Lead

DOC316.53.01055

USEPA[1] Dithizone Method[2] **Method 8033**

3 to 300 µg/L **Powder Pillows**

Scope and Application: For water and wastewater

[1] USEPA accepted for reporting for wastewater analysis (digestion is required)

[2] Procedure is equivalent to Standard Method 3500-Pb D for wastewater analysis.

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 209 Instrument-specific information

Instrument	Sample cell	Cell orientation
DR 6000	2612602	Fill line faces right
DR 5000	2612602	Fill line faces user
DR 3900	2612602	Fill line faces user
DR 3800, DR 2800, DR 2700	2612602	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 a 1:1 Nitric Acid Solution. Rinse with deionized water.
Cloudy and turbid samples may require filtering before running the test. Report results as µg/L soluble lead. Use glass membrane type filter to avoid loss of lead 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.
For more accurate results, adjust the sample to pH 11.0–11.5 using a pH meter in step 11. Omit the five additional drops of Sodium Hydroxide Standard Solution in step 12
The DithiVer powder will not completely dissolve in the chloroform. For further notes see *DithiVer solution preparation, storage and reagent blank*.
Read the MSDS before testing. Spilled reagent will affect test accuracy and is hazardous to skin and other materials.
In bright light conditions (e.g. direct sunlight) it may be necessary to close the cell compartment with the protective cover during measurements.
Digestion is required to for determine the total lead for EPA reporting purposes. Use mild or vigorous digestion.

Collect the following items:

Description	Quantity
Citrate Buffer Powder Pillows	1
Chloroform	50 mL
DithiVer Metals Reagent Powder Pillows	1
Potassium Cyanide	2 g
Sodium Hydroxide Standard Solution, 5.0 N	varies
Cotton Balls	1
Clippers	1
Cylinder, 50 mL graduated mixing	1
Cylinder, 5 mL graduated	1
Cylinder, 50 mL graduated	1
Cylinder, 250 mL graduated	1
Funnel, 500 mL separatory	1
Sample Cells (see *Instrument-specific information*)	2
Spoon, measuring, 1.0 g	1
Support Ring (4 inch) and Stand (5 x 8 inch base)	1

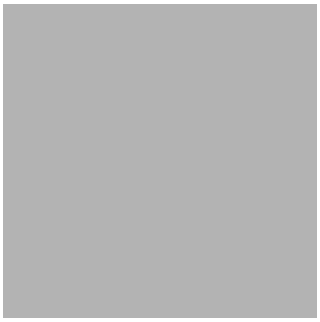
See *Consumables and replacement items* for reorder information.

Dithizone method for powder pillows

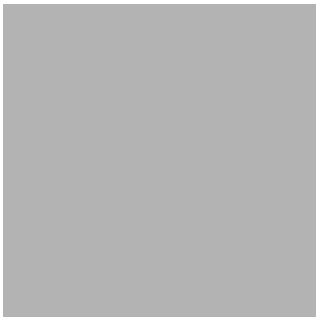
1. Select the test.

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

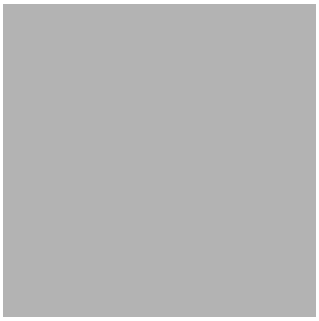
Refer to the user manual for orientation.



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

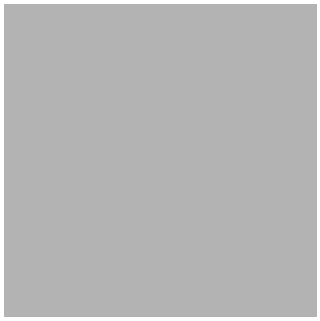


3. Transfer the sample into 500 mL separatory funnel.

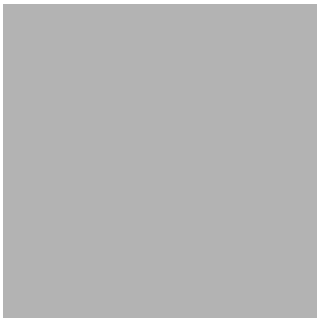


4. Add the contents of one Buffer Powder Pillow, citrate type.

Dithizone method for powder pillows (continued)

