



Method 10072

Persulfate Digestion Method

Test 'N Tube™ Vials

HR (10 to 150 mg/L N)

Scope and Application: For water and wastewater.

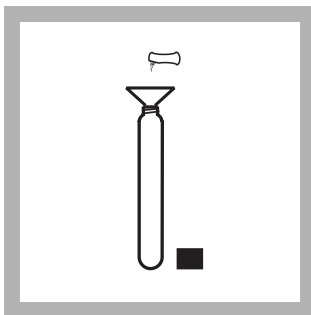
Digestion is required for determining total nitrogen. The digestion procedure is included in the method



1. Turn on the COD Reactor. Heat to 103-106 °C (optimal temperature is 105 °C). Place the plastic shield in front of the reactor.

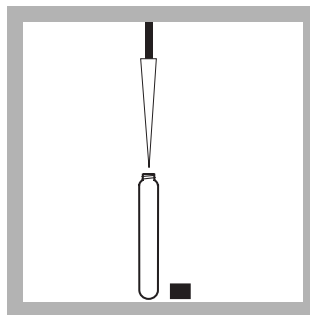
Note: Ensure safety devices are in place to protect the analyst should splattering and leakage occur.

Note: For proof of accuracy, run a 125 mg/L $\text{NH}_3\text{-N}$ standard through digestion and analysis.



2. Prepare a reagent blank: Using a funnel, add the contents of one Total Nitrogen Persulfate Reagent Powder Pillow to one HR Total Nitrogen Hydroxide Digestion Vial.

Note: Wipe off any reagent that gets on the lid or the tube threads.



3. Add 0.5 mL of the deionized water provided. Cap and shake vigorously for about 30 seconds.

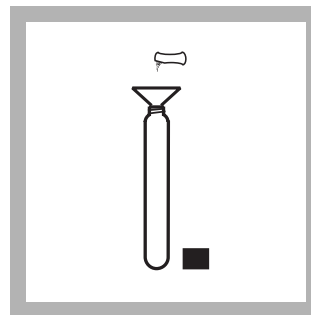
Process this reagent blank exactly the same as the sample, including digestion and color finish. Proceed to step 6.

Note: Alternate water must be free of all nitrogen-containing species.

Note: The persulfate reagent may not dissolve completely after shaking.

Note: One reagent blank is sufficient for each set of samples using the same lots of reagents.

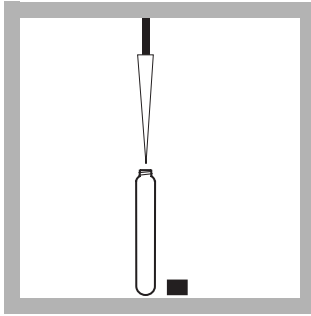
Note: The reagent blank is stable for as long as seven days when stored in the dark; see Blanks for Colorimetric Measurement following this procedure.



4. Prepare the sample: Using a funnel, add the contents of one Total Nitrogen Persulfate Reagent Powder Pillow to one HR Total Nitrogen Hydroxide Digestion Vial.

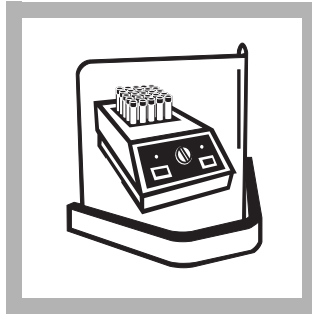
Note: Wipe off any reagent that gets on the lid or the tube threads.

NITROGEN, Total, continued

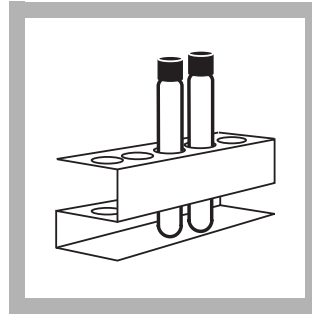


5. Add 0.5 mL of sample to the vial. Cap the vial, shake vigorously for about 30 seconds.

Note: The persulfate reagent may not dissolve completely after shaking.

