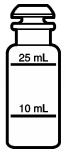
Test preparation

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
DR6000 DR3800 DR2800 DR2700 DR1900	The fill line is to the right.	2612602 
DR5000 DR3900	The fill line is toward the user.	

Before starting

The reagents that are used in this test contain potassium cyanide. **Keep cyanide solutions at pH > 11 to prevent exposure to hydrogen cyanide gas.** Collect the reacted samples for safe disposal.
Clean all glassware with 6.0 N (1:1) hydrochloric acid, then fully rinse with deionized water to remove contaminants.
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.
Filter samples that are turbid before the test. Use glass membrane filters because cadmium can adsorb on paper filters. Report results as soluble cadmium.
Do not use the Pour-Thru Cell or sipper module (for applicable instruments) with this test.
The DithiVer® powder will not completely dissolve in the chloroform. Refer to DithiVer solution preparation and storage on page 6.
In bright light conditions (e.g., direct sunlight), close the cell compartment, if applicable, with the protective cover during measurements.
To make sure that all forms of the metal are measured, digest the sample with heat and acid. Use the mild or vigorous digestion. Refer to the *Water Analysis Guide* for more information.
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.

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Items to collect

Description	Quantity
Buffer Powder Pillows, citrate	1
Chloroform, ACS	30 mL
DithiVer Metals Reagent Powder Pillows	1
Potassium Cyanide	0.1 g
Sodium Hydroxide Solution, 50%	20 mL
Cotton balls, absorbent	1
Clippers for plastic pillows	1
Cylinder, graduated, 25-mL, glass stopper	1
Cylinder, graduated, 250-mL	1
Mixing cylinder, graduated, 50 mL, with glass stopper	1
Funnel, separatory, 500 mL	1
Spoon, measuring, 0.1-g	1
Support ring (4-inch) and stand (5 x 8-inch base)	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

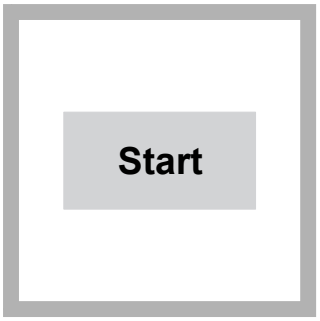
- Collect samples in clean glass or plastic bottles that have been cleaned with 6 N (1:1) hydrochloric acid and rinsed with deionized water.
- To preserve samples for later analysis, adjust the sample pH to less than 2 with concentrated nitric acid (approximately 2 mL per liter). No acid addition is 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 2.5 with 5 N sodium hydroxide solution.
- Correct the test result for the dilution caused by the volume additions.

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Test procedure

⚠WARNING

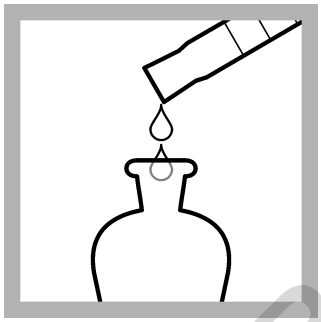
Gas inhalation hazard. Operate the instrument in a fume hood to prevent exposure to hazardous gas.



1. Start program **60 Cadmium, Dithizone**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



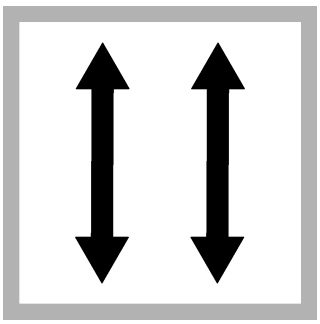
2. Fill a 250-mL graduated cylinder to the 250-mL mark with sample.



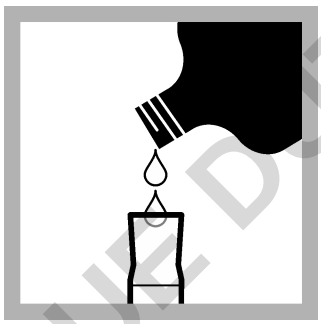
3. Pour the sample into a 500-mL separatory funnel.



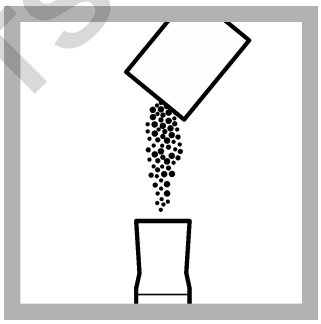
4. Add the contents of one Buffer Powder Pillow, citrate type.



