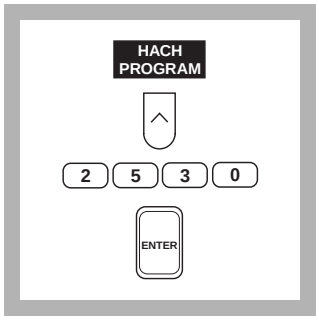
Method 8039 **Cadmium Reduction Method**

Powder Pillows or AccuVac® Ampuls **HR (0 to 30.0 mg/L NO_3^-–N)**

Scope and Application: *For water, wastewater and seawater.*
The estimated detection limits for program numbers 2530 and 2535 are 0.5 and 0.3 mg/L NO_3^-–N, respectively.

Using Powder Pillows



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

Select the stored program number for high range nitrate by pressing **2530** with the numeric keys.

Press: **ENTER**

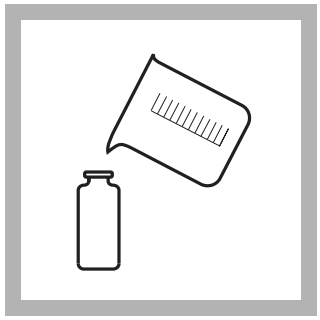
Note: *If samples cannot be analyzed immediately, see Sample Collection, Storage and Preservation following these steps. Adjust the pH of preserved samples before analysis.*

2. The display will show:

HACH PROGRAM: 2530 N, Nitrate HR

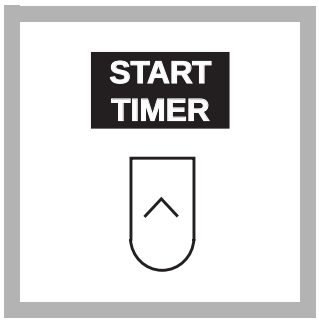
The wavelength (λ), **500 nm**, is automatically selected.

Note: *For best results, determine a reagent blank for each new lot of reagent as follows. Prepare a reagent blank by repeating steps 3 through 9, using deionized water as the sample. Zero the instrument on deionized water by pressing the soft key under* ***ZERO****. Insert the reagent blank and the blank value will be displayed. Correct for the reagent blank by pressing the soft keys under* ***OPTIONS, (MORE)****, and then* ***BLANK:OFF****. Enter the reagent blank value and press* **ENTER***. Repeat for each new lot of reagent.*



3. Fill a sample cell with 10 mL of sample.

4. Add the contents of one NitraVer 5 Nitrate Reagent Powder Pillow (the prepared sample). Stopper.

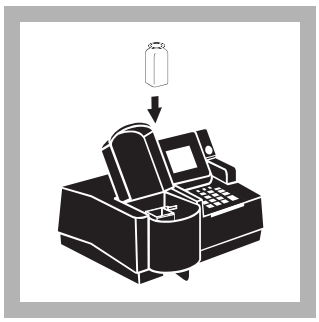


5. Press the soft key under ***START TIMER***.

Shake the cell vigorously until the timer beeps in one minute.

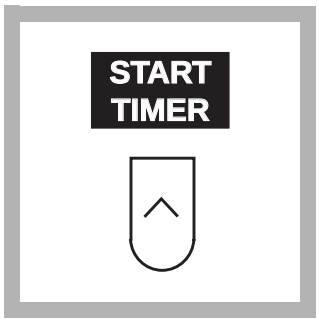
Note: *A deposit of unoxidized metal will remain after the NitraVer 5 dissolves. The deposit will not affect results.*

Note: *Shaking time and technique influence color development. For most accurate results, make successive tests on a 10-mg/L Nitrate Nitrogen Standard Solution listed under OPTIONAL REAGENTS AND STANDARDS. Adjust shaking times to obtain the correct result.*



9. Place the prepared sample into the cell holder. Close the light shield. The result in mg/L nitrate nitrogen (NO_3^-–N) will be displayed.

Note: *Measure sample within one minute after timer beeps.*



6. When the timer beeps, press the soft key under ***START TIMER***.

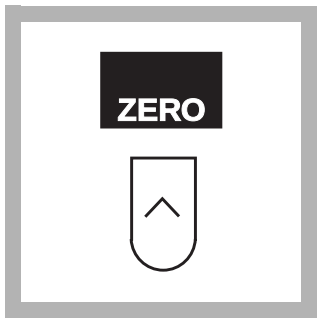
A 5-minute reaction period will begin.

