



Method 8027

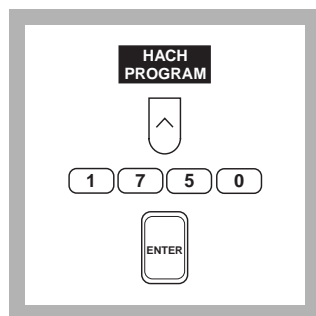
Pyridine-Pyrazalone Method*

Powder Pillows

(0 to 0.240 mg/L CN⁻)

Scope and Application: For water, wastewater and seawater. The estimated detection limit for program number 1750 is 0.003 mg/L CN⁻.

* Adapted from Epstein, Joseph, *Anal. Chem.* 19 (4), 272 (1947)



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

Select the stored program for cyanide by pressing **1750** 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 can be used for this procedure.



2. The display will show: **HACH PROGRAM: 1750 Cyanide**

The wavelength (λ), **612 nm**, is automatically selected.

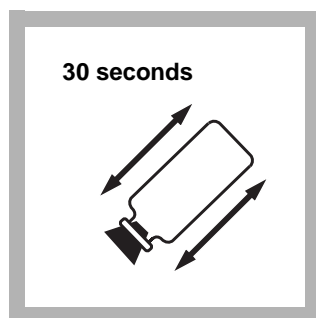


3. Using a graduated cylinder, fill a sample cell with 10 mL of sample.

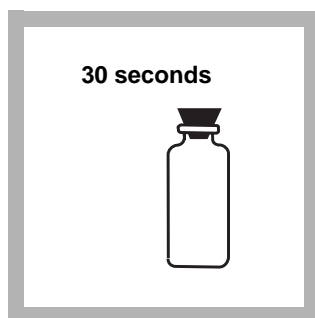
Note: For proof of accuracy, use a 0.10-mg/L cyanide standard solution (preparation given in the Accuracy Check section) in place of the sample.



4. Add the contents of one CyaniVer 3 Cyanide Reagent Powder Pillow. Stopper the sample cell.



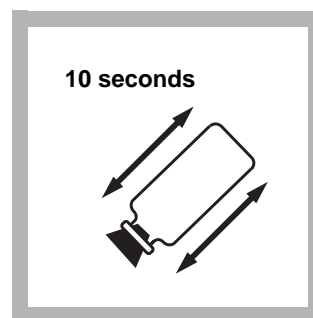
5. Shake the sample cell for 30 seconds.



6. Wait an additional 30 seconds, leaving the sample cell undisturbed.



7. Add the contents of one CyaniVer 4 Cyanide Reagent Powder Pillow. Stopper the sample cell.



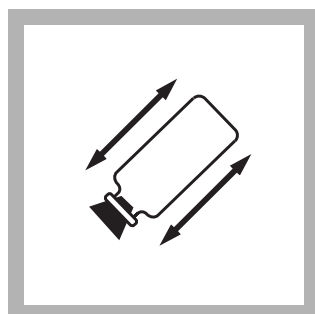
8. Shake the sample cell for 10 seconds. Immediately proceed with Step 9.

Note: Delaying the addition of the CyaniVer 5 Cyanide Reagent Powder for more than 30 seconds after the addition of the CyaniVer 4 Cyanide Reagent Powder will give lower test results.

Note: Accuracy is not affected by undissolved CyaniVer 4 Cyanide Reagent Powder.

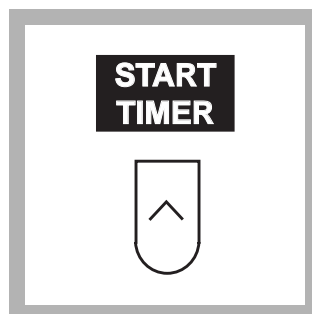


9. Add the contents of one CyaniVer 5 Cyanide Reagent Powder Pillow. Stopper the cell.



10. Shake the cell vigorously.

Note: If cyanide is present, a pink color will develop which then turns blue after a few minutes.



11. Press the soft key under **START TIMER**.

A 30-minute reaction period will begin.