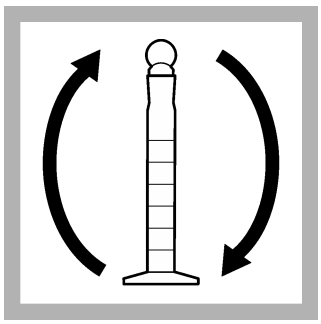
5. Put the stopper on the funnel. Shake to dissolve.



6. Prepare the DithiVer solution: Add 30 mL of chloroform to a 50-mL mixing cylinder.



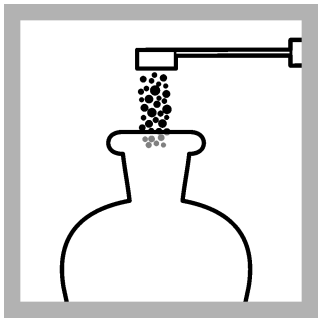
7. Add the contents of one DithiVer Metals Reagent Powder Pillow.



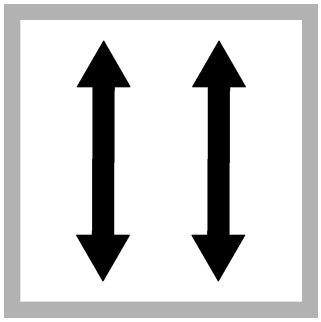
8. Put the stopper on the mixing cylinder. Invert the mixing cylinder several times to mix.



9. Add 20 mL of 50% Sodium Hydroxide Solution to the funnel.



10. Add one 0.1-g scoop of potassium cyanide to the funnel.



11. Put the stopper on the funnel. Shake vigorously for 15 seconds.

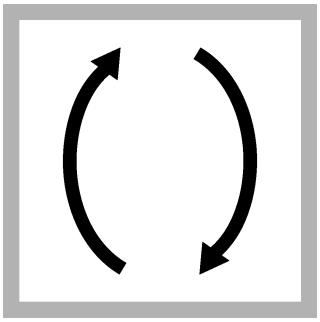


12. Remove the stopper. Start the instrument timer. A 1-minute reaction time starts.

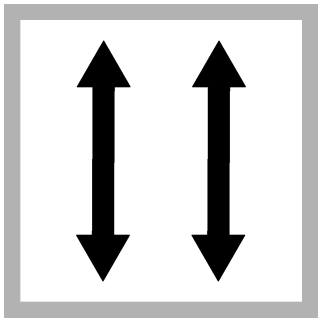
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13. Add 30 mL of the DithiVer solution to the 500-mL separatory funnel.



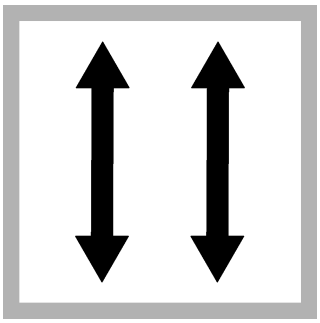
14. Put the stopper on the funnel and invert to mix. Invert the funnel and open the stopcock to vent.



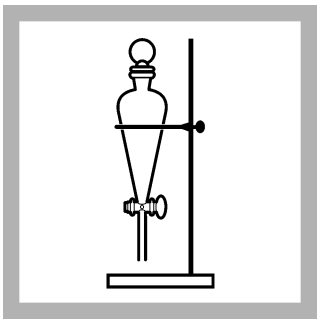
15. Close the stopcock. Shake the funnel once or twice. Invert the funnel and open the stopcock to vent.



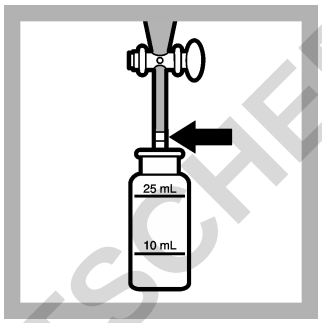
16. Start the instrument timer. A 1-minute reaction time starts.



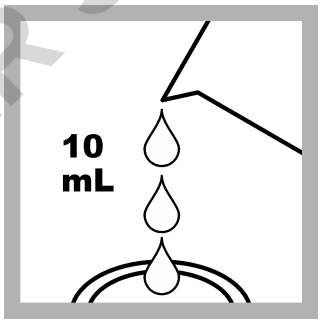
17. Close the stopcock and shake the funnel vigorously during the 1-minute time period.



