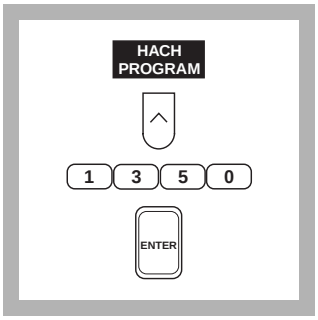
CADMIUM

Method 8017 **Dithizone Method***

Powder Pillows **(0 to 80.0 µg/L)**

Scope and Application: *For water and wastewater; digestion is required to determine total cadmium. See Section 2 for digestion procedure. The estimated detection limit for program number 1350 is 1.3 µg/L Cd.*

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



1. Press the soft key under ***HACH PROGRAM***.

Select the stored program number for cadmium (Cd) by pressing **1350** with the numeric keys.

Press: **ENTER**

Note: *If samples cannot be analyzed immediately, see Sample Collection, Storage and Preservation following these steps. Adjust the pH of preserved samples before analysis.*

Note: *The Flow Cell and Sipper Modules cannot be used with this procedure.*

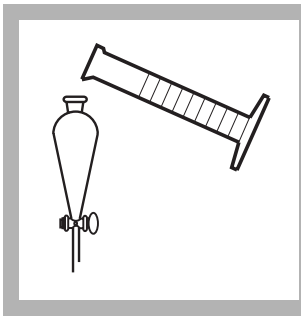
2. The display will show:

HACH PROGRAM: 1350
Cadmium

The wavelength (λ), **515 nm**, is automatically selected.

Note: *For proof of accuracy, use a 40 µg/L cadmium standard solution (preparation given in the Accuracy Check) in place of the sample.*

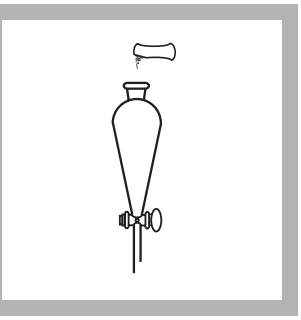
Note: *For best results, determine a reagent blank for each new lot of reagent as follows. Prepare a reagent blank by repeating steps 3 through 14, using deionized water as the sample. Zero the instrument on chloroform by pressing the soft key under* ***ZERO****. Insert the reagent blank and the blank value will be displayed. Correct for the reagent blank by pressing the soft keys under* ***OPTIONS, (MORE),*** *and then* ***BLANK:OFF****. Enter the reagent blank value and press* **ENTER***. Repeat for each new lot of reagent.*



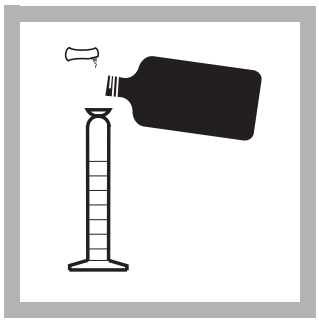
3. Fill a 250-mL graduated cylinder to the 250-mL mark with sample. Pour the sample into a 500-mL separatory funnel.

Note: *Clean all glassware with 6 N Hydrochloric Acid Solution and rinse with deionized water.*

Note: *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.*



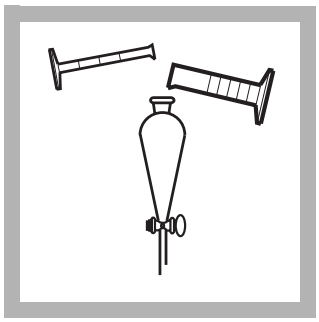
4. Add the contents of one Buffer Powder Pillow for heavy metals, citrate type. Stopper the funnel and shake to dissolve.



5. 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 (this is the DithiVer solution).