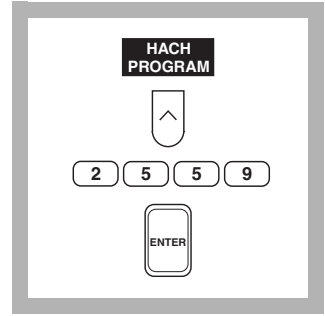


6. Place the vials in the COD Reactor. Heat for 30 minutes.



7. Using finger cots or gloves, remove the hot vials from the reactor and allow to cool to room temperature.

Note: It is very important to remove the vials from the COD Reactor after exactly 30 minutes.



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

Select the stored program for Test 'N Tube HR Total Nitrogen by pressing **2559** with the numeric keys.

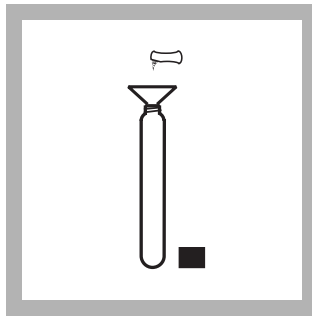
Press: **ENTER**

Note: A software update disc may be required to install this method.



9. The display will show:
HACH PROGRAM: 2559
N, Total, HR, TNT

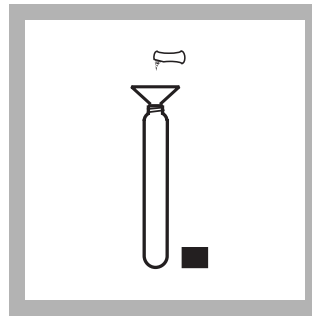
The wavelength (λ), **410 nm**, is automatically selected.



10. Add the contents of one Total Nitrogen Reagent A Powder Pillow to the vial containing the digested blank or sample. Cap the vial and shake for 15 seconds.

Press the soft key under **START TIMER** after shaking.

A 3-minute reaction period will begin.

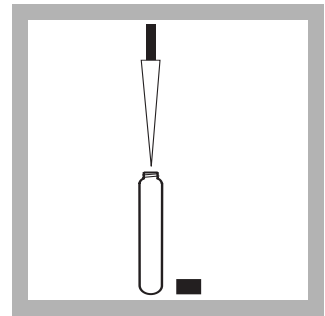


11. After the timer beeps, add one Total Nitrogen Reagent B Powder Pillow to the vial. Cap the vial and shake for 15 seconds.

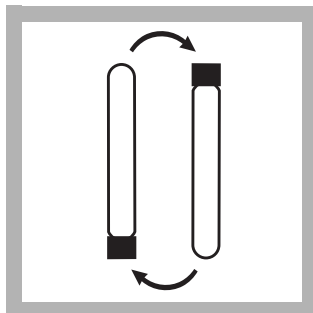
Press the soft key under **START TIMER** after shaking.

A 2-minute reaction period will begin.

Note: The reagent will not completely dissolve. The solution will begin to turn yellow.

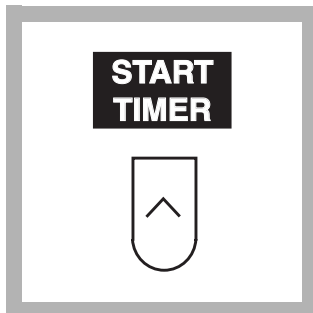


12. After the timer beeps, remove the cap from one Total Nitrogen Reagent C Vial. Add 2 mL of digested, treated sample (or reagent blank) to the vial. The vial will be warm.



13. Cap and invert slowly 10 times to mix.

Note: Proper mixing is important for complete recovery. Hold the vial vertical with the cap up. Invert the vial and wait for all of the solution to flow to the cap end. Pause. Return the vial to the upright position and wait for all of the solution to flow to the vial bottom. This is one inversion (10 inversions = 30 seconds).