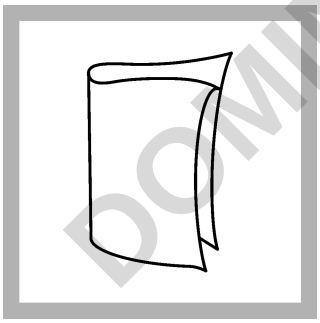
18. Put the funnel in the stand. Do not move the funnel until the timer expires.
If there is cadmium in the sample, the bottom (chloroform) layer becomes orange or pink.



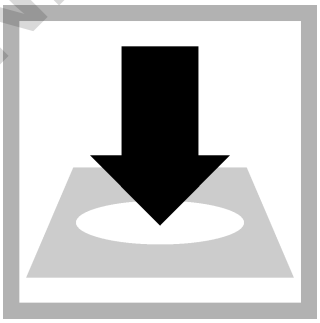
19. Prepare the sample: Put a cotton plug the size of a pea into the funnel delivery tube. Slowly drain the bottom (chloroform) layer into a dry 25-mL sample cell. Put the stopper on the sample cell.
The Cd-dithizone complex is stable for more than 1 hour if the sample cell is closed tightly and kept out of direct sunlight.



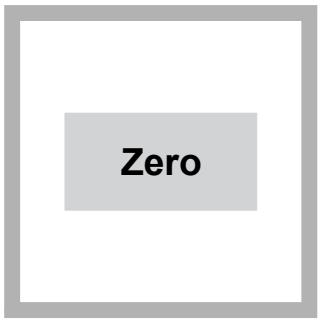
20. Prepare the blank: Put at least 10 mL of chloroform in a dry sample cell. Put the stopper on the sample cell.



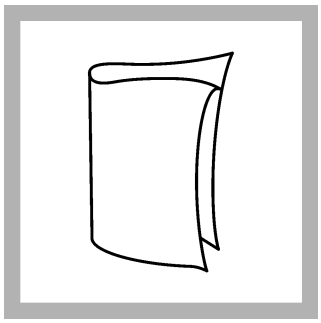
21. Clean the blank sample cell.



22. Insert the blank into the cell holder.

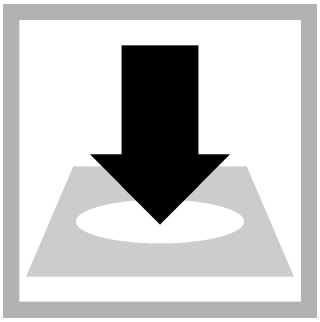


23. Push **ZERO**. The display shows 0.0 µg/L Cd.

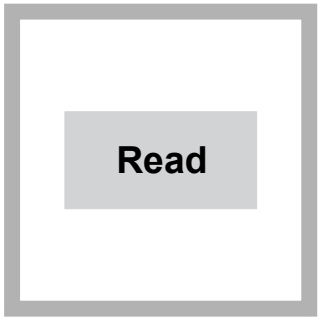


24. Clean the prepared sample cell.

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25. Insert the prepared sample into the cell holder.



26. Push **READ**. Results show in µg/L Cd.

Interferences

To eliminate interference from the metals shown in Table 2, complete the steps that follow after step 8 of the procedure.

1. Measure approximately 5 mL of the DithiVer solution into the separatory funnel.
2. Put the stopper on the funnel, invert and open the stopcock to vent.
3. Close the stopcock and shake the solution vigorously for 15 seconds.
4. Do not move the funnel until the layers separate (about 30 seconds). A yellow, red, or bronze color in the bottom (chloroform) layer confirms the presence of interfering metals. Draw off and collect the bottom (chloroform) layer for proper disposal.
5. Do the extraction with fresh 5-mL portions of the DithiVer solution again (discarding the bottom layer each time) until the bottom layer develops a pure dark green color for three successive extracts. These extractions remove only a very small amount of cadmium from the sample.
6. Extract the solution with 2- or 3-mL portions of pure chloroform to remove any DithiVer solution that remains. Collect the bottom layer each time for a correct disposal.
7. Continue with step 9 of the procedure.
8. In step 13, substitute 28.5 mL of DithiVer solution for the 30 mL.
9. Continue with step 16 of the procedure.

Table 2 Interfering substances

Interfering substance	Interference level
Highly buffered samples or extreme sample pH	Can be more than the buffering capacity of the reagents and sample pretreatment is necessary.
Bismuth	More than 80 mg/L.
Copper	More than 2 mg/L.
Mercury	All levels.
Silver	More than 2 mg/L.

