

Direct ISE Method¹

Method 10001
0.1 to 10.0 mg/L NH₃-N
Ammonia ISE
Scope and application: For wastewater².

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 information

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
HQ4100 and HQ30d portable one input, multi-parameter HQ4200 and HQ40d portable two input, multi-parameter HQ4300 portable three input, multi-parameter HQ430d benchtop one input, multi-parameter HQ440d benchtop two input, multi-parameter	Intellical ISENH3181 ammonia ISE
Sension+ MM340 lab two input, pH/mV/ISE Sension+ MM374 lab two input, pH/mV/EC/ISE Sension+ MM378 lab two input, pH/ISE/EC/DO	Sension+ 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.

When an Intellical probe is connected to an HQ meter or an HQd meter, the meter automatically identifies the measurement parameter and is prepared for use.

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.

Calibrate the probe before initial use. Refer to [Calibration](#) on page 3.

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.

During calibration, measure the standard solutions from lowest to highest concentration for best results.

Make sure that the calibration solutions and the samples are at the same temperature (± 2 °C (± 3.6 °F)) for best results.

Immediately before the test, adjust the sample pH to more than 11 with 10 N Sodium Hydroxide (or equivalent ISA), then analyze the samples immediately for the best results. At high pH, ammonia solutions release ammonia into the atmosphere.

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.

This procedure is specified for the HQ meters and HQd meters. The Sension+ meters can be used, but the menus and navigation will be different.

Items to collect

Description	Quantity
Ammonia ISA (TISAB)—powder pillow or solution (1 pillow or 0.5 mL for each 25 mL of solution)	1
Ammonia Nitrogen Standard Solution, 100 mg/L as NH ₃ -N	25 mL
Beaker, polypropylene, 50 mL, low form	3 or 4 (USEPA)
Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.)	3 or 4 (USEPA)
Stirrer, magnetic	1
Wash bottle with deionized water	1
Lint-free cloth	1

Refer to [Consumables and replacement items](#) on page 6 for order information.

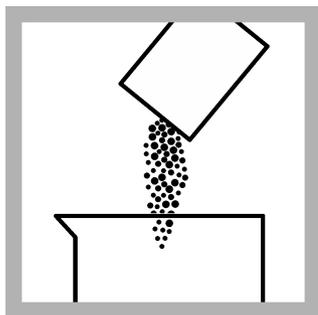
Sample collection

- 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

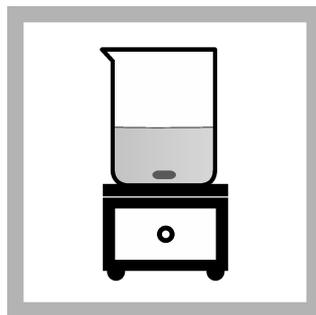


1. Add 25 mL of sample to a beaker.

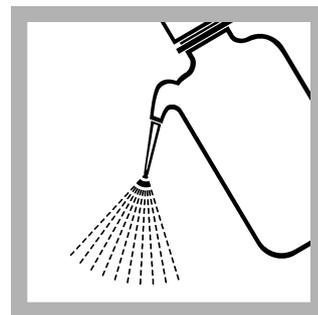


2. Add the contents of one Ammonia ISA Powder Pillow.

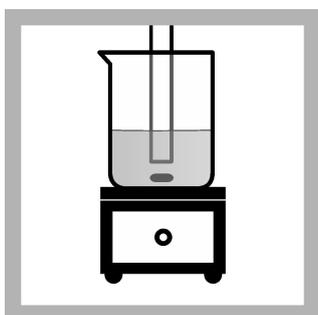
Note: As an alternative, add 0.5 mL of Ammonia ISA Solution.



