



Method 10200

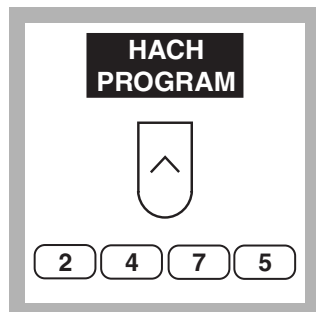
(0–4.50 mg/L Cl₂ and 0–0.50 mg/L NH₃-N)

Indophenol Method*

Scope and Application: Finished chloraminated drinking water

* U.S. Patent 6,315,950

Note: For more accurate chloramine results, determine a reagent blank for each lot of reagent using deionized water in place of the sample. Correct for the reagent blank in program 2475 by pressing the **OPTIONS (MORE)** soft keys, and then **BLANK:OFF**. Enter the reagent blank value and press **ENTER**. Repeat for each lot of reagent.



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

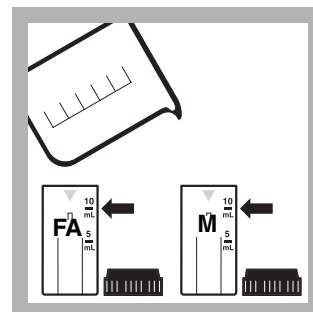
Press: **2475**, the stored program number for Monochloramine, LR.



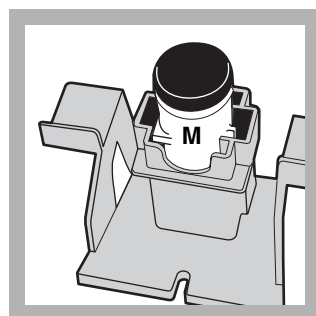
2. Press: **ENTER**.
The display will show:
**HACH PROGRAM 2475
Chloramine, Mono LR**
The wavelength (λ), **655 nm**, is automatically selected.



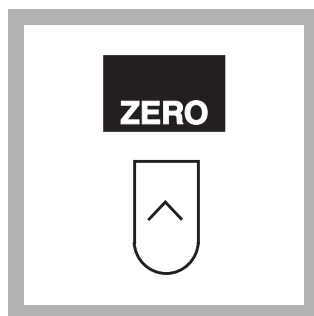
3. Insert the AccuVac[®] adapter into the sample cell module by sliding it under the thumbscrew and into the alignment grooves. Fasten with the thumbscrew.



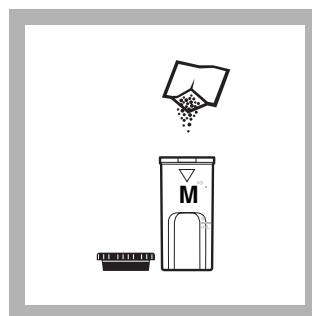
4. Fill two 10-mL/1-cm cells to the 10-mL line with sample.
Label one cell “Free Ammonia” and one cell “Monochloramine”.



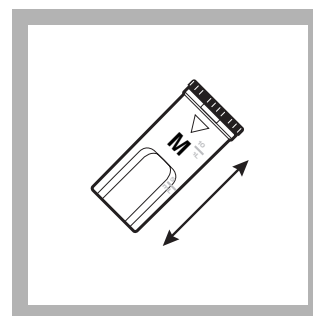
5. Place the Monochloramine cell into the cell holder so that the locking ridge on the cell is oriented to the left.
Press the top rim of the cell on the right side to lock it in place. Close the light shield.



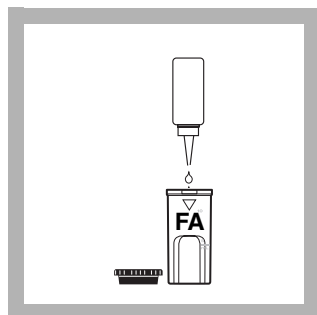
6. Press the **ZERO** soft key.
The display will show:
mg/L Cl₂
Remove the cell from the instrument.