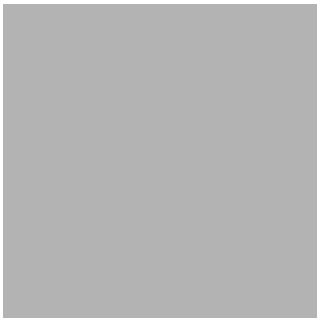


5. Insert the stopper into the funnel and shake to dissolve.

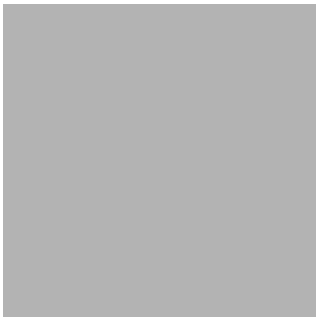


6. DithiVer Solution preparation:

Add 50 mL of chloroform to a 50-mL mixing graduated cylinder. Add the contents of one DithiVer Metals Reagent Powder Pillow.

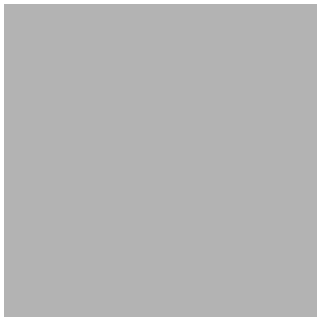


7. Stopper the cylinder. Invert several times to mix.

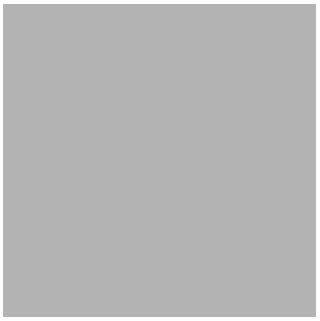


8. Measure 30 mL of the prepared dithizone solution with a second graduated cylinder and add to the separatory funnel.

Insert the stopper and invert to mix. Open stopcock to vent. Close the stopcock.



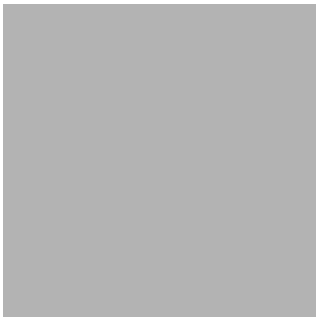
9. Add 5 mL of 5.0 N Sodium Hydroxide Standard Solution.



10. Stopper. Invert. Open stopcock to vent. Close the stopcock and shake the funnel once or twice and vent again.

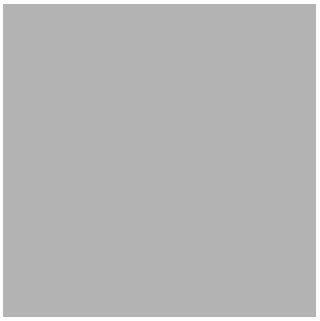
If the solution turns orange after shaking, the pH is too high. Add a few drops of 5.25 N Sulfuric Acid to the solution to decrease the pH.

The blue-green color will reappear (alternatively, to avoid higher blanks, repeat on new sample and use less sodium hydroxide in step 9).



11. Continue adding 5.0 N Sodium Hydroxide Standard Solution dropwise and shaking the funnel after every few drops until the color of the solution being shaken changes from blue-green to orange.

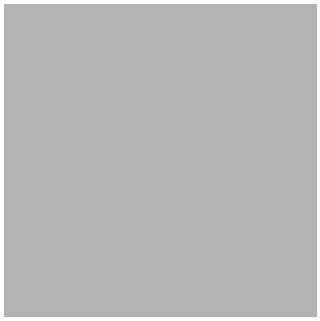
Large amounts of zinc cause the color transition at the end point to be indistinct.



12. Add 5 more drops of 5.0 N Sodium Hydroxide Standard Solution.

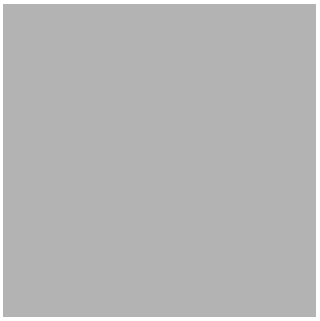
A pink color in the bottom (chloroform) layer at this point does not necessarily indicate lead is present. Only after adding the potassium cyanide in the next step will the presence of lead be confirmed by a pink color.

Dithizone method for powder pillows (continued)

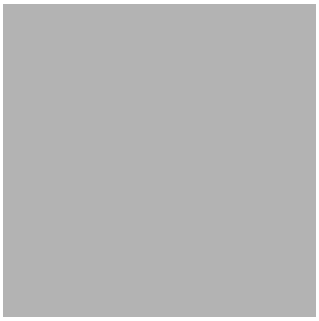


13. Add 2 heaping 1.0 g scoops of potassium cyanide to the funnel. Stopper.

Shake vigorously until the potassium cyanide is all dissolved (about 15 seconds).