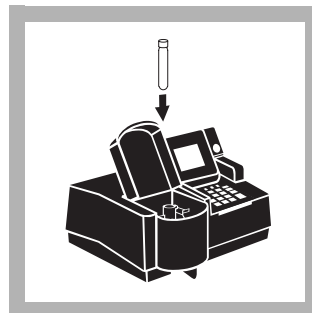
14. Press the soft key under **START TIMER**.

A 5-minute reaction period will begin. Do not invert the vial again.

Note: The yellow color will intensify.

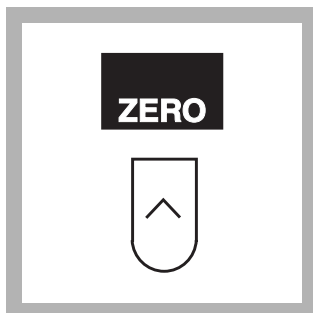


15. Insert the Test 'N Tube Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.



16. When the timer beeps, clean the outside of the Total Nitrogen Reagent C Vial containing the reagent blank. Place the vial in the adapter with the Hach logo facing the front of the instrument and close the light shield.

Note: Wipe with a damp towel, followed by a dry one, to remove fingerprints or other marks.

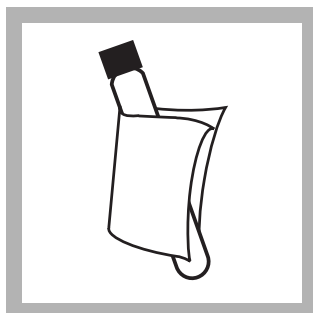


17. Press the soft key under **ZERO**.

The display will show:

0 mg/L N

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.



18. Wipe the Total Nitrogen Reagent C vial containing the sample.

Note: Wipe with a damp towel, followed by a dry one, to remove fingerprints or other marks.



19. Place the vial into the cell holder with the Hach logo facing the front of the instrument and close the light shield. The result in mg/L total nitrogen will be displayed.

Note: Multiple samples may be read after zeroing on one reagent blank.

Note: Results may be expressed as N, NH₃ or NO₃⁻. Press the soft keys under **OPTIONS** and then **FORM** to scroll through the available options. Press **ENTER** to return to the read screen.

Note: If the test overranges, repeat the digestion and measurement with diluted sample. The digestion must be repeated for accurate results.

NITROGEN, Total, continued

Interferences

The substances in the following table have been tested and found **not** to interfere up to the indicated levels (in mg/L):

Substance	Maximum Level Tested (mg/L)
Barium	10.4
Calcium	1200
Chromium (3+)	2
Iron	8
Lead	26.4 ppb
Magnesium	2000
Organic Carbon	600
pH	13 pH units
Phosphorus	400
Silica	600
Silver	3.6
Tin	6

Interfering substances that resulted in a concentration change of $\pm 10\%$:

Substance	Level and Effect
Bromide	> 240 ppm; positive interference
Chloride	≥ 3000 ppm; positive interference

The large amounts of nitrogen-free organic compounds in some samples may decrease digestion efficiency by consuming some of the persulfate reagent. Samples known to contain high levels of organics should be diluted and re-run to verify digestion efficiency.

Sample Collection, Storage and Preservation

Collect samples in clean plastic or glass bottles. Best results are obtained with immediate analysis.

Preserve the sample by reducing the pH to 2 or less with concentrated sulfuric acid (at least 2 mL/L). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Warm samples to room temperature and neutralize with 5 N Sodium Hydroxide before analysis. Correct the test result for volume additions; see Section 1.2.2 *Correcting For Volume Additions*.

Accuracy Check

This method generally yields 95–100% recovery on organic nitrogen standards. For proof of accuracy Hach offers a set of three Primary Standards for Kjeldahl Nitrogen.