7. Add the contents of one Monochlor F pillow to the cell for the Monochloramine measurement.



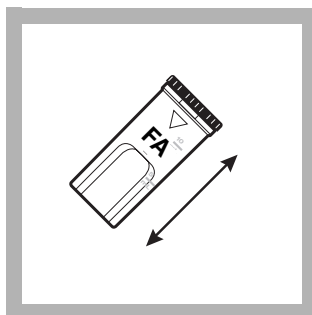
8. Cap the cell and shake for 20 seconds to dissolve the reagent.
A green color will form if monochloramine is present.



9. Add one drop of Free Ammonia Reagent Solution to the cell for Free Ammonia measurement.

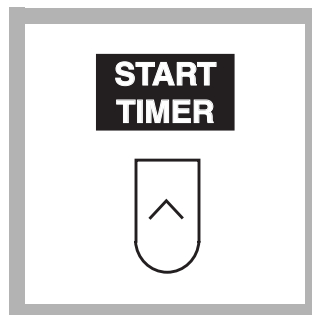


10. Cap the reagent bottle to maintain reagent performance and stability.



11. Cap the cell and mix.

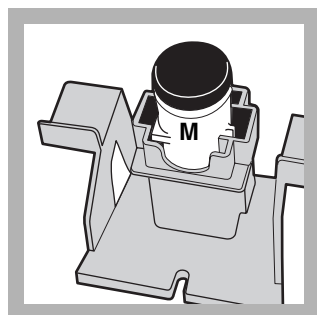
Note: If the sample becomes cloudy by the end of the reaction period, pretreat the sample and retest. See Interferences on page 4.



12. Press the **START TIMER** soft key.

A 5-minute reaction period will begin.

Note: Color development time depends on sample temperature. See Table 1. For accurate results allow the full reaction period to occur.



13. After the timer expires, place the Monochloramine cell into the cell holder so the locking ridge on the cell is oriented to the left. Press the top rim of the cell on the right side to lock it in place.

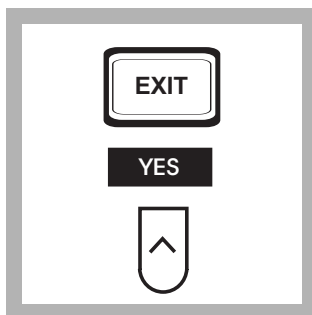


14. Close the light shield and read the result.

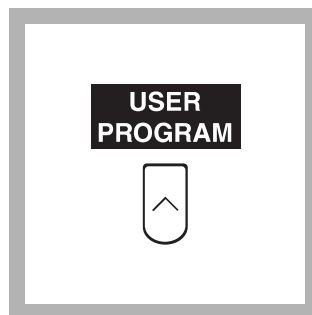
The result in mg/L Monochloramine (as Cl_2) will be displayed.

Leave the cell in the instrument.

*Note: Results may be expressed as NH_2Cl or N. Press the soft keys under **OPTIONS (MORE)** and then **FORM** to scroll through the available options. Press **ENTER** to return to the read screen.*



15. Press **EXIT**, then **YES** to return to the main menu.



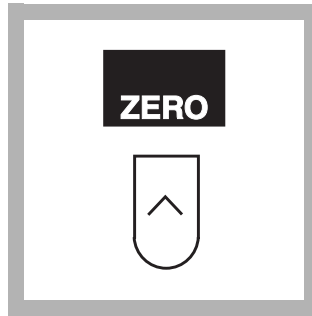
16. Press the **USER PROGRAM** soft key.

Use the **UP** or **DOWN** arrow keys to scroll to the *user-entered program* for N, Ammonia Free, or key in the program number with the numeric keypad.

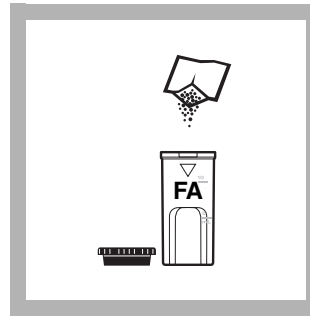
See Entering the User Programs on page 7 for more information.



