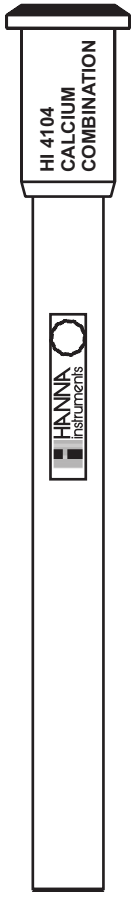


Instruction Manual

HI 4004
HI 4104

Calcium Ion
Selective Electrode

Half-cell
Combination

HANNA® instruments
With Great Products, Come Great Results™

HI 4004 Calcium Half-cell
HI 4104 Calcium Combination Electrode

I. Introduction:

The Hanna HI 4004 and HI 4104 are ion selective electrodes designed for the measurement of calcium ions in aqueous solutions. They utilize a replaceable sensing module that contains an organic polymer membrane that is sensitive to calcium ions. The HI 4004 is a half-cell electrode that requires a separate reference. The HI 4104 is a combination ion selective electrode.

II. Specifications

Type:	PVC membrane with organic ion exchanger
Ion measured:	Calcium (Ca^{2+})
Measurement range:	1.0 M to 3 X 10^{-6} M 40080 to 0.12 ppm

Interference:
Organic solvents and cationic detergents must be absent. Ratio of interfering ion to Ca^{2+} must be less than the ratio indicated below:

15000	for Na^{+}	sodium
7000	for Mg^{3+}	magnesium
700	for Ni^{2+}	nickle
300	for Fe^{2+}	ferrous
250	for Al^{3+}	aluminum
200	for NH_4^{+}	ammonium
35	for Cu^{2+}	cupric
0.001	for Pb^{2+}	lead

Operating Temperature:	0-40°C
Operating pH:	4 to 10 pH (see Section XIII)
Dimensions:	12 mm (OD) X 120 mm nominal insertion (0.47" X 4.72")
Connection:	BNC

III. Theory of Operation:

The HI 4004 and HI 4104 calcium electrodes are potentiometric devices used for the rapid determination of free calcium ions in water, sea water and beverages. The electrode functions as a sensor or ionic conductor. The HI 4004 requires a separate reference electrode to complete its electrolytic circuit. The HI 4104 is a combination electrode with a Ag/AgCl reference electrode with gel stabilized Cl^- electrolyte in it's inner chamber. The external reference chamber is refillable. The PVC membrane used on the sensor is impregnated with the organic ion exchanger.

This organic ion exchanger is considered a carrier ionophore in that it is capable of shielding and carrying the charged calcium ion in it's polar cage freely through the apolar regions of the membrane. A charge imbalance developes between the test solution and internal cell of the sensor.

This voltage changes in response to the sampleís 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)

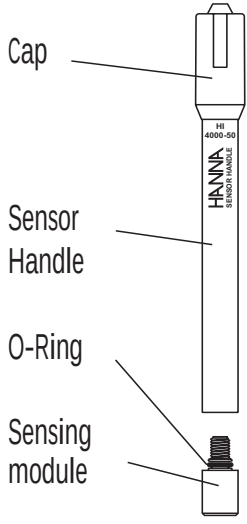
n = Charge on ion (2+)

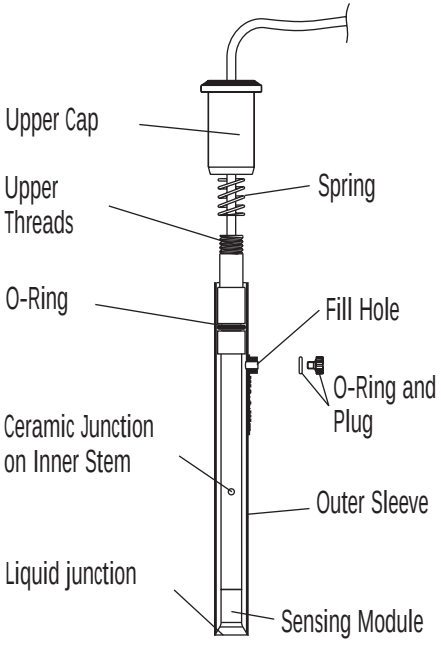
A_{ion} = ion activity in sample

T = absolute temperature in K

F = Faraday constant (9.648×10^4 C/equivalent)

IV. Design elements of the HI 4004 and HI 4104 electrodes





V. Equipment required:

- The HI 4004 requires the Hanna HI 5315 Double junction reference electrode with HI 7082 as external electrolyte.
- Hanna HI 4222 pH/ISE/mV meter or other suitable ion or pH/mV meter (Note: log/linear graph paper is useful if an ISE (ion) meter is not available).
- Hanna HI 180 magnetic stirrer or equivalent with magnetic stirring bars (Note: Isolate beakers from stirrer motor heat by placing insulating material such as foam or cork between them).
- Hanna HI 76404 electrode holder or equivalent.
- Plastic beakers (HI 740036P) or other suitable measurement vessel.

