# Nitrogen, Ammonia

DOC316.53.01234

## Known Addition ISE Method[1]

## Minimum of 0.8 mg/L $NH_3$–N

**Method 10002**

**Ammonia ISE**

**Scope and application:** For wastewater[2].

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

[2] This procedure can be used for *Standard Methods for the Examination of Water and Wastewater* 4500-NH3 E for USEPA NPDES reporting.

## Test preparation

### Instrument-specific table

This procedure is applicable to the meters and probes that are shown in Table 1. Procedures for other meters and probes can be different.

**Table 1 Instrument-specific information**

| Meter | Probe |
|---|---|
| sens***ion*** 4 | sens***ion*** combination ammonia ISE (5192700) |

### Before starting

| |
|---|
| Refer to the meter documentation for meter settings and operation. Refer to probe documentation for probe preparation, maintenance and storage information. |
| Prepare the probe before initial use. Refer to probe documentation. |
| Calibration is not necessary for this method. Use this method when there is a linear relationship between concentration and response. |
| It is necessary to know the sample concentration within a factor of three. |
| As an alternative, use this method to verify the results of a direct measurement. |
| Condition the probe before use. To condition the probe, put the probe in 100 mL of the lowest concentration standard solution for a maximum of 1 hour. |
| Stir the standards and samples at a slow and constant rate to prevent the formation of a vortex. |
| Air bubbles under the sensor tip can cause slow response or measurement errors. To remove the bubbles, carefully shake the probe. |
| Small differences in concentration between samples can increase the stabilization time. Make sure to condition the probe correctly. Try different stir rates to see if the stabilization time decreases. |
| 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 |
|---|---|
| Nitrogen Ammonia Standard Solution, 1000 mg/L as $NH_3$–N | varies |
| Sodium Hydroxide Solution, 10 N | 1.0 mL |
| Beaker, polypropylene, 150 mL | 3 or 4 (USEPA) |

## Items to collect (continued)

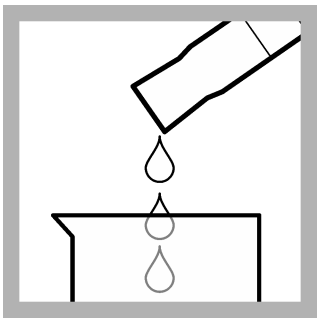
| Description | Quantity |
|---|---|
| Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.) | 3 or 4 (USEPA) |
| Stirrer, magnetic | 1 |
| TenSette pipet, 1.0–10.0 mL and pipet tips | 1 |
| Wash bottle with deionized water | 1 |
| Lint-free cloth | 1 |

Refer to Consumables and replacement items on page 5 for order information.

## Sample collection

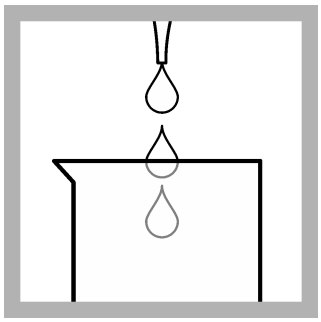
- Collect samples in clean glass or plastic bottles with tight-fitting caps. Completely fill the bottle and immediately tighten the cap.
- Collect samples at less than 40 °C (104 °F). Ammonia is quickly released from samples at more than 50 °C (122 °F). Use a cooling coil between the bottle and the sampling point if necessary.
- If chlorine is in the sample, immediately add 1 drop of 0.1 N Sodium Thiosulfate Standard Solution for each 0.3 mg of chlorine in a 1-liter sample.
- Analyze the samples as soon as possible for best results.
- If prompt analysis is not possible, adjust the sample pH to between 2 and 1.5 with concentrated sulfuric acid.
- Keep the preserved samples at or below 6 °C (43 °F) for a maximum of 28 days.
- Do not use mercuric chloride as a preservative because ammonia forms a complex with mercuric ions.
- Do not let the sample pH go to more than 10 before the test. At high pH, ammonia solutions release ammonia into the atmosphere.
- Correct the test result for the dilution caused by the volume additions.

## Test procedure

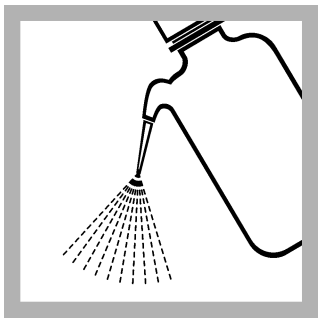


**1.** Add 100 mL of sample to a 150-mL beaker.

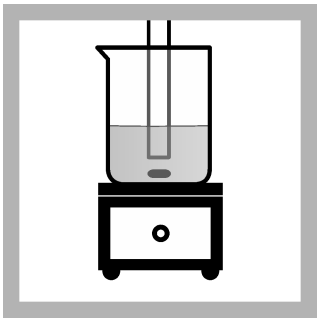
**2.** Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



**3.** Use a pipet to add 1.0 mL of 10 N Sodium Hydroxide Solution to the sample.



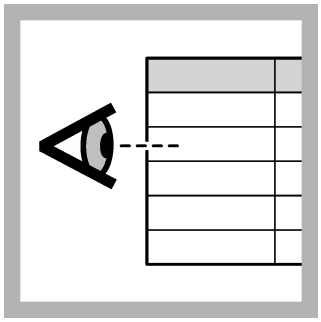
**4.** Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



**5.** Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.

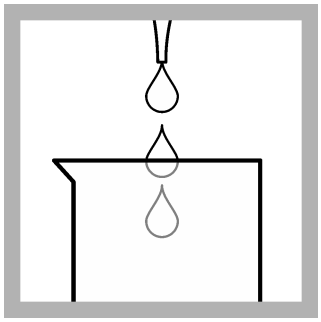

**6.** Push **std addn**. Use the arrow keys to select the units.
The slope for the last calibration shows on the display (default: 59.2 mV). Change the slope value if necessary.