1. Prepare one or more of the following 3 solutions. Each preparation is for an equivalent 120-mg/L N standard. Use the deionized water included in the kit or water that is free of all organic and nitrogen-containing species.
 - a. Weigh 1.6208 g of Ammonium p-Toluenesulfonate (PTSA). Dissolve in a 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.

- b. Weigh 2.1179 g of Glycine p-Toluenesulfonate. Dissolve in a 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.
 - c. Weigh 2.5295 g of Nicotinic p-Toluenesulfonate. Dissolve in a 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.
2. Analyze each of these solutions using the test procedure above. Calculate the percent recovery for each using this formula:

$$\% \text{ recovery} = \frac{\text{measured concentration}}{120} \times 100$$

The percent recovery should be:

Compound	Lowest Expected % Recovery
Ammonia-PTSA	95%
Glycine-PTSA	95%
Nicotinic-PTSA	95%

Hach analysts have found Ammonia-PTSA to be the most difficult to digest. Other compounds may yield different percent recoveries.

Standard Solution Method

For proof of accuracy, substitute 0.5 mL of a 125-mg/L ammonia nitrogen standard solution for the sample in the procedure*.

To adjust the calibration curve using the reading obtained with a 120 mg/L N standard solution, press the soft keys under **OPTIONS, (MORE)**, then **STD: (OFF)**. Press **KEEP** to retain the default concentration. If an alternate concentration is used, enter the actual concentration and press **ENTER** to return to the read screen. See *Adjusting the Standard Curve* in the DR/4000 Procedures Manual for more information.

Standard Additions Method

- a. Fill three 25-mL graduated mixing cylinders with 25 mL of sample.
- b. Open an Ammonia Nitrogen Standard Solution, 1000-mg/L as NH₃-N.
- c. Use the TenSette® Pipet to add 0.1, 0.2 and 0.3 mL of standard, respectively, to the three mixing cylinders.
- d. Stopper each cylinder and mix thoroughly.
- e. Add 0.5 mL of each prepared solution, respectively, to three HR Total Nitrogen Hydroxide Digestion vials.
- f. Analyze each standard addition sample as described in the procedure. The nitrogen concentration should increase by approximately 4 mg/L N for each 0.1 mL of standard added.
- g. If these increases do not occur, see *Standard Additions in Section 1* of the Procedure Manual for troubleshooting information.

* To prepare a 125-mg/L ammonia nitrogen standard, use a 25-mL Class A pipet to transfer 25.00 mL of a 1000-mg/L Ammonia Nitrogen Standard Solution (see *OPTIONAL REAGENTS AND STANDARDS*) to a 200-mL Class A volumetric flask. Dilute to the line with organic-free water.

NITROGEN, Total, continued

Blanks for Colorimetric Measurement

The reagent blank may be used repeatedly for measurements using the same lots of reagents. Store the reagent blank in the dark at room temperature (18–25 °C) for a maximum of seven days. If a small amount of white floc appears prior to the end of one week, discard the reagent blank and prepare a new one.

Calibration Standard Preparation

To perform a HR total nitrogen calibration using the Test 'N Tube Persulfate Digestion method, prepare calibration standards containing 20.00, 50.00, 80.00 and 125 mg/L nitrogen (NH₃-N) as follows:

- a. Using Class A glassware, pipet 5.00 mL of a 1000-mg/L Ammonia Nitrogen Standard Solution into a 250-mL Class A volumetric flask.
- b. Using Class A glassware, pipet 25.00 mL of a 1000-mg/L Ammonia Nitrogen Standard Solution into a 500-mL Class A volumetric flask.
- c. Using Class A glassware, pipet 8.00 mL of a 1000-mg/L Ammonia Nitrogen Standard Solution into a 100-mL Class A volumetric flask.
- d. Using Class A glassware, pipet 25.00 mL of a 1000-mg/L Ammonia Nitrogen standard solution into a 200-mL class A volumetric flask.
- e. Using the Basic Persulfate Digestion 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.

