INSTRUCTION MANUAL

HI4013 Half-Cell

HI4113 Combination

Nitrate
Ion Selective Electrodes

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Dear Customer,

Thank you for choosing a Hanna Instruments® product.

Please read this instruction manual carefully before using this instrument as it provides the necessary information for correct use of this instrument, and a precise idea of its versatility.

If you need additional technical information, do not hesitate to e-mail us at tech@hannainst.com.
Visit www.hannainst.com for more information about Hanna Instruments and our products.

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1. PRELIMINARY INTRODUCTION

HI4013 and HI4113 are ion selective electrodes designed for the measurement of nitrate ions in aqueous solutions.
They utilize a replaceable sensing module that contains an organic polymer membrane, sensitive to nitrate ions.

Each HI4113 combination ISE is supplied with:

- HI4113-53 Set of 3 replacement sensing modules
- HI7078S Electrolyte solution 0.5M $(NH_4)_2SO_4$ (4 x 30 mL)
- Pipette
- Quick reference guide
- Quality certificates (electrode & sensing module)

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2. SPECIFICATIONS

Type	PVC membrane with organic ion exchanger
Ion measured	Nitrate (NO_3^-)
Measurement range	0.1 M to 1×10^{-5} M 6200 to 0.62 ppm
Interference	Organic solvents and cationic detergents must be absent. Ratio of interfering ion to NO_3^- must be less than the ratio indicated below: 300 for F^- fluoride 100 for Cl^- chloride 4 for CO_3^{2-} carbonate 2 for NO_2 nitrite 0.01 for I^- iodide 0.0045 for ClO_4^- perchlorate
Operating temperature	0 to 40 °C (32 to 104 °F)
Operating pH	3 to 8 pH (see pH and Interferents section)
Dimensions	12 mm (OD) × 120 mm nominal insertion (0.47" × 4.72")
Connection	BNC

3. THEORY OF OPERATION

The HI4013 and HI4113 nitrate electrodes are potentiometric devices used for the rapid determination of free nitrate ions in water, emulsified foods, and plant samples. The electrode functions as a sensor or ionic conductor.

The HI4013 is a half-cell electrode that requires a separate reference electrode to complete its electrolytic circuit.

The HI4113 is a combination electrode with a Ag/AgCl reference electrode with gel stabilized Cl^- electrolyte in its inner chamber. The external reference chamber is refillable.

The PVC membrane used on the sensor is impregnated with the organic ion exchanger. The ion exchanger is considered a carrier ionophore in that it is capable of shielding and carrying the charged nitrate ion in its polar cage, freely, through the apolar regions of the membrane. A charge imbalance develops between the test solution and internal cell of the sensor. This voltage changes in response to the sample's ion activity. When the ionic strength of the sample is fixed, the voltage is proportional to the concentration of nitrate ions in solution.

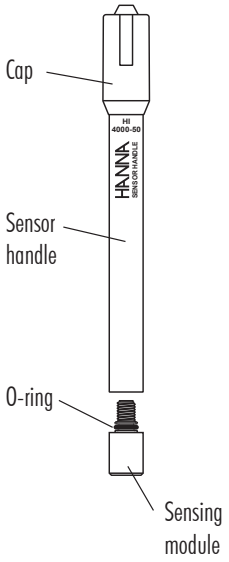
The sensor follows the Nernst Equation:

$$E = E_a + 2.3\ RT/nF \log A_{ion}$$

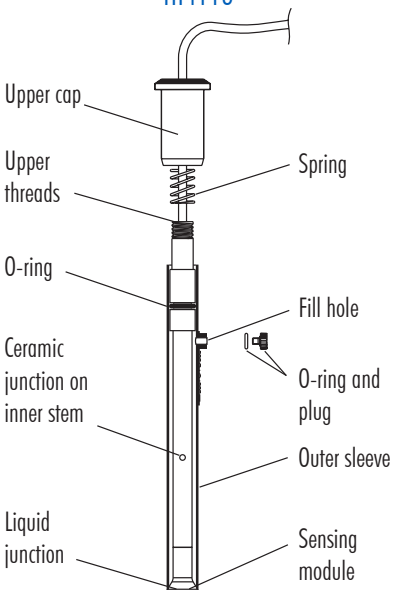
E = observed potential
E_a = reference and fixed internal voltages
R = gas constant (8.314 J/K Mol)
n = charge on ion (−1)
A_{ion} = ion activity in sample
T = absolute temperature in K
F = Faraday constant (9.648×10^4 C/equivalent)

