Cyanide

DOC316.53.01040

Pyridine-Pyrazalone Method[1]

Method 8027

0.002 to 0.240 mg/L CN^-

Powder Pillows

Scope and application: For water, wastewater and seawater.

[1] Adapted from Epstein, Joseph, Anal. Chem. 19(4), 272 (1947).

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.	2495402 
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The orientation mark is toward the user.	2401906 

Before starting

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
All samples to be analyzed for cyanide should be treated by acid distillation except when experience has shown that there is no difference in results obtained with or without distillation.
Use a water bath to keep the temperature for the reaction in this test at the optimum 25 °C for best results. Samples less than 23 °C need longer reaction times and samples more than 25 °C give low results.
The timing during the test procedure is critical. Open the necessary reagents before this procedure is started for best results.
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.
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
CyaniVer® Cyanide 3 Reagent Powder Pillow, 10-mL	1
CyaniVer® Cyanide 4 Reagent Powder Pillow, 10-mL	1
CyaniVer® Cyanide 5 Reagent Powder Pillow, 10-mL	1
Cylinder, graduated, 10-mL	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.
- The presence of oxidizing agents, sulfides and fatty acids can cause the loss of cyanide during sample storage. Samples that contain these substances must be pretreated as described in the sections that follow before preservation with sodium hydroxide. If the sample contains sulfide and is not pretreated, it must be analyzed within 24 hours.
- To preserve samples for later analysis, adjust the sample pH to a minimum pH 12 with 5.0 N sodium hydroxide standard solution (about 4 mL per liter). Use a glass serological pipet and pipet filler. Measure the pH and add more sodium hydroxide if necessary.
- Keep the preserved samples at or below 6°C (43 °F) for up to 14 days.
- Before analysis, adjust the pH to 7 with 2.5 N hydrochloric acid standard solution.
- Let the sample temperature increase to room temperature before analysis.
- Correct the test result for the dilution caused by the volume additions.

Oxidizing agents

Oxidizing agents such as chlorine decompose cyanides during storage. To test for and remove oxidizing agents, pretreat the sample as follows:

1. Measure 25-mL of the sample and add one drop of 10-g/L m-Nitrophenol Indicator Solution. Swirl to mix.
2. Add 2.5 N Hydrochloric Acid Standard Solution by drops until the color changes from yellow to colorless. Swirl the sample thoroughly after the addition of each drop.
3. Add two drops of Potassium Iodide Solution, 30-g/L and two drops of Starch Indicator Solution to the sample. Swirl to mix. The solution will turn blue if oxidizing agents are present.
4. If the color is blue, add two level, 1-g measuring spoonfuls of ascorbic acid per liter of sample.
5. Remove a 25-mL portion of the treated sample and repeat steps 1 to 3. If the sample turns blue, repeat steps 4 and 5.
6. If the 25-mL sample remains colorless, preserve the remaining sample to pH 12 for storage with 5 N Sodium Hydroxide Standard Solution.
7. Complete the procedure given under Interfering Substances and Levels, Reducing Agents, to eliminate the effect of excess ascorbic acid, before the cyanide procedure is started.

Sulfides

Sulfides will quickly convert cyanide to thiocyanate (SCN–). To test for and remove sulfide, pretreat the sample as follows:

1. Put a drop of sample on a disc of Hydrogen Sulfide Test Paper that has been wetted with pH 4 Buffer Solution.
2. If the test paper darkens, add a 1-g measuring spoon of Lead Acetate to the sample. Repeat step 1.
3. If the test paper continues to turn dark, keep adding Lead Acetate until the sample tests negative for sulfide.
4. Filter the lead sulfide precipitate through Filter Paper and a Funnel. Preserve the sample for storage with 5 N Sodium Hydroxide Standard Solution or neutralize to a pH of 7 for analysis.

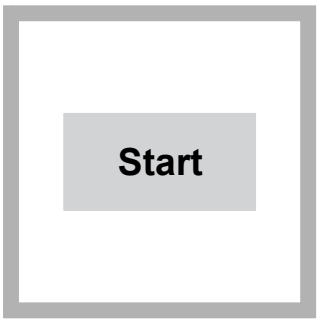
Fatty acids

CAUTION Perform this operation under a ventilation hood and complete as quickly as possible.