Method Performance

Precision:

Standard: 125 mg/L NH₃-N

Program	95% Confidence Limits
2559	122.5–127.5 mg/L N

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

Estimated Detection Limit:

Program	EDL
2559	7 mg/L N

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 40CFR, part 136, Appendix B, see *Section 1.5.1*.

Sensitivity:

Program Number: 2559

Program	ΔAbs	ΔConcentration
Entire Range	0.010	2 mg/L

See *Section 1.5.3 Sensitivity Explained* for more information.

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.

Summary of Method

An alkaline persulfate digestion converts all forms of nitrogen to nitrate. Sodium metabisulfite is added after the digestion to eliminate halogen oxide interferences. Nitrate then reacts with chromotropic acid under strongly acidic conditions to form a yellow complex with an absorbance maximum at 410 nm.

REQUIRED REAGENTS

Test ³N Tube HR Total Nitrogen Reagent Set (50 vials).....27141-00
 Includes: (1) 26718-46, (1) 26719-46, (1) 26720-46, (1) 272-42, (50) Hydroxide digestion vials,*
 (50) Acid Solution vials*, (1) 272-42

Description	Quantity Required		Cat. No.
	Per Test	Unit	
HR Total Nitrogen Hydroxide Digestion Vials	1 vial	50/pkg	*
Total Nitrogen Persulfate Reagent Powder Pillows	1 pillow	50/pkg	26718-46
Total Nitrogen Reagent A, Bisulfite Powder Pillows.....	1 pillow	50/pkg	26719-46
Total Nitrogen Reagent B, Indicator Powder Pillows	1 pillow	50/pkg	26720-46
Total Nitrogen Reagent C Vials, Acid Solution	1 vial	50/pkg	*
Water, deionized	1 mL	100 mL.....	272-42

REQUIRED EQUIPMENT AND SUPPLIES

COD Reactor, 115/230 VAC, North American Plug.....	1	each.....	45600-00
COD Reactor, 230 VAC, European Plug	1	each.....	45600-02
DR/4000 Test Tube Adapter.....	1	each.....	48189-00
Funnel, micro	1	each.....	25843-35
Pipet, TenSette, 0.1- to 1.0-mL	1	each.....	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	2	50/pkg.....	21856-96
Safety Shield	1	each.....	23810-00
Test Tube Cooling Rack	1-3	each.....	18641-00

* These items are not sold separately. Please reorder the complete set (Cat. No. 27141-00).

NITROGEN, Total, continued

OPTIONAL REAGENTS AND STANDARDS

Description	Unit	Cat. No.
Ammonia Standard Solution as N, 1000-mg/L.....	500 mL.....	23541-53
Primary Standard Set, for Kjeldahl Nitrogen.....	set of 3.....	22778-00
Sodium Hydroxide Standard Solution, 5.0 N.....	59 mL SCDB.....	2450-26
Sulfuric Acid, ACS, concentrated.....	500 mL.....	979-49
Water, organic-free.....	500 mL.....	26415-49

OPTIONAL EQUIPMENT AND SUPPLIES

Balance, analytical, 115 VAC.....	each.....	26103-00
Balance, analytical, 230 VAC.....	each.....	26103-02
Cylinder, mixing, graduated, 25-mL.....	each.....	20886-40
Flask, volumetric, Class A, 100-mL.....	each.....	14574-42
Flask, volumetric, Class A, 200-mL.....	each.....	14574-45
Flask, volumetric, Class A, 250 mL.....	each.....	14574-46
Flask, volumetric, Class A, 500-mL.....	each.....	14574-49
Flask, volumetric, Class A, 1000-mL.....	each.....	14574-53
pH Paper, pH 1.0 to 11.0.....	5 rolls/pkg.....	391-33
Pipet, volumetric, Class A, 5-mL.....	each.....	14515-37
Pipet, volumetric, Class A, 8-mL.....	each.....	14515-08
Pipet, volumetric, Class A, 20-mL.....	each.....	14515-20
Pipet, volumetric, Class A, 25-mL.....	each.....	14515-40



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