Cyanide

DOC316.53.01495

USEPA[1] Pyridine Barbituric Acid Method[2] — Method 10265

0.01 to 0.60 mg/L CN^- — TNTplus® 862

Scope and application: For wastewater, seawater, drinking water, surface water and process water. Distillation is necessary to determine total cynaide.

[1] USEPA procedure is equivalent to USEPA method 335.2 for surface and saline waters, domestic and industrial wastes.
[2] Adapted from *Standard Methods for the Examination of Water and Wastewaters (4500-CN^- E)*

Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows the adapter and light shield requirements for the applicable instruments that can use TNTplus vials.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information for TNTplus vials

Instrument	Adapters	Light shield
DR 6000, DR 5000	—	—
DR 3900	—	LZV849
DR 3800, DR 2800	—	LZV646
DR 1900	9609900 or 9609800 (A)	—

Before starting

DR 3900, DR 3800, DR 2800: Install the light shield in Cell Compartment #2 before this test is started.
Review the safety information and the expiration date on the package.
The recommended sample pH is 2–10.
The sample temperature must be 15–25 °C (59–77 °F) for accurate results.
The recommended temperature for reagent storage is 2–8 °C (35–46 °F).
To determine total cyanide, distill all the samples and the standards[1] with a Micro Dist distillation block. Refer to Distillation procedure for total cyanide determination on page 3.
DR 1900: Go to All Programs>LCK or TNTplus Methods>Options to select the TNTplus number for the test. Other instruments automatically select the method from the barcode on the vial.
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.

[1] Always distill the standards with the samples. For the most accurate results, complete a user calibration with the distilled standards.

Items to collect

Description	Quantity
Cyanide TNTplus Reagent Set	1
Pipet, adjustable volume, 1.0–5.0 mL	1
Pipet tips, for 1.0–5.0 mL pipet	1
Pipet, TenSette, 1.0–10.0 mL	1
Pipet tips, for TenSette Pipet, 1.0–10.0 mL	1

Refer to Consumables and replacement items on page 6 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.

Distillation procedure for total cyanide determination

Items to collect:

- Micro Dist distillation block
- Micro Dist tubes, user-fill
- Pipet, adjustable volume, 1.0–5.0 mL and tips
- Pipet, TenSette, 1.0–10.0 mL and tips

Distill all samples and the standards with a Micro Dist distillation block. Refer to the Micro Dist documentation for the distillation procedure and Table 2. Always distill the standards with the samples. For the most accurate results, complete a user calibration with distilled standards.

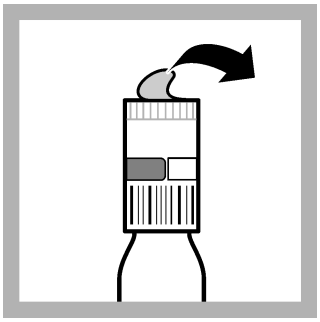
Note: *Before the releasing agent is added, fill the pipet with the releasing agent multiple times and discard into a waste container.*

Table 2 Micro Dist information for cyanide analyzed with TNT862

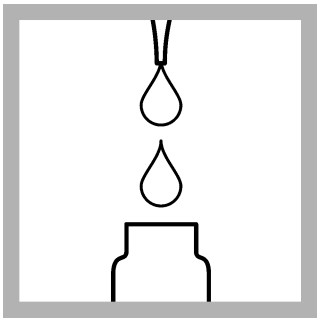
Specification	Value
Block temperature	120 °C
Trapping solution	1.5 mL of 0.1 M NaOH
Sample or standard solution	6.0 mL
Releasing agent[2]	0.75 mL of 7.11 M sulfuric acid / 0.79 M magnesium chloride solution
Distillation time	30 minutes
Diluted concentration	0.025 M NaOH

[2] Releases the free cyanide as HCN (g) and digests the complexed cyanide

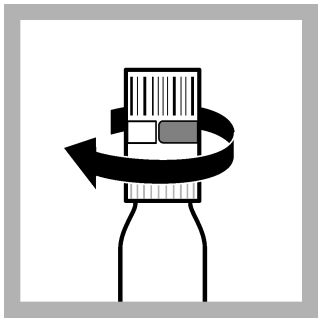
Test procedure



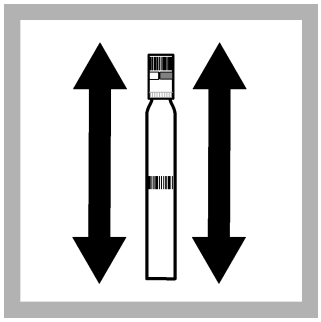
1. Carefully remove the lid from the DosiCap™ Zip cap. Remove the cap from the test vial.



