Nitrate

DOC316.53.01239

Direct ISE Method

Method 8359

0.04 to 4.00 mg/L NO_3–N

Nitrate ISE

Scope and application: For drinking water.

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
HQ30d portable single input, multi-parameter HQ40d portable dual input, multi-parameter HQ430d benchtop single input, multi-parameter HQ440d benchtop dual input, multi-parameter	IntelliCAL ISENO3181 nitrate ISE
sensION™+ MM340 lab dual input, pH/mV/ISE sensION™+ MM374 lab dual input, pH/mV/EC/ISE sensION™+ MM378 lab dual input, pH/ISE/EC/DO	sensION+ 9662 nitrate ISE with sensION+ 5044 reference sensION+ 9662C nitrate ISE

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 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 procedure on page 3.
Use Nitrate Nitrogen Standard Solutions of 0.04 mg/L and 1.2 mg/L or 2.0 mg/L to calibrate the probe.
During calibration, measure the standard solutions from lowest to highest concentration for best results.
The result is NO_3–N mg/L (nitrate-nitrogen) shown as elemental nitrogen (N). To change the results to NO_3^- mg/L (nitrate), multiply the results by 4.4.
Make sure that the calibration solutions and the samples are at the same temperature (± 2 °C (± 3.6 °F)) for best results.
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.
A white precipitate forms if chloride or other ions are in the sample. The white precipitate will not cause damage to the probe or interfere with the analysis.
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 HQd meters. The sensION+ meters can be used, but the menus and navigation will be different.

Items to collect

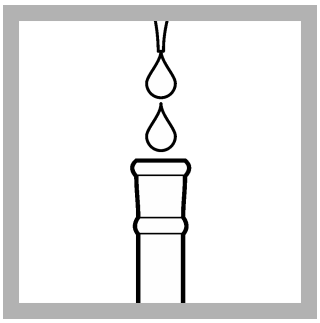
Description	Quantity
Nitrate ISA (TISAB) solution	5 mL
Nitrate Nitrogen Standard Solution, 10 mg/L	varies
Beaker, polypropylene, 150 mL	3 or 4 (USEPA)
Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.)	3 or 4 (USEPA)
Stirrer, magnetic	1
TenSette pipet, 1.0–10.0 mL and pipet tips	1
Wash bottle with deionized water	1
Lint-free cloth	1

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

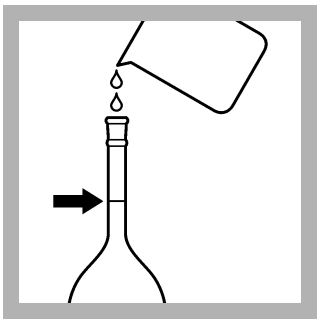
Sample collection

- Collect samples in clean glass or plastic bottles.
- Analyze the samples as soon as possible for best results.
- If immediate analysis is not possible, keep the samples at or below 6 °C (43 °F) for a maximum of 24 hours.
- Do not adjust the sample pH.
- Let the sample temperature increase to room temperature before analysis.

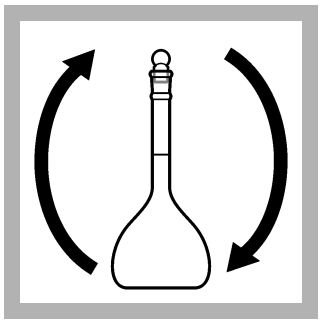
Test procedure



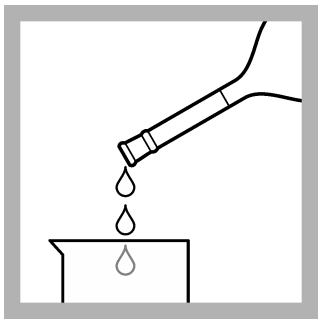
1. Use a pipet to add 5 mL of Nitrate ISA solution into a 100-mL volumetric flask.



