Nitrogen, Ammonia

DOC316.53.01234

USEPA[1] Known Addition ISE Method[2] **Method 10002**

≥0.8 mg/L NH_3-N **ISE Electrode**

Scope and Application: For wastewater

[1] USEPA Accepted for reporting wastewater analyses

[2] Adapted from *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, Method 4500NH3E (with distillation). Manual distillation is not required if comparability data on representative samples in company files show the distillation is not necessary. Manual distillation will be required to resolve any controversies.

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 458 Instrument-specific information

Meter	Electrode
*sens**ion***™ 4 meters	5192700

Before starting the test:

Refer to the meter manual for meter operation. Refer to electrode manual for electrode maintenance and care.
Prepare the electrode:
New electrodes or electrodes stored more than 7 days
Electrodes stored 1 to 7 days
Refer to the Distillation Apparatus manual to perform sample distillation, if necessary.
Prepare spiking solutions according to the Nitrogen and Ammonia in the Wastewater section.
When there is a linear relationship between concentration and response, the known addition method can be used to measure occasional samples because calibration is not required. The sample concentration must be known within a factor of three, in order to get accurate measurements, because the concentration of ammonia in the sample must be approximately doubled by the standard addition.

Collect the following items:

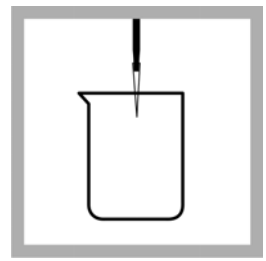
Description	Quantity
Ammonia electrode filling solution	varies
Ammonia electrode storage solution	20 mL
Ammonia nitrogen standard, 1000 mg/L NH_3–N	varies
Ammonia ISA solution	2 mL per 100 mL sample
Ammonia electrode, combination BNC	1
Wash bottle	1
TenSette® pipet, 1.0–10.0 mL	1
*sens**ion*** 4 laboratory pH/ISE meter	1
Stir bar, 22.2 x 4.76 mm (7/16 x 3/16 in.)	1
Select on based on available voltage:	
Stirrer, electromagnetic, 115 V, with stand and stir bar	1
Stirrer, electromagnetic, 230 V, with stand and stir bar	1

See *Consumables and replacement items* for reorder information.

Nitrogen, Ammonia known addition method

1. Accurately transfer 100 mL of sample to a 150-mL beaker using a volumetric pipet or graduated cylinder. Add a stir bar to the beaker.

2. Stir at a constant and moderate rate on a magnetic stirrer to improve response time and accuracy.



3. Use a TenSette Pipet to add 1.0 mL of 10 N NaOH solution into the sample.

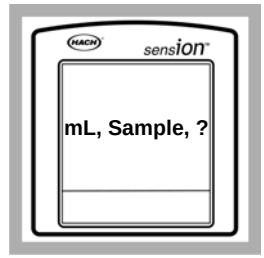
4. Remove the electrode from the storage solution. Rinse it with deionized water and blot dry. Put the electrode in the sample.

Make sure that no air bubbles are trapped under the tip of the electrode. Remove bubbles by lightly tapping the electrode or by tilting the electrode to 20°.

Nitrogen, Ammonia known addition method (continued)

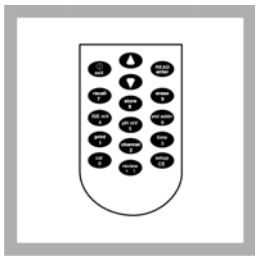
5. Turn the meter on. Press **STD ADDN**. Use the **ARROW** keys to select the required units. Accept the units.

6. The display will show the slope value for the last calibration (the default is –59.2 mV). Accept the numerical value or change the slope value.



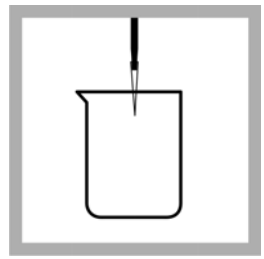
7. The meter will prompt for the sample volume (in mL). Enter the sample volume and press **ENTER** to accept the volume.

8. The display will show **Stabilizing...** until the baseline reading is stable. The meter will then prompt for the standard volume.

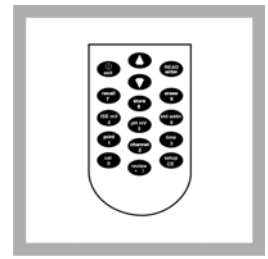


9. Enter the volume of standard to be used (for example, 1.0 mL). Press **ENTER** and accept the volume.

10. Obtain the standard concentration and volume from Table 4 on page 48 after estimating the sample concentration.



11. Add the volume of a known standard (listed in Table 4) to the beaker and proceed as quickly as possible through the rest of the procedure.



12. Enter the concentration of the standard used (for example, 1000 mg/L).

Press **ENTER** and accept the concentration.