When distilled, fatty acids will pass over with cyanide and under the alkaline conditions of the absorber, will form soaps. If the presence of fatty acid is suspected, use the following pretreatment before preserving samples with sodium hydroxide.

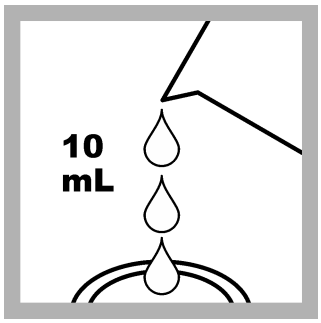
1. Acidify 500 mL of sample to pH 6 or 7 with a 4:1 dilution of glacial Acetic Acid.
2. Pour the sample into a 1000-mL separation funnel and add 50 mL of Hexane.
3. Stopper the funnel and shake for 1 minute. Allow the layers to separate.
4. Drain off the lower sample layer into a 600-mL beaker. If the sample is to be stored, add enough 5 N Sodium Hydroxide Standard Solution to raise the pH to a minimum pH 12.

Powder pillow procedure

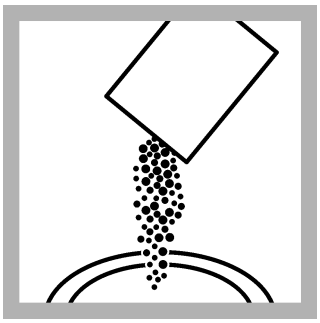


1. Start program **160 Cyanide**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

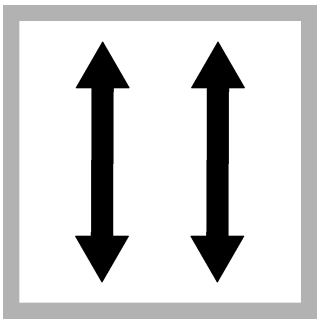
Note: *Although the program name can be different between instruments, the program number does not change.*



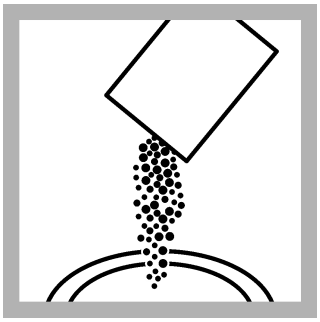
2. Prepare the sample: Fill a sample cell with 10 mL of sample.



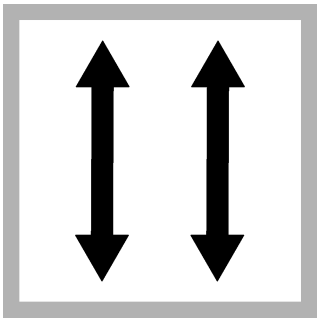
3. Add the contents of one CyaniVer 3 Cyanide Reagent Powder Pillow.



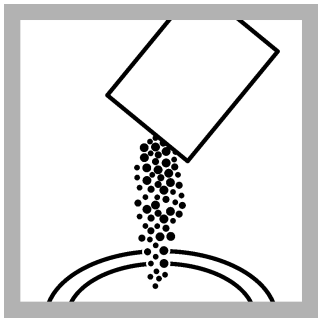
4. Put the stopper on the sample cell. Shake the sample cell for 30 seconds. Let the sample cell sit for another 30 seconds.



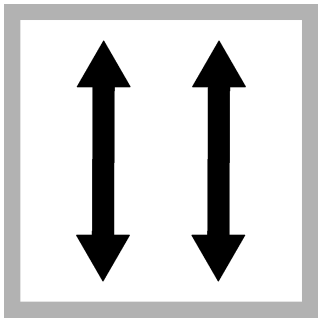
5. Add the contents of one CyaniVer 4 Cyanide Reagent Powder Pillow.



6. Close the sample cell. Shake the sample cell for 10 seconds. Immediately do the next step. A delay of more than 30 seconds will produce low test results.



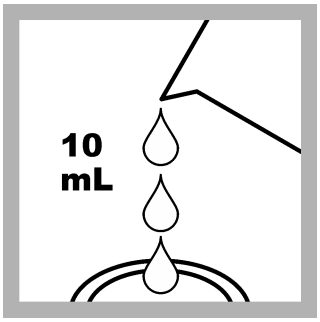
7. Add the contents of one CyaniVer 5 Cyanide Reagent powder Pillow.



