

## Instruction Manual

**HI 4015**

**HI 4115**

Silver/Sulfide Ion  
Selective Electrode

Half-cell

Combination

## HI 4015 Silver/ Sulfide Half-cell HI 4115 Silver/ Sulfide Combination Electrode

### I. Introduction:

The Hanna HI 4015 and HI 4115 are ion selective electrodes designed for the measurement of Silver/ Sulfide ions in aqueous solutions. The HI 4015 is a solid state half-cell sensor that requires a separate reference. The HI 4115 is a combination ion selective electrode.

### II. Specifications

Type:	Solid State electrode with a Silver/ Sulfide pellet.				
Ion(s) measured:	Silver ( $\text{Ag}^+$ ), Sulfide ( $\text{S}^{2-}$ )				
Measurement range:	<table> <tr> <td>Silver</td><td>1.0 M to <math>1 \times 10^{-6}</math> M (107,900 to 0.11 ppm)</td></tr> <tr> <td>Sulfide</td><td>1.0 M to <math>1 \times 10^{-7}</math> M (32,100 to 0.003 ppm)</td></tr> </table>	Silver	1.0 M to $1 \times 10^{-6}$ M (107,900 to 0.11 ppm)	Sulfide	1.0 M to $1 \times 10^{-7}$ M (32,100 to 0.003 ppm)
Silver	1.0 M to $1 \times 10^{-6}$ M (107,900 to 0.11 ppm)				
Sulfide	1.0 M to $1 \times 10^{-7}$ M (32,100 to 0.003 ppm)				
Interfering ions:	Mercury must be absent. Ions that complex with measured species will reduce measured ion concentrations.				
Operating Temperature:	0-80°C				
Operating pH:	2-8 pH (For Silver) 12-14 pH (For Sulfide)				
Dimensions:	12 mm (OD) X 120 mm nominal insertion (0.47" X 4.72")				
Connection:	BNC				

2

### III. Theory of Operation:

The HI 4015 or HI 4115 Silver/ Sulfide electrodes are potentiometric devices used for the rapid determination of free silver or sulfide ions. They can be used as an indicator following the progress of a halide titration with silver nitrate. Sulfide ion determinations are made in ground waters, soils and paper liquors. The electrode functions as a sensor or ionic conductor. The HI 4015 requires a separate reference electrode to complete its electrolytic circuit. The HI 4115 has a double junction reference electrode incorporated in its design. The silver/ silver- sulfide 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 silver or sulfide ions in solution and the electrode follows the Nernst equation.

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

E = observed potential

$E_a$  = Reference and fixed internal voltages

R = gas constant (8.314 J/K Mol)

n = Charge on ion (2- for sulfide), (1+ for silver)

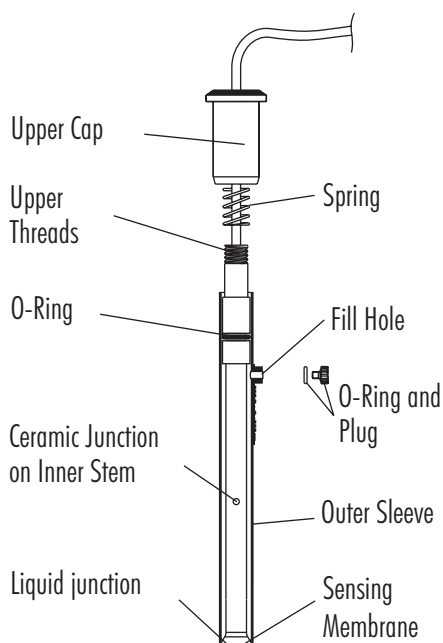
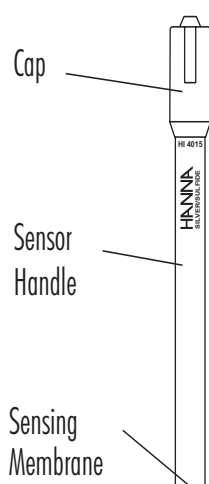
$A_i$  = ion activity in sample

T = absolute temperature in K

F = Faraday constant ( $9.648 \times 10^4$  C/mol)

3

#### IV. Design elements of the HI 4015 and HI 4115 electrodes



#### V. Equipment required:

- Hanna HI 5315 Double Junction Reference Electrode with HI 7072 Fill Solution for use with HI 4015.
- 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 Teflon 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 Calibration

Select appropriate Hanna Instruments standard and ISA from the list below:

0.1 M Silver Standard, 500 mL	HI 4015-01
ISA for Silver measurement, 500 mL	HI 4000-00
SAOB for Sulfide measurement, 500 mL	HI 4015-00

Note: For Sulfide standard, see directions that follow.