VI. Solutions Required

Standards for Calcium Measurements

0.1 M calcium standard,500 mL	HI 4004-01

Ionic Strength Adjuster

ISA, 500 mL	HI 4004-00

Conditioning and Storage Solution

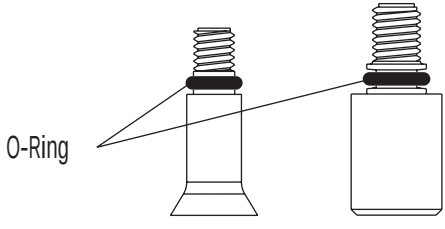
Calcium storage solution, 500 mL	HI 4004-45

Using volumetric pipettes and glassware make dilutions to bracket the concentration of the samples. Store samples in plastic bottles. Standards with concentrations $< 10^{-3}$ M should be prepared daily.

Two mL of Hanna ISA HI 4004-00 should be added to 100 mL sample or standard.

VII. General Guidelines

- Ensure the o-ring is installed on modules before screwing into the sensor handle or inner stem.



- Due to shipping or storage the internal solution inside the PVC modules may have developed an air pocket near the membrane. Gently shaking the sensor down (like the old style mercury thermometer) will place the internal solution next to the membrane.
- Presoaking the Calcium sensor in HI 4004-45 solution for at least half-hour before calibration will help to optimize the sensor response.
- Do not leave your sensors in standard or samples with ISA for long periods of time.
  Note: The electrode membrane will develop a opaque appearance when it becomes wetted. This is normal.
- 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 same temperature.
- Thermally insulate solution vessel from magnetic stirrer.
- Calibration standards and sample solutions should be stirred at the same rate using identical sized TFE coated stir bars.
- 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 sensing surface (due to solution temperature changes). Tap off gently.
- Avoid large changes in temperature (thermal shock) as it may damage the sensor.

Additional HI 4104 guidelines

- Remove the protective plastic wrap that covers the ceramic junction before assembling sensor for the first time.
- Add reference HI 7082 fill solution to bottom of fill hole or empty and refill fill solution daily before using.
- During measurement always operate electrode with the fill hole open.
- During normal use, fill solution will slowly drain out of the tapered cone 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 a good head pressure. For optimum response, this level should be maintained and not be 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 and rinse internal body with deionized water. Reassemble and refill with fresh fill solution.
- If an erratic measurement occurs, check to see if foreign matter is seen trapped near the internal cone. Drain by depressing the electrode cap then refill with fresh fill solution.

VIII. Electrode Preparation

HI 4004

The Hanna HI 4004 is a 2 piece design comprised of a sensor handle (HI4000-50) and a sensing module (HI 4004-51).

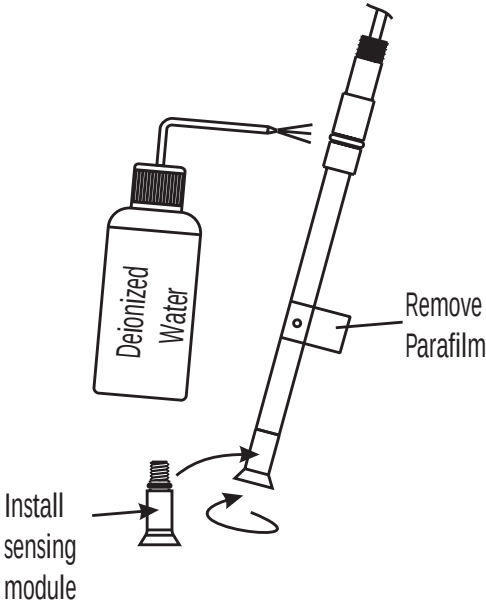
1. Remove sensing module from shipping vial. Do not touch the sensing membrane with the "H" hole pattern on it.
2. Screw the module into the sensor handle finger tight. Do not overtighten.

3. Holding the assembled electrode at the cable end, shake the sensor to ensure internal fill solution that may have separated during shipping is in contact with inner membrane surface.
4. Prepare HI 5315 reference electrode by filling electrolyte reservoir with HI 7082 fill solution.
5. Place sensor and reference electrodes into electrode holder and connect cable connectors to meter.
6. Soak the Calcium electrodes membrane in HI 4004-45 conditioning solution or a calcium standard (0.01M) without ISA before calibration.