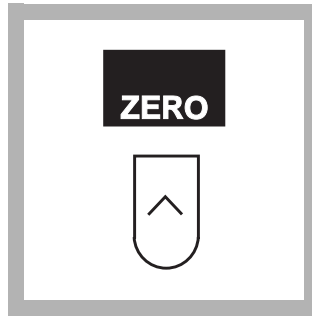
Note: Samples at less than 23 °C require longer reaction time and samples at greater than 25 °C give low test results.



12. When the timer beeps, fill another sample cell (the blank) with 10 mL of sample.



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

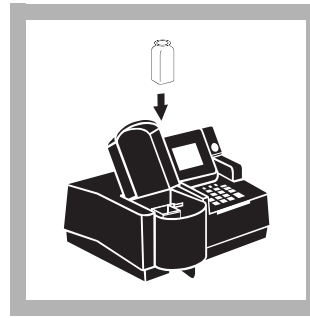


14. Press the soft key under **ZERO**.

The display will show:

0.000 mg/L Cu

Note: For alternate 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 to the read screen.



15. Place the prepared sample into the cell holder. Close the light shield. Results in mg/L cyanide (or chosen units) will be displayed.

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

Do not pour these solutions down the drain!

Interferences

Table 1 Interfering Substances and Suggested Treatments for Powder Pillows

Interfering Substance	Interference Levels and Treatments
Chlorine	Large amounts of chlorine in the sample will 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 testing using 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 by adding the contents of one HexaVer Chelating Reagent Powder Pillow to the sample and then mixing before adding the CyaniVer 3 Cyanide Reagent Powder Pillow in Step 4. Prepare a reagent blank of deionized water and reagents to zero the instrument in Step 14.
Oxidizing Agents	a) 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. b) 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. c) Add Sodium Arsenite Solution drop-wise until the sample turns colorless. Swirl the sample thoroughly after each drop. Count the number of drops. d) Take another 25-mL sample and add the total number of drops of Hydrochloric Acid Standard Solution counted in Step a. e) Subtract one drop from the amount of Sodium Arsenite Solution added in Step c. Add this amount to the sample and mix thoroughly. Continue with Step 4 of the cyanide procedure.
Reducing Agents	a) 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. b) 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. c) Add Bromine Water drop-wise until a blue color appears. Swirl the sample thoroughly after each addition. Count the number of drops. d) Take another 25-mL sample and add the total number of drops of Hydrochloric Acid Standard Solution counted in Step a. e) Add the total number of drops of Bromine Water counted in Step c to the sample and mix thoroughly. f) Continue with Step 4 of the cyanide procedure.
Turbidity	Large amounts of turbidity will cause high readings. Filter highly turbid water samples before use in Steps 3 and 12, using the labware listed under <i>OPTIONAL EQUIPMENT AND SUPPLIES</i> . The test results should then be recorded as soluble cyanide.

Sample Collection, Storage and Preservation

Collect samples in glass or plastic bottles and analyze as quickly as possible.

The presence of oxidizing agents, sulfides and fatty acids can cause the loss of cyanide during sample storage. Samples containing these substances must be pretreated as described in the following procedures before preservation with sodium hydroxide. If the sample contains sulfide and is not pretreated, it must be analyzed within 24 hours.

Preserve the sample by adding 4.0 mL of 5.0 N Sodium Hydroxide Standard Solution to each liter (or quart) of sample, using a glass serological pipet and pipet filler. Check the sample pH. An addition of 4-mL of sodium hydroxide is usually enough to raise the pH of most water and wastewater samples to 12. Add more 5.0 N Sodium Hydroxide if necessary. Store the samples at 4 °C (39 °F) or less. Samples preserved in this manner can be stored for 14 days.

Before testing, samples preserved with 5.0 N Sodium Hydroxide or samples that are highly alkaline due to chlorination treatment processes or sample distillation procedures should be adjusted to approximately pH 7 with 2.5 N Hydrochloric Acid Standard Solution. Where significant amounts of preservative

are used, a volume correction should be made; see Section 1.2.2 *Correcting for Volume Additions*.