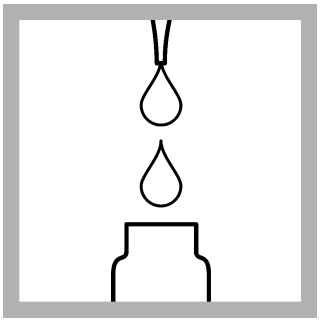
2. Use a pipet to add 1.0 mL of sample to the test vial. Immediately continue to the next step.



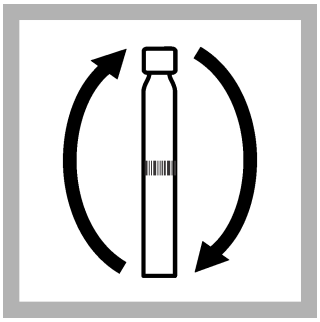
3. Turn the DosiCap Zip over so that the reagent side goes on the test vial. Tighten the cap on the vial.



4. Shake the vial 2–3 times to dissolve the reagent in the cap.
Look through the open end of the DosiCap to make sure that the reagent has dissolved.

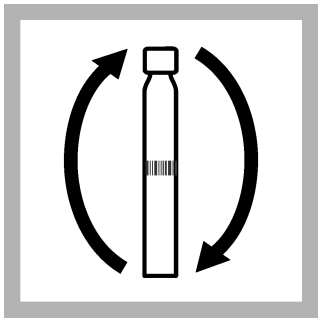


5. Use a pipet to add 1.0 mL of Solution A to the test vial.

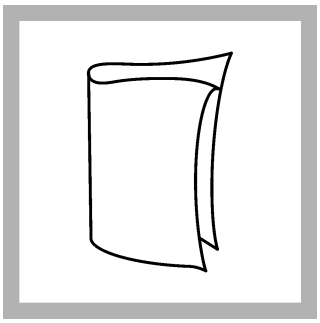


6. Tighten the cap on the vial and invert the vial 2–3 times.

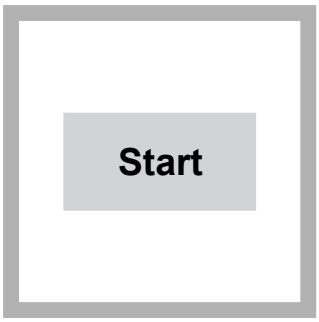
7. Start the reaction time of 3 minutes.



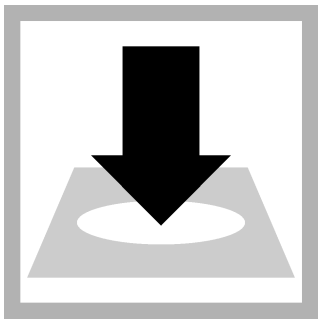
8. When the timer expires, invert the vial 2–3 times.



9. Clean the vial.



10. DR 1900 only: Select program 862. Refer to Before starting on page 1.



11. Insert the vial into the cell holder. DR 1900 only: Push **READ**.
Results show in CN^-.

Interferences

Interfering substance	Interference level
Chlorine	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.

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.

Summary of Method

Cyanides react with chlorine to form cyanogen chloride. Cyanogen chloride reacts with pyridine when barbituric acid is in the sample and forms a violet color. The measurement wavelength is 590 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Cyanide TNTplus Reagent Set	1	25/pkg	TNT862

Required apparatus

Description	Quantity/test	Unit	Item no.
Pipet, adjustable volume, 1.0–5.0 mL	1	each	BBP065
Pipet tips, for 1.0–5.0 mL pipet	1	75/pkg	BBP068
Pipet, TenSette, 1.0–10.0 mL	1	each	1970010
Pipet tips, for TenSette Pipet, 1.0–10.0 mL	1	50/pkg	2199796
Light shield, DR 3900	1	each	LZV849
Light shield, DR 3800, DR 2800, DR 2700	1	each	LZV646

Micro Dist apparatus

Description	Quantity/test	Unit	Item no.
Micro Dist distillation block, 100 VAC	1	each	A17102
OR			
DRB200 Reactor Block	1	each	DRB200-04
DRB200 adapter sleeves, Micro Dist	1	8/pkg	LZT144
Micro Dist tubes, user-fill	varies	50/pkg	A17517
Micro Dist tubes, user-fill	varies	100/pkg	A17117

Recommended standards

Description	Unit	Item no.
Potassium Cyanide, ACS	100 g	76714

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
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
Water, deionized	4 L	27256

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HACH COMPANY
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Telephone: (970) 669-3050
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