**7.** Enter the sample volume (mL), then push **enter**.



**8.** Refer to Table 2 on page 3 to identify the volume of standard solution to add.

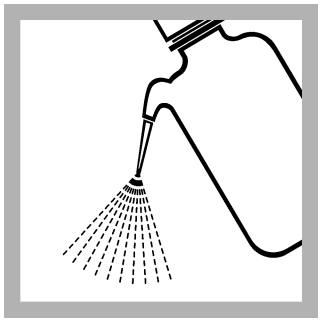

**9.** Enter the volume of standard solution (mL), then push **enter**.



**10.** Add the standard solution to the beaker. Complete the remaining steps within 5 minutes.


**11.** Enter the concentration of the standard solution, then push **enter**.
The display shows the adjusted value for the original sample (mg/L).

The display shows "STANDARD ADDITIONS" when data is shown again for standard additions.



**12.** Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

## Standard volumes

Select a range in Table 2, then read across the row to find the volume of 1000-mg/L Nitrogen Ammonia Standard Solution ($NH_3$–N) to add to the prepared sample.

**Table 2 Standard volumes**

| Expected sample concentration | Standard volume to add | Increase in sample concentration after addition |
|---|---|---|
| 0.8 to 4.0 mg/L | 2 mL | 20 mg/L |
| 2.5 to 7.5 mg/L | 5 mL | 50 mg/L |
| 5 to 15 mg/L | 10 mL | 100 mg/L |
| 12 to 50 mg/L | 25 mL | 250 mg/L |
| 25 to 75 mg/L | 50 mL | 500 mg/L |
| 50 to 150 mg/L | 100 mL | 1000 mg/L |

## Interferences

Distillation before ammonia analysis removes all inorganic interferences that form a complex with ammonia.

| Interfering substance | Interference level |
|---|---|
| Amines | Volatile low molecular weight gives a positive interference. |
| Mercury | Forms a metal complex with ammonia. |
| Silver | Forms a metal complex with ammonia. |

## Accuracy check

### Slope method

Use the slope method to validate the electrode response.

1. Prepare two standard solutions that are one decade apart in concentration (e.g., 1 mg/L and 10 mg/L or 10 mg/L and 100 mg/L). The minimum concentration is 0.2 mg/L.
2. Use the test procedure to measure the mV value of each standard solution.
3. Compare the mV value of each standard solution. The expected difference is 58 (± 3) mV at 25 °C (77 °F).

### Standard solution method

Use the standard solution method to validate the test procedure, the reagents (if applicable) and the instrument.

Items to collect:

- Standard solution within the test range

1. Use the test procedure to measure the concentration of the standard solution.
2. Compare the expected result to the actual result.

## Clean the probe

Clean the probe when:

- Drifting/inaccurate readings occur as a result of contamination on the sensing element or incorrect storage conditions.
- Slow response time occurs as a result of contamination on the sensing element.
- The slope is out of range as a result of contamination on the sensing element.

For general contamination, complete the steps that follow.

1. Rinse the probe with deionized water. Blot dry with a lint-free cloth. Do not touch the tip of the probe.
2. If harsh contaminants are attached to the probe, polish the probe tip with a soft cloth or cotton swab to remove the contaminants.
3. Soak the probe for 30 seconds in 25 mL of Ammonia Probe Storage Solution.

## Method performance

The accuracy of the measurements is dependent on many factors that are related with the overall system, which includes the meter, the probe and calibration solutions. Refer to the meter or probe documentation for more information.

## Summary of method

The ammonia electrode measures ammonia gas or ammonium ions in solutions. When a strong base is added, ammonium ions in solutions become 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

### Probe

| Description | Unit | Item no. |
|---|---|---|
| sens***ion***™ combination ammonia probe | each | 5192700 |

### Recommended reagents and standards

| Description | Unit | Item no. |
|---|---|---|
| Nitrogen Ammonia Standard Solution, 1000-mg/L as $NH_3$–N | 1 L | 2354153 |
| Sodium Hydroxide Solution, 5 N | 50 mL | 245026 |
| Sodium Hydroxide Standard Solution, 10 N | 500 mL | 2545049 |
| Sodium Thiosulfate Standard Solution, 0.1 N | 100 mL | 32332 |
| Sulfuric Acid, ACS | 500 mL | 97949 |

### Accessories

| Description | Unit | Item no. |
|---|---|---|
| Beaker, 150 mL, polypropylene | each | 108044 |
| Bottle, wash, 500 mL | each | 62011 |
| Flask, volumetric, Class A, 100-mL | each | 1457442 |
| Graduated cylinder, 100 mL | each | 50842 |
| Pipet, TenSette®, 0.1–1.0 mL | each | 1970001 |
| Pipet tips for TenSette® Pipet, 0.1–1.0 mL | 50/pkg | 2185696 |
| Probe clips, color-coded, for IntelliCAL probes | 50/pkg | 5818400 |
| Probe holder, 3 probes, for sensION+ benchtop meters | each | LZW9321.99 |
| Probe stand, universal | each | 8508850 |
| Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.) | each | 4531500 |
| Stirrer, electromagnetic, 120 VAC, with electrode stand | each | 4530001 |
| Stirrer, electromagnetic, 230 VAC, with electrode stand | each | 4530002 |

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