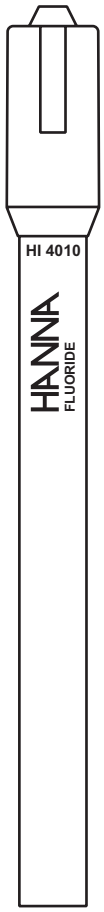


Instruction Manual

HI 4010
HI 4110

Fluoride Ion
Selective Electrode

Half-cell
Combination

HANNA® instruments
With Great Products, Come Great Results™

HI 4010 Fluoride Half-cell
HI 4110 Fluoride Combination Electrode

I. Introduction:

The Hanna HI 4010 and HI 4110 are ion selective electrodes designed for the measurement of fluoride ions in aqueous solutions. The HI 4010 is a solid state half-cell sensor that requires a separate reference. The HI 4110 is a combination ion selective electrode.

II. Specifications

Type:	Solid State electrode with a Lanthanum Fluoride crystal membrane.
Ion(s) measured:	Fluoride (F^-)
Measurement range:	Saturated to $1X\ 10^{-6}M$ Saturated to 0.02 ppm
Interfering ions:	OH^-

Note:

Several other ions (Al^{3+}, Fe^{3+}) that complex with the measured species will reduce the ion concentrations measured directly. TISAB reagent should be used in most of these cases. H^+ ion also forms HF species below pH 5. Increase pH in these cases above 5 for a total fluoride measurement.

Operating Temperature:	0-80°C
Operating pH:	5 to 8 pH
Dimensions:	12 mm (OD) X 120 mm nominal insertion (0.47" X 4.72")
Connection:	BNC

III. Theory of Operation:

The HI 4010 or HI 4110 fluoride electrodes are potentiometric devices used for the rapid determination of free fluoride ions in water, soft drinks, wine, emulsified foods, and plating and pickling acids. The electrode functions as a sensor or ionic conductor. The HI 4010 requires a separate reference electrode to complete its electrolytic circuit. The HI 4110 has a reference electrode incorporated in its design. The lanthanum fluoride crystalline pellet is practically insoluble in the test solutions being measured and produces a potential change due to changes in the sample's ion activity. When the ionic strength of the sample is fixed, the voltage is proportional to the concentration of fluoride ions in solution and the electrode 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)

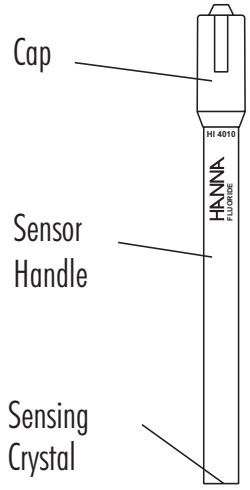
n = Charge on ion (1-)

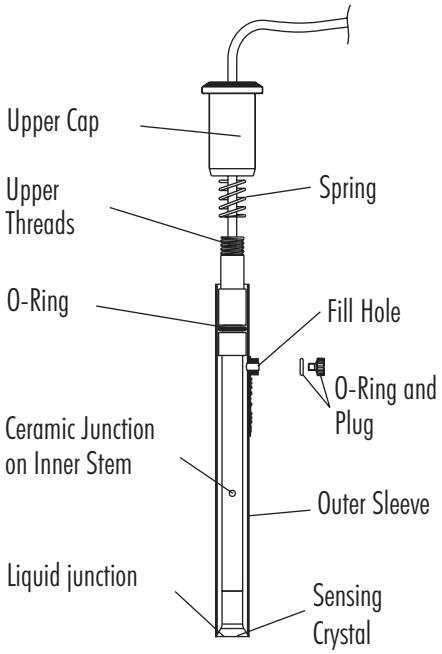
A_{ion} = ion activity in sample

T = absolute temperature in K

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

IV. Design elements of the HI 4010 and HI 4110 electrodes





V. Equipment required:

- Hanna HI 5315 double junction reference electrode with HI 7075 fill solution for measurements with HI 4010.
- 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 stirring bars (HI 731320). (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