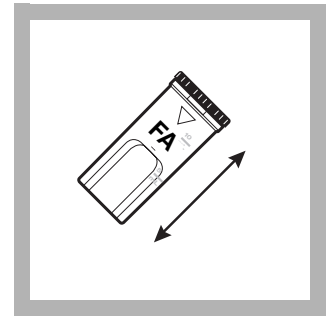
17. Press: **ENTER**.
The display will show:
**USER PROGRAM XXX
N, Ammonia Free**
where XXX is the User Program number assigned to the Free Ammonia test.



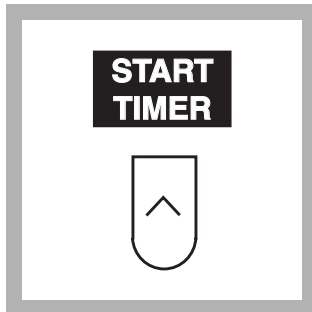
18. With the Monochloramine sample still in the adapter, press the **ZERO** soft key.
The display will show:
NH₃-N f
Remove the cell from the cell holder



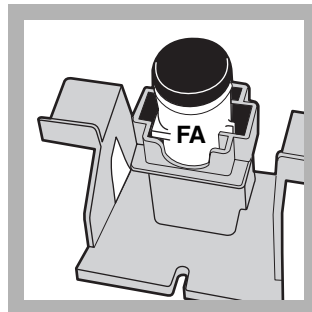
19. Add the contents of one pillow of Monochlor-F to the cell for the Free Ammonia measurement.
Note: *The reaction period indicated in step 12 must be complete before the addition of Monochlor F to the cell for free ammonia measurement.*



20. Cap and shake the cell about 20 seconds to dissolve.
A green color will form if Monochloramine or Ammonia is present.



21. Press the **START TIMER** soft key.
A 5-minute reaction period will begin.
Note: *Color development time depends on sample temperature. See Table 1 on page 4.*



22. After the timer expires, place the Free Ammonia cell into the cell holder so the locking ridge on the cell is oriented to the left. Press the top rim of the cell on the right side to lock it in place.



23. Close the light shield.
The result in mg/L Free Ammonia as Nitrogen (NH₃-N) will be displayed.
Note: *Press the **OPTIONS (MORE)** soft keys and then **FORM:** to scroll through the available options. Press **ENTER** to return to the read screen.*

Sampling and Storage

Collect samples in clean glass bottles. Most reliable results are obtained when samples are analyzed as soon as possible after collection.

Nitrogen, Free Ammonia and Chloramine (Mono), continued

Color Development Time

Test results are strongly influenced by sample temperature. **Both reaction periods in the procedure are the same and depend on the temperature of the sample.** The reaction periods indicated in the procedure are for a sample temperature of 18–20 °C (68–73 °F). Adjust both reaction periods according to Table 1.

Table 1 Reaction Period

| Sample Temperature | | Reaction Periods (Minutes) |
|--------------------|-----|-------------------------------|
| ° C | ° F | |
| 5 | 40 | 10 |
| 7 | 42 | 9 |
| 9 | 48 | 8 |
| 10 | 50 | 8 |
| 12 | 54 | 7 |
| 14 | 58 | 7 |
| 16 | 61 | 6 |
| 18 | 68 | 5 |
| 20 | 73 | 5 |
| 23 | 75 | 2.5 |
| 25 | 77 | 2 |
| >25 | >77 | 2 |

Interferences

This method is intended for finished, chloraminated drinking water samples that have a measurable combined (total) chlorine disinfectant residual. Samples where the disinfectant residual has disappeared and samples which exhibit a chlorine demand may produce low ammonia test results. Blanks and ammonia standards analyzed without a disinfectant residual must be prepared using high quality, reagent grade water.

