Lead

DOC316.53.01055

USEPA[1] Dithizone Method[2]

Method 8033

3 to 300 µg/L Pb^{2+}

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.

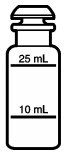
Test preparation

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
DR 6000 DR 3800 DR 2800 DR 2700 DR 1900	The fill line is to the right.	2612602 
DR 5000 DR 3900	The fill line is toward the user.	

Before starting

Clean all glassware with 1:1 nitric acid, then 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 cloudy and turbid samples if necessary before the test. Report results as µg/L soluble lead. Use glass membrane type filters to prevent loss of lead by absorption onto the filter paper.
For more accurate results, adjust the sample to pH 11.0 to 11.5 with a pH meter in step 15. Omit the five additional drops of Sodium Hydroxide Standard Solution in step 16.
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.

Items to collect

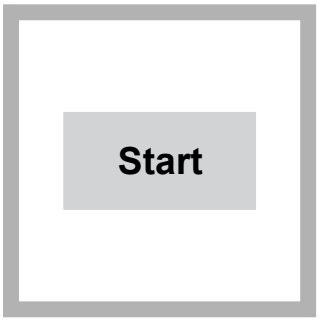
Description	Quantity
Buffer Powder Pillows, citrate	1
Chloroform, ACS	50 mL
DithiVer Metals Reagent Powder Pillows	1
Potassium Cyanide	2 g
Sodium Hydroxide Standard Solution, 5.0 N	varies
Cotton balls, absorbent	1
Clippers for plastic pillows	1
Cylinder, graduated, 5-mL	1
Mixing cylinder, graduated, 50-mL, with glass stopper	1
Cylinder, graduated, 50-mL	1
Cylinder, graduated, 250-mL	1
Funnel, separatory, 500-mL	1
Spoon, measuring, 1.0-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.

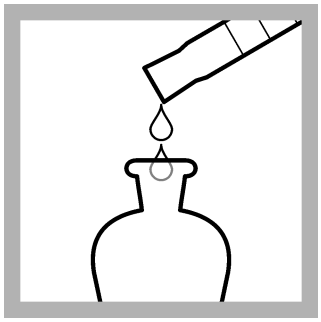
Test procedure



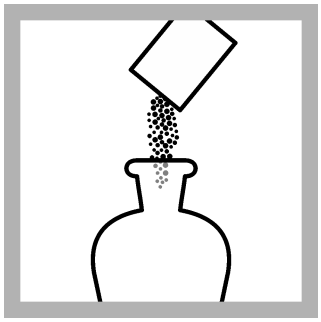
1. Start program **280 Lead, Dithizone**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

Note: *Although the program name can be different between instruments, the program number does not change.*

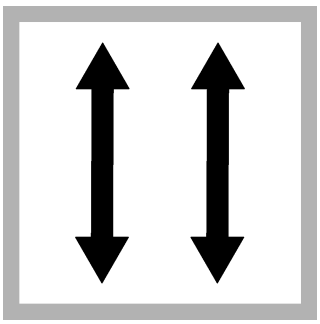
2. Fill a 250-mL graduated cylinder to the 250-mL mark with sample.



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

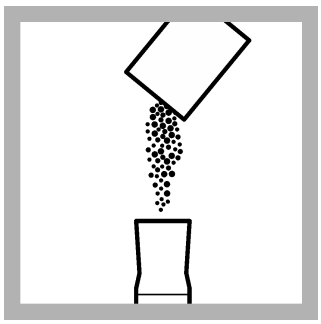


4. Add the contents of one Buffer Powder Pillow, citrate type.

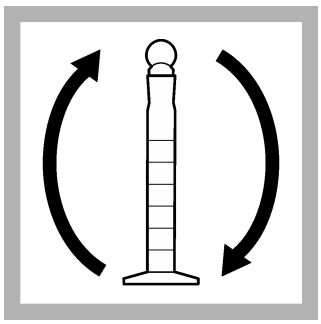


5. Put the stopper on the funnel. Shake to dissolve.

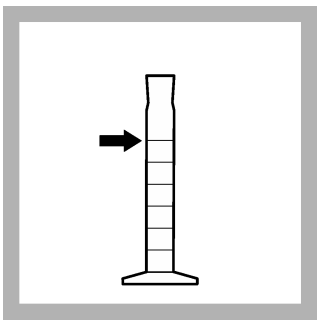
6. Prepare the DithiVer solution: Add 50 mL of chloroform to a 50-mL mixing cylinder.