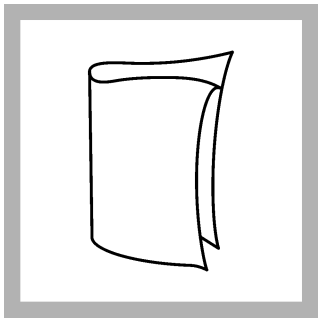
8. Close the sample cell. Shake the sample cell vigorously.
If cyanide is in the sample, a pink color will show.

9. Start the instrument timer. A 30-minute reaction time starts.

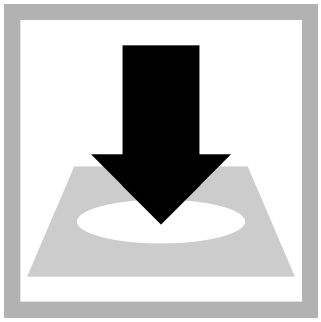
The solution will show pink, then will show blue. Samples less than 25 °C require a longer reaction time. Samples greater than 25 °C give low test results..



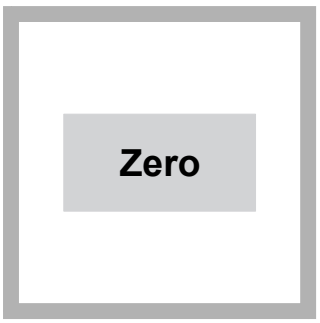
10. Prepare the blank: When the timer expires, fill a second sample cell with 10 mL of sample.



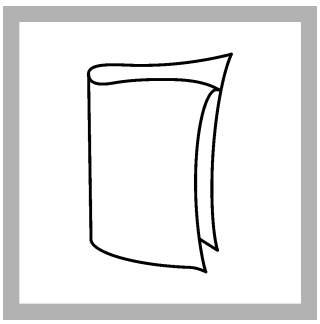
11. Clean the blank sample cell.



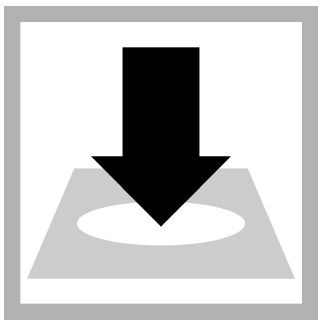
12. Insert the blank into the cell holder.



13. Push **ZERO**. The display shows 0.000 mg/L CN^-.



14. Clean the prepared sample cell.



15. Insert the prepared sample into the cell holder.

16. Push **READ**. Results show in mg/L CN^-.

Interferences

Interfering substance	Interference level
Chlorine	Large amounts of chlorine in the sample cause a milky white precipitate after the addition of the CyaniVer® 5 Reagent. If chlorine or other oxidizing agents are known to be present, pretreat the sample before the test with the procedure in this table for oxidizing agents.
Metals	Nickel or cobalt in concentrations up to 1 mg/L do not interfere. Eliminate the interference from up to 20 mg/L copper and 5 mg/L iron: add the contents of one HexaVer Chelating Reagent Powder Pillow to a fresh portion of sample and mix. Use this treated sample in the test procedure. Prepare a reagent blank of deionized water and reagents to zero the instrument.
Oxidizing agents	**1.** Adjust a 25-mL portion of the alkaline sample to pH 7–9 with 2.5 N Hydrochloric Acid Standard Solution. Count the number of drops of acid added. **2.** Add two drops of Potassium Iodide Solution and two drops of Starch Indicator Solution to the sample. Swirl to mix. The sample will turn blue if oxidizing agents are present. **3.** Add Sodium Arsenite Solution drop-wise until the sample turns colorless. Swirl the sample thoroughly after each drop. Count the number of drops. **4.** Take another 25-mL sample and add the total number of drops of Hydrochloric Acid Standard Solution counted in step 1. **5.** Subtract one drop from the amount of Sodium Arsenite Solution added in step 3. Add this amount to the sample and mix thoroughly. Use this treated sample in the cyanide test procedure.
Reducing agents	**1.** Adjust a 25-mL portion of the alkaline sample to pH 7–9 with 2.5 N Hydrochloric Acid Standard Solution. Count the number of drops added. **2.** Add four drops of Potassium Iodide Solution and four drops of Starch Indicator Solution to the sample. Swirl to mix. The sample should be colorless. **3.** Add Bromine Water drop-wise until a blue color shows. Swirl the sample thoroughly after each addition. Count the number of drops. **4.** Take another 25-mL sample and add the total number of drops of Hydrochloric Acid Standard Solution counted in step 1. **5.** Add the total number of drops of Bromine Water counted in step 3 to the sample and mix thoroughly. **6.** Use this treated sample in the cyanide test procedure.
Turbidity	Large amounts of turbidity will cause high readings. Use filter paper and a funnel to filter highly turbid water samples. Use the filtered sample for the blank and sample preparation in the test procedure. The test results should then be recorded as soluble cyanide.

