

Instruction Manual

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**HI 4009**

**HI 4109**

Cyanide Ion

Selective Electrode

Half-cell

Combination

## HI 4009 Cyanide Half-cell

## HI 4109 Cyanide Combination Electrode

### I. Introduction:

The Hanna HI 4009 and HI 4109 are ion selective electrodes designed for the measurement of Cyanide ions in aqueous solutions. The HI 4009 is a solid state half-cell sensor that requires a separate reference. The HI 4109 is a combination ion selective electrode.

### II. Specifications

Type:	Solid State electrode with a Silver halide pellet.
Ion(s) measured:	Cyanide ( $\text{CN}^-$ )
Measurement range:	$10^{-2}\text{M}$ to $1 \times 10^{-6}\text{M}$ 260 to 0.026 ppm
Interfering ions:	Silver, Sulfide and Mercury must be absent. Ratio of interfering ion to $\text{CN}^-$ must be less than the ratio indicated below: 1.0 for $\text{I}^-$ Iodide 500 for $\text{Br}^-$ Bromide 500 for $\text{Cl}^-$ Chloride
Operating Temperature:	0-80°C
Operating pH:	11 to 14 pH (recommended)
Dimensions:	12 mm (OD) X 120 mm nominal insertion (0.47" X 4.72")
Connection:	BNC

#### WARNING:

HCN GAS IS TOXIC IF BREATHED, OR ABSORBED THROUGH SKIN. USE OF A HOOD AND PROTECTIVE CLOTHING IS STRONGLY ADVISED. USE ISA TO ADJUST pH ABOVE 11.

### **III. Theory of Operation:**

The HI 4009 or HI 4109 Cyanide electrodes are potentiometric devices used for the rapid determination of free Cyanide ions in effluent, for electroplating bath analysis and as a detector for titration of cyanide with silver nitrate.

The electrode functions as a sensor or ionic conductor. The HI 4009 requires a separate reference electrode to complete its electrolytic circuit. The HI 4109 incorporates a reference electrode. The silver halide 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 by the addition of ISA, the voltage is proportional to the concentration of Cyanide 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 volt coulomb/K Mole)

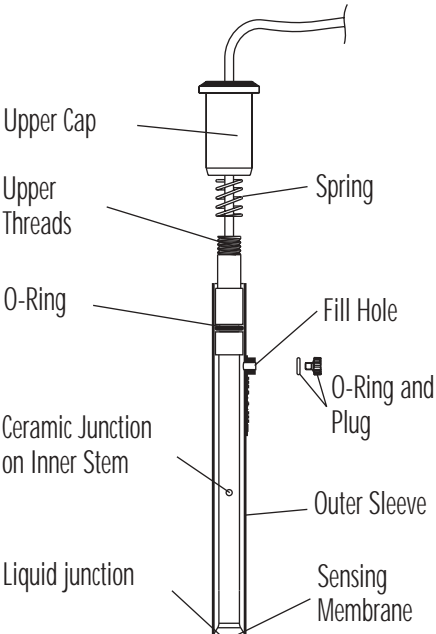
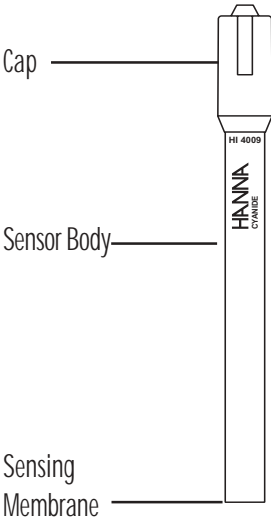
n = Charge on ion (1-)

$A_i$  = ion activity in sample

T = absolute temperature in K

F = Faraday constant ( $9.648 \times 10^4$  coulomb/mole)

IV. Design elements of the HI 4009 and HI 4109 electrodes



## **V. Equipment required:**

- Hanna HI 5315 Double Junction Reference Electrode with HI 7072 Fill Solution for HI 4009.
- 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 TFE coated 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 for Cyanide Measurements**

ISA, 500 mL

HI 4001-00

User supplied standards:

Note: These solutions should only be used for making more dilute standards. The sensing surface will be damaged if submersed in this high a concentration.