##### Silver Standards

##### For Molar solutions:

Using volumetric pipettes and glassware make serial dilutions of HI 4015-01 to approximately bracket the concentration of the samples. Standards with concentrations  $< 10^{-3}$  M should be prepared daily. Store in dark plastic bottles.

Two mL of Hanna ISA for Halide electrodes (HI 4000-00) should be added to 100 mL of sample or standard.

##### For ppm solutions:

Prepare 1078.7 ppm Silver standard by diluting HI 4015-01: Pipette 100 mL standard to a 1 liter volumetric flask. Add deionized water to volume. Using additional pipettes and glassware make serial dilutions of this 1078.7 ppm standard to bracket the sample concentra-

tions. Standards with concentrations < 100 ppm should be made daily.

#### Solutions for Sulfide Measurements

SAOB, Hanna HI 4015-00: Add content of SAOB reagent B bottle to the bottle with SAOB reagent A. Cap bottle and mix well until completely dissolved. Reagent that is brown has been oxidized and should be discarded.

#### Sulfide Standards:

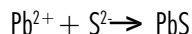
Sulfide standards are susceptible to air oxidation and therefore are not commercially available.

Sulfide stock solution: Weigh approximately 100 gram of reagent grade Sodium Sulfide nonahydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) into a 1 liter volumetric flask that contains a volume of distilled or deionized /deareated water. Swirl to dissolve, bring to volume, then transfer to a tightly sealed 1 L container with minimal head space and allow solution to equilibrate overnight.

#### 133.5 ppm standard (approximate concentration):

Transfer 5.00 mL stock solution and 250 mL Sulfide Antioxidant buffer SAOB (Hanna HI 4015-00) to a 500 mL volumetric flask. Mix well then bring to volume with distilled or deionized /deareated water. Hanna HI 4015-00 SAOB, should be clear to pale straw in color after mixing. Note: higher concentrations of standard can also be prepared and titrated if samples are greater in concentration. The sensor is useable from 32,100 to 0.003 ppm.

Determine exact concentration of the prepared standard by doing a titration with Lead Perchlorate standard (user prepared) on a weekly basis. The exact concentration of the standard is found by titrating 10 mL of the standard with 0.01 M Lead Perchlorate standard; ( $\text{Pb}(\text{ClO}_4)_2$ ).



Use the electrode pair as an indicator for  $\text{S}^{2-}$  to determine the endpoint. See Section XII.

Calculate as follows:

Weekly standard in Molar concentration

$$C \text{ (moles/liter)} = (0.01) * V_t / V_s$$

$V_t$  = Volume of the Lead Perchlorate titrant used to reach endpoint (mL)

Weekly standard in ppm

$$C \text{ (ppm)} = (0.01) * 32.07 V_t / V_s$$

Using volumetric pipettes and glassware make dilutions daily from the titrated standard whose value has been determined. Choose standards to bracket the concentration of the samples.

50 mL of HI 4000-00 ISA should be added to each 100 mL flask of standard before being brought to volume.

#### **VII. General Guidelines**

- Calibration standards and sample solutions should have the same ionic strength. ISA or SAOB should be added to both samples and standards in the same 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 identically sized TFE coated stir bars.
- Rinse electrode pair with distilled or deionized water between samples and gently dab off using soft disposable absorbent toweling. Do not rub sensor surface.
- Presoaking silver sensor in a dilute standard ( $<10^{-3}\text{M}$ ) will help to optimize response.
- A scratched, pitted, or tarnished pellet surface can cause drift, poor repeatability or a loss of low level response. Restore optimum response can be 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.
- Avoid leaving electrode in SAOB containing solutions for long periods of time as it will damage the electrode.