Note: *An amber color will develop if nitrate nitrogen is present.*

Note: *The result can be expressed as mg/L nitrate (NO_3^-). Press the soft keys under* ***OPTIONS*** *and then* ***FORM:*** *to scroll through the available options.*

Note: *Rinse the sample cell immediately after use to remove all cadmium particles. Retain the spent sample for proper hazardous waste disposal for cadmium.*

7. When the timer beeps, fill a second sample cell with 10 mL of sample (the blank). Place the blank into the cell holder.



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

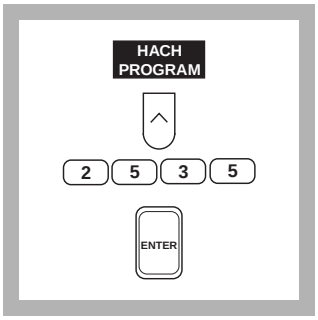
The display will show:

0.0 mg/L NO_3^-–N

Note: *If you are using a reagent blank correction, the display will show the correction.*

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.*

Using AccuVac Ampuls



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

Select the stored program number for high range nitrate by pressing **2535** with the numeric keys.

Press: **ENTER**

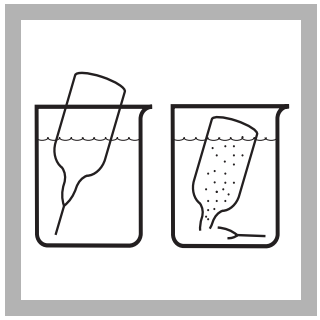
Note: *If samples cannot be analyzed immediately, see Sample Collection, Storage and Preservation following these steps. Adjust the pH of preserved samples before analysis.*

2. The display will show:

HACH PROGRAM: 2535 N, Nitrate HR AV

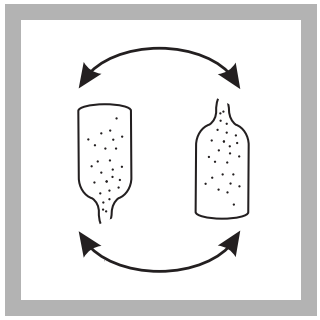
The wavelength (λ), **500 nm**, is automatically selected.

Note: *For best results, determine a reagent blank for each new lot of reagent as follows. Prepare a reagent blank by repeating steps 3 through 10, using deionized water as the sample. Zero the instrument on deionized water by pressing the soft key under* ***ZERO****. Insert the reagent blank and the blank value will be displayed. Correct for the reagent blank by pressing the soft keys under* ***OPTIONS, (MORE)****, and then* ***BLANK:OFF****. Enter the reagent blank value and press* **ENTER***. Repeat for each new lot of reagent.*



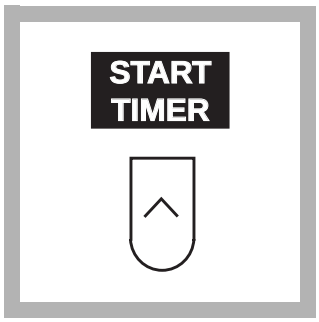
3. Collect at least 40 mL of sample in a 50-mL beaker. Fill a NitraVer 5 Nitrate AccuVac Ampul with sample. Place a stopper over the tip of the ampul.

Note: *Keep the tip immersed while the ampul fills.*



4. Press the soft key under ***START TIMER***. Invert the ampul repeatedly until the timer beeps in one minute. Wipe off any liquid or fingerprints.

Note: *Inversion rate can influence color development. For most accurate results, make successive tests on a 10-mg/L Nitrate Nitrogen Standard Solution listed under OPTIONAL REAGENTS AND STANDARDS. Adjust inversion rate to obtain the correct result.*

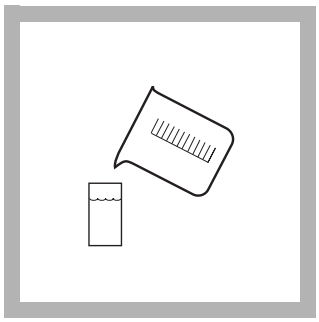


5. When the timer beeps, press the soft key under ***START TIMER***.

A 5-minute reaction period will begin.