Table 3 Substances that do not interfere

Aluminum	Lead
Antimony	Magnesium
Arsenic	Manganese
Calcium	Nickel
Chromium	Tin

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Table 3 Substances that do not interfere (continued)

Cobalt	Zinc
Iron	

DithiVer solution preparation and storage

- Keep DithiVer Powder Pillows away from heat.
- To prepare large quantities of this solution, add the contents of 10 DithiVer Metals Reagent Powder Pillows to a 500-mL bottle of chloroform and invert several times until well mixed (powder may not dissolve completely).
- Keep dithizone solution in an amber glass bottle for storage. This solution is stable for 24 hours.

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:

- Cadmium Standard Solution, 100-mg/L Cd
- 100-mL volumetric flask, Class A
- 25.0-mL volumetric pipet, Class A
- Pipet, TenSette, 0.1–1.0 mL
- Pipet tips for TenSette Pipet, 0.1–1.0 mL

1. Prepare a 25-mg/L cadmium standard solution as follows:
   a. Use a 25.0-mL volumetric pipet to add 25.0 mL of a 100-mg/L cadmium standard solution to a 100-mL volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare this solution weekly.
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 250-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:

- Cadmium Standard Solution, 100-mg/L Cd
- 100-mL volumetric flask, Class A
- 5.00-mL volumetric pipet, Class A
- 2.00-mL volumetric pipet, Class A
- Pipet filler safety bulb

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- Cylinder, graduated, 250-mL
- Separatory funnel, 500-mL
- Deionized water

1. Prepare a 5.0-mg/L cadmium stock solution as follows:
   a. Use a pipet to add 5.00 mL of a 100-mg/L cadmium standard solution to a 100-mL volumetric flask.
   b. Dilute to the mark with deionized water. Mix well.
2. Prepare a 40 µg/L cadmium standard solution as follows:
   a. Use a graduated cylinder to add 248 mL of deionized water into a 500-mL separatory funnel.
   b. Use a pipet to add 2.00 mL of the 5.0-mg/L cadmium stock solution into the separatory funnel. Mix well.
3. Use the test procedure to measure the concentration of the prepared standard solution.
4. Compare the expected result to the actual result.

   Note: *The factory calibration can be adjusted slightly with the standard calibration 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.*

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
60	40 µg/L Cd	39.3–40.7 µg/L Cd	0.73 µg/L Cd

Summary of Method

The dithizone method measures cadmium in water and wastewater. The DithiVer Metals Reagent is a stable powder form of dithizone. Cadmium ions in basic solution react with dithizone to form a pink to red cadmium-dithizonate complex, which is extracted with chloroform. The measurement wavelength is 515 nm.

Pollution prevention and waste management

Do not pour chloroform, cadmium and cyanide solutions down the drain. Collect the chloroform solutions and the cotton plug that are used in the delivery tube of the separatory funnel for disposal with laboratory solvent waste. Collect the cyanide solution as a reactive waste. Be sure that cyanide solutions are kept in a caustic solution with a pH > 11 to prevent potential release of hydrogen cyanide gas. These solutions 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.
Cadmium Reagent Set (100 Tests), includes:	—	—	2242200
Buffer Powder Pillows, citrate	1	100/pkg	1420299
Chloroform, ACS	30 mL	500 mL x 8	1445849
DithiVer Metals Reagent Powder Pillows	1	100/pkg	1261699
Potassium Cyanide	0.1 g	100 g	76714

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Consumables and replacement items (continued)

Description	Quantity/test	Unit	Item no.
Sodium Hydroxide solution, 50%	20 mL	500 mL	218049
Cotton balls, absorbent	1	100/pkg	257201

Required apparatus

Description	Quantity/test	Unit	Item no.
Clippers for plastic pillows	1	each	93600
Cylinder, graduated, 25 mL	1	each	50840
Cylinder, graduated, 250 mL	1	each	50846
Mixing cylinder, graduated, 50 mL, with glass stopper	1	each	189641
Funnel, separatory, 500 mL	1	each	52049
Spoon, measuring, 0.1 g	1	each	51100
Support Ring, 4-inch	1	each	58001
Support, Ring Stand, 5-inch x 8-inch base	1	each	56300

Recommended standards

Description	Unit	Item no.
Cadmium Standard Solution, 100-mg/L Cd	100 mL	1402442

Optional reagents and apparatus

Description	Unit	Item no.
Hydrochloric Acid Solution, 6.0 N	500 mL	88449
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	245032
Nitric Acid, concentrated	500 mL	15249
Water, deionized	4 L	27256
Filter Discs, glass, 47-mm	100/pkg	253000
Filter Holder, glass, for 47-mm filter	each	234000
Flask, filtering, 500 mL	each	54649
Flask, volumetric, Class A, 100 mL	each	1457442
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696

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