Note: *Use adequate ventilation for the extraction, preferably a fume hood.*

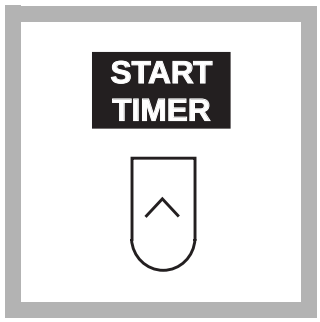
Note: *The DithiVer powder will not completely dissolve in the chloroform. For further notes see Dithiver Solution Preparation and Storage.*



6. Add 20 mL of 50% Sodium Hydroxide Solution. Add a 0.1-g scoop of potassium cyanide to the funnel. Stopper. Shake vigorously for 15 seconds.

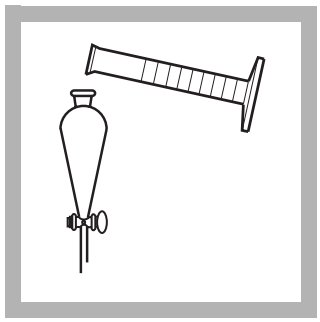
Warning: Cyanide is a deadly poison. Use a fume hood. Maintain cyanide solutions at pH 11 or greater to prevent formation of cyanide gas.

Note: *Spilled reagent will affect test accuracy and is hazardous to skin and other materials. Please read the MSDS before testing.*



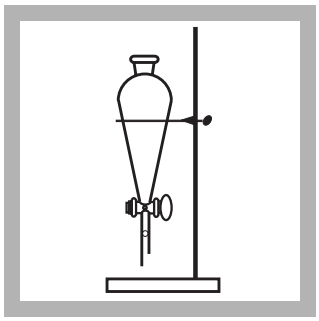
7. Remove the stopper. Press the soft key under ***START TIMER.***

A 1-minute reaction period will begin.



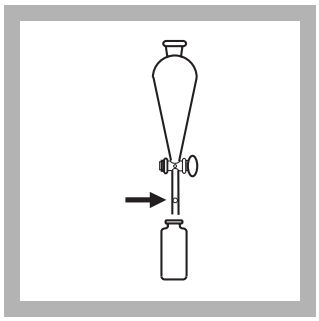
8. Add 30 mL of the DithiVer solution to the 500-mL separatory funnel. Stopper, invert, and open stopcock to vent. Close the stopcock and shake funnel once or twice; vent again.

Press the soft key under ***START TIMER***. Close the stopcock and shake the funnel vigorously during the 1 minute time period.



9. Press the soft key under ***START TIMER***, and allow the funnel to stand undisturbed until the timer beeps.

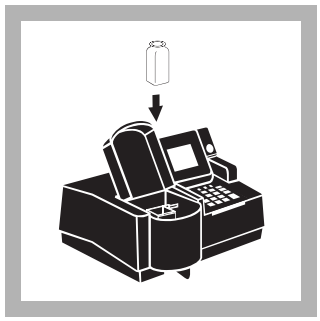
Note: *The bottom (chloroform) layer will be orange to pink if cadmium is present.*



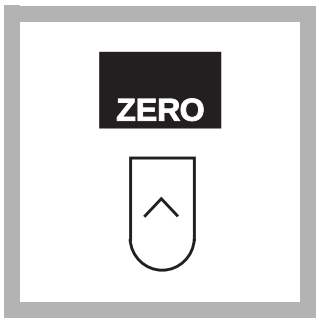
10. Insert a cotton plug the size of a pea into the delivery tube of the funnel and slowly drain the bottom (chloroform) layer into a dry 25-mL sample cell (the prepared sample). Stopper.

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

11. Fill a dry 25-mL sample cell with chloroform (the blank). Stopper.



12. Place the blank into the cell holder. Close the light shield.



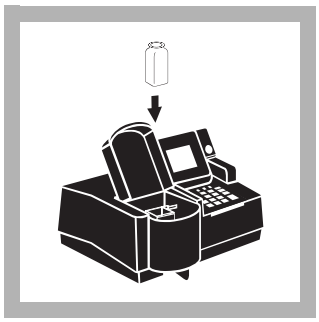
13. Press the soft key under ***ZERO***.