2. Add sample to the mark.

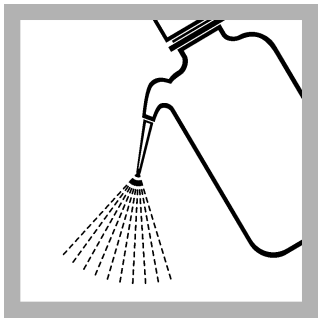


3. Insert the stopper. Invert the flask to mix.

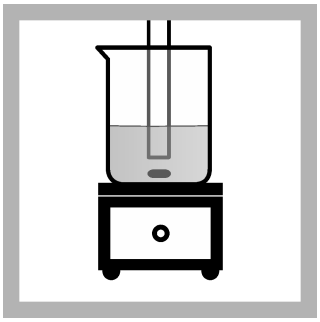


4. Pour the solution into a 150-mL beaker.

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

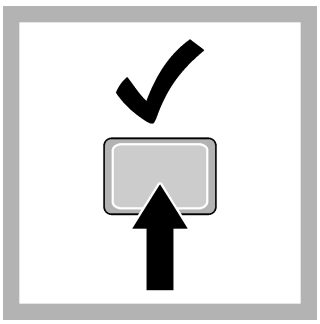


6. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

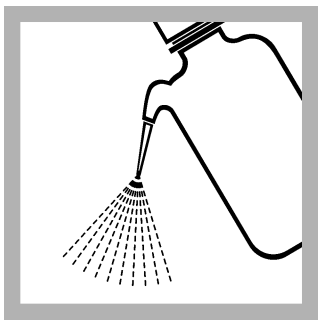


7. Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.

8. Wait 5 to 10 minutes to let the probe adjust.

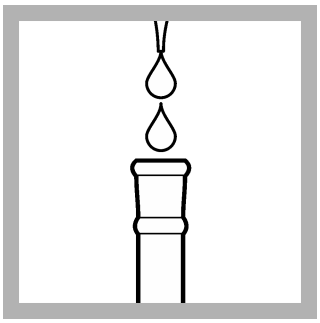


9. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.

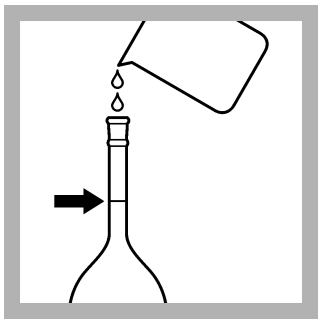


10. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

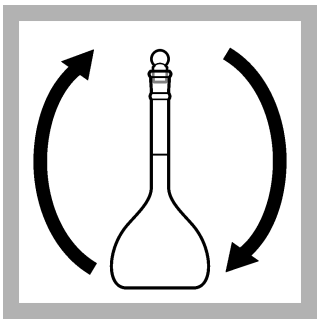
Calibration procedure



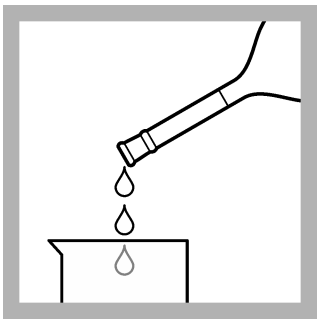
1. Use a pipet to add 5 mL of Nitrate ISA Solution into a plastic 100-mL volumetric flask.