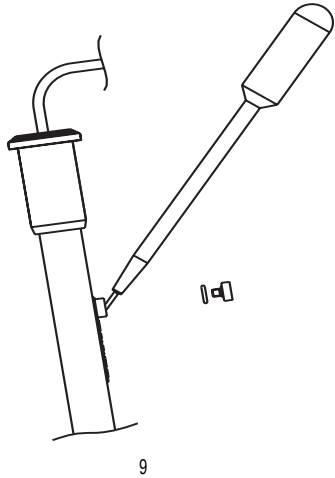
HI 4104

The Hanna HI 4104 is shipped disassembled. The sensing module is found in the glass storage vial.

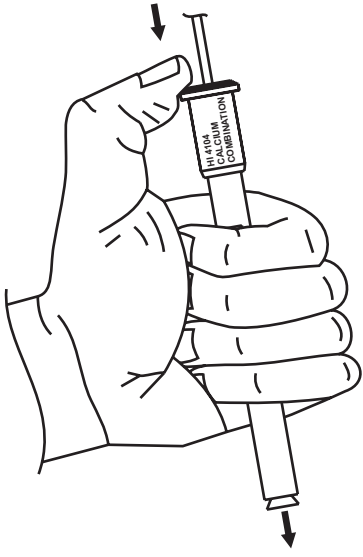
1. Unwrap Parafilm® seal found over ceramic junction on inner stem and discard. This is only used for shipping or long term storage.
2. Remove sensing cone from shipping vial. Do not touch the sensing membrane with the "H" hole pattern on it.
3. Screw the cone into the inner stem finger tight. Do not over tighten.



4. Rinse inner stem with deionized water making certain to wet o-ring found on the inner stem.
5. Reassemble electrode by gently pushing the inner assembly into the outer body, sliding spring down cable, and screwing cap into place.
6. Remove fill hole cover and o-ring on fill hole spout. Using the dropper pipette provided, add a few drops HI 7082 fill solution to the electrode. Invert the electrode to wet the o-ring and rinse the fill solution chamber.



7. Holding the body of the electrode gently press upper cap with your thumb. This permits the fill solution to drain out of the body. Release cap and verify electrode returns to its original position. (You may need to gently assist for this to occur).



8. Tighten the electrode cap onto the body and fill electrode body until fill solution volume is just below fill hole.
9. Position electrode in a Hanna HI 76404 electrode holder (or equivalent) and connect BNC connector to meter.

IX. Quick Check of Electrode Slope

- Connect electrode(s) to pH/mV/ISE meter
- Place meter in mV mode.
- Place 100 mL of deionized water into a beaker with stir bar.
- Place reference and measuring half-cell or combination electrode into prepared sample.
- Add 1 mL of a standard to beaker. Record the mV value when stable.
- Add an additional 10 mL of standard to the solution. Record the mV when reading has stabilized. This

value should be more positive than the previous value noted.

- Determine the difference between the two mV values. An acceptable value for this slope is 26 ± 4 mV (20-25°C).

X. Corrective action

- Verify module has been screwed into sensor handle or inner stem.
- Verify Parafilm® seal has been removed from ceramic junction (HI 4104 or HI 5315 reference).
- Verify fill solution has been added to reference chamber.
- Verify electrodes are connected properly to meter and meter is powered.
- Verify dilute standards are freshly made and stored. Remake solutions if appropriate. Store in plastic bottles.
- If the reading is jumpy or unstable, shake sensor down (see section VII).
- If the sensor slope just misses the suggested slope window, soaking the sensor in a standard solution without ISA may solve the problem.
- If the membrane is damaged, the response becomes extremely sluggish, or the slope of the electrode has decreased significantly, and procedures above have not helped, the module should be replaced.

For HI 4004

1. Dry off module and sensor handle.
2. Unscrew sensing module and replace with a new one. (HI 4004-51).
3. Soak new module in calcium solution to condition it before calibration.

For HI 4104

1. Drain the fill solution by depressing cap. Rinse electrode with distilled or deionized water. Drain.

2. Unscrew upper cap and slide down cable toward connector.
3. Move spring and outer body down cable also.
4. Dry off inner stem and module with a soft tissue.
5. Hold inner stem and unscrew module and replace with a new one. (HI 4104-51).
6. Reassemble electrode (see section VII), and refill with electrolyte. Soak new membrane in calcium solution without ISA to condition before calibration.

XI. Direct Calibration and Measurement

This method is a simple procedure for measuring many samples. A direct reading ISE meter (HI 4222 or equivalent) determines concentration of the unknown by a direct reading after calibrating the meter with the standards. Add HI 4004-00 to adjust ionic strength at a dose of 2 mL of per 100 mL sample or standard. The meter is calibrated 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 calibration will need to be repeated more frequently.