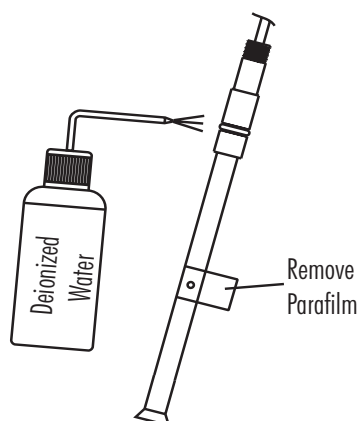
### VIII. **Electrode Preparation**

#### HI 4015

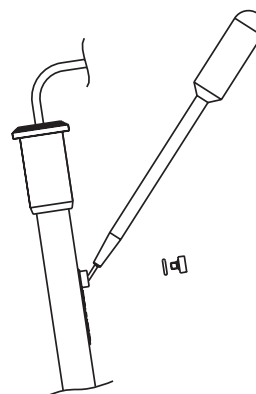
1. Remove protective cover from sensor tip.
2. Prepare reference electrode by filling outer electrolyte reservoir with HI 7072.
3. Place sensor and reference electrodes into electrode holder and connect cable connectors to meter.

#### HI 4115

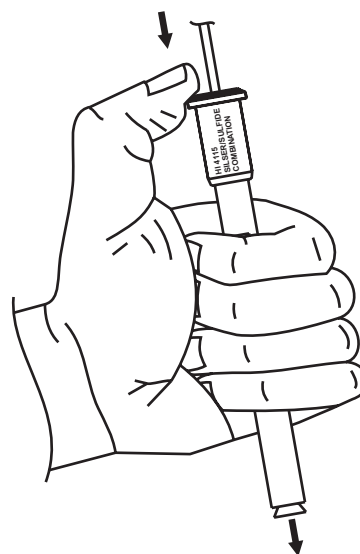
1. Unwrap plastic film seal found over ceramic junction on inner stem and discard. This is only used for shipping and long term storage.
2. Rinse inner stem with deionized water making certain to wet the o-ring found on the inner stem.



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

### **Ag<sup>+</sup>**

- 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 electrode (s) into prepared sample.
- Add 1 mL of a standard (0.1 M or 1078.7 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 greater than the previous noted (more positive).
- Determine the difference between the two mV values. An acceptable value for this slope is  $56 \pm 4$  mV. If sensor does not have appropriate mV change, corrective action must be taken.

### **S<sup>2-</sup>**

- Connect sensors to pH/mV/ISE meter.
- Place meter in mV mode.
- Place 50 mL of deaerated water into a beaker with 50 mL of the premixed SAOB, Hanna HI 4015-00. Add stir bar and mix thoroughly.
- Place electrode (s) into prepared sample.
- Add 1 mL of the titrated 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  $-28 \pm 4$  mV for freshly made solution. Solution exposed to air will be degraded and lower slopes will be observed. If sensor does not have appropriate mV change, corrective action must be taken.

## X. Corrective action

- Verify protective cap has been removed. (HI 4015)
- Verify plastic film has been removed from inner stem. (HI 4115)
- Verify electrodes are connected properly to meter and meter is powered.
- Verify dilute standards are freshly made and stored. Remake solutions if appropriate.
- Verify SAOB was added to sulfide standards and they have been stored appropriately. Remake solutions if necessary.
- If the silver sensor slope just misses the suggested slope window, soaking the sensor in a dilute standard may solve the problem. (Choose a dilute value equal or less than  $10^{-3}$  M).
- 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 thumb against the shiny backing and slowly rotate back and forth while applying gentle pressure. Check to see if small scratches have been eliminated and coatings have been removed. Rinse in deionized water and dab dry. Continue polishing until you are satisfied with the surface.  
Warning: Silver Sulfide dust is considered corrosive. Protective hand coverings are strongly recommended during this procedure.
- 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

The direct calibration technique 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. The meter is calibrated with two or more freshly made standards that are in the linear measurement range of the unknowns. Unknowns are read directly. At very low levels of silver, special precautions must be employed for reproducible measurements. Water used for standards must be free of halides and sensors and glassware must be rinsed repeatedly with this water to prevent carry over. Plastic beakers are recommended. In the region where the electrode response appears curved, more calibration points are needed, and calibration will need to be repeated more frequently. See "Procedure for Silver" below for additional instructions.

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.