Molar Stock solution:

0.01M stock solution (1 Liter): To a one liter volumetric flask add approximately 300 mL deionized water and 10-mL of HI 4001-00 ionic strength (pH) adjuster. On an analytical balance weigh 0.490g of dry NaCN salt and transfer to the volumetric flask. Swirl contents until dissolved. Add deionized water to bring the flask to its 1 liter calibrated mark. Mix thoroughly and store in tightly capped plastic bottle.

ppm stock solution:

1000 ppm stock solution (1 Liter): To a one liter volumetric flask add approximately 300 mL deionized water and 10 mL of HI 4001-00 ionic strength (pH) adjuster. On an analytical balance weigh 1.88g of dry NaCN salt and transfer to the 1-liter volumetric flask. Swirl contents until dissolved. Add deionized water to bring the flask to its 1 liter calibrated marking. Mix thoroughly and store in tightly

capped plastic bottle. Using volumetric pipettes and glassware make dilutions to bracket the concentration of the samples. Store standards in plastic bottles. Standards with concentrations  $< 10^{-3}\text{M}$  should be prepared daily. One mL of Hanna ISA and pH adjuster (HI 4001-00) should be added to each 100 mL of sample or standard.

## **VII. General Guidelines**

- Use of a hood and protective clothings is strongly advised. Use ISA to adjust pH above 11.
- Calibration standards and sample solutions should have the same ionic strength. ISA should be added to both samples and standards in the same ratio. 1 part ISA to 100 parts standard is the normal dosing.
- Concentrated samples ( $> .005\text{ M}$ ) should be diluted before measurement. Multiply the final result by the corresponding dilution factor.
- For high ionic strength samples, use standard addition or titration methods.
- Calibration standards and sample solutions should be at same temperature and at elevated pH.
- The magnetic stirrer may generate heat. Thermally insulate beaker containing standard or sample from magnetic stirrer by placing cork or other insulative sheet between beaker and stirrer plate.
- Calibration standards and sample solutions should be stirred at the same rate using identical sized TFE coated stir bars.
- Rinse electrode pair with distilled or deionized water between samples and gently dab dry with soft disposable absorbent toweling. Do not rub electrodes.
- Presoaking cyanide sensor in a dilute standard will optimize response. Use concentrations approximately  $10^{-3}\text{M}$  or less with ISA added.
- A scratched, pitted, or tarnished pellet surface can cause drift, a loss of low level response, or poor repeatability. Optimum response can be restored by removing the damaged surface with the microabrasive strip

HI 4000-70.

- Avoid large changes in temperature (thermal shock) as it may damage the sensor.
- Gas bubbles may form from solution out-gassing due to temperature change. Gently tap body of sensor to dislodge them from sensing membrane.

#### HI 4009

- Remove protective cover from sensor tip.
- Prepare HI 5315 reference electrode by filling electrolyte reservoir with HI 7072 fill solution.
- Place sensor and reference electrodes into electrode holder and connect cable connectors to meter.

#### HI 4109

- Remove the protective plastic wrap that covers the ceramic junction before assembling sensor for the first time.
- HI 7072 reference fill solution should be added daily to electrolyte reservoir before electrode use.
- 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 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. It must cover the ceramic found on the inner stem.
- 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.

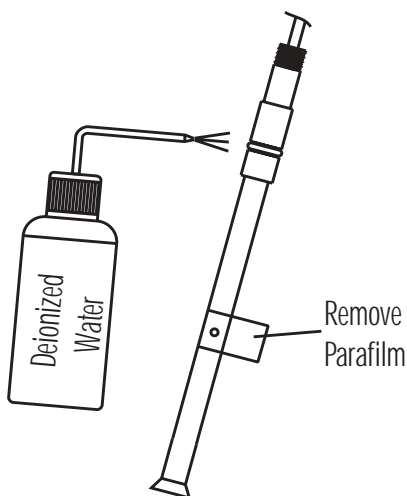
## VIII. Electrode Preparation

### HI 4009

1. Remove protective cover from sensor tip.
2. Prepare reference electrode by filling outer electrolyte reservoir with HI 7072.
3. Place sensor and reference electrodes into electrode holder and connect cable connectors to meter.

