Nitrogen, Free Ammonia

DOC316.53.01084

Indophenol Method

Method 10201

0.01 to 0.50 mg/L NH_3–N

Powder Pillows

Scope and application: To monitor free ammonia levels during the production of chloramines, at booster stations and in potable distribution system waters.

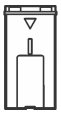
Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows requirements that can change between instruments, such as adapter and sample cell requirements.

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

Table 1 Instrument-specific information

Instrument	Adapter	Sample cell orientation	Sample cell
DR6000	—	The orientation key is toward the arrow on the universal cell adapter.	4864302 
DR5000	A23618	The orientation key is toward the user.	
DR3900	LZV846 (A)	The orientation key is away from the user.	
DR1900	9609900 or 9609800 (C)	The orientation key is toward the arrow on the adapter.	
DR/850, DR/890	—	The orientation key is at the 2 o'clock position.	
DR900	—	The orientation key is toward the user.	
DR3800 DR2800 DR2700	LZV585 (B)	The 1-cm path is aligned with the arrow on the adapter.	5940506 

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Use Method 10200, Nitrogen, Free Ammonia and Chloramine (Mono) to determine free ammonia and monochloramine simultaneously on the same sample.
In bright light conditions (e.g., direct sunlight), close the cell compartment, if applicable, with the protective cover during measurements.
For the best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to determine the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option.
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.

Items to collect

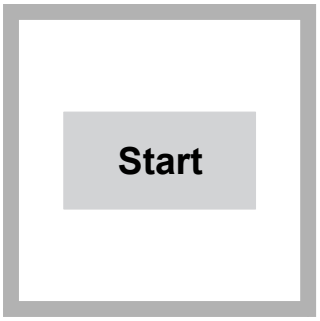
Description	Quantity
Free Ammonia Chlorinating Solution	1 drop
Monochlor F Reagent Pillows	2
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

Refer to Consumables and replacement items on page 7 for order information.

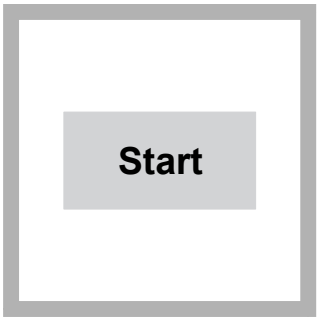
Sample collection and storage

- Analyze samples immediately after collection.
- Collect samples in clean glass bottles.
- Open the sample valve or spigot and let the water flow for a minimum of 5 minutes.
- Rinse the sample bottle several times with the sample and let the sample overflow each time, then cap the container so that there is no head space (air) above the sample.

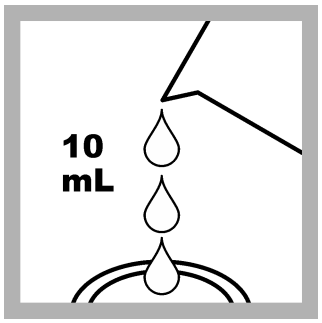
Test procedure



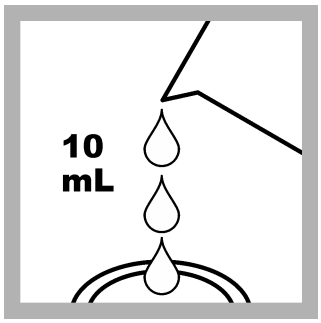
1. For the DR 800 series, enter and start program **133**.



2. For other instruments, start program **389, N, Ammonia Free**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

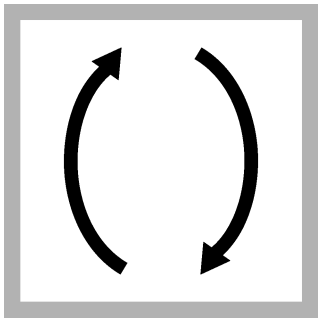


3. Fill two sample cells to the 10-mL line with sample. Write **Free Ammonia** on one sample cell. Write **Monochloramine** on the second sample cell.



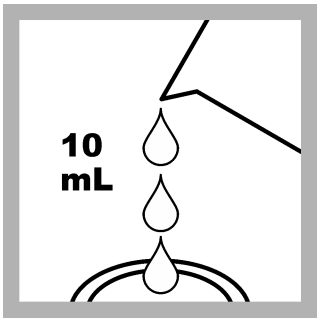
4. Prepare the sample: Fill a sample cell with 10 mL of sample.