4. DESIGN ELEMENTS

HI4013



HI4113



5. EQUIPMENT REQUIRED

- Suitable ion or pH/mV meter » HI6XXX
  ***Note**: Log/linear graph paper is useful if an ISE (ion) meter is not available.*
- HI5315 reference electrode, teamed with HI4113 combination ISE or HI4013 half cell ISE
- Magnetic stirrer » HI6000180
  ***Note**: Isolate beakers from stirrer motor heat by placing insulating material (foam or cork) between.*
- Electrode holder » HI764060
- Plastic beakers » HI740036P

6. SOLUTIONS REQUIRED

Standards for Nitrate Measurements

0.1 M sodium nitrate standard, 500 mL	HI4013-01
100 ppm nitrate standard (as N), 500 mL	HI4013-02
1000 ppm nitrate standard (as N), 500 mL	HI4013-03

Ionic Strength Adjuster

ISA, 500 mL	HI4013-00
ISISA, 500 mL	HI4013-06

- Use volumetric pipettes and glassware to make dilutions to bracket the concentration of the samples.
- Store samples in plastic bottles.
- Standards with concentrations $< 10^{-3}$ M should be prepared daily.
- Add 2 mL of HI4013-00 (Hanna Instruments ISA) to 100 mL sample or standard.

HI4013-06 ISISA is Interferent Suppressant ISA.

Prepare by following below steps:

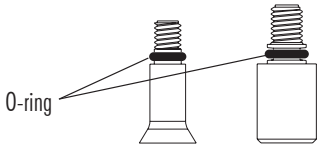
- Dissolve 17.32 g $Al_2(SO_4)_3 18\,H_2O$, 3.43 g Ag_2SO_4, 1.28 g H_3BO_3, 2.52 g H_2NSO_3H in $\approx$ 800 mL DI water.
- Adjust pH to 3 by slowly adding 0.1 N NaOH.
- Dilute to 1 liter.
- Store in a dark-colored container.

For drinking water:

- Add 10 mL of HI4013-06 (Hanna Instruments ISISA) to each 50 mL sample (or standard).

7. GENERAL GUIDELINES

- Ensure the O-ring sits correctly on the module(s) before screwing into the sensor handle or inner stem.



- Due to shipping (storage) the internal solution inside the PVC modules may have developed an air pocket near the membrane.
  To ensure electrical continuity, hold the top of electrode and whip the electrode downward.
- Presoak the nitrate sensor in a 10^{-2} M standard (or HI4013-02 solution) without ISA, for at least half-hour before calibration, to help optimize the sensor response.
- Do not leave sensors in standard or samples with ISA (or ISISA) for long periods of time.
- Calibration standards and sample solutions should have the same ionic strength.
  ISA should be added to both samples and standards.
- Calibration standards and sample solutions should be at the same temperature.
- Calibration standards and sample solutions should be stirred at the same rate using identically-sized, TFE-coated stir bars.
- Thermally insulate solution vessel from magnetic stirrer.
- Rinse electrodes with distilled or deionized water between samples and gently dab dry with lab wipe (or other soft, disposable absorbent toweling). Do not rub the sensing surface.
- Check for gas bubbles that may form near the sensing surface (due to solution temperature changes).
  Tap off gently.
- Avoid large changes in temperature (thermal shocks) as it may damage the sensor.