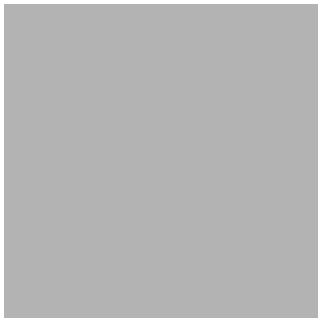


14. Wait one minute for the layers to separate. The bottom (chloroform) layer will be pink if lead is present.



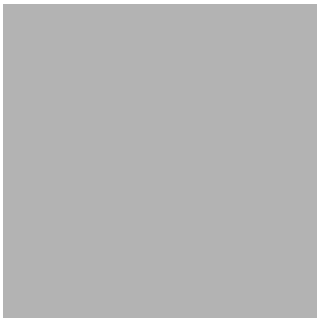
15. Prepared sample: Insert a cotton plug the size of a pea into the delivery tube of the funnel and slowly drain the bottom (chloroform) layer into a dry sample cell. Insert the stopper.

The lead-dithizone complex is stable for at least thirty minutes if the sample cell is kept tightly capped and out of direct sunlight.

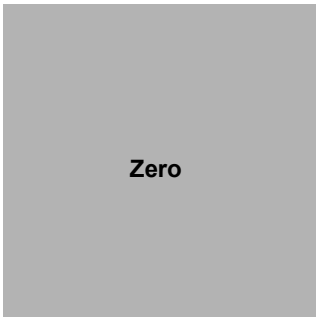


16. Blank preparation: Measure 10 mL of chloroform into another sample cell.

Insert the stopper.



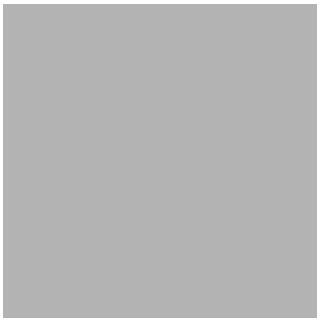
17. Insert the blank into the cell holder.



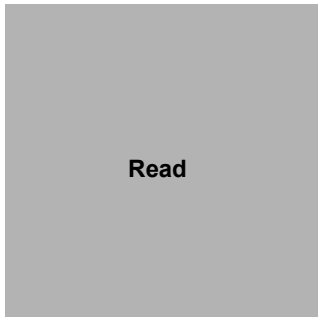
18. ZERO the instrument.

The display will show:

0 µg/L Pb^{2+}



19. Insert the prepared sample into the cell holder



20. READ the results in µg/L Pb^{2+}.

Interferences

Table 210 Substances that do not interfere

Non-interfering substance	Non-interfering substance
Aluminum	Lead
Antimony	Magnesium
Arsenic	Manganese
Calcium	Nickel
Chromium	Tin
Cobalt	Zinc
Iron	

Interference from the metals in the *Interfering substances* table can be eliminated by inserting the *Interference treatment for metals* procedure after step 6 of the *Dithizone method for powder pillows* procedure.

Table 211 Interfering substances

Interfering substance	Interference level
Highly buffered samples or extreme sample pH	All levels. See *Interference treatment for metals*.
Bismuth	All levels. See *Interference treatment for metals*.
Copper	All levels. See *Interference treatment for metals*.
Mercury	All levels. See *Interference treatment for metals*.
Silver	All levels. See *Interference treatment for metals*.
Tin	All levels. See *Interference treatment for metals*.

Interference treatment for metals

1. 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.
2. Repeat extraction with fresh 5 mL portions of prepared dithizone solution (collecting the bottom layer each time in appropriate waste collection vessel) until the bottom layer shows a pure dark green color for three successive extracts. Extractions can be repeated a number of times without appreciably affecting the amount of lead in the sample.
3. Extract the solution with several 2 or 3 mL portions of pure chloroform to remove any remaining dithizone, again collecting the bottom layer each time for proper disposal.
4. Continue the procedure, substituting 28.5 mL of prepared dithizone solution for the 30 mL in step 8.

