



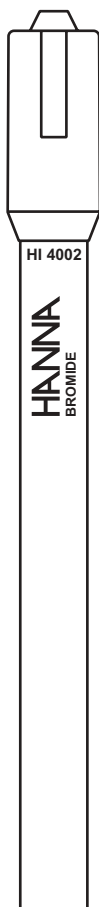
Instruction Manual

HI 4002

HI 4102

Bromide Ion

Selective Electrode



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Half-cell

Combination

HI 4002 Bromide Half-cell

HI 4102 Bromide Combination Electrode

I. Introduction:

The Hanna HI 4002 and HI 4102 are ion selective electrodes designed for the measurement of Bromide ions in aqueous solutions. The HI 4002 is a solid state half-cell sensor that requires a separate reference. The HI 4102 is a combination ion selective electrode.

II. Specifications

Type:	Solid State electrode with a Silver Bromide pellet.
Ion(s) measured:	Bromide (Br^-)
Measurement range:	1.0 M to 1×10^{-6} M 79,910 to 0.08 ppm
Interfering ions:	Cyanide, and Mercury must be absent. Ratio of interfering ion to Br^- must be less than the ratio indicated below: 0.01 for I^- iodide 0.01 for CN^- cyanide 50 for Cl^- Chloride
Operating Temperature:	0-80°C
Operating pH:	2-12.5 pH
Dimensions:	12 mm (OD) X 120 mm nominal insertion (0.47" X 4.72")
Connection:	BNC

III. Theory of Operation:

The HI 4002 or HI 4102 Bromide electrodes are potentiometric devices used for the rapid determination of free Bromide ions in food products, beverages, plants, soils and as an indicator in titrations. The electrode functions as a sensor or ionic conductor. The HI 4002 requires a separate reference electrode to complete its electrolytic circuit. The HI 4102 incorporates a reference electrode. The silver Bromide 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 bromide 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)

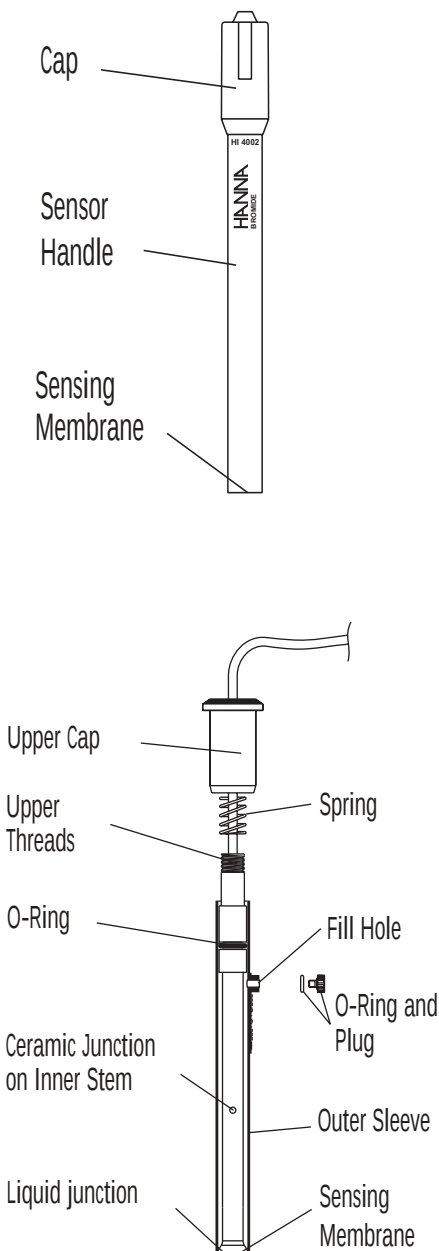
n = Charge on ion (1-)

A_i = ion activity in sample

T = absolute temperature in K

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

IV. Design elements of the HI 4002 and HI 4102 electrodes



V. Equipment required:

- Hanna HI 5315 Double Junction Reference Electrode with HI 7072 Fill Solution for HI 4002.
- 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 Bromide Measurements

0.1 M Bromide Standard, 500 mL	HI 4002-01
ISA, 500 mL	HI 4000-00

For Molar solutions:

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

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 799 ppm bromide standard by diluting HI4002-01: Pipette 100 mL standard to a 1 liter volumetric flask. Add deionized water to volume. Using additional volumetric pipettes and glassware make serial dilutions of this 799 ppm standard to approximately bracket the concentration of the samples. Standards with concentrations < 80 ppm should be prepared daily.

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

VII. General Guidelines

- 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 50 parts standard is the normal dosing.
- Concentrated samples ($> 1\text{ M}$