The following do not interfere in the free ammonia determination when at or below the stated concentration.

| Substance | Level Tested |
|-----------|-------------------------------|
| Aluminum | 0.2 mg/L Al |
| Chloride | 1200 mg/L Cl |
| Copper | 1 mg/L Cu |
| Iron | 0.3 mg/L Fe |
| Manganese | 0.05 mg/L Mn |
| Nitrate | 10 mg/L NO ₃ -N |
| Nitrite | 1 mg/L NO ₂ -N |
| Phosphate | 2 mg/L -PO ₄ |
| Silica | 100 mg/L SiO ₂ |
| Sulfate | 1600 ppm as CaCO ₃ |
| Zinc | 5 ppm Zn |

Samples containing high levels of both Total Hardness and Alkalinity may become cloudy after the addition of the Free Ammonia Reagent Solution. If this occurs by the end of the first reaction period, the sample for Free Ammonia measurement must be pretreated as follows:

Nitrogen, Free Ammonia and Chloramine (Mono), continued

Note: The sample for Monochloramine measurement does not need pretreatment.

1. Measure 10 mL of sample into the cell for Free Ammonia measurement.
2. Add the contents of one Hardness Treatment Reagent Powder Pillow (Cat. No. 28823-46) to the sample.
3. Cap the cell and invert until the reagent is dissolved.
4. Remove the cap.
5. Continue with the analysis at step 4 using the pretreated sample as the Free Ammonia cell.

Accuracy Check (Monochloramine, Program 2475)

1. Prepare the following monochloramine standard fresh before use.
2. Add the contents of one Buffer Powder Pillow, pH 8.3 to about 50-mL of organic-free water in a clean 100-mL Class A volumetric flask. Swirl to dissolve the powder.
3. Using a Class A volumetric pipet, transfer 2.00 mL of Nitrogen, Ammonia Standard Solution, 100 mg/L as $\text{NH}_3\text{-N}$ into the flask.
4. Dilute to volume with organic-free water, cap and mix thoroughly. This is a 2.00 mg/L buffered ammonia standard.
5. Pipet 50.0 mL of the buffered ammonia standard into a clean 100-mL beaker. Add a stir bar.
6. Obtain a recent lot of Chlorine Solution Ampules, 50–75 mg/L, and note the actual free chlorine concentration for this lot.
7. Calculate the amount of Chlorine Solution to be added to the ammonia standard using the following equation:
$$\text{mL chlorine solution required} = \frac{455}{\text{free chlorine concentration}}$$
8. Open an ampule and, using a glass Mohr pipet, add the calculated amount of Chlorine Solution slowly to the ammonia standard, while mixing at medium speed on a stir plate.
9. Allow the monochloramine solution to mix for 1 minute after all the Chlorine Solution is added.
10. Quantitatively transfer the monochloramine solution to a clean 100-mL Class A volumetric flask. Dilute to the mark with organic-free water, cap, and mix thoroughly. This is a nominal 4.5 mg/L (as Cl_2) monochloramine standard.

Use this standard within 1 hour of preparation.

Important Note: Because of the strong buffer used in the preparation of this standard, it cannot be used for accuracy verification of the Free Ammonia test.

Accuracy Check (Free Ammonia, User Program)

Dilution water is required when testing a diluted sample and preparing standard solutions. Dilution water must be free of ammonia, chlorine and chlorine demand. A convenient source is a recirculating, deionizer system with carbon filtration which produces 18 megaohm-cm water.

Standard Additions Method

1. Measure 50 mL of sample into three 50-mL mixing cylinders.
2. Use the TenSette Pipet to add 0.3, 0.6, and 1.0 mL of Ammonium Nitrogen Standard, 10 mg/L as $\text{NH}_3\text{-N}$ to the three samples. Mix well.
3. Analyze each spiked sample following all the steps of the Monochloramine and Free Ammonia procedure. The ammonia nitrogen concentration should increase 0.02 mg/L for each 0.1 mL of standard added.
4. If these increases do not occur, see the Standard Additions Section of the *DR/4000 Procedures Manual* for more information.

