Cadmium

DOC316.53.01012

Dithizone Method[1] **Method 8017**

(0.7 to 80.0 µg/L) **Powder Pillows**

Scope and Application: For water and wastewater; digestion is required to determine total cadmium.

[1] Adapted from Standard Methods for the Examination of Water and Wastewater (method 3500 Cd D).

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 61 Instrument-specific information

Instrument	Sample cell	Cell orientation
DR 6000	2495402	Fill line faces right
DR 5000	2495402	Fill line faces user
DR 3900	2495402	Fill line faces user
DR 3800, DR 2800, DR 2700	2495402	Fill line faces right

Before starting the test:

For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water instead of the sample.
Clean all glassware with 6 N Hydrochloric Acid Solution and rinse with deionized water.
Sample cell orientation may vary. Refer to the instrument user manual for correct cell orientation.
Cloudy and turbid samples may require filtering before running the test. Report results as µg/L soluble cadmium. Use glass membrane type filter to avoid loss of cadmium by adsorption onto the filter paper.
If samples cannot be analyzed immediately, see *Sample collection, preservation and storage*. Adjust the pH of preserved samples before analysis.
The Flow Cell and Sipper Modules cannot be used with this procedure.
The DithiVer powder will not completely dissolve in the chloroform. For further notes see *Dithiver solution preparation and storage*.
Read the MSDS before testing. Spilled reagent will affect test accuracy and is hazardous to skin and other materials. Goggles and gloves are recommended.
In bright light conditions (e.g. direct sunlight) it may be necessary to close the cell compartment with the protective cover during measurements.

Collect the following items:

Description	Quantity
Citrate buffer powder pillows	1
Chloroform	30 mL
DithiVer Metals Reagent powder pillows	1
Potassium Cyanide	0.1 g
Sodium Hydroxide solution, 50%	20 mL
Cotton balls	1
Clippers	1
Cylinder, 25-mL graduated	1
Cylinder, 250-mL graduated	1
Cylinder, 50-mL graduated mixing	1
Funnel, 500-mL separatory	1
Sample Cells	2
Spoon, measuring, 0.1-g	1
Support ring (4-inch) and stand (5 x 8-inch base)	1

See *Consumables and replacement items* for reorder information.

Dithizone method with powder pillows

DANGER
Cyanide is a deadly poison. Use a fume hood. Maintain cyanide solutions at pH 11 or greater to prevent formation of cyanide gas.

1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).

Refer to the user manual for orientation.

2. Fill a 250-mL graduated cylinder to the 250-mL mark with sample. Pour the sample into a 500-mL separatory funnel.

3. Add the contents of one Buffer Powder Pillow for heavy metals, citrate type. Stopper the funnel and shake to dissolve.

4. DithiVer Solution Preparation:
Add 30 mL of chloroform to a 50-mL mixing graduated cylinder. Add the contents of one DithiVer Metals Reagent Powder Pillow. Stopper the cylinder. Invert several times to mix.

Dithizone method with powder pillows (continued)

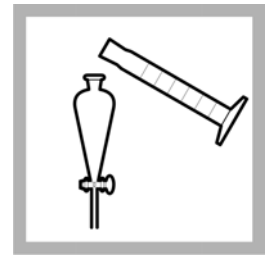
5. Add 20 mL of 50% Sodium Hydroxide Solution to the funnel.

6. Add a 0.1-g scoop of potassium cyanide to the funnel. Stopper. Shake vigorously for 15 seconds.

7. Remove the stopper.

Start the instrument timer.

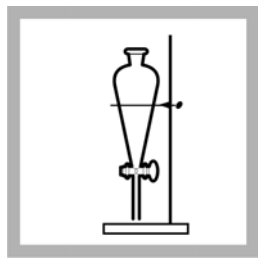
A 1-minute reaction period will begin.



8. Add 30 mL of the DithiVer solution to the 500-mL separatory funnel. Stopper, invert, and open stopcock to vent. Close the stopcock and shake funnel once or twice; vent again.

9. Start the instrument timer.

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

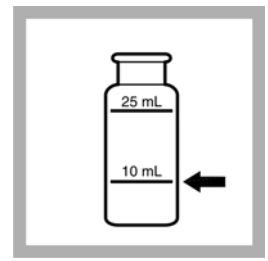


10. Start the instrument timer and allow the funnel to stand undisturbed until the timer expires.

The bottom (chloroform) layer will be orange to pink if cadmium is present.

11. Prepared Sample: Insert a cotton plug the size of a pea into the delivery tube of the funnel and slowly drain the bottom (chloroform) layer into a dry 25-mL sample cell (the prepared sample). Stopper.