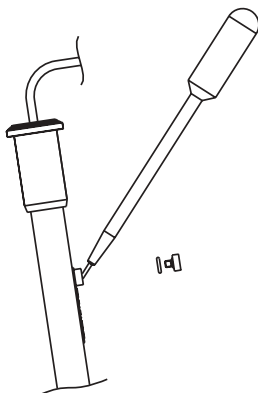
### HI 4109

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. Rinse inner stem with deionized water making certain to wet the o-ring found on the inner stem.



3. Reassemble electrode by gently pushing the inner assembly into the outer body, sliding spring down cable, and screwing cap into place.
4. Remove fill hole cover and o-ring on fill hole spout.
5. Using the dropper pipette provided, add a few drops HI 7072 fill solution to the electrode, wetting the o-ring and rinsing out the fill solution chamber.





6. 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).



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

## **IX. Quick Check of Electrode Slope**

Use of a hood and protective clothing is strongly advised.

- Connect sensors to pH/mV/ISE meter
- Place meter in mV mode.
- Place 100 mL of deionized water into a beaker with stir bar and 1 mL of HI 4001-00 ISA.
- Place electrodes into prepared sample.
- Add 1 mL of the stock standard (either M or ppm) to the beaker. Record the mV value when stable.
- Add an additional 10 mL of stock 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 4009).
- Verify plastic film has been removed from inner stem (HI 4109).
- Verify electrodes are connected properly to meter and meter is powered.
- 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 dilute standard may solve the problem. ( $<10^{-3}$  M standard).
- A scratched sensing surface can be polished with HI 4000-70 polishing strip. Cut off approximately 1 inch of the micro-abrasive strip. Wet the frosted side with deionized water and place against damaged membrane of the electrode. Place your gloved thumb against the shiny backing and slowly rotate back and forth while applying gentle pressure. Continue polishing until you are satisfied with the surface. If dark deposits appear on polishing strip move the paper slightly and continue polishing.

- 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 should be replaced.

## **XI. Direct Calibration and Measurement**

This method is a simple procedure for measuring many samples. Use of a hood and protective clothing is strongly advised when handling cyanide samples and standards. 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. The meter is calibrated with two or more freshly made standards that are in the linear measurement range of the unknowns. One mL of ISA (HI 4001-00) is added to each 100 mL volume of standard or sample. More calibration standards are required in non-linear regions. Unknowns are read directly.

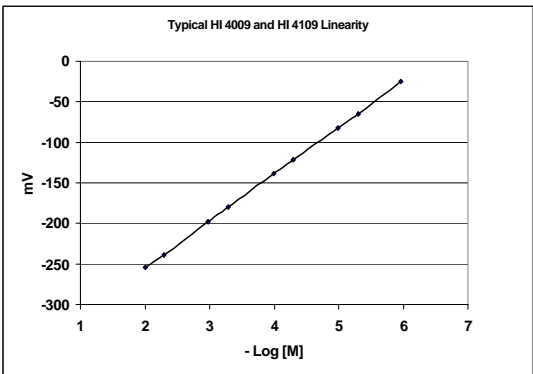
Samples with higher concentration should be diluted to be within the working range of the electrodes. The final result must be multiplied by the corresponding dilution factor to determine the actual concentration.

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.

## Procedure

- 1) Follow sections VIII and IX to prepare sensors for measurement.
- 2) Follow section VI to prepare standards / solution. Standards should bracket and fall within the range of interest.  
One mL HI 4001-00 ISA 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 measurement before recording values. Slightly longer equilibrations are required at lower concentrations.
- 5) To prevent carry over and contamination of samples, rinse sensors with deionized and dab dry between samples.