Standard for Fluoride Measurements

Select appropriate Hanna Instruments standard and ISA from the list below:	Part number
0.1 M Sodium Fluoride, 500 mL	HI 4010-01
100 ppm, 500 mL	HI 4010-02
1000 ppm, 500 mL	HI 4010-03
10 ppm with TISAB II, 500 mL	HI 4010-10 *
1 ppm with TISAB II, 500 mL	HI 4010-11 *
2 ppm with TISAB II, 500 mL	HI 4010-12 *

ISA

TISAB II, 500 mL	HI 4010-00
TISAB II, 1 gallon	HI 4010-05
TISAB III , 500 mL	HI 4010-06

KIT:	HI 4010-30
Contains four 500 mL bottles of:	
TISAB II	HI 4010-00
10 ppm with TISAB II	HI 4010-10 *
1 ppm with TISAB II	HI 4010-11 *

*Standards that are asterisked contain TIASB II and are ready to use withour further additions.

Using volumetric pipettes and glassware make dilutions to bracket the concentration of the samples. Standards with concentrations < 10^{-4} M (1.9 ppm) should be prepared daily. Standards that are asterisked * contain TISAB II and should be used directly with no additional TISAB II added. Samples used with these standards should have TISAB II added. To 50 parts standard or sample add 50 parts TISAB II (HI 4010-00, HI 4010-05) or to 50 parts standard or sample add 5 parts of TISAB III concentrate (HI 4010-06). Note: TISAB is formulated for water sample analysis to provide samples and standards a constant ionic strength and pH background that stabilizes the solutions activity coefficient and permits concentration to be measured directly. It preferentially complexes various metal ions (i.e. Aluminum; Al^{3+}, Iron; Fe^{3+}) that also complex with fluoride thus permitting a total fluoride measurement. Contact Hanna Instruments for guidelines with other applications.

VII. General Guidelines

- Calibration standards and sample solutions should have the same ionic strength. Use the same TISAB (II or III) for both samples and standards. Always prepare samples and standards with the same ISA to volume ratio.
- Calibration standards and sample solutions should be at same temperature.
- Thermally insulate beaker with standard or sample 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 crystal.
- Presoaking fluoride sensor in a standard near sample concentrations will activate crystal and optimize response.

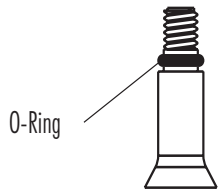
- A slightly scratched crystal may benefit from a treatment with a fluoride containing toothpaste (without baking soda). Lightly wipe the sensor tip with the mild abrasive. Rinse well with deionized and soak in a fluoride standard near measurement value.
- Avoid large changes in temperature (thermal shock) as it may damage the sensor.

HI 4010

- Remove protective cover from sensor tip.

HI 4110

- Remove the protective plastic wrap that covers the ceramic junction before assembling sensor for the first time.
- Ensure o-ring is installed on sensing module before screwing into the inner stem.



- Add reference HI 7075 fill 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.
- 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.
- If an erratic measurement occurs, check to see if foreign matter is seen trapped near the internal cone. Drain and refill with fresh fill solution.