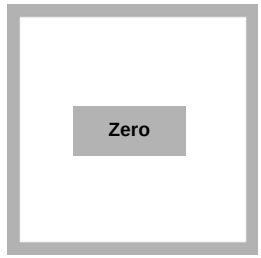
The cadmium-dithizone complex is stable for more than one hour if the sample cell is kept tightly capped and out of direct sunlight.



12. Blank Preparation: Fill a dry sample cell with at least 10 mL of chloroform. Stopper.

Dithizone method with powder pillows (continued)

13. Insert the blank into the cell holder.

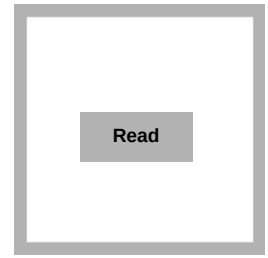


14. **ZERO** the instrument.

The display will show:

0.0 µg/L Cd

15. Insert the prepared sample into the cell holder.



16. **READ** the results in µg/L cadmium.

Interferences

Table 62 Interfering substances

Interfering substance	Interference level
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment.
Bismuth	Greater than 80 mg/L. See treatment below.
Copper	Greater than 2 mg/L. See treatment below.
Mercury	All levels. See treatment below.
Silver	Greater than 2 mg/L. See treatment below.

To eliminate interference from the metals listed in the *Interfering substances* table, insert the following steps into the procedure after step 4.

1. Measure approximately 5 mL of the DithiVer solution into the separatory funnel. Stopper the funnel, invert and open the stopcock to vent. Close the stopcock and shake the solution vigorously for 15 seconds. Allow the funnel to stand undisturbed 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.
2. Repeat the extraction with fresh 5-mL portions of the DithiVer solution (discarding the bottom layer each time) until the bottom layer shows a pure dark green color for three successive extracts. Extractions can be repeated several times without appreciably affecting the amount of cadmium in the sample.
3. Extract the solution with several 2- or 3-mL portions of pure chloroform to remove any remaining DithiVer, collecting the bottom layer each time for proper disposal.
4. Continue with step 5 of the procedure.
5. In step 8, substitute 28.5 mL of DithiVer solution for the 30 mL.
6. Continue with step 9 of the procedure.

Table 63 Substances that do not interfere

Aluminum	Lead
Antimony	Magnesium
Arsenic	Manganese
Calcium	Nickel
Chromium	Tin
Cobalt	Zinc
Iron	

Sample collection, preservation and storage

Collect samples in an acid-washed glass or plastic containers. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Store preserved samples up to six months at room temperature. Adjust the pH to 2.5 with 5.0 N sodium hydroxide before analysis. Correct the test result for volume additions.

Dithiver solution preparation and storage

Store DithiVer Powder Pillows away from light and heat. A convenient way to prepare this solution is to add the contents of 16 DithiVer Metals Reagent Powder Pillows to a 500-mL bottle of chloroform and invert several times until well mixed (carrier powder may not dissolve completely). Store dithizone solution in an amber glass bottle. This solution is stable for 24 hours.

Accuracy check

Required for accuracy check:

- Cadmium Voluette Ampule Standard, 25-mg/L Cd
- TenSette® Pipet, 0.1–1.0 mL and tips

1. After reading test results, leave the sample cell (unspiked sample) in the instrument.
2. Select Options>More>Standard Additions from the instrument menu.
3. Accept the default values for standard concentration, sample volume, and spike volumes. After the values are accepted, the unspiked sample reading will appear in the top row. See the user manual for more information.
4. Open the standard solution ampule.
5. Use the TenSette Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively to three 250-mL samples and mix each thoroughly.
6. Follow the *Dithizone method with powder pillows* test procedure for each of the spiked samples, starting with the 0.1 mL sample spike. Measure each of the spiked samples in the instrument.
7. Select **GRAPH** to view the results. Select **IDEAL LINE** (or best-fit) to compare the standard addition results to the theoretical 100% recovery.

Standard Solution Method
Required for accuracy check:

- Cadmium Standard Solution, 100-mg/L Cd.
- Deionized water
- 100-mL Volumetric flask

- Class A volumetric pipet and bulb

1. Prepare a 5.0-mg/L cadmium standard solution:
   a. Pipet 5.00 mL of Cadmium Standard Solution, 100-mg/L Cd, into a 100-mL volumetric flask.
   b. Dilute to the mark with deionized water. Prepare this solution daily.
2. Pipet 2.00 mL of the 5.0-mg/L Cadmium Standard Solution into 248 mL of deionized water in a 500-mL separatory funnel. This is a 40-µg/L cadmium solution. Perform *Dithizone method with powder pillows* on this solution beginning with step 3 of the procedure.
3. To adjust the calibration curve using the reading obtained with the standard solution, elect Options>More>Standard Adjust from the instrument menu.
4. Turn on the Standard Adjust feature and accept the shown concentration. If an alternate concentration is used, enter the concentration and adjust the curve to that value.