HI4113 Guidelines

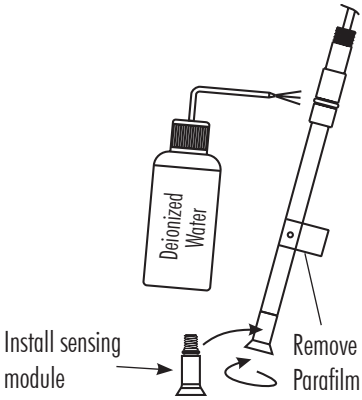
- Remove the protective seal that covers the ceramic junction before assembling the sensor for the first time.
- Empty existing fill solution and refill before using.
- Add HI7078 reference fill solution to bottom of the fill hole.
- Always operate electrode with the fill hole open during measurement.
- During use, fill solution will slowly drain out of the tapered junction at the lower portion of the electrode.
  Excessive loss (>4 cm drop within 24 hours) is not normal.
  If this occurs, verify cap is tightened and the interface between the internal cone and outer body is free of debris.
- Add filling solution daily to maintain good head pressure.
  For optimum response, fill solution level should be maintained and not allowed to drop more than 2-3 cm (1 inch) below fill hole.
- Do not use an electrode if crystallized salts are visible inside the electrode.
  Drain electrode, disassemble, rinse internal body with DI water. Reassemble and refill with fresh fill solution.
- If an erratic measurement occurs, check for trapped foreign matter near the internal cone.
  Depress the electrode cap to drain. Refill with fresh fill solution.

8. ELECTRODE PREPARATION

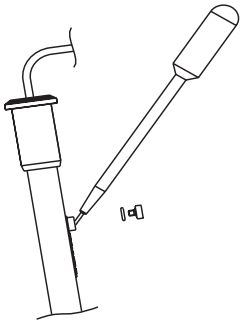
HI4013

1. Remove sensing module from shipping vial.
   Do not touch the sensing membrane with the "H" hole pattern on it!
2. Screw the module into the sensor handle finger tight. Do not overtighten.
3. Hold the electrode at the cable end and whip the sensor downward to ensure fill solution, that may have separated during shipping, is in contact with inner membrane surface.
4. Prepare HI5315 reference electrode by filling electrolyte reservoir with HI7078 fill solution.
5. Place the sensor and reference electrodes into the electrode holder and connect cable connectors to meter.
6. Soak the nitrate-electrode membrane in a 0.001 M nitrate-containing standard (or HI4013-02 solution) without ISA, before calibration.

HI4113



1. Unwrap Parafilm® seal found over ceramic junction, on inner stem, and discard.
   This is only used for shipping (or long term storage).
2. Remove the sensing module from the shipping vial.
   Do not touch the sensing membrane with the "H" hole pattern on it!
3. Screw the cone into the inner stem, finger tight.
   Do not overtighten.
4. Rinse inner stem with DI water making certain to wet the O-ring.
5. Gently push the inner stem into the outer body, sliding the spring down cable, and screwing the cap into place.
6. Remove fill hole cover and O-ring on fill hole spout.
7. Using the dropper pipette provided, add a few drops of HI7078 fill solution to the electrode.
8. Invert the electrode to wet the O-ring and rinse the fill solution chamber.



9. Holding the electrode body, gently press the upper cap with thumb.
   This permits the fill solution to drain out of the body.
10. Release the cap and verify electrode returns to its original position.
    Users may need to gently assist for this to occur.
11. Tighten the electrode cap onto the body and fill electrode body until fill solution volume is just below fill hole.
12. Position electrode in HI76404 electrode holder (or equivalent) and connect BNC connector to meter.

9. QUICK CHECK OF ELECTRODE SLOPE

- Connect electrode(s) to pH/mV/ISE meter.
- Place the meter in mV mode.
- Pour 100 mL of DI water into a beaker with stir bar.
- Place reference and measuring (half-cell or combination) electrodes into prepared sample.
- Add 1 mL of HI4013-01 (0.1M nitrate standard solution) or HI4013-03 (1000 ppm (mg/L) nitrate standard solution) to beaker.
  Record the mV value when stable.
- Add an additional 10 mL of standard to the solution.
  Record the mV when the reading has stabilized.
  This value should be less than the previous value noted (more negative).
- Determine the difference between the two mV values. An acceptable value for this slope is 56 $\pm$ 4 mV (20-25 °C).