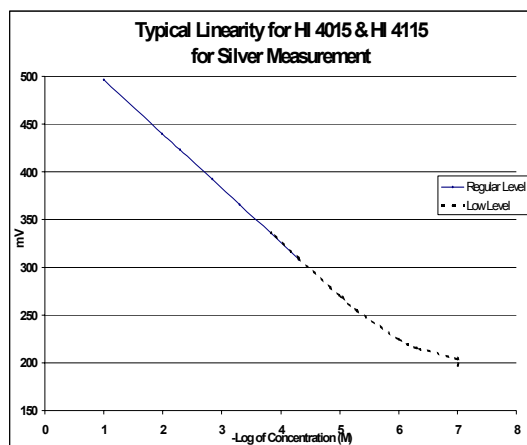
### Procedure for Silver

- 1) Follow sections VIII and IX to prepare sensors for measurement.
- 2) Follow section VI to prepare standard solution. Standards should bracket and fall within the range of interest.

Two mL HI 4000-00 ISA is added to 100 mL of both samples and standards for measurements equal or above  $10^{-4}$  M silver. At concentrations equal or less than  $10^{-4}$  M silver, prepare a separate calibration curve and use 1 mL of a diluted ISA in sample and stan-

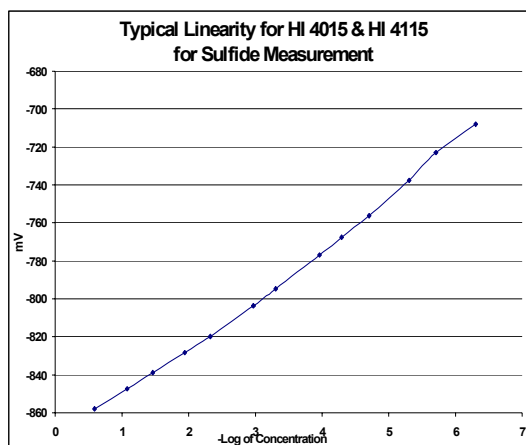
dards. Add stir bar and mix thoroughly and continuously before taking measurements. A lower level ionic strength adjuster is prepared by diluting HI 4000-00 ISA (20 mL diluted to 100 mL). This should be used at a dose of 1 part per 100 parts sample or standard. Sample ionic strengths will be approximately  $10^{-2}$  M.

- 3) Follow section VII 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 water and dab dry between samples.



### Procedure for Sulfide

- 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.  
Fifty mL HI 4015-00 ISA is added to the beaker with 50 mL sample or standard. Add stir bar and mix thoroughly and continuously before making measurements. Protect these solutions from air and use promptly.
- 3) Follow section VII 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 water and dab dry between samples.



## XII. Other Measurement Techniques

### Known Addition (for $\text{Ag}^+$ or $\text{S}^{2-}$ )

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. This method is preprogrammed in the Hanna HI 4222 pH/ISE/mV meter, which simplifies the method greatly. This technique is useful for high ionic strength samples.

Example: Silver ion determination with known addition.

1. A 50 mL sample of unknown ( $V_{\text{sample}}$ ) is placed in a clean plastic beaker with a HI 4115 sensor. 2 mL of HI 4000-00 ISA ( $V_{\text{ISA}}$ ) is added and the sample is mixed well. The stable mV value ( $V_1$ ) is then recorded.
2. 5 mL ( $V_{\text{std}}$ ) of  $10^{-3}\text{M}$  ( $C_{\text{std}}$ ) standard is added to the beaker and the mV value increases. The unknown silver 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 multiple samples.

### Analyte Subtraction ( $\text{S}^{2-}$ )

This method is based on a titration reaction, with the electrode responding to a reagent that reacts with the sample being added.

A known concentration of sulfide in a sample can be determined by using this method. A silver standard is used as the reagent. Ions that complex with silver cannot be present. These include  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ , or SAOB. This method assumes an ideal sensor slope, but actual



determined slopes at the temperature of measurement should be used if known.

Example: Sulfide ion determination by sample subtraction.