The display will show:

0.0 µg/L Cd

Note: *If you are using a reagent blank correction, the display will show the correction.*

Note: *For other concentration units, press the soft key under* ***OPTIONS****. Then press the soft key under* ***UNITS*** *to scroll through the available options. Press* **ENTER** *to return the read screen.*



14. Place the prepared sample into the cell holder. Close the light shield. Results in µg/L cadmium (or chosen units) will be displayed.

Note: *See Pollution Prevention and Waste Management following these steps for proper disposal of chloroform solutions.*

Interferences

The following do not interfere:

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

Table 1 Interfering Substances and Suggested Treatments

Interfering Substance	Interference Levels and Treatments
Highly buffered samples or Extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment; see Section *1.3.1 pH Interference*.
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.

Eliminate interference from the metals in the table by the following treatment, beginning after Step 5.

a. Measure about 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.

b. Repeat 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.

c. 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.

d. Continue with Step 6 of the procedure.

e. In Step 8, substitute 28.5 mL of DithiVer solution for the 30 mL.

f. Continue with Step 9 of the procedure.

Sample Collection, Storage and Preservation

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; see Section *1.2.2 Correcting 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

Standard Additions Method

a. Leave the unspiked sample in the sample compartment. Verify that the units displayed are in µg/L. Select standard additions mode by pressing the soft keys under ***OPTIONS, (MORE)*** and then ***STD ADD***.

b. Press **ENTER** to accept the default sample volume (mL), 250.

c. Press **ENTER** to accept the default standard concentration (µg/L), 25,000.

d. Press the soft key under ***ENTRY DONE***.

e. Snap the neck off a Cadmium Voluette Ampule Standard, 25-mg/L Cd (25,000-µg/L Cd).

f. 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.

g. Analyze each standard addition sample as described above. Accept the standard additions reading by pressing the soft key under ***READ*** each time. Each addition should reflect approximately 100% recovery.

h. After completing the sequence, the display will show the extrapolated concentration value and the "best-fit" line through the standard additions data points, accounting for matrix interferences.

i. See Section *1.4.1 Standard Additions* for more information.

Standard Solution Method
Prepare a 5.0-mg/L cadmium standard solution by pipetting 5.00 mL of Cadmium Standard Solution, 100-mg/L Cd, into a 100-mL volumetric flask. Dilute to the mark with deionized water. Prepare this solution daily. 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 the cadmium test on this solution beginning with Step 4 of the procedure.

Method Performance

Precision
Standard: 40.0 µg/L Cd

Program	95% Confidence Limits
1350	39.3–40.7 µg/L Cd

For more information on determining precision data and method detection limits, refer to Section *1.5*.

Estimated Detection Limit

Program	EDL
1350	1.3 µg/L Cd

For more information on derivation and use of Hach's estimated detection limit, see Section *1.5.2*. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, Appendix B, see Section *1.5.1*.

Sensitivity
Program Number: 1350

Portion of Curve:	ΔAbs	ΔConcentration
Entire Range	0.010	0.73 µg/L

See Section *1.5.3 Sensitivity Explained* for more information.

Calibration Standard Preparation

To perform a cadmium calibration using the dithizone method, prepare a 1,000-µg/L cadmium stock solution by pipetting 10.00 mL of a 100-mg/L Cadmium Standard Solution (Cat. No. 14024-42) into a 1000-mL volumetric flask using Class A glassware. Dilute to the mark with deionized water and mix thoroughly.

Prepare calibration standard containing 12.00, 36.00, 64.00 and 80.00 µg/L Cd as follows:

a. Into four different 250-mL volumetric flasks, pipet 3.00, 9.00, 16.00 and 20.00 mL of the 1,000-µg/L Cd stock solution using Class A glassware.

b. Dilute to the mark with deionized water and mix thoroughly.

c. Using the dithizone method and the calibration procedure described in the *User-Entered Programs* section of the *DR/4000 Spectrophotometer Instrument Manual*, generate a calibration curve from the standards prepared above.