Oxidizing Agents

Oxidizing agents such as chlorine decompose cyanides during storage. To test for their presence and to eliminate their effect, pretreat the sample as follows:

- a. Take a 25-mL portion of the sample and add one drop of m-Nitrophenol Indicator Solution, 10-g/L. Swirl to mix.
- b. Add 2.5 N Hydrochloric Acid Standard Solution drop-wise until the color changes from yellow to colorless. Swirl the sample thoroughly after the addition of each drop.
- c. 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.
- d. If *Step c* suggests the presence of oxidizing agents, add two level 1-g measuring spoonfuls of ascorbic acid per liter of sample.
- e. Withdraw a 25-mL portion of sample treated with ascorbic acid and repeat *Steps a to c*. If the sample turns blue, repeat *Steps d and e*.
- f. If the 25-mL sample remains colorless, preserve the remaining sample to pH 12 for storage with 5 N Sodium Hydroxide Standard Solution (usually 4 mg/L).
- g. Perform the procedure given under *Interferences, Reducing Agents* to eliminate the effect of excess ascorbic acid, before following the cyanide procedure.

Sulfides

Sulfides will quickly convert cyanide to thiocyanate (SCN). To test for the presence of sulfide and eliminate its effect, pretreat the sample as follows:

- a. Place a drop of sample on a disc of hydrogen sulfide test paper that has been wetted with pH 4 Buffer Solution.
- b. If the test paper darkens, add a 1-g measuring spoon of lead acetate to the sample. Repeat *Step a*.
- c. If the test paper continues to turn dark, keep adding lead acetate until the sample tests negative for sulfide.
- d. 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 in a hood as quickly as possible

When distilled, fatty acids will pass over with cyanide and form soaps under the alkaline conditions of the absorber. If the presence of fatty acid is suspected, do not preserve samples with sodium hydroxide until the following pretreatment is performed. The effect of fatty acids can be minimized as follows:

- a. Acidify 500 mL of sample to pH 6 or 7 with Acetic Acid Solution.
- b. Pour the sample into a 1000-mL separatory funnel and add 50 mL of hexane.

- c. Stopper the funnel and shake for one minute. Allow the layers to separate.
- d. Drain off the sample (lower) layer into a 600-mL beaker. If the sample is to be stored, add 5 N Sodium Hydroxide Standard Solution to raise the pH to above 12.

Accuracy Check

Standard Additions Method

Caution: Cyanides and their solutions, and the hydrogen cyanide liberated by acids, are very poisonous. Both the solutions and the gas can be absorbed through the skin.

Prepare a 100-mg/L cyanide stock solution weekly by dissolving 0.1884 grams or an equivalent amount of pure sodium cyanide in deionized water and diluting to 1000 mL.

Immediately before use prepare a 0.200-mg/L cyanide working solution by diluting 2.00 mL of the 100-mg/L stock solution to 1000 mL using deionized water.

To adjust the calibration curve using the reading obtained with the 0.200 mg/L standard solution press the soft keys under **OPTIONS, (MORE)** and then **STD:OFF**. Press **ENTER** to accept the default concentration, the value of which will depend on the selected units. If an alternate concentration is used, enter the actual concentration and press **ENTER** to return to the read screen. See Section 1.5.5 *Adjusting the Standard Curve* for more information.

Method Performance

Precision

Standard: 0.200 mg/L CN⁻

Program	95% Confidence Limits
1750	0.198–0.202 mg/L CN ⁻

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

Estimated Detection Limit

Program	EDL
1750	0.003 mg/L CN ⁻

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: 1750

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	0.0013 mg/L CN ⁻

See Section 1.5.3 *Sensitivity Explained* for more information.

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. A one-hour reflux is adequate with most compounds.

If thiocyanate is present in the original sample, a distillation step is absolutely necessary because 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.