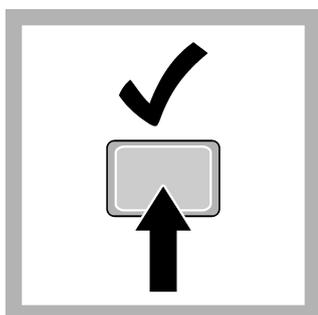
3. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



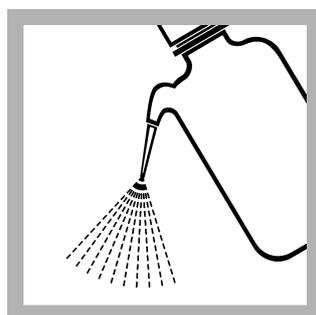
4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



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.

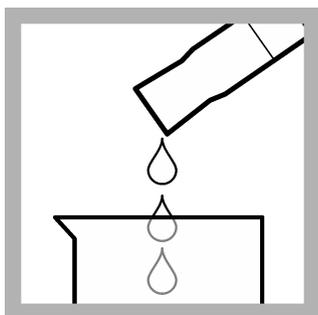


6. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.

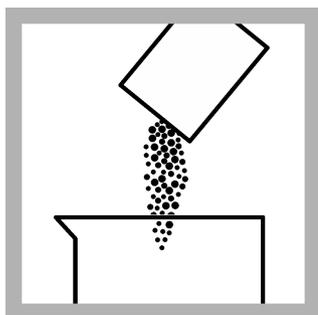


7. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

Calibration

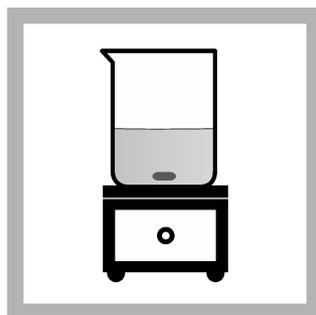


1. Add 25 mL of the lowest concentration standard solution to a beaker.

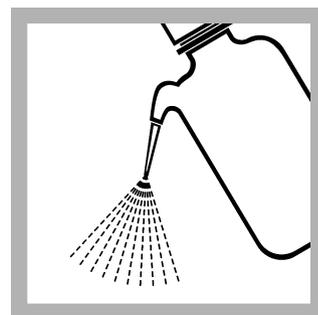


2. Add the contents of one Ammonia ISA Powder Pillow.

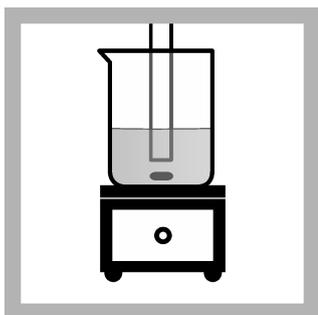
Note: As an alternative, add 0.5 mL of Ammonia ISA Solution.



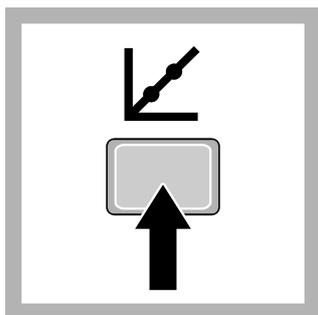
3. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



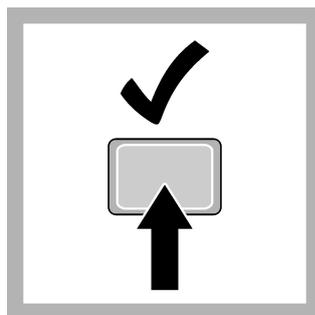
4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



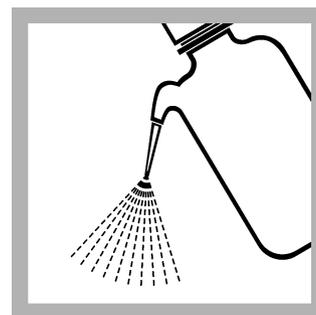
5. Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.



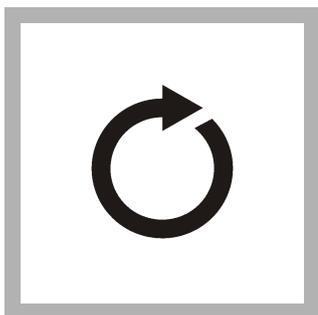
6. Push **Calibrate**. The standard solution value is shown.