2. Add deionized water that is at room temperature to the mark.

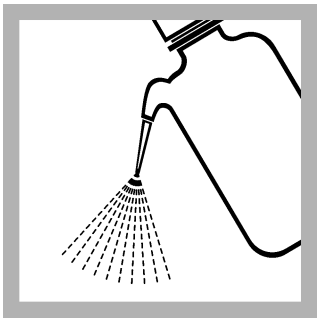


3. Insert the stopper. Invert the flask to mix.

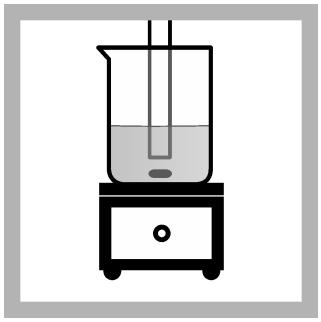


4. Pour the solution into a 150-mL beaker.

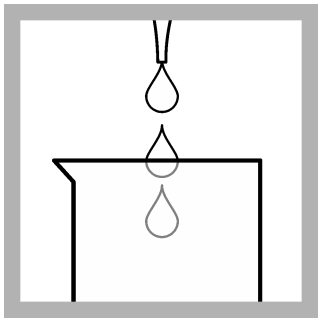
5. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.



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

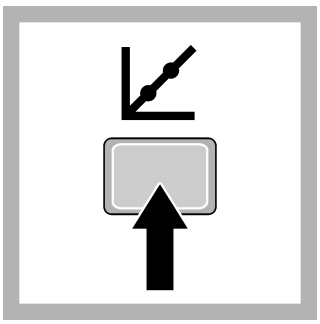


7. Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.

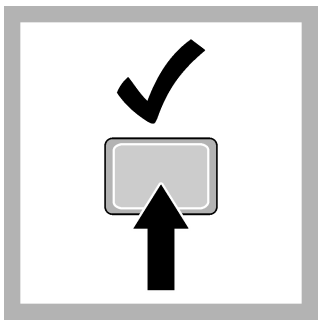


8. Add 0.4 mL of 10-mg/L Nitrate Nitrogen Standard Solution to make a 0.04-mg/L standard solution.

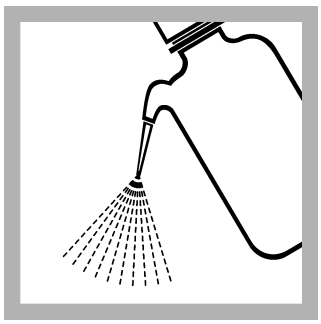
9. Wait 30 minutes to let the probe adjust to the low level of nitrate.



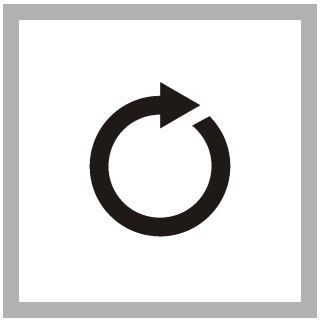
10. Push **Calibrate**. The standard solution value is shown.



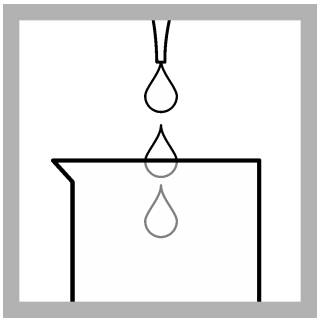
11. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.



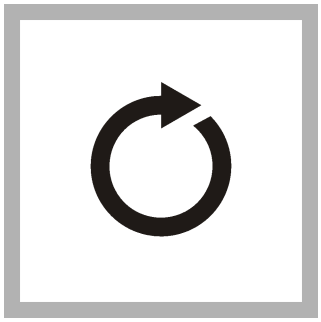
12. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.



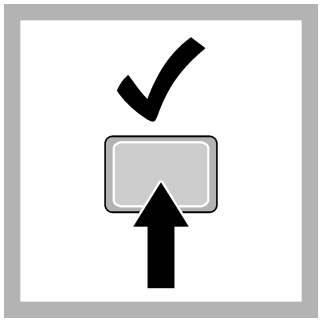
13. Do steps 1–7 again.



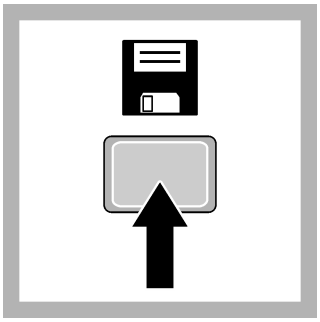
14. Add 1.2 mL or 2.0 mL of 100-mg/L Nitrate Nitrogen Standard Solution to make a 1.2-mg/L or 2.0-mg/L standard solution.