Acid distillation

All samples to be analyzed for cyanide should be treated by acid distillation except when experience has shown that there is no difference in results obtained with or without distillation. With most compounds, a 1-hour reflux is adequate.

If thiocyanate is present in the original sample, a distillation step is absolutely necessary as thiocyanate causes a positive interference. High concentrations of thiocyanate can yield a substantial quantity of sulfide in the distillate. The “rotten egg” smell of hydrogen sulfide will accompany the distillate when sulfide is present. The sulfide must be removed from the distillate prior to testing.

If cyanide is not present, the amount of thiocyanate can be determined. The sample is not distilled and the final reading is multiplied by 2.2. The result is mg/L SCN^-.

The distillate can be tested and treated for sulfide after the last step of the distillation procedure by using the following lead acetate treatment procedure.

1. Put a drop of the distillate (already diluted to 250 mL) on a disc of Hydrogen Sulfide Test Paper that has been wetted with pH 4 Buffer Solution.
2. If the test paper darkens, add 2.5 N Hydrochloric Acid Standard Solution by drops to the distillate until a neutral pH is obtained.

3. Add a 1-g measuring spoon of Lead Acetate to the distillate and mix. Repeat step 1.
4. If the test paper continues to turn dark, keep adding lead acetate until the distillate tests negative for sulfide. Filter the black lead sulfide precipitate through filter paper and a funnel. Neutralize the liquid filtrate to pH 7 and immediately analyze for cyanide.

Distillation procedure

The following steps describe the distillation process using distillation apparatus and cyanide glassware offered by the manufacturer:

1. Set up the distillation apparatus for cyanide recovery, leaving off the thistle tube. Refer to the Distillation Apparatus Manual. Turn on the water and make certain it is flowing steadily through the condenser.
2. Fill the distillation apparatus cylinder to the 50-mL mark with 0.25 N Sodium Hydroxide Standard Solution.
3. Fill a clean 250-mL graduated cylinder to the 250-mL mark with sample and pour it into the distillation flask. Put a stir bar in the flask and attach the thistle tube.
4. Arrange the vacuum system as shown in the Distillation Apparatus Manual, but do not connect the vacuum tubing to the gas bubbler. Turn on the water to the aspirator to full flow and adjust the flow meter to 0.5 SCFH.
5. Connect the vacuum tubing to the gas bubbler, making certain that air flow is maintained (check the flow meter) and that air is bubbling from the thistle tube and the gas bubbler.
6. Turn the power switch on and set the stir control to 5. Using a 50-mL graduated cylinder, pour 50 mL of 19.2 N Sulfuric Acid Standard Solution through the thistle tube and into the distillation flask.
7. Using a water bottle, rinse the thistle tube with a small amount of deionized water.
8. Allow the solution to mix for 3 minutes, then add 20 mL Magnesium Chloride Reagent through the thistle tube and rinse again. Allow the solution to mix for 3 more minutes.
9. Make sure that there is a constant flow of water through the condenser.
10. Turn the heat control to 10.
11. Carefully monitor the distillation flask at this point in the procedure. Once the sample begins to boil, slowly lower the air flow to 0.3 SCFH. If the contents of the distillation flask begin to back up through the thistle tube, increase the air flow by adjusting the flow meter until the contents do not back up through the thistle tube. Boil the sample for 1 hour.
12. After 1 hour, turn off the still, but maintain the air flow for 15 minutes more.
13. After 15 minutes, remove the rubber stopper on the 500-mL vacuum flask to break the vacuum and turn off the water to the aspirator. Turn off the water to the condenser.
14. Remove the gas bubbler/cylinder assembly from the distillation apparatus. Separate the gas bubbler from the cylinder and pour the contents of the cylinder into a 250-mL, Class A volumetric flask. Rinse the gas bubbler, cylinder and J-tube connector with deionized water and add the washings to the volumetric flask.
15. Fill the flask to the mark with deionized water and mix thoroughly. Neutralize the contents of the flask. Use the distilled sample in the test procedure for cyanide.