Nitrogen, Ammonia known addition method (continued)

13. The display will show **Sample+Standard** and **Stabilizing...** until the reading is stable.

14. The meter will calculate and display the concentration of the adjusted value for the original sample in mg/L. Record or store this value.

The display will show **STANDARD ADDITONS** when data is recalled for standard additions.

Nitrogen ammonia in wastewater

Known addition is also a convenient check on the results of direct measurement. Because an accurate measurement requires that the concentration approximately double as a result of the addition, the approximate sample concentration must be known within a factor of three. Make a spiking solution before beginning the procedure.

1. Use the *Spiking solutions* table to determine how to dilute a 1000 mg/L NH_3-N stock solution to use as a spiking solution.
2. Pipet the appropriate amount of 1000-mg/L NH_3-N standard into a 100-mL volumetric flask.
3. Dilute to the mark with ammonia-free water.
4. Determine the slope before performing standard additions of the sample.
   a. Use the 100 mg/L and 1000-mg/L NH_3-N stock solutions to determine the slope.
   b. Check the electrode occasionally to determine if it is functioning properly and to determine its exact slope value. The frequency of this operation depends on the harshness of the sample.

Table 459 Spiking solutions

Expected Sample Concentration (mg/L)	mL of 1000-mg/L NH_3-N	Standard Concentration
0.8–4.0	2	20 mg/L
2.5–7.5	5	50 mg/L
5–15	10	100 mg/L
12–50	25	250 mg/L
25–75	50	500 mg/L
50–150	100	1000 mg/L

Electrode preparation

New electrodes or electrodes stored more than 7 days

Before using a new Ammonia Electrode or an electrode that has been stored dry, remove the protective cap from the end.

1. Unscrew the top cap. Carefully remove the internal glass electrode from the outer body. A white membrane is mounted at the tip of the outer body.
2. Fill the outer body with 3.5 mL of Internal Fill Solution.
3. Rinse the internal glass electrode with deionoized water. Blot dry. Return the electrode to the filled outer body. Make sure that the key pin at the top of the internal glass electrode is seated in the slot at the top of the outer body.
4. Reinstall the threaded top cap onto the top of the ammonia electrode body. Finger-tighten the cap until snug. **Do not over-tighten.**
5. Hold the fully assembled electrode securely by one end and shake with an abrupt downward motion (like shaking the mercury down in a thermometer) to remove bubbles.
6. Place the assembled electrode into the Ammonia Electrode Storage Solution or 1000 mg/L Ammonia Standard for at least 60 minutes.

Electrodes stored 1 to 7 days

- Keep the electrode in 1000 mg/L ammonia standard without Ionic Strength Adjustor (ISA).
- Alternatively, keep the electrode in the Ammonia Electrode Storage Solution.
- Never let the membrane dry out. Cover the storage beaker and electrode body with Parafilm® to prevent solution evaporation.

Electrodes stored between samples

Place the electrode in Ammonia Electrode Storage Solution for at least one minute. This reinitializes the electrode for the next measurement.

Interferences

Distillation prior to ammonia analysis removes all inorganic interferences that complex ammonia.

Table 460 Interfering substances

Interfering substance	Interference level
Amines	Volatile low molecular weight gives a positive interference
Mercury	Complexes with ammonia
Silver	Complexes with ammonia

Sample collection, preservation and storage

- Collect samples in glass or plastic containers of convenient size. Clean new bottles by washing with deionized or distilled water. Fill the sample bottle completely and stopper immediately. Analyze the sample as soon as possible.
- Ammonia may be lost more quickly from samples at temperatures above 50 °C, so it is important to collect samples at less than 40 °C or use a cooling coil between the bottle and sampling point if necessary.
- If chlorine is present, treat the sample immediately with sodium thiosulfate. Add one drop of 0.1 N Sodium Thiosulfate Standard Solution for each 0.3 mg of chlorine present in a one liter sample.

- If prompt analysis is not possible, preserve the sample with 0.8 mL of concentrated sulfuric acid per liter. Use a sension pH meter to be sure the pH of the preserved sample is between 1.5 and 2. Some wastewater samples may require more sulfuric acid to achieve this pH. Store the sample at 4 °C. Samples preserved in this manner may be stored up to 28 days.
- Before analysis, neutralize the sample to pH 7 with 5 N sodium hydroxide. Do not let the pH go above 10. Correct the test results for the volume addition.
- Do not use mercuric chloride as a preservative because ammonia complexes with mercuric ions.

Accuracy check

Standard additions method (sample spike)
To verify measurement accuracy, perform a standard addition spike on the sample. The spike should roughly double the measured concentration without significantly diluting the sample.