## XII. Other Measurement Techniques

### Known Addition (for CN<sup>-</sup>)

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 called Known Addition. The method can use an ideal sensor slope, but actual determined slopes at the temperature of measurement should be used if known. The volume and concentration of the added standard must cause a mV change of at least 30 mV. This method is preprogrammed in the Hanna HI 4222 pH/ISE/mV meter, which simplifies the method greatly. The method is recommended for samples with higher ionic strengths.

Example: Cyanide ion determination in samples with concentrations less than  $5 \times 10^{-4}$  M using known addition.

1. A 50 mL sample of unknown ( $V_{\text{sample}}$ ) is placed in a clean plastic beaker with a cyanide sensor. 500  $\mu\text{L}$  (0.5 mL) of HI 4001-00 ISA ( $V_{\text{ISA}}$ ) is added to the 50 mL sample and allowed to mix. The stable mV value ( $mV_1$ ) is recorded.
2. 10 mL ( $V_{\text{std}}$ ) of  $10^{-2}$ M ( $C_{\text{std}}$ ) stock standard is added to the beaker and the mV value decreases. The unknown cyanide concentration in the original sample ( $C_{\text{sample}}$ ) can then be determined by the following equation.

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

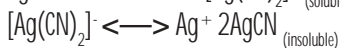
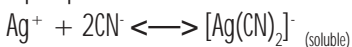
$$(V_{\text{sample}} + V_{\text{standard}} + V_{\text{ISA}}) = V_T$$

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

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

## Titration

A cyanide electrode may be used as an indicator to follow the progress and detect the endpoint of a complexation titration of  $\text{CN}^-$  with silver nitrate standard. Time must be allowed for the alkali salt to redissolve and mV to settle. The end point is reached when the formation of insoluble silver cyanoargentate precipitates occurs. The electrode can be used in colored samples, or high or variable ionic strength samples to increase accuracy of the determination. During the titration the sensor follows the decrease in cyanide concentration while small additions of silver nitrate titrant are added. The silver reacts with the cyanide ions forming a precipitate.



At the stoichiometric end point, a large change in mV occurs. This technique may be useful in obtaining the actual value of cyanide standards. Measurements may be automated by use of the Hanna Titrator HI 901 or titrated manually.

## **XIII. pH**

The HI 4109 and HI 4009 electrodes may be used in solutions with pH values between 11 and 13. Samples that fall beyond this range should be adjusted.

## **XIV. Storage and Care of the HI 4009 and HI 4109 sensors**

The HI 4009 sensor can be stored in very dilute standards ( $< 10^{-3}\text{M}$ ) for short periods of time and should be stored dry with the protective cap on when not in use.

The model HI 4109 combination electrode can be left in dilute standards ( $< 10^{-3}\text{M}$ ) for short time periods.

For long term storage, the electrode should be drained and washed of salts with distilled or deionized water. Unscrew the upper cap and move outer sleeve up cable. Wrap the ceramic junction on the inner stem with Parafilm® or other sealing wrap. Place the protective cap provided over the

sensor membrane. Store dry disassembled electrode in storage box provided with electrode.

## **XV. Conversion Tables**

<b><u>For CN<sup>-</sup></u></b>	<b>Multiply by</b>
Moles/L (M) to ppm (mg/L)	$2.602 \times 10^4$
ppm (mg/L) to M (moles/L)	$3.843 \times 10^{-5}$

## **XVI. Disposal of Cyanides**

Sodium Cyanide is a deadly poison and extreme care must be taken during use and in disposal after use.

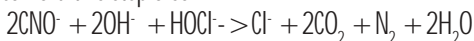
Test solutions and standards may be neutralized before discharging. Consult your waste manager for exact procedures. The overview of the process is below.

Caution: Neutralization reactions should be carried out in a hood.

- 1) Cyanide is oxidized to cyanate at an elevated pH. pH and ORP measurements can aid the progress of this reaction.



- 2) Cyanate is then oxidized to N<sub>2</sub> and CO<sub>2</sub> which bubble off as harmless gases. pH and ORP measurements can aid this step also.





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## 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.

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

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