Pollution prevention and waste management

Reacted samples may contain cyanide and must be disposed of as a hazardous waste. It is imperative that these materials be handled safely to prevent the release of hydrogen cyanide gas (an extremely toxic material with the smell of almonds). Most cyanide compounds are stable and can be safely stored for disposal in highly alkaline solutions (pH >11) such as 2 N sodium hydroxide. Never mix these wastes with other laboratory wastes which may contain lower pH materials such as acids or even water. Dispose of reacted solutions according to local, state and federal regulations.

Accuracy check

Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

Items to collect:

- 0.2503 g potassium cyanide
- 1-L volumetric flask, Class A (2)
- 2-mL volumetric pipet, Class A and pipet filler safety bulb
- Deionized water

1. Prepare a 100-mg/L cyanide stock solution as follows:
   a. Add 0.2503 g of potassium cyanide into a 1-L volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare the stock solution each week.
2. Prepare a 0.200 mg/L cyanide standard solution as follows:
   a. Use a pipet to add 2.00 mL of the 100-mg/L cyanide stock solution into a 1-L volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare the standard solution immediately before use.
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
160	0.100 mg/L CN^-	0.090–0.110 mg/L CN^-	0.002 mg/L CN^-

Summary of method

The Pyridine-Pyrazalone method used for cyanide measurements gives an intense blue color with free cyanide. A sample distillation is necessary to determine cyanide that is complexed with transition and heavy metals. The measurement wavelength is 612 nm for spectrophotometers or 610 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Cyanide Reagent Set, CyaniVer, 10-mL	1	1	2430200
Includes:			
CyaniVer® 3 Cyanide Reagent Powder Pillow, 10-mL	1	100/pkg	2106869
CyaniVer® 4 Cyanide Reagent Powder Pillow, 10-mL	1	100/pkg	2106969
CyaniVer® 5 Cyanide Reagent Powder Pillow, 10-mL	1	100/pkg	2107069

Required apparatus

Description	Quantity/test	Unit	Item no.
Cylinder, graduated, 10-mL	1	each	50838
Sample cells, 10-mL square, matched pair	2	2/pkg	2495402
Stoppers for 18-mm tubes and AccuVac Ampul	1	6/pkg	1448000

Recommended standards

Description	Unit	Item no.
Potassium Cyanide, ACS	125 g	76714
Water, deionized	4 L	27256

Optional reagents and apparatus

Description	Unit	Item no.
Acetic Acid, ACS	500 mL	10049
Ascorbic Acid	100 g	613826
Bromine Water, 30 g/L	29 mL	221120
Buffer Solution, pH 4	500 mL	1222349
Filter paper, 2–3-micron, pleated, 12.5-cm	100/pkg	189457
Funnel, poly, 65-mm	each	108367
Hexane Solution, ACS	500 mL	1447849
HexaVer Chelating Reagent Powder Pillows	100/pkg	24399
Hydrochloric Acid Standard Solution, 2.5 N	100 mL MDB	141832
Hydrogen Sulfide Test Paper	100/pkg	2537733
m-Nitrophenol Indicator Solution	100 mL	247632
Magnesium Chloride Reagent	1 L	1476253
Potassium Iodide, 30-g/L	100 mL	34332
Sodium Arsenite, 5-g/L	100 mL	104732
Sodium Hydroxide Standard Solution, 0.25 N	1000 mL	1476353
Sodium Hydroxide Standard Solution, 5.0 N	1 L	245053
Starch Indicator Solution	100 mL MDB	34932
Sulfuric Acid Standard Solution, 19.2 N	500 mL	203849
Cyanide glassware	each	2265800
Distillation heater and support for apparatus set, 115 VAC option	each	2274400
Distillation heater and support for apparatus set, 230 VAC option	each	2274402
Distillation apparatus set, general purpose	each	2265300
Pipet, serological, 5-mL	each	53237
Pipet filler, safety bulb	each	1465100
Paper, pH, 0–14 pH range	100/pkg	2601300
Spoon, measuring, 1-g	each	51000
Thermometer, non-mercury, –10 to +225 °C	each	2635700

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