Note: *A deposit of unoxidized metal will remain after the NitraVer 5 dissolves. The deposit will not affect results.*

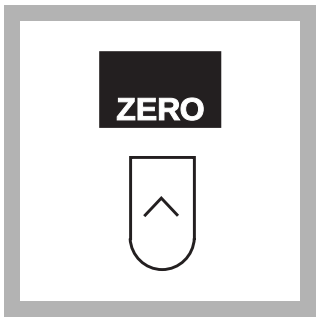
Note: *An amber color will develop if nitrate nitrogen is present.*



6. When the timer beeps, fill a zeroing vial (the blank) with at least 10 mL of sample.

7. Insert the AccuVac Ampul Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.

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



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

The display will show:

0.0 mg/LNO_3^-–N

Note: *If you have entered a reagent blank correction, the display will show the correction.*

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.*

10. Place the AccuVac Ampul into the cell holder. Close the light shield. Results in mg/L nitrate expressed as nitrogen (NO_3^-–N) will be displayed.

Note: *Measure sample within 1 minute after timer beeps.*

Note: *The results can be expressed as mg/L nitrate (NO_3^-). Press the soft keys under* ***OPTIONS****, then* ***FORM:*** *to scroll through the available options.*

Interferences

Table 1 Interfering Substances and Suggested Treatments

Interfering Substance	Interference Level and Treatment
Chloride	Chloride concentrations above 100 mg/L will cause low results. The test may be used at high chloride concentrations (seawater) but a calibration must be done using standards spiked to the same chloride concentration.
Ferric iron	All levels
Nitrite	All levels Compensate for nitrite interference as follows: **1.** Add 30-g/L Bromine Water dropwise to the sample in Step 3 until a yellow color remains. **2.** Add one drop of 30-g/L Phenol Solution to destroy the color. **3.** Proceed with Step 4. Report the results as total nitrate and nitrite.
pH	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.
Strong oxidizing and reducing substances	Interfere at all levels

Sample Collection, Storage and Preservation

Most reliable results are obtained when samples are analyzed as soon as possible after collection. If prompt analysis is impossible, store samples in clean plastic or glass bottles for up to 24 hours at 4 °C. To preserve samples for longer periods, add 2 mL of concentrated sulfuric acid (H_2SO_4) per liter and store at 4 °C.

Before analysis, warm the sample to room temperature and adjust the pH to 7 with 5.0 N Sodium Hydroxide Standard Solution. Do not use mercury compounds as preservatives. Correct the test result for volume additions by dividing the total volume (acid + base + sample) by the original sample volume and multiplying the test result by this factor.

Accuracy Check

Standard Solution Method

To test accuracy, use a 10.0 mg/L Nitrate Nitrogen Standard Solution in place of the sample and perform the procedure as described.

To adjust the calibration curve using the reading obtained with the 10.0 mg/L Nitrate Nitrogen Standard Solution, press the soft keys under ***OPTIONS, (MORE)*** then ***STD: OFF***. Press **ENTER** to accept the default concentration, 10.0-mg/L NO_3^-–N. 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.

Standard Additions Method

a. Leave the unspiked sample in the sample compartment. Verify that the units displayed are in mg/L. Select standard additions mode by pressing the soft keys under ***OPTIONS, (MORE)*** and then ***STD ADD***.

b. Press **ENTER** to accept the default sample volume (mL), 25. (This is the volume to which standard addition aliquots are added.)

c. Press **ENTER** to accept the default standard concentration (mg/L), 500.

d. Press the soft key under ***ENTRY DONE***.

e. Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

f. Snap the neck off a Nitrate Nitrogen PourRite Ampule Standard, 500-mg/L NO_3^-–N.

g. Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard, respectively, to the three mixing cylinders. Stopper each and mix thoroughly.

h. For analysis with AccuVac Ampuls, transfer solutions to dry, clean 50-mL beakers to facilitate filling of the ampules. For analysis with powder pillows, transfer only 10 mL of solution to the 10-mL sample cells.

i. Analyze each standard addition sample as described above. Accept the standard additions readings by pressing the soft key under ***READ*** each time. Each addition should reflect approximately 100% recovery.

j. After completing the sequence, the display will show the extrapolated concentration value and the "best-fit" line through the standard additions data points, accounting for matrix interferences.

k. See Section *1.4.1 Standard Additions* for more information.