Standard Solution Method

Prepare a 0.20 mg/L ammonia nitrogen standard by diluting 2.00 mL of the Ammonia Nitrogen Standard Solution, 10 mg/L, to 100 mL with dilution water. Or, using the TenSette Pipet, prepare a 0.20 mg/L ammonia nitrogen standard by diluting 0.4 mL of a Ammonia Nitrogen Voluette Standard Solution, 50 mg/L as $\text{NH}_3\text{-N}$, to 100 mL with dilution water. Analyze the standard solution following every step of the Monochloramine and Free Ammonia procedure.

Method Performance

Monochloramine Test

Precision

In a single laboratory, using a monochloramine standard of 2.10 mg/L Cl_2 and representative lots of reagent, a single operator obtained a standard deviation of ± 0.06 mg/L Cl_2 .

Estimated Detection Limit

The estimated detection limit (EDL) for Method 10200 is 0.09 mg/L Cl_2 .

Free Ammonia Test

Precision

In a single laboratory using a solution containing 1.86 mg/L Cl_2 plus 0.054 mg/L $\text{NH}_3\text{-N}$ and one representative lot of reagent with the DR/4000, a single operator obtained a standard deviation of ± 0.004 mg/L $\text{NH}_3\text{-N}$ for eight replicates.

Estimated Detection Limit

The estimated detection limit (EDL) for Method 10200 is 0.015 mg/L $\text{NH}_3\text{-N}$.

For more information on the EDL, see *Section 1 of the DR/4000 Procedures Manual*.

Summary of Method

Monochloramine (NH_2Cl) and “free ammonia” (NH_3 and NH_4^+) can exist in the same water sample. Added hypochlorite combines with free ammonia to form more monochloramine. In the presence of a cyanoferrate catalyst, monochloramine in the sample reacts with a substituted phenol to form an intermediate monoimine compound. The intermediate couples with excess substituted phenol to form a green-colored indophenol, which is proportional to the amount of monochloramine present in the sample. Free ammonia is determined by comparing the color intensities, with and without added hypochlorite.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for information specific to the reagent used.

Entering the User Programs

1. Press the **USER PROGRAM** soft key.
2. Press the **CREATE** soft key. The prompt line will ask for a new program number.
3. Enter the number using the numeric keypad and press **ENTER**.

When a valid number is entered, the display will change and prompt the user to select the program type. Each user-entered program may be assigned a unique number between 1 and 999. This number is displayed in front of the specified program as part of the user program. The prompt line will flash “**INVALID ENTRY**” if the number is already in use.

4. To assign the next available number, press the **NEXT UNUSED** soft key and then press **ENTER**.

***Note:** Four-digit program numbers are reserved for Hach user-calibration templates.*

5. Press **EXIT** at any time to return to the main menu.
6. Press the **SINGLE WAVELENGTH** soft key.

Nitrogen, Free Ammonia and Chloramine (Mono), continued

Settings for Monochloramine

Table 2 shows the setting to be entered for each parameter of the Monochloramine User Program.

Table 2 Monochloramine Parameter Settings

| Parameter | Setting |
|------------------|---|
| Name: | Chloramine, Mono |
| Format: | XXX.XX |
| Units: | mg/L |
| Chemical Form: | Cl ₂ |
| Lower Limit: | -0.05 mg/L |
| Upper Limit: | 4.50 mg/L |
| Wavelength: | 655.0 nm |
| Calib. Table: | Off |
| Calib. Formula: | C=a+bA Coefficients: a=0.0000, b=3.8598 |
| Chemical Form 2: | NH ₂ Cl factor = 0.7257 |
| Chemical Form 3: | N factor = 0.1975 |
| Timer 1: | Wait 05:00 |
| Timer 2: | Off |
| Timer 3: | Off |
| Timer 4: | Off |

Settings for Free Ammonia

Table 3 shows the setting to be entered for each parameter of the Free Ammonia User Program.