- a. Place a drop of the distillate (already diluted to 250 mL) on a disc of hydrogen sulfide test paper that has been wetted with pH 4.0 Buffer Solution.
- b. If the test paper darkens, add 2.5 N Hydrochloric Acid Standard Solution drop-wise to the distillate until a neutral pH is obtained.
- c. Add a 1-g measuring spoon of lead acetate to the distillate and mix. Repeat Step a.
- d. If the test paper continues to turn dark, keep adding lead acetate until the distillate tests negative for sulfide.
- e. Filter the black lead sulfide precipitate through filter paper and funnel. Neutralize the liquid filtrate to pH 7 and analyze for cyanide without delay.

Distillation Procedure

The following steps describe the distillation process using apparatus offered by Hach:

- a. Set up the distillation apparatus for cyanide recovery, leaving off the thistle tube. Refer to the *Hach Distillation Apparatus Manual*. Turn on the water and make certain it is flowing steadily through the condenser.
- b. Fill the distillation apparatus cylinder to the 50-mL mark with 0.25 N Sodium Hydroxide Standard Solution.
- c. Fill a clean 250-mL graduated cylinder to the 250-mL mark with sample and pour it into the distillation flask. Place a stirring bar into the flask and attach the thistle tube.
- d. Arrange the vacuum system as shown in the *Hach 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.
- e. 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.

- f. 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.
- g. Using a water bottle, rinse the thistle tube with a small amount of deionized water.
- h. Allow the solution to mix for three minutes; then add 20 mL Magnesium Chloride Reagent through the thistle tube and rinse again. Allow the solution to mix for 3 more minutes.
- i. Verify that there is a constant flow of water through the condenser.
- j. Turn the heat control to 10.
- k. It is very important to 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 no longer back up through the thistle tube. Allow the sample to boil for one hour.
- l. When one hour has elapsed, turn the still off but maintain the air flow for 15 minutes.
- m. 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.
- n. 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, the cylinder, and J-tube connector with deionized water and add the washings to the volumetric flask.
- o. Fill the flask to the mark with deionized water and mix thoroughly. Neutralize the contents of the flask and analyze for cyanide.

Calibration Standard Preparation

To perform a cyanide calibration using the Pyridine-Pyrazalone method, prepare calibration standard containing 0.05, 0.100, and 0.200 mg/L cyanide as follows:

- a. Prepare a 100-mg/L cyanide stock solution as described in the *Accuracy Check*.
- b. Into three different 1000-mL Class A volumetric flasks, pipet 0.50, 1.00 and 2.00 mL of the 100-mg/L cyanide stock solution, respectively. Use Class A pipets.
- c. Dilute each flask to volume with deionized water. Stopper and invert several times to mix.
- d. Using the Pyridine-Pyrazalone 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 Pyridine-Pyrazalone method used for measuring cyanide gives an intense blue color with free cyanide. A sample distillation is required to determine cyanide from transition and heavy metal cyanide complexes.

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 1.

Pollution Prevention and Waste Management

Special Considerations for Cyanide Containing Materials

Samples analyzed by this procedure may contain cyanide, which is regulated as reactive (D003) waste by the federal RCRA. It is imperative these materials be handled safely to prevent 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.

In the event of a spill or release, special precautions must be taken to prevent exposure to hydrogen cyanide gas. The following steps may be taken to destroy the cyanide compounds in the event of an emergency:

- a. Use a fume hood or supplied air or self contained breathing apparatus.
- b. While stirring, add the waste to a beaker containing a strong solution of sodium hydroxide and calcium hypochlorite or sodium hypochlorite (household bleach).
- c. Maintain a strong excess of hydroxide and hypochlorite. Let the solution stand for 24 hours.
- d. Neutralize and flush the solution down the drain with a large excess of water. Note: if the solution contains other regulated materials such as chloroform or heavy metals, it may still need to be collected for hazardous waste disposal. Never flush hazardous wastes down the drain.