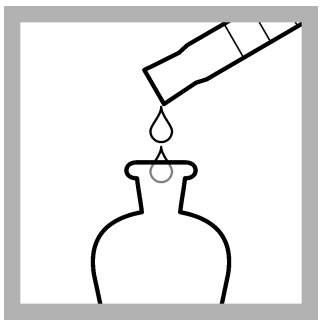
7. Add the contents of one DithiVer Metals Reagent Powder Pillow.



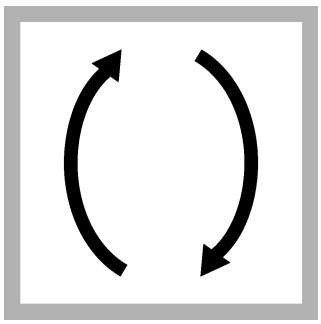
8. Put the stopper on the mixing cylinder. Invert the mixing cylinder several times to mix.



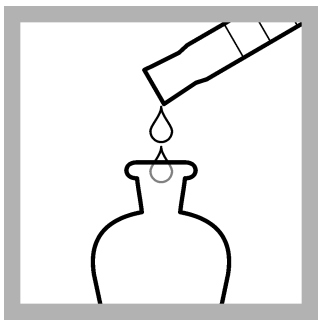
9. Measure 30 mL of the prepared DithiVer solution with a second graduated cylinder.



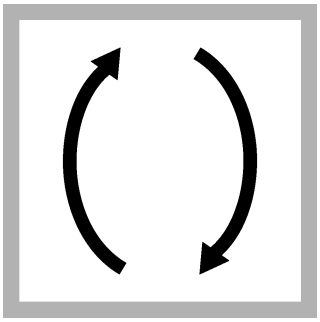
10. Add 30 mL of the DithiVer solution to the 500-mL separatory funnel.



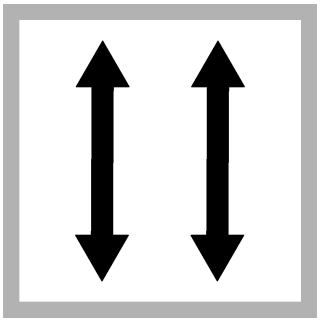
11. Put the stopper on the funnel and invert to mix. Invert the funnel and open the stopcock to vent. Close the stopcock.



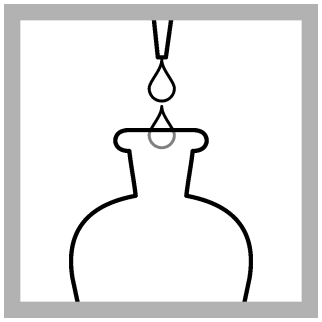
12. Add 5 mL of 5.0 N Sodium Hydroxide Solution to the funnel.



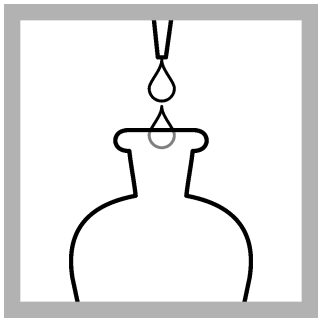
13. Put the stopper on the funnel and invert to mix. Invert the funnel and open the stopcock to vent.



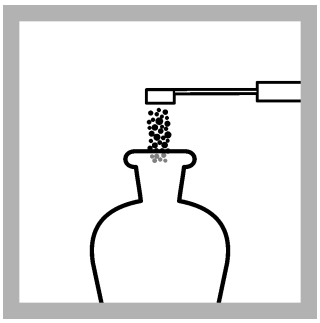
14. Close the stopcock. Shake the funnel once or twice. Invert the funnel and open the stopcock to vent. If the solution is orange after shaking, the pH is too high. Add a few drops of 5.25 N Sulfuric Acid. The color should become blue-green. As an alternative, to prevent higher blanks, start the procedure again with a new sample and use less sodium hydroxide in step 12.