5. Add one drop of Free Ammonia Chlorinating Solution to the sample. Immediately tighten the cap on the reagent bottle.

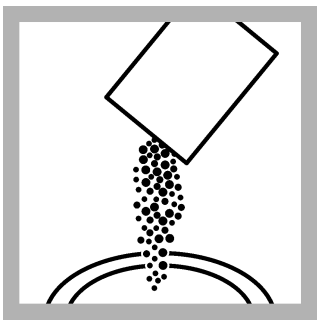


6. Put the stopper on the sample cell. Invert the sample cell to mix the reagent for 15 seconds.

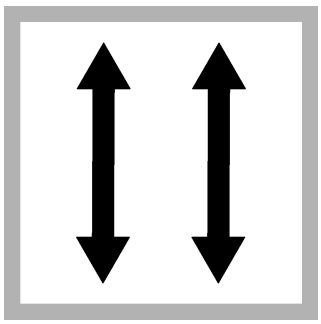
7. Start the instrument timer. A 1-minute reaction time starts. Adjust the reaction time for the sample temperature. Refer to Color development time on page 5. If the sample pH is more than 9.5, increase the reaction time to 2 minutes. If the sample becomes cloudy by the end of the reaction period, pretreat the sample and start over. Refer to Interferences on page 4.



8. Prepare the blank: Fill a second sample cell with 10 mL of sample.

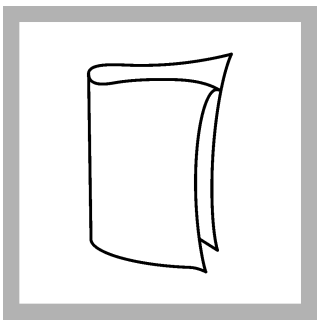


9. After the timer expires, add the contents of one Monochlor F Reagent Powder Pillow to each sample cell.

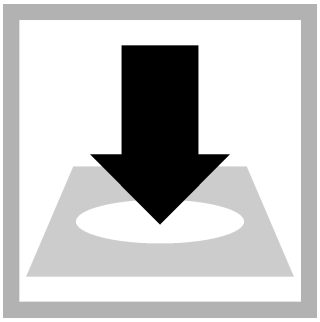


10. Close the sample cells. Shake the sample cells for approximately **20 seconds** to dissolve the reagent. A green color will show if monochloramine or free ammonia is in the sample.

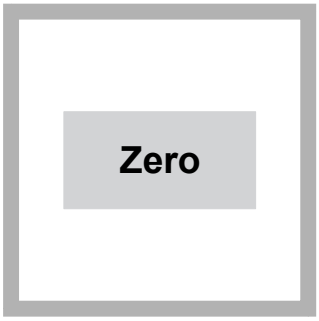
11. Start the instrument timer. A 5-minute reaction time starts. Adjust the reaction time for the sample temperature. Refer to Color development time on page 5.



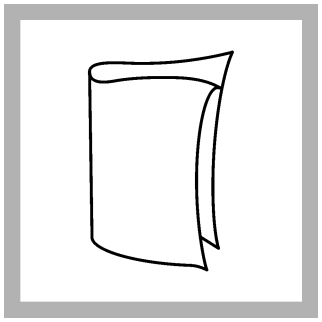
12. When the timer expires, clean the blank sample cell. Make sure that there are no air bubbles in the sample cell after the reaction. If there are bubbles, invert the sample cell to remove the bubbles.



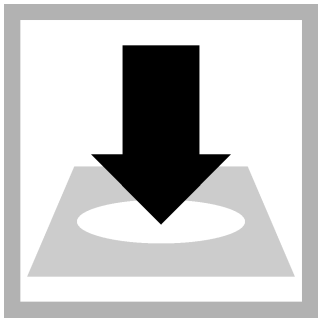
13. Insert the blank into the cell holder.



14. Push **ZERO**. The display shows 0.00 mg/L NH_3–N f.



15. Clean the prepared sample cell.
Make sure that there are no air bubbles in the sample cell after the reaction. If there are bubbles, invert the sample cell to remove the bubbles.



16. Insert the prepared sample into the cell holder.

17. Push **READ**. Results show in mg/L NH_3–N f.

Interferences

This method is intended for finished, chloraminated drinking water samples that have a measurable combined (total) chlorine disinfectant residual. Samples that do not have a disinfectant residual and samples that have a chlorine demand can cause low ammonia test results. Blanks and ammonia standards that are analyzed without a disinfectant residual must be prepared with high quality, reagent grade water.

The substances that are shown in Table 2 do not interfere in the free ammonia determination at or below the given concentration.