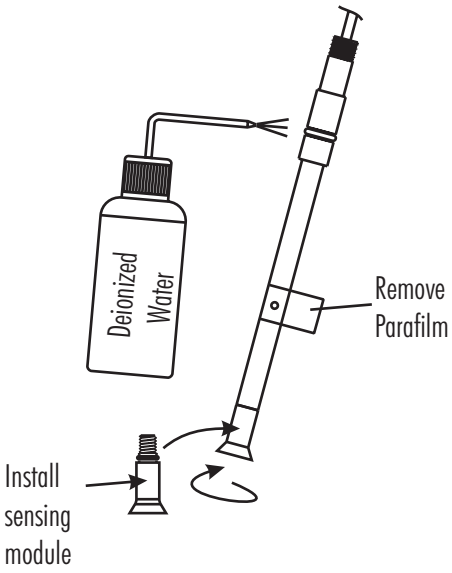
VIII. Electrode Preparation

HI 4010

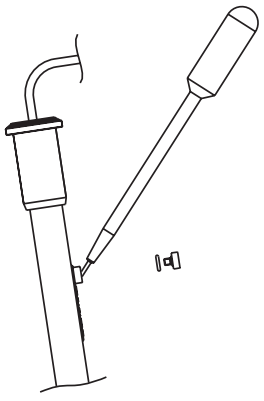
1. Remove protective cover from HI 4010 sensor tip.
2. Due to shipping or storage the internal solution inside the electrode may have developed an air pocket near the membrane. Gently shaking the sensor down (like the old style mercury thermometer) will place the internal solution next to the membrane. Note: when the sensor is inverted an air pocket will be seen which is normal.
3. Prepare HI 5315 reference electrode by filling outer electrolyte reservoir with HI 7072.
4. Place sensor and reference electrodes into electrode holder and connect cable connectors to meter.

HI 4110

1. Unwrap plastic film seal found over ceramic junction on inner stem and discard. This is only used for shipping and long term storage.
2. Open the glass vial that contains the fluoride module (HI 4110-51) and remove from container.
3. Ensure the o-ring is installed on module before screwing into inner stem. Do not over tighten.
4. Due to shipping or storage the internal solution inside the module 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. Note: When inverted, an air pocket will be visible inside the sensor which is normal.
5. Rinse inner stem with deionized water making certain to wet the o-ring found on the inner stem.



6. Reassemble electrode by gently pushing the inner assembly into the outer body, sliding spring down cable, and screwing cap into place. DO NOT TOUCH OR PUT PRESSURE ON LANTHANUM CRYSTAL.
7. Remove fill hole cover and o-ring on fill hole spout.
8. Using the dropper pipette provided, add a few drops of HI 7075 fill solution to the electrode, wetting the o-ring and rinsing out the fill solution chamber.



9. 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).

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

IX. Quick Check of Electrode Slope

- Connect sensors to pH/mV/ISE meter.
- Place meter in mV mode.
- Place 100 mL of deionized water into a beaker with stir bar.
- Place the electrodes into prepared sample.
- Add 1 mL of a standard (0.1 M or 1000 ppm 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 less than the previous noted (more negative).

- Determine the difference between the two-mV values. An acceptable value for this slope is -56 $\pm$ 4 mV.

X. Corrective action

- Verify protective cap has been removed (HI 4010).
- Verify plastic film has been removed from inner stem (HI 4110 or HI 5315 electrode).
- Verify electrodes are connected properly to meter and meter is powered. For HI 4110 verify sensor is screwed into the inner stem.
- Verify dilute standards are freshly made and stored. Remake solutions if appropriate.
- If the sensor slope just misses the suggested slope window, soaking the sensor in a standard may solve the problem. (Choose 10^{-2} M fluoride or 1000 ppm standard).
- A scratched sensing surface can be polished with fluoride toothpaste (without baking soda). Use a small drop of the paste and a soft wipe. Using a circular motion, and gentle pressure, rub the surface of the electrode with this micro abrasive material. Rinse with water. Check to see if small scratches have been eliminated. Rinse in deionized water and blot dry. Soak in a fluoride standard for 1 hour. Repeat section IX.
- If the reading is jumpy or unstable, shake sensor down (see section VIII).
- 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 sensor (or module) should be replaced.

For HI 4110 module replacement

1. Drain the fill solution by pressing the upper 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 4110-51).
6. Reassemble electrode (see section VIII), and refill with electrolyte. Soak new membrane in fluoride solution 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 4212 or equivalent) determines concentration of the unknown by a direct reading after calibrating the meter with the standards. The meter is calibrated with two or more freshly made standards that are in the linear measurement range of the unknowns. More calibration standards are required in non-linear regions. Unknowns are read directly.