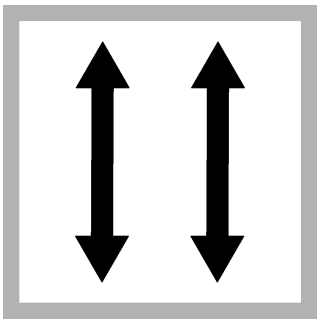
15. Add 3 drops of 5.0 N Sodium Hydroxide Standard Solution. Put the stopper on the funnel and shake to mix. Continue to add 3 drops and shake until the solution is orange. Large amounts of zinc cause the color change at the end point to be indistinct.



16. Add 5 more drops of 5.0 N Sodium Hydroxide Standard Solution.
A pink color in the bottom (chloroform) layer in this step does not necessarily indicate that lead is in the sample. Only after potassium cyanide is added in the next step does a pink color confirm the presence of lead.

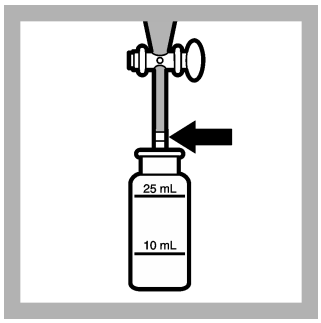


17. Add two heaping 1.0-g scoops of potassium cyanide to the funnel.

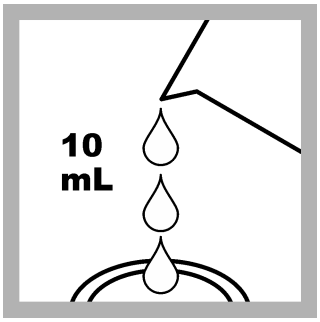


18. Put the stopper on the funnel. Shake vigorously until the powder is dissolved (approximately 15 seconds).

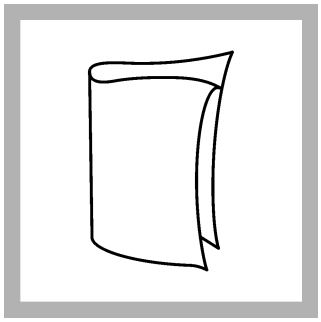
19. Wait 1 minute for the layers to separate. The bottom (chloroform) layer will be pink if lead is in the sample.



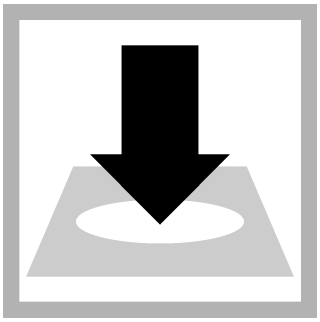
20. Prepare the sample: Put a cotton plug the size of a pea into the funnel delivery tube. Slowly drain the bottom (chloroform) layer into a dry 25-mL sample cell. Put the stopper on the sample cell.
The lead-dithizone complex is stable for a minimum of 30 minutes if the sample cell is closed tightly and kept out of direct sunlight.



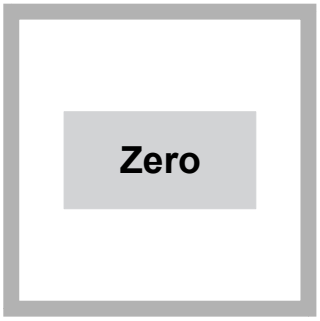
21. Prepare the blank: Fill a dry sample cell with 10 mL of chloroform. Put the stopper on the sample cell.



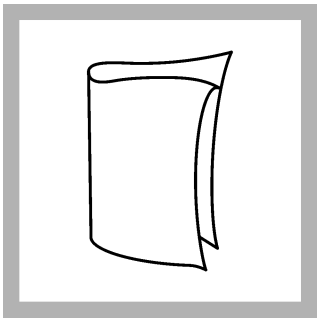
22. Clean the blank sample cell.



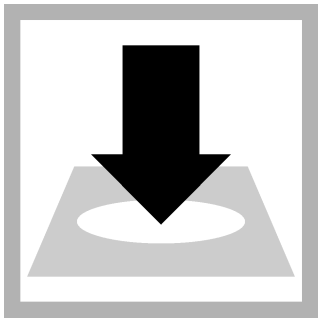
23. Insert the blank into the cell holder.