Table 2 Non-interfering substances

Substance	Maximum level tested
Al	0.2 mg/L
Cl^-	1200 mg/L
Cu	1 mg/L
Fe	0.3 mg/L
Mn	0.05 mg/L
NO_3^-–N	10 mg/L
NO_2^-–N	1 mg/L
PO_4^{3-}	70 mg/L
SiO_2	100 mg/L

Table 2 Non-interfering substances (continued)

Substance	Maximum level tested
SO_4^{2-}	1600 mg/L
Zn	5 mg/L

Samples that contain high levels of both total hardness and alkalinity may become cloudy after the addition of the Free Ammonia Chlorinating Solution. If this occurs by the end of the first reaction period, the sample for Free Ammonia measurement must be pretreated as follows:

1. Measure 10 mL of sample into the sample cell for Free Ammonia.
2. Add the contents of one Hardness Treatment Reagent Powder Pillow to the sample.
3. Tighten the cap on the sample cell and invert until the reagent is dissolved.
4. Remove the cap.
5. Use the pretreated sample in the test procedure for the Free Ammonia sample.

For samples with a pH less than 8, monochloramine may not form after Free Ammonia Chlorinating Solution is added. If this occurs, add one drop of 1 N Sodium Hydroxide Standard Solution to the sample before Free Ammonia Chlorinating Solution is added. The addition of Sodium Hydroxide Standard Solution increases the pH to appropriate levels to form monochloramine.

Note: *The blank does not need pretreatment.*

Color development time

Test results are strongly influenced by the sample temperature. The reaction times in the procedure are for samples at 18–20 ºC (64–68 ºF). Adjust the reaction times for the sample temperature as shown in Table 3. The color is stable for a maximum of 15 minutes after the specified development time.

If the sample temperature is less than 10 °C (50 °F), especially if the sample is measured outdoors in cold weather, measure the prepared sample again 5 to 10 minutes after the development time given in Table 3. Measure the prepared sample again to make sure that the reaction has completed. The colorimetric reaction has completed if the results do not increase by more than 10% within 10 minutes of the development time.

Table 3 Color development time

Sample temperature (°C)	Sample temperature (°F)	Development time (minutes)
5	41	10
7	45	9
9	47	8
10	50	8
12	54	7
14	57	7
16	61	6
18	64	5
20	68	5
23	73	2.5
25	77	2
> 25	> 77	2

Accuracy check

Standard additions method (sample spike)

Use the standard additions method (for applicable instruments) to validate the test procedure, reagents and instrument and to find if there is an interference in the sample.

Items to collect:

- Ammonium Nitrogen Standard Solution, 10-mg/L NH_3–N
- 50-mL mixing cylinders (3)
- Pipet, TenSette®, 0.1–1.0 mL and tips

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.3 mL, 0.6 mL and 1.0 mL of the standard solution, respectively, to three 50-mL portions of fresh sample. Mix well.
6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

Items to collect:

- Ammonium Nitrogen Standard Solution, 10-mg/L NH_3–N
- 100-mL volumetric flask, Class A
- 2-mL volumetric pipet, Class A and pipet filler
- Deionized water—must be free of ammonia, chlorine and chlorine demand, for example 18 MΩ-cm water from a deionizer system with carbon filtration.

1. Prepare a 0.20-mg/L ammonia nitrogen standard solution as follows:
   a. Use a pipet to add 2.00 mL of 10-mg/L ammonia nitrogen standard solution into the volumetric flask. *(Alternate preparation: add 0.4 mL of a 50-mg/L ammonia nitrogen standard solution to the volumetric flask.)*
   b. Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
2. Use the test procedure to measure the concentration of the prepared standard solution.
3. Compare the expected result to the actual result.

   Note: *The factory calibration can be adjusted slightly with the standard calibration adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are small variations in the reagents or instruments.*

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
389	0.20 mg/L NH_3–N	0.19–0.21 mg/L NH_3–N	0.01 mg/L NH_3–N

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 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. The measurement wavelength is 655 nm or 610 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Free Ammonia Reagent Set, includes:	—	50/pkg	2879200
Free Ammonia Chlorinating Solution	1 drop	4 mL SCDB	2877436
Monochlor F Reagent Pillows	2	100/pkg	2802299

Recommended standards

Description	Unit	Item no.
Nitrogen, Ammonia Standard Solution, 10-mg/L NH_3-N	500 mL	15349
Nitrogen Ammonia Standard Solution, 10-mL Voluette® Ampule, 50-mg/L NH_3–N	16/pkg	1479110

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
Flask, volumetric, Class A, 100 mL, glass	each	1457442
Hardness Treatment Reagent Pillows	50/pkg	2882346
Sodium Hydroxide Standard Solution, 1.00 N	100 mL MDB	104532
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet, volumetric, Class A, 2 mL	each	1451536
Pipet filler, safety bulb	each	1465100
Water, organic-free	500 mL	2641549

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