Table 3 Free Ammonia Parameter Settings

| Parameter | Setting |
|------------------|---|
| Name: | N, Ammonia Free |
| Format: | XXX.XX |
| Units: | mg/L |
| Chemical Form: | NH ₃ -N |
| Lower Limit: | -0.01 mg/L |
| Upper Limit: | 0.55 mg/L |
| Wavelength: | 655.0 nm |
| Calib. Table: | Off |
| Calib. Formula: | C=a+bA Coefficients: a=0.0000, b=0.9490 |
| Chemical Form 2: | NH ₃ factor = 1.216 |
| Chemical Form 3: | Cl ₂ factor = 5.0600 |
| Timer 1: | Wait 05:00 |
| Timer 2: | Off |
| Timer 3: | Off |
| Timer 4: | Off |

Nitrogen, Free Ammonia and Chloramine (Mono), continued

REQUIRED REAGENTS

| Description | Quantity Required Per Test | Unit | Cat. No. |
|--|-------------------------------|----------------|----------|
| Free Ammonia Reagent Set (50 tests) Includes: (1) 28022-99, (1) 28773-36..... | | | 28797-00 |
| Free Ammonia Reagent Solution | 1 drop | 4 mL SCDB..... | 28773-36 |
| Monochlor F Reagent Pillows..... | 2 pillows | 100/pkg..... | 28022-99 |

REQUIRED APPARATUS

| | | | |
|---|---------|------------|----------|
| Sample Cell, 1-cm/10-mL, with cap | 2 | 2/pkg..... | 48643-02 |
|---|---------|------------|----------|

OPTIONAL REAGENTS

| | | | |
|---|--|-------------|----------|
| Buffer, pH 8.3, Powder Pillows..... | | 25/pkg..... | 898-68 |
| Chlorine Solution, Voluette® Ampule, 50–75 mg/L..... | | 16/pkg..... | 14268-10 |
| Hardness Treatment Reagent Pillows (1 per test) | | 50/pkg..... | 28823-46 |
| Nitrogen Ammonia Standard Solution, 10 mg/L as NH ₃ -N..... | | 500 mL..... | 153-49 |
| Nitrogen Ammonia Standard Ampule, 50 mg/L as NH ₃ -N, 10 mL..... | | 16/pkg..... | 14791-10 |
| Nitrogen Ammonia Standard Solution, 100 mg/L as NH ₃ -N..... | | 500 mL..... | 24065-49 |
| Water, Organic Free..... | | 500 mL..... | 26415-49 |

OPTIONAL APPARATUS

| | | | |
|--|--|-------------|----------|
| Ampule Breaker Kit | | each..... | 21968-00 |
| Beaker, 100 mL, Polypropylene..... | | each..... | 1080-42 |
| Beaker, 100 mL, Glass | | each..... | 500-42H |
| Cylinder, 50 mL, mixing | | each..... | 20886-41 |
| Flask, Volumetric, Class A, 100 mL | | each..... | 14574-42 |
| Pipet Filler, Safety Bulb | | each..... | 14651-00 |
| Pipet, TenSette®, 0.1 to 1.0 mL..... | | each..... | 19700-01 |
| Pipet Tips, for 19700-01 TenSette Pipet | | 50/pkg..... | 21856-96 |
| Pipet, Mohr, Glass, 10 mL | | each..... | 20934-38 |
| Pipet, Volumetric, Class A, 2.0 mL..... | | each..... | 14515-36 |
| Pipet, Volumetric, Class A, 50.00 mL..... | | each..... | 14515-41 |
| Scissors..... | | each..... | 28831-00 |
| Stir Bar, Octagonal | | each..... | 20953-52 |
| Stirrer, Magnetic..... | | each..... | 28812-00 |
| Thermometer, –10 to 110 °C..... | | each..... | 1877-01 |
| Wipers, Disposable Kimwipes®, 30 x 30 cm, 280/box..... | | box..... | 20970-01 |



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Outside the U.S.A. – Contact the HACH office or distributor serving you.

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