To perform a standard addition sample:

1. Use the *Spike volumes for known additions* table to determine the concentration and volume of standard to spike the sample. The volume of sample transferred must be accurate.
2. Add the amount and concentration specified in the *Spike volumes for known additions* table to the sample while performing the standard addition method on the sample. Do not allow the sample to stand too long before spiking or ammonia will be lost to the atmosphere. T
3. After adding the standard, proceed with the calculations. Results from 90–110% recovery are typically considered acceptable. Calculate percent recovery as follows:

$$\% \text{ Recovery} = \frac{100(X_s - X_u)}{K}$$

Where:

X_s = measured value for spiked sample in mg/L

X_u = measured value for unspiked sample adjusted for dilution by the spike, in mg/L

K = known value of the spike in the sample in mg/L

Calculations

1. $X_u = \frac{X_i \times V_u}{V_u + V}$

Where:

X_i = measured value of unspiked sample in mg/L

V_u = volume of separate unspiked portion in mL

V = volume of spike in mL

2. $K = \frac{C \times V}{V_u + V}$

Where:

C = concentration of standard used in spike in mg/L

V = volume of spike in mL

V_u = volume of separate portion before spike in mL

3. Final calculation plugging in X_u and K: $\% \text{ Recovery} = \frac{100(X_s - X_u)}{K}$

Example:

A sample was analyzed and read 5.0 mg/L NH_3–N. As directed in the *Spike volumes for known additions* table, a 4.0-mL spike of 100-mg/L NH_3–N standard was added to another 100-mL sample, giving a final standard addition result of 8.75 mg/L.

Calculate the percent recovery as follows:

1. $X_u = \frac{5.0\ mg/L \times 100\ mL}{100\ mL + 4\ mL} = 4.81\ mg/L$

2. $K = \frac{100\ mg/L \times 4\ mL}{100\ mL + 4\ mL} = 3.85\ mg/L$

3. $\%R = \frac{100 \times (X_s - X_u)}{K} = \frac{100 \times (8.75 - 4.81)}{3.85} = 102.3\ \%\ Recovery$

Table 461 Spike volumes for known additions

Measured Sample Concentration (mg/L)	Measured Sample Volume (mL)	Standard Concentration (mg/L)	Standard Volume (mL)
0.8–1.0	100	100	1.0
1–3	100	100	2.0
3–6	100	100	4.0
6–9	100	100	8.0
9–12	100	100	10.0
12–20	100	1000	2.0
20–40	100	1000	4.0
40–60	100	1000	6.0
60–75	100	1000	8.0

Method performance

Instrument	Standard	Precision 95% Confidence Limits of Distribution
*sens**ion*** 4	5.00 mg/L	4.81–5.19 mg/L
*sens**ion*** 2		4.81–5.19 mg/L

Summary of method

The ammonia electrode measures ammonia gas or ammonium ions in aqueous solutions that have been converted to gas by the addition of a strong base. The electrode is a complete electrochemical cell consisting of a glass pH electrode and a reference electrode.

The gas-permeable membrane separates the sample from a thin layer of electrolyte that is pressed between the pH bulb and the membrane. At high pH, ammonium ion is converted to ammonia gas.

The gas diffuses through the membrane and causes a pH change in the thin layer of electrolyte. The potential across the pH glass changes as a result of the pH change and the electrode measures the change in potential. The measured pH change is proportional to the ammonia concentration in the solution.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Ammonia Electrode Filling Solution	3 mL	50 mL	4447226
Ammonia Electrode Storage Solution	5 mL	500 mL	2541249
Ammonia Nitrogen Standard, 1000 mg/L NH_3-N	varies	1 L	2354153
Sodium Hydroxide Solution, 10 N	10 mL	500 mL	2545049
Water, deionized	100 mL	4 L	27256

Required apparatus

Description	Quantity/Test	Unit	Catalog number
Ammonia Electrode	1	each	5192700
Beaker, 150 mL, polypropylene	1	each	108044
Bottle, wash, 500 mL	1	each	62011
Cylinder, graduated, 100-mL	1	each	50842
*sens**ion*** 4 Laboratory pH/ISE Meter	1	each	5177500
Stir Bar, 22.2 x 4.76 mm	1	each	4531500
TenSette® Pipet, 1.0–10.0 mL	1	each	1970010
Pipet tips for 1970010 TenSette Pipet	varies	50/pkg	2199796
Select one based on available voltage:			
Stirrer, electromagnetic 115 V, with stand and stir bar	1	each	4530001
Stirrer, electromagnetic 230 V, with stand and stir bar	1	each	4530002

Optional reagents

Description	Unit	Catalog number
pH Paper, pH 9.0-12.0	5 rolls/pkg	38533
Sulfuric Acid, concentrated	500 mL	97949
5.0 N NaOH	1000 mL	245053

Optional apparatus

Description	Unit	Catalog number
Ammonia Electrode Membrane Modules	4/pkg	5192711
Electrode Washer	each	2704700
Pipet, Volumetric, Class A, 1.00 mL	each	1451535
Pipet, Volumetric, Class A, 10.00 mL	each	1451538
Pipet, Volumetric, Class A, 100.0 mL	each	1451542
Pipet tips for 1970001 TenSette Pipet	50/pkg	2185696

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