24. Push **ZERO**. The display shows 0 µg/L Pb^{2+}.



25. Clean the prepared sample cell.



26. Insert the prepared sample into the cell holder.

27. Push **READ**. Results show in µg/L Pb^{2+}.

Interferences

Use the steps that follow to remove the interferences that are shown in Table 2. Table 3 shows the substances that do not interfere.

1. Complete steps 2–8 of the test procedure.
2. Measure approximately 5 mL of the DithiVer solution into the separatory funnel.
3. Stopper the funnel, invert and open the stopcock to vent.
4. Close the stopcock and shake the solution vigorously for 15 seconds.
5. Do not move the funnel until the layers separate (approximately 30 seconds). A yellow, red or bronze color in the bottom (chloroform) layer confirms the presence of interfering metals.
6. Draw off and collect the bottom (chloroform) layer for proper disposal.
7. Do the extraction with fresh 5 mL portions of prepared dithizone solution again. Collect the bottom layer each time in applicable waste collection vessels until the bottom layer develops a pure dark green color for three successive extracts. These extractions remove only a very small amount of lead from the sample.
8. Extract the solution with 2- or 3-mL portions of pure chloroform to remove any dithizone solution that remains. Collect the bottom layer each time for correct disposal. Continue the procedure, but use 28.5 mL of prepared dithizone solution instead of the 30 mL in step 9 of the procedure.

Table 2 Interfering substances

Interfering substance	Interference level
Highly buffered samples or extreme sample pH	All levels
Bismuth	All levels
Copper	All levels

Table 2 Interfering substances (continued)

Interfering substance	Interference level
Mercury	All levels
Silver	All levels
Tin	All levels

Table 3 Substances that do not interfere

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

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:

- 50-mg/L (50,000 µg/L) Lead Voluette Ampule Standard
- Ampule breaker
- TenSette Pipet and pipet tips

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the 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:

- 100-mg/L Lead Standard Solution
- 100-mL volumetric flask, Class A
- 10-mL volumetric pipet, Class A and pipet filler safety bulb
- Deionized water

1. Prepare a 10-mg/L Lead Stock Solution as follows:
   a. Use a pipet to add 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:
   a. Use a graduated cylinder to measure 245 mL of deionized water into the 500 mL separatory funnel (step 3 on page 3 of the procedure). Use a pipet to add 5.00 mL of the 10.0-mg/L Lead Standard Solution into the funnel.
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 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 slight 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
280	150 µg/L Pb	140–160 µg/L Pb	2.3 µg/L

Summary of Method

The dithizone method measures 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. The measurement wavelength is 515 nm.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Lead Reagent Set, includes:	—	100/pkg	2243100
Buffer Powder Pillows, citrate	1	100/pkg	1420299
Chloroform, ACS	40 mL (2x)	4L	1445817
DithiVer Metals Reagent Powder Pillows	1	100/pkg	1261699
Potassium Cyanide	2 g (2x)	125 g	76714
Sodium Hydroxide Standard Solution, 5.0 N	5 mL	1000 mL	245053
Sodium Hydroxide Standard Solution, 5.0 N	varies (2x)	50 mL SCDB	245026

Required apparatus

Description	Quantity/test	Unit	Item no.
Clippers for plastic pillows	1	each	96800
Cylinder, graduated, 5-mL	1	each	50837
Cylinder, graduated, 50-mL	1	each	50841
Cylinder, graduated, 250-mL	1	each	50846
Cotton balls, absorbent	1	100/pkg	257201
Mixing cylinder, graduated, 50-mL, with glass stopper	1	each	189641
Funnel, separatory, 500-mL	1	each	52049
Spoon, measuring, 1.0-g	1	each	51000
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.
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	Item no.
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
Chloroform, ACS	500 mL	1445849
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
Nitric Acid Solution, 1:1	500 mL	254049
Nitric Acid, concentrated	500 mL	15249
Sulfuric Acid Standard Solution, 5.25 N	100 mL	244932
Pipet, serological, 2-mL	each	53236
Pipet, volumetric 5.00-mL	each	1451537
Pipet, volumetric, Class A, 10-mL	each	1451538
Pipet filler, safety bulb	each	1465100
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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