REQUIRED REAGENTS AND STANDARDS

	Cat. No.
Cyanide Reagent Set	
Includes: (1) 21068-69, (1) 21069-69, (1) 21070-69	24302-00

Description	Quantity Required		Unit	Cat. No.
	per test			
CyaniVer 3 Cyanide Reagent Powder Pillows	1 pillow	100/pkg		21068-69
CyaniVer 4 Cyanide Reagent Powder Pillows	1 pillow	100/pkg		21069-69
CyaniVer 5 Cyanide Reagent Powder Pillows	1 pillow	100/pkg		21070-69

REQUIRED EQUIPMENT AND SUPPLIES

Cylinder, graduated, 10-mL	1	each	508-38
DR/4000 1-Inch Cell Adapter	1	each	48190-00
Stoppers, rubber, No. 1	1	12/pkg	2118-01

CYANIDE, continued

OPTIONAL REAGENTS AND STANDARDS

Acetic Acid Solution, 10%, Alpha.....	500 mL.....	14816-49
Ascorbic Acid.....	100 g.....	6138-26
Bromine Water, 30-g/L.....	29 mL.....	2211-20
Buffer Solution, pH 4.00.....	500 mL.....	12223-49
Hexanes, ACS.....	4 liters.....	14478-17
HexaVer Chelating Reagent Powder Pillows.....	100/pkg.....	243-99
Hydrochloric Acid Standard Solution, 2.5 N.....	100 mL MDB.....	1418-32
Lead Acetate, trihydrate, ACS.....	500 g.....	7071-34
Magnesium Chloride Solution, 51%.....	1000 mL.....	14762-53
m-Nitrophenol Indicator Solution, 10-g/L, pH 7.0-8.4.....	100 mL MDB.....	2476-32
Potassium Iodide Solution, 30-g/L.....	100 mL MDB.....	343-32
Sodium Arsenite Solution, APHA, 5-g/L.....	100 mL MDB.....	1047-32
Sodium Cyanide, ACS.....	28 g.....	184-20
Sodium Hydroxide Standard Solution, 0.250 N.....	1000 mL.....	14763-53
Sodium Hydroxide Standard Solution, 5.0 N.....	1 L.....	2450-53
Starch Indicator Solution.....	100 mL MDB.....	349-32
Sulfuric Acid Standard Solution, 19.2 N.....	500 mL.....	2038-49
Water, deionized.....	4 liters.....	272-56

OPTIONAL EQUIPMENT AND SUPPLIES

Description	Unit	Cat. No.
Beaker, glass, 600-mL.....	each.....	500-52
Bottle, wash, 500-mL.....	each.....	620-11
Cylinder, graduated, 50-mL.....	each.....	508-41
Cylinder, graduated, 250-mL.....	each.....	508-46
Distillation Apparatus Set, Cyanide.....	each.....	22658-00
Distillation Apparatus Set, general purpose.....	each.....	22653-00
Distillation Apparatus Heater and Support Set, 115 VAC, 50/60 Hz.....	each.....	22744-00
Distillation Apparatus Heater and Support Set, 230 VAC, 50/60 Hz.....	each.....	22744-02
DR/4000 Carousel Module Kit.....	each.....	48090-02
DR/4000 Flow Cell Module Kit, 1-inch.....	each.....	48090-04
DR/4000 Sipper Module Kit, 1-inch.....	each.....	48090-03
Dropper, plastic.....	each.....	6080-00
Filter Paper, folded, 12.5-cm.....	100/pkg.....	1894-57
Flask, volumetric, Class A, 250-mL.....	each.....	14574-46
Flask, volumetric, Class A, 1000-mL.....	each.....	14574-53
Funnel, poly, 65-mm.....	each.....	1083-67
Funnel, separatory, 500-mL.....	each.....	520-49
Hydrogen Sulfide Test Papers.....	100/pkg.....	25377-33
pH Meter, <i>sension</i> TM 1, portable.....	each.....	51700-00
Pipet, volumetric, Class A, 0.5-mL.....	each.....	14515-34
Pipet, volumetric, Class A, 1.00-mL.....	each.....	14515-35
Pipet, volumetric, Class A, 2.00-mL.....	each.....	14515-36
Pipet, serological, 5-mL.....	each.....	532-37
Pipet Filler, safety bulb.....	each.....	14651-00
Scoop, double ended, 7.....	each.....	12257-00
Spoon, measuring, 1.0 g.....	each.....	510-00
Support Ring, 4-inch.....	each.....	580-01
Support Ring Stand, 5 x 8 in. base.....	each.....	563-00



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