15. Do steps 10–12 again.



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



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

Interferences

The sensing element responds to nitrate as well as other ions. Typically, probe response to another ion increases the potential, and causes a positive error. The response to other ions can be semi-quantitatively determined through the Nikolsky equation, an extended Nernst equation:

$E = E^o + (RT/(zF))\ln(aNa + KNax \times ax)$

Where:

- ax—The activity of the interfering ion
- KNax—The selectivity coefficient for the interfering ion relative to nitrate

For the nitrate ISE, the major interferences are shown in Table 2. To eliminate most of these interferences, add the Nitrate ISA and adjust the pH to between 3 and 5. The measurements are usually made at this pH range to eliminate carbonate and bicarbonate interference and reduce organic acid interference.

The selectivity coefficient is the approximate apparent increase in the measured concentration caused by one unit of the interfering ion (e.g., 1 unit of ClO_4^- raises the nitrate concentration by 0.1). The approximate selectivity coefficients for some ions with the IntelliCAL® Nitrate ISE are shown in Table 2.

Table 2 Interfering substances

Interfering substance	K (selectivity coefficient) value
Perchlorate (ClO_4^-)	1200 (interferes more)
Iodide (I^-)	10
Bromide (Br^-)	0.1
Chloride (Cl^-)	0.006
Nitrite (NO_2^-)	0.001 (interferes less)

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:

- Nitrate Nitrogen Standard Solution, 10 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 0.2 mg/L NO_3–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 (± 2 °C (± 3.6 °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.
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 minutes in 10-mg/L Nitrate Nitrogen Standard Solution. Rinse the probe with deionized water. Dry with a lint-free cloth. Install the sensor protection cap on the probe.

Summary of method

Nitrate ions are selectively absorbed by the ISE membrane. The absorbed nitrate ions cause a potential (voltage) that is proportional to the concentration of nitrate in the sample. The ISE membrane is a solvent-polymer membrane that is a nitrate ion-exchanger in an inert polyvinyl chloride (PVC) plastic matrix. The nitrate electrode has an internal silver/silver chloride element, which results in a fixed-potential when it touches the internal filling solution.

Consumables and replacement items

HQd meters and probes

Description	Unit	Item no.
HQ30d portable single input, multi-parameter meter	each	HQ30D53000000
HQ40d portable dual input, multi-parameter meter	each	HQ40D53000000
HQ430d benchtop single input, multi-parameter meter	each	HQ430D
HQ440d benchtop dual input, multi-parameter meter	each	HQ440D
IntelliCAL™ ISENO3181 nitrate ISE probe, 1 m cable	each	ISENO318101
IntelliCAL™ ISENO3181 nitrate ISE probe, 3 m cable	each	ISENO318103

sensION+ meters and probes

Description	Unit	Item no.
sensION™+ MM340 lab dual input, pH/mV/ISE meter	each	LPV2200.97.0002
sensION™+ MM374 lab dual input, pH/mV/EC/ISE meter	each	LPV4110.97.0002
sensION™+ MM378 lab dual input, pH/ISE/EC/DO meter	each	LPV4130.97.0002
sensION™+ 9662 nitrate ISE probe	each	LZW9662.97.0002
sensION™+ 9662C nitrate ISE probe	each	LZW9662C.97.0002
sensION™+ 5044 reference electrode	each	LZW5044.97.0002

Recommended reagents and standards

Description	Unit	Item no.
Nitrate Ionic Strength Adjustor (ISA) Solution	500 mL	2488349
Nitrate Nitrogen Standard Solution, 1-mg/L NO_3-N	500 mL	204649
Nitrate Nitrogen Standard Solution, 10.0-mg/L NO_3–N	500 mL	30749
Nitrate Nitrogen Standard Solution, 100-mg/L NO_3–N	500 mL	194749

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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