Method performance

Program	Standard	Precision 95% Confidence Limits of Distribution	Sensitivity Concentration change per 0.010 Abs change
60	40.0 µg/L Cd	39.3–40.7 µg/L Cd	0.73 µg/L

Summary of method

The dithizone method is designed for the determination of 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. Test results are measured at 515 nm.

Pollution prevention and waste management

Both chloroform (D022) and cyanide (D003) solutions are regulated as hazardous wastes by the Federal RCRA. Do not pour these solutions down the drain. Chloroform solutions and the cotton plug used in the delivery tube of the separatory funnel should be collected for disposal with laboratory solvent waste. Collect the cyanide solution as a reactive waste. Be sure that cyanide solutions are stored in a caustic solution with a pH >11 to prevent potential release of hydrogen cyanide gas. See the current MSDS for disposal information.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Cadmium Reagent Set	—	100/pkg	2242200
Includes:(1) 14202-99, (1) 14458-17, (1) 12616-99, (1) 767-14, (4) 2180-49, (1) 2572-01			
Buffer Powder Pillows, citrate	1	100/pkg	1420299
Chloroform, ACS	40 mL	4 L	1445817
DithiVer Metals Reagent Powder Pillows	1	100/pkg	1261699
Potassium Cyanide	0.1 g	125 g	76714
Sodium Hydroxide Solution, 50%	20 mL	500 mL	218049

Required reagents (continued)

Description	Quantity/Test	Unit	Catalog number
Cotton Balls, absorbent	1	100/pkg	257201

Required apparatus

Description	Quantity	Unit	Catalog number
Clippers, for opening powder pillows	1	each	96800
Cylinder, graduated, 25-mL	1	each	50840
Cylinder, graduated, 250-mL	1	each	50846
Cylinder, graduated, mixing, 50-mL	1	each	189641
Funnel, separatory, 500-mL	1	each	52049
Sample cell, 25 mL square, matched pair with cap	2	2/pkg	2612602
Spoon, measuring, 0.1-g	1	each	51100
Support Ring, 4"	1	each	58001
Support Ring Stand, 5" x 8" base	1	each	56300

Recommended standards

Description	Unit	Catalog number
Cadmium Standard Solution, 100-mg/L Cd	100 mL	1402442
Chloroform, ACS	500 mL	1445849
Hydrochloric Acid Solution, 6.0 N	500 mL	88449
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	245032
Sodium Hydroxide Standard Solution, 5.0 N	59 mL SCDB	245026
Water, deionized	4 L	27256

Optional reagents and apparatus

Description	Unit	Catalog number
Cylinder, graduated, 5-mL	each	50837
Filter Discs, glass, 47 mm	100/pkg	253000
Filter Holder, glass, for 47-mm filter	each	234000
Flask, Erlenmeyer, 500-mL	each	50549
Flask, filtering, 500-mL	each	54649
Flask, volumetric, Class A, 100-mL	each	1457442
Flask, volumetric, Class A, 250-mL	each	1457446
Flask, volumetric, Class A, 1000-mL	each	1457453
Gloves, chemical resistant, size 9 to 9.5[1]	pair	2410104
Goggles, safety, vented	each	2550700
Hot Plate, 3½-in. diameter, 120 VAC, 50/60 Hz	each	1206701
pH Paper, pH 1.0 to 11.0	5 rolls/pkg	39133
Pipet Filler, safety bulb	each	1465100
Pipet, serological, 2-mL	each	53236
Pipet, TenSette®, 0.1 to 1.0 mL	each	1970001
Pipet Tips, for TenSette Pipet 1970001	50/pkg	2185696
Pipet Tips, for TenSette Pipet 1970001	1000/pkg	2185628
Pipet, volumetric, 2.00-mL, Class A	each	1451536
Pipet, volumetric, 3.00-mL, Class A	each	1451503
Pipet, volumetric, 6.00-mL, Class A	each	1451506
Pipet, volumetric, 8.00-mL, Class A	each	1451508
Pipet, volumetric, 9.00-mL, Class A	each	1451509
Pipet, volumetric, 10.00-mL, Class A	each	1451538
Pipet, volumetric, 20.00-mL, Class A	each	1451520
Tongs, crucible, 9-inch	each	56900

[1] Other sizes available.

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