Method Performance

Precision

Standard: 20.0 mg/L NO_3^-–N_2

Program	95% Confidence Limits
2530	19.5–20.5 mg/L NO_3^-–N
2535	19.6–20.4 mg/L NO_3^-–N

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

Estimated Detection Limit

Program	EDL
2530	0.5 mg/L NO_3^-–N
2535	0.3 mg/L NO_3^-–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 40 CFR part 136, Appendix B, see Section *1.5.1*.

Sensitivity

Program Number: 2530

Portion of Curve	ΔAbs	ΔConcentration
0.4 mg/L NO_3^-–N	0.010	0.35 mg/L NO_3^-–N
15.0 mg/L NO_3^-–N	0.010	0.59 mg/L NO_3^-–N
27.0 mg/L NO_3^-–N	0.010	0.72 mg/L NO_3^-–N

Program Number: 2535

Portion of Curve	ΔAbs	ΔConcentration
0.3 mg/L NO_3^-–N	0.010	0.35 mg/L NO_3^-–N
15.0 mg/L NO_3^-–N	0.010	0.56 mg/L NO_3^-–N
27.0 mg/L NO_3^-–N	0.010	0.68 mg/L NO_3^-–N

See Section *1.5.3 Sensitivity Explained* for more information.

Calibration Standard Preparation

To perform a nitrate calibration using the NitraVer 5 method, prepare calibration standards containing 4, 14, and 30 mg/L NO_3^-–N as follows:

a. Into three different 500-mL Class A volumetric flasks, pipet 2.00, 7.00, and 15.00 mL of a 1000-mg/L Nitrate Nitrogen Standard Solution using Class A glassware.

b. Dilute to the mark with deionized water. Mix thoroughly.

c. Using the NitraVer 5 Powder Pillow or AccuVac 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

Cadmium metal reduces nitrates in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt. The salt couples with gentisic acid to form an amber colored solution.

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

Prepared samples will contain cadmium and must be disposed of according to Federal, State and local hazardous waste regulations. For information on pollution prevention and waste management, refer to Section *1*.

REQUIRED REAGENTS AND STANDARDS (Using Powder Pillows)

Description	Quantity Required per test	Unit	Cat. No.
NitraVer 5 Nitrate Reagent Powder Pillows for 10 mL sample	1 pillow	100/pkg	21061-69

REQUIRED REAGENTS AND STANDARDS (Using AccuVac Ampuls)

NitraVer 5 Nitrate Reagent AccuVac Ampul	1 ampul	25/pkg	25110-25

REQUIRED EQUIPMENT AND SUPPLIES (Using Powder Pillows)

DR/4000 1-Inch Cell Adapter	1	each	48190-00
Sample Cells, matched pair, 1-inch, glass, with stoppers	2	pair	26126-02

REQUIRED EQUIPMENT AND SUPPLIES (Using AccuVac Ampuls)

Beaker, 50-mL	1	each	500-41
DR/4000 AccuVac Ampul Adapter	1	each	48187-00
Sample Cell, 10-mL with cap (zeroing vial)	1	each	21228-00
Stopper	1	6/pkg	1731-06

OPTIONAL REAGENTS AND STANDARDS

Bromine Water, 30-g/L	29 mL*	2211-20
Nitrate Nitrogen Standard Solution, 10.0-mg/L NO_3^-–N	500 mL	307-49
Nitrate Nitrogen Standard Solution, 1000-mg/L NO_3^-–N	500 mL	12792-49
Nitrate Nitrogen Standard Solution, PourRite Ampule, 500-mg/L NO_3^-–N, 2 mL	20/pkg	14260-20
Phenol Solution, 30-g/L	29 mL*	2112-20
Sodium Hydroxide Standard Solution, 5.0 N	1 liter	2450-53
Sulfuric Acid, ACS	500 mL*	979-49
Water, deionized	4 liters	272-56

OPTIONAL EQUIPMENT AND SUPPLIES

AccuVac Snapper	each	24052-00
Cylinder, graduated, mixing, 25 mL	each	20886-40
Dropper, for 29-mL bottle	each	2258-00
DR/4000 Carousel Module Kit	each	48070-02
Flask, volumetric, 500-mL, Class A	each	14574-49
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 2.00-mL	each	14515-36
Pipet, volumetric, Class A, 7.00-mL	each	14515-07
Pipet, volumetric, Class A, 15.00-mL	each	14515-39
Pipet Filler, safety bulb	each	14651-00
pH Paper, pH 1.0 to 11.0	5/pkg	391-33
PourRite Ampule Breaker	each	24846-00

* Larger sizes available

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