DithiVer solution preparation, storage and reagent blank

- Store DithiVer Powder Pillows away from light and heat.
- A convenient way to prepare this solution is to add the contents of 10 DithiVer Metals Reagent Powder Pillows to a 500 mL bottle of chloroform.
- Invert several times until well mixed (carrier powder may not dissolve).
- Store dithizone solution in an amber glass bottle. This solution is stable for 24 hours.
- Carry out a reagent blank using deionized water through the entire method to obtain the most accurate results.

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.

Accuracy check

Standard additions method (sample spike)
Required for accuracy check:

- Lead Voluette Ampule Standard, 50 mg/L Pb
- Ampule breaker
- TenSette Pipet and Pipet Tips

1. After reading test results, leave the sample cell (unspiked sample) in the instrument.Verify that units are in µg/L.
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 prepare spiked samples: add 0.1 mL, 0.2 mL and 0.3 mL of standard to three 250 mL portions of fresh sample.
6. Follow the *Dithizone method for 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
Note: *Refer to the instrument user manual for specific software navigation instructions.*

Required for accuracy check:

- Lead Standard Solution, 100 mg/L
- Deionized water
- 100 mL Class A volumetric flask

- Class A volumetric pipet, 10 mL
- Pipet filler

1. Prepare a 10 mg/L lead standard solution as follows:
   a. Pipet 10.00 mL of Lead Standard, 100 mg/L, into a 100 mL volumetric flask.
   b. Dilute to the mark with deionized water. Mix well.
2. Prepare a 200 µg/L lead standard solution as follows:

   Use a graduated cylinder to measure 245 mL of deionized water into the 500 mL separatory funnel (step 3 of the *Dithizone method for powder pillows* test). Pipet 5.00 mL of the 10.0 mg/L Lead standard into the funnel.
3. Follow the *Dithizone method for powder pillows* test procedure.
4. To adjust the calibration curve using the reading obtained with the 200 µg/L Standard Solution, select Options>More>Standard Adjust from the instrument menu.
5. Turn on the Standard Adjust feature and accept the displayed 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
280	150 µg/L Pb	140–160 µg/L Pb	2.3 µg/L

Summary of method

The dithizone method is designed for the determination of lead in water and wastewater. The DithiVer Metals Reagent is a stable powder form of dithizone. Lead ions in basic solution react with dithizone to form a pink to red lead-dithizonate complex, which is extracted with chloroform. Test results are measured at 515 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Lead Reagent Set (100 Tests)	—	—	2243100
Includes: (1) 1420299, (2) 1445817, (1) 1261699, (2) 76714, (1) 245053, (2) 245026			
Buffer Powder Pillows, citrate	1	100/pkg	1420299
Chloroform, ACS	30 mL	4 L	1445817
DithiVer Metals Reagent Powder Pillows	1	100/pkg	1261699
Potassium Cyanide	0.1 g	125 g	76714
Sodium Hydroxide Solution, 5.0 N	5 mL	1000 mL	245053
Sodium Hydroxide Standard Solution, 5.0 N	varies	59 mL DB	245026

Lead

Required apparatus

Description	Quantity	Unit	Catalog number
Clippers, for opening powder pillows	1	each	96800
Cotton Balls, absorbent	1	100/pkg	257201
Cylinder, graduated, 5 mL	1	each	50837
Cylinder, graduated, 50 mL	1	each	50841
Cylinder, graduated, 250 mL	1	each	50846
Cylinder, graduated, mixing, 50 mL	1	each	189641
Funnel, separatory, 500 mL	1	each	52049
pH Meter, sens***ion***™1, portable, with electrode	1	each	5170010
Spoon, measuring,1 g	1	each	51000
Support Ring, 4"	1	each	58001
Support Ring Stand, 5" x 8" base	1	each	56300
Sample Cell, 1-inch square, w/stopper, matched pair	2	2/pkg	2612602

Recommended standards

Description	Unit	Catalog number
Lead Standard Solution, 100 mg/L Pb	100 mL	1261742
Lead Standard Solution, 10 mL Voluette Ampules, 50 mg/L Pb	16/pkg	1426210

Optional reagents and apparatus

Description	Unit	Catalog number
Ampule Breaker Kit	each	2196800
Chloroform, ACS	500 mL	1445849
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
Nitric Acid Solution, 1:1	500 mL	254049
Nitric Acid, ACS	500 mL	15249
pH Paper, pH 1.0 to 11.0	5 rolls/pkg	39133
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, volumetric, 5.00 mL, Class A	each	1451537
Pipet, volumetric, 10.00 mL, Class A	each	1451538
Pipet Filler, safety bulb	each	1465100
Sulfuric Acid, 5.25 N	100 mL MDB	244932
Water, deionized	4 L	27256