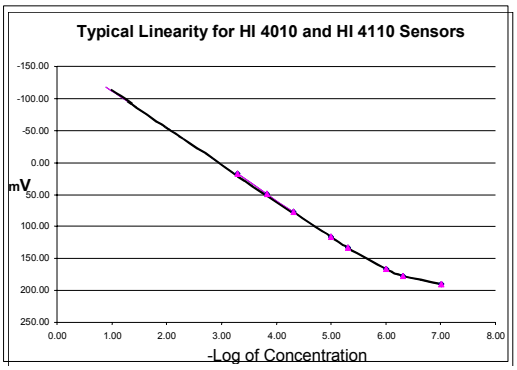
A pH/mV meter in mV mode with semi log graph paper may also be used. Two or more freshly prepared standards that are in the measurement range of the unknowns are measured in mV mode on the meter.

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.

At very low levels of fluoride, special precautions must be employed for reproducible measurements. Water used for standards must be fluoride free and sensors and glassware must be rinsed repeatedly with this water to prevent carry over. In the region where the electrode calibration becomes curved, many more calibration points are needed, and calibration will need to be repeated more frequently.

If no fluoride complexing species are in the sample, TISAB needn't be added at the same proportions. Add 1 parts TISAB to 100 parts sample or standard. Ionic strength will be fixed at approximately 0.02M. Attention: Always prepare samples and standards with the same ISA to volume ratio.

1) Follow sections VIII and IX to prepare sensors for measurement.
2) Follow section VI to prepare standards/solution. Standards should bracket the sample concentration. Standards and solutions should be at the same temperature.
   1 part of TISAB is added to 100 parts 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 measurement before recording values. Longer equilibrations are required at lower concentrations (4-5 minutes).
5) To prevent carry over and contamination of samples, rinse sensors with deionized water and dab dry between samples.



XII. Other Measurement Techniques

Known addition (for F^-)

An unknown concentration can be determined by adding a known amount (volume and concentration) of measured ion to a known volume of the sample. This technique is useful for very low F^- concentration samples. It can use an ideal sensor slope, but actual determined slopes at the temperature of measurement should be used if known. This method is preprogrammed in the Hanna HI 4222 pH/ISE/mV meter, which simplifies the method greatly.

Example: Fluoride ion determination with known addition.

1. A 50 mL sample of unknown (Vsample) is placed in a clean plastic beaker with cleaned electrodes. The mV 1 is recorded. If fluoride metal complexes are present add 50 mL TISAB II (V_{TISAB}). Mix well then take mV value.
2. 5 mL (Vstd) of 10^{-3}M (Cstd) standard is added to the beaker and the mV value decreases. The unknown fluoride concentration in the original sample (Csample) can then be determined by the following equation.

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

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

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

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

Titration

Titration can be used to measure an ion that doesn't have an ion selective sensor. An example of this is the use of the Hanna HI 4110 or HI 4010 fluoride electrode for aluminum (Al^{3+}) determination. Because the stoichiometry between the two species is variable fixing the pH and titrating to a fixed endpoint is advised.

Five mL acetate buffer (3.7 M HOAC/0.76M OAC^- in composition) is added to 100 mL of sample. A standard aluminum solution is first titrated with a fluoride solution to determine the endpoint value. Measurements may be automated by use of the Hanna Titrator HI 901 or titrated manually.

XIII. pH

The HI 4110 and HI 4010 sensors measure fluoride ions between 5 and 8 pH.

XIV. Storage and Care of the HI 4010 and HI 4110 sensors

The HI 4010 sensor can be stored in standards near measured values for short periods of time and should be stored dry with the protective cap on when not in use for long periods of time. The model HI 4110 combination electrode can be left in standards that were used for calibration 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, and replace o-ring and plug on fill hole opening. Place sensor tip in a dilute fluoride standard, positioned upright. Prior to use, drain electolyte chamber and refill with fresh 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 fluoride module and store dry in the shipping vial. Store disassembled electrode in storage box provided with electrode.

XV. Conversion tables

For F^-	Multiply by
Moles/Liter (M) to ppm (mg/L)	1.900×10^4
ppm (mg/L) to M (Moles/Liter)	5.263×10^{-5}

MAN4110 07/06R2

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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