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.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheet* for information specific to the reagents used. For additional information, refer to Section *3*.

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 Section *3* for more information on proper disposal of these materials.

REQUIRED REAGENTS AND STANDARDS

	Cat. No.
Cadmium Reagent Set (100 Tests)	22422-00
Includes: (1) 14202-99, (1) 14458-17, (1) 12616-99, (1) 767-14, (4) 2180-49, (1) 2572-01	

Description	Quantity Required per test	Unit	Cat. No.
Buffer Powder Pillows, citrate	1 pillow	100/pkg	14202-99
Chloroform, ACS	30 mL	4 L	14458-17
DithiVer Metals Reagent Powder Pillows	1 pillow	100/pkg	12616-99
Potassium Cyanide	0.1 g	125 g	767-14
Sodium Hydroxide Solution, 50%	20 mL	500 mL	2180-49
Cotton Balls, absorbent	1	100/pkg	2572-01

REQUIRED EQUIPMENT AND SUPPLIES

Clippers, for opening powder pillows	1	each	968-00
Cylinder, graduated, 25-mL	1	each	508-40
Cylinder, graduated, 250-mL	1	each	508-46
Cylinder, graduated, mixing, 50-mL	1	each	1896-41
Sample Cells, matched pair, 1-inch, glass, with stopper	2	pair	26126-02
DR/4000 1-Inch Cell Adapter	1	each	48190-00
Funnel, separatory, 500-mL	1	each	520-49
Spoon, measuring, 0.1-g	1	each	511-00
Support Ring, 4"	1	each	580-01
Support Ring Stand, 5" x 8" base	1	each	563-00

OPTIONAL REAGENTS AND STANDARDS

Cadmium Standard Solution, 100-mg/L Cd	100 mL	14024-42
Cadmium Standard Solution, 10-mL Voluette Ampule, 25-mg/L Cd	16/pkg	14261-10
Hydrochloric Acid Solution, 6.0 N	500 mL	884-49
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sodium Hydroxide Standard Solution, 5.0 N	59 mL SCDB	2450-26
Water, deionized	4 liters	272-56
Chloroform, ACS	500 mL	14458-49

OPTIONAL EQUIPMENT AND SUPPLIES

Description	Unit	Cat. No.
Ampule Breaker Kit	each	21968-00
Cylinder, graduated, 5-mL	each	508-37
DR/4000 Carousel Module Kit	each	48090-02
Filter Discs, glass, 47 mm	100/pkg	2530-00
Filter Holder, glass, for 47-mm filter	each	2340-00
Flask, Erlenmeyer, 500-mL	each	505-49
Flask, filtering, 500-mL	each	546-49
Flask, volumetric, Class A, 100-mL	each	14574-42
Flask, volumetric, Class A, 250-mL	each	14574-46
Flask, volumetric, Class A, 1000-mL, with glass stopper	each	14574-53
Hot Plate, 3½-in. diameter, 120 VAC, 50/60 Hz	each	12067-01
Hot Plate, 3½-in. diameter, 240 VAC, 50/60 Hz, variable control	each	12067-02
pH Paper, pH 1.0 to 11.0	5 rolls/pkg	391-33
pH Meter, *sens**ion***™***1,*** portable	each	51700-00
Pipet, serological, 2-mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, 2.00-mL, Class A	each	14515-36
Pipet, volumetric, 3.00-mL, Class A	each	14515-03
Pipet, volumetric, 6.00-mL, Class A	each	14515-06
Pipet, volumetric, 8.00-mL, Class A	each	14515-08
Pipet, volumetric, 9.00-mL, Class A	each	14515-09
Pipet, volumetric, 10.00-mL, Class A	each	14515-38
Pipet, volumetric, 20.00-mL, Class A	each	14515-20
Pipet Filler, safety bulb	each	14651-00
Tongs, crucible, 9-inch	each	569-00

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