10. CORRECTIVE ACTION

- Verify module has been screwed into the sensor handle (or inner stem).
- HI4113 measuring electrode (or HI5315 reference electrode)
  Verify seal has been removed from ceramic junction.
- Verify reference chamber has been filled.
- Verify the electrode is correctly connected to the meter and the meter is powered on.
- Ensure diluted standards are freshly made. Remake solutions if necessary. Store in plastic bottles.
- If the reading is unstable, hold the top of the electrode and whip the electrode downward (see General Guidelines section).
- If the sensor slope misses the suggested slope window, soak the sensor in a standard solution without ISA.
- If the membrane is damaged, electrode response becomes extremely sluggish, or electrode slope has decreased significantly, and procedures above have not helped, replace the module.

HI4013

1. Dry off module and sensor handle.
2. Unscrew sensing module and replace with a new one.
3. Soak new module in nitrate solution to condition it before calibration.

HI4113

1. Depress the cap to drain the fill solution. Rinse the electrode with distilled or DI water. Drain.
2. Unscrew the upper cap and slide down cable toward connector.
3. Move the spring and outer body down cable also.
4. Dry off the inner stem and module with a soft tissue.
5. Hold the inner stem and unscrew the module. Replace with a new one.
6. Reassemble the electrode (see General Guidelines section). Refill with electrolyte.
7. Soak new membrane in nitrate solution without ISA to condition before calibration.

11. DIRECT CALIBRATION & MEASUREMENT

This method serves as a simple procedure for measuring several samples.
A direct reading ISE meter determines concentration of the unknown after meter calibration.

- Add HI4013-00 to adjust ionic strength at a dose of 2 mL per 100 mL sample (or standard).
  ISISA* may also be used at a dose of 10 mL for 50 mL of sample (or standard).
- Meter calibration is done using freshly made standards that are in the measurement range of the unknowns.
  Unknowns are read directly.
- In the region where the electrode calibration becomes less linear, more calibration points are needed, and frequent calibrations are required.
- A pH/mV meter in mV mode and semi-log graph paper may also be used.
- Two (or more) freshly-prepared standards (within measurement range of the unknowns) are measured on the meter. Values are plotted on the semi-log paper and the points are connected to form a straight-line curve.
- When samples are measured, their mV values are converted to concentration by following the mV to the concentration axis on the semi-log plot.

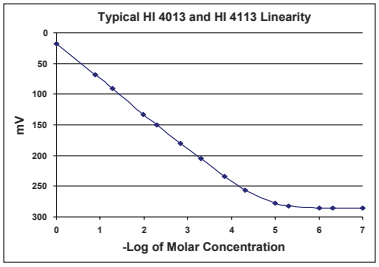
Procedure

1. Follow Electrode Preparation and Quick Check of Electrode Slope sections to prepare for measurement.
2. Follow Solutions Required section to prepare standards/solutions.
   Standards should bracket and fall within the range of interest.
   Standards and solutions should be at the same temperature.
   - 2 mL of HI4013-00 is added to 100 mL of both samples and standards.
     or
   - 10 mL of ISISA are added to 50 mL both of both samples and standards.
     Add stir bar and mix before taking measurements.
3. Follow General Guidelines section to optimize test set-up.

* Note: ISISA is the recommended ISA used for procedure 4500-NO_3-D. published in Standard Methods for the Examination of Water and Wastewater. It is an EPA accepted method for drinking water analysis.

4. During calibration it is best to start with lower concentration samples first.
   Wait for a stable reading before reading/recording values.
   Permit longer equilibration times at these levels (3 or 4 minutes).

***Note**: To prevent sample contamination, rinse sensors with deionized water. Remove moisture with absorbent tissue between samples.*



12. OTHER MEASUREMENT TECHNIQUES

Known Addition

Known Addition and other incremental methods are done automatically on ISE meters such as HI6222, HI6522, or HI6542.

An unknown concentration can be determined by adding a known volume and concentration of NO_3^- standard to the sample. mV values are noted before and after the addition of standard (ΔE).

An ideal sensor slope can be used in the equation but actual determined slopes at the temperature of measurement should be used if known (S).

Example of nitrate ion determination with Known Addition

1. Place 50 mL sample of unknown (V_{SAMPLE}) in a clean, plastic beaker with an electrode (s).
2. Add 50 mL of ISISA* to sample and mix. mV1 is recorded.
3. Add 5 mL ($V_{STANDARD}$) of 10^{-1} M ($C_{STANDARD}$) standard to the beaker. The mV value decreases.

   ***Note**: for samples with different concentrations, add a known volume and concentration of standard to produce approximately 30 mV change.*

   The unknown Nitrate concentration in the original sample (C_{SAMPLE}) can then be determined using the equation given here.

$$C_{sample} = \frac{C_{standard} V_{standard}}{(V_T)10^{\Delta E/S} - (V_{S'})} \left(\frac{V_{S'}}{V_{sample}} \right)$$

$$(V_{sample} + V_{standard} + V_{ISA}) = V_T$$

$$(V_{sample} + V_{ISA}) = V_{S'}$$

4. The procedure can be repeated with a second standard addition to verify slope and operation of the method.

* Note: ISISA is Interferent suppressant ISA, see Solutions Required section.

13. pH & INTERFERENTS

HI4013 and HI4113 nitrate electrodes operate over a pH range of 3 pH to 8 pH.
For best results, keep the pH constant throughout calibration and test.
Sulfuric acid (NaOH) can be used for pH adjustment. Alternatively, use ISISA to suppress interferences and buffer pH.
Limit the exposure time to samples containing interferences to prolong electrode life.
If the sensor has been exposed to ions above recommended levels, soak in pure nitrate solutions without ISA to aid recovery of function.

14. STORAGE & CARE

Short-term storage recommendations

- The HI4013 sensor can be stored in standards that do not contain ISA.
- The HI4113 sensor can be stored in diluted standards that do not contain ISA.

If the electrode is used frequently and needs to be ready for use, prevent evaporation of fill solution.

- Top off fill solution, replace the O-ring and the fill hole cover on the fill hole opening; and place the sensor in dilute nitrate solution that does not contain ISA.
- Store the electrode upright.
- Prior to use, drain the electrolyte chamber and refill with fresh HI7078 fill solution.

Long-term storage recommendations

- Disassemble and wash off salts.
- Wrap the junction on the inner stem, remove and store module in glass vial; and store the sensor in the provided box.
- Refrigerate the module to extend its life.

15. CONVERSION TABLES

For NO_3^-	Multiply by
Moles/L (M) NO_3^- to ppm NO_3^- (mg/L)	62000
ppm (mg/L) to M (moles/L)	1.61×10^{-5}
ppm NO_3 to ppm NO_3 (as N) mg/L	0.2258
ppm NO_3 (as N) mg/L to ppm NO_3	4.4286

CERTIFICATION

All Hanna® instruments conform to the **CE European Directives.**

RoHS compliant

Disposal of Electrical & Electronic Equipment. The product should not be treated as household waste. Instead, hand it over to the appropriate collection point for the recycling of electrical and electronic equipment, which will conserve natural resources. Ensuring proper product disposal prevents potential negative consequences for the environment and human health.
For more information, contact your city, your local household waste disposal service, or the place of purchase.

RECOMMENDATIONS FOR USERS

Before using this product, make sure it is entirely suitable for your specific application and for the environment in which it is used. Any variation introduced by the user to the supplied equipment may degrade its performance. Do not use or store the product in hazardous environments.

WARRANTY

Hanna Instruments® Ion Selective Electrodes are warranted for six months against defects in workmanship and materials when used for their intended purpose and maintained according to instructions. This warranty is limited to repair or replacement free of charge. Damage due to accidents, misuse, tampering, or lack of prescribed maintenance is not covered.
If service is required, contact your local Hanna Instruments office. If under warranty, report the model number, date of purchase, serial number, and the nature of the problem. If the repair is not covered by the warranty, you will be notified of the charges incurred. If the product is to be returned to Hanna Instruments, first obtain a Returned Goods Authorization (RGA) number from the Technical Service department and then send it with shipping costs prepaid. When shipping any product, make sure it is properly packed for complete protection.