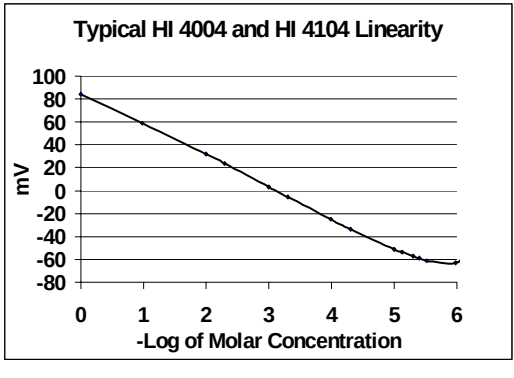
A pH/mV meter in mV mode and semi log graph paper may also be used. Two or more freshly prepared standards that are in the measurement range of the unknowns are measured in mV mode on the meter.
These values are plotted on the semi-log paper and the points are connected to form a straight-line curve. 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:

Follow sections VIII and IX to prepare electrodes for measurement.

1) Follow section VI to prepare standards/ solution. Standards should bracket and fall within the range of interest. Standards and solutions should be at the same temperature.
2) 2 mL of HI 4004-00 is added to 100 mL of both samples and standards.
   Add stir bar and mix before taking measurements.
3) Follow section VII; General Guidelines to optimize test set-up.
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).

To prevent carry over and contamination of samples, rinse sensors with deionized water and remove moisture with absorbant tissue between samples.



XII. Other Measurement Techniques

Known addition

An unknown concentration can be determined by adding a known volume and concentration of Ca^{2+} 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). This method is preprogrammed in the Hanna HI 4222 pH/ISE/mV meter, which simplifies the method greatly.

Example:

Calcium ion determination with known addition.

1. A 50 mL sample of unknown (V_{SAMPLE}) is placed in a clean plastic beaker with an electrode (s). One mL of ISA is added to the sample and permitted to mix. mV 1 is recorded.
2. 10 mL ($V_{STANDARD}$) of 10^{-1} M ($C_{STANDARD}$) standard is added to the beaker and the mV value increases. (Note: for other concentration samples, add a known volume and concentration of standard to produce approximately 30 mV change).

   The unknown calcium concentration in the original sample (C_{SAMPLE}) can then be determined by using the equation that follows.
3. The procedure can be repeated with second standard addition to verify slope and operation of the method.

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

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

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

XIII. pH and Interferents

HI 4004/ HI 4104 calcium electrodes can operate over a

pH range of 4-10 . The electrode responds to free calcium ions only. Precipitates with oxalate, carbonate, phosphate and complexes with hydroxide, sulfate, and bicarbonate reduce measureable calcium from solution. Using Known Addition (section XII) with complexing reagents and pH adjustments may permits total calcium to be measured. Limiting the length of time of exposure to samples containing interferences will prolong useful life of your electrode. If sensor has been exposed to ions above recommended levels, soaking in pure calcium solutions without ISA or HI 4004-45 will aid recovery of function.

XIV. Storage and Care of the HI 4004 and HI 4104 electrodes

The HI 4004 sensor can be stored in HI 4004-45 for short time periods. For long term storage, unscrew sensing module from sensor handle and store dry in the shipping vial. The model HI 4104 combination electrode can be left in HI 4004-45 for short time periods. If the electrode will be used frequently and needs to be ready for use, take measures to prevent evaporation of fill solution. Top off fill solution, replace o-ring, fill hole cover on the fill hole opening, and place sensor in HI 4004-45 storage and conditioning solution. Store electrode upright. Prior to use, drain electolyte chamber and refill with fresh HI 7082 fill solution.

For long term storage, the electrode should be drained, disassembled and washed of salts with deionized water. Wrap the ceramic junction in Parafilm® or other sealing wrap. Unscrew the module and store dry in the shipping vial. Refrigeration of module will extend its life. Store disassembled electrode in storage box provided with electrode.

XV. Conversion tables

	Multiply by
Moles/L (M) Ca^{2+} to ppm Ca^{2+} (mg/L)	40080
ppm (mg/L) to M (moles/L)	2.49×10^{-5}

MAN4104 07/06R1

WARRANTY

Hanna Instruments Ion Selective Electrodes are warranted to be free of defects in material and workmanship for 6 months from date of purchase when used for their intended purpose and maintained according to instructions. If they fail to work when first used contact your dealer immediately. Damage due to accidents, misuse, misapplication, tampering or lack of prescribed maintenance is not covered.

Hanna Instruments reserves the right to modify the design, construction or appearance of its products without advance notice.

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