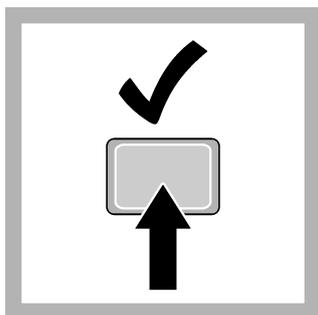
7. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.



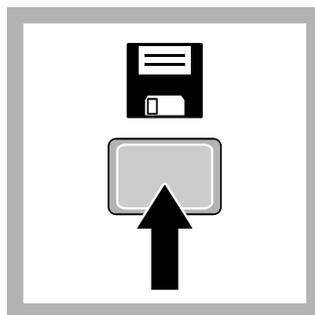
8. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



9. Measure the remaining standard solutions.



10. Push **Done**. A calibration summary is shown when the minimum number of calibration standards are measured.



11. Push **Store** to accept the calibration.

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.

Standard additions method

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

Items to collect:

- Nitrogen Ammonia Standard Solution, 100 mg/L
 - Graduated cylinder, 25 mL, polypropylene
 - TenSette pipet
 - Pipet tips
1. Use a graduated cylinder to measure 25 mL of sample into a beaker.
 2. Use the test procedure to measure the concentration of the sample.
 3. Use the TenSette pipet to add 0.5 mL of the standard solution to the sample.
 4. Measure the concentration of the spiked sample.
 5. Compare the results before and after the standard solution addition. The concentration should increase by 2 mg/L $\text{NH}_3\text{-N}$.

Temperature check

For probes that do not have a temperature sensor, measure the temperature of the standard solutions and samples. Make sure that the calibration solutions and the samples are at the same temperature ($\pm 2\text{ }^\circ\text{C}$ ($\pm 3.6\text{ }^\circ\text{F}$)) for best results.

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 for 30 seconds in 25 mL of Ammonia Probe Storage Solution.

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

HQ meters, HQd meters and probes

Description	Unit	Item no.
HQ4100 portable one input, multi-parameter meter	each	LEV015.53.4100A
HQ4200 portable two input, multi-parameter meter	each	LEV015.53.4200A
HQ4300 portable three input, multi-parameter meter	each	LEV015.53.4300A
HQ430d benchtop one input, multi-parameter meter	each	HQ430D
HQ440d benchtop two input, multi-parameter meter	each	HQ440D
Intellical ISENH3181 digital ammonia ISE probe, 1 m cable	each	ISENH318101
Intellical ISENH3181 digital ammonia ISE probe, 3 m cable	each	ISENH318103

Sension+ meters and probes

Description	Unit	Item no.
Sension+ MM340 lab two input, pH/mV/ISE meter	each	LPV2200.97.0002
Sension+ MM374 lab two input, pH/mV/EC/ISE meter	each	LPV4110.97.0002
Sension+ MM378 lab two input, pH/ISE/EC/DO meter	each	LPV4130.97.0002
Sension+ Ammonia ISE probe	each	5192700

Recommended reagents and standards

Description	Unit	Item no.
Ammonia Ionic Strength Adjustor (ISA) Powder Pillows	100/pkg	4447169
Ammonia Ionic Strength Adjustor (ISA) Solution	500 mL	2824349
Nitrogen Ammonia Standard Solution, 100-mg/L as NH ₃ -N	500 mL	2406549
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, polypropylene, 50 mL, low form	each	108041
Bottle, wash, 500 mL	each	62011
Graduated cylinder, polypropylene, 25 mL	each	108140
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

Accessories (continued)

Description	Unit	Item no.
Stirrer, electromagnetic, 120 VAC, with electrode stand	each	4530001
Stirrer, electromagnetic, 230 VAC, with electrode stand	each	4530002



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