- 1) A volume of standard solution of silver reagent ( $V_{std}$ ) ( $C_{std}$ ) plus ISA ( $V_{ISA}$ ) is placed in a beaker with the sensor pair. The mV1 is recorded.
- 2) A known volume ( $V_{sam}$ ) of the unknown sulfide sample is added (mV should change at least 10 — 30 mV). The new mV is recorded (mV2) and the difference is calibrated using the equation below  $\Delta mV = |mV2 - mV1|$ . S is the slope of the silver electrode.
- 3) The unknown sulfide concentration in the sample ( $C_{sam}$ ) can then be determined by the following equation. For an example a sensor is placed into 100 mL of a 0.001 M  $Ag^+$  standard. 1.0 mL of unknown was added. The mV changed 12.5 mV. The unknown sulfide value is found to be  $1 \times 10^{-2}$  M.  $n = \frac{1}{2}$  because  $\frac{1}{2}$  mole of sulfide reactions with 1 mole of silver ion.

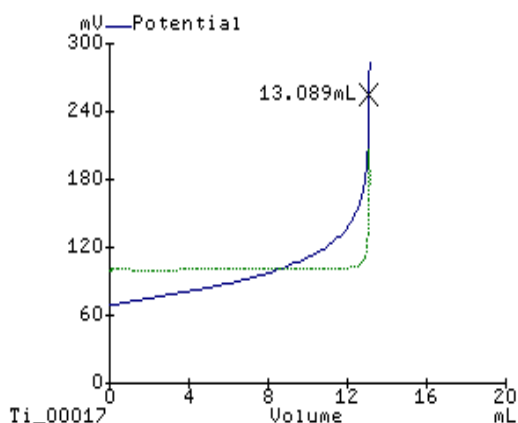
$$C_{sample} = n * \left( \frac{V_{std} * C_{std}}{V_{std} + V_{ISA}} - \frac{V_{std} * C_{std}}{V_{std} + V_{ISA} + V_{sam}} \right) * \left( \frac{V_{std} + V_{ISA} + V_{sam}}{V_{sam}} \right)$$

$n =$  Mole ratio of ions in sample that react with 1 mole of standard

### Titration of Chloride

A silver electrode may be used as an indicator to follow the progress of a chloride (or other halide) titration with silver nitrate. The electrode can be used in colored samples where other indicators suffer from interferences. During the titration the sensor follows the decrease in the halide concentration while small additions of silver nitrate titrant are added. The silver reacts with the chloride ions forming a precipitate of silver chloride. At the stoichiometric end point, a large change in mV occurs as the silver is in excess. Measurements may be automated by use of the Hanna Titrator HI 901 or titrated manually.

**Plot generated on Hanna HI 901 Titrator during automated chloride titration using HI 4115 electrode.**



$$C_{S^{2-}} = C_{Pb^{2+}} * \frac{V_{Pb^{2+}}}{V_{S^{2-}}}$$

### Titration of Sulfide

A silver/sulfide electrode may be used as an indicator to follow the progress of a sulfide titration with lead perchlorate. The lead perchlorate should be 10 to 20 times greater in concentration than that of the sulfide sample. The sample is first mixed with an equal volume of SAOB. During the titration the sensor follows the decrease in the sulfide concentration while small additions of lead perchlorate titrant are added and react with the sulfide ions. Permit sufficient time for solution reaction and electrode equilibration. The largest mV change for given increment is the endpoint.

### **XIII. pH**

For Silver measurements:

HI 4115 and HI 4015 electrodes may be used in solutions with pH values between 2 and 8. Samples that fall beyond this range should be adjusted with acid ( $\text{HNO}_3$ ) or base ( $\text{NaOH}$ ).

For Sulfide measurements:

Sulfide measurements are made in the presence of SAOB; HI 4015-00 which adjusts the pH between 12 and 14 pH.

### **XIV. Storage and Care of the HI 4015 and**

#### **HI 4115 sensors**

The HI 4015 sensor can be stored in very dilute standards ( $< 10^{-4} \text{ M}$ ) for short periods of time and should be stored dry with the protective cap on when not in use.

The model HI 4115 combination electrode can be left in dilute standards ( $< 10^{-4} \text{ M}$ ) 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**

#### **For $\text{Ag}^+$**

#### **Multiply by**

Moles/L (M) to ppm (mg/L)  
ppm (mg/L) to M (moles/L)

$1.0787 \times 10^5$   
 $9.27 \times 10^{-6}$

#### **For $\text{S}^{2-}$**

Moles/L (M) to ppm (mg/L)  
ppm (mg/L) to M (moles/L)

$3.207 \times 10^4$   
 $3.12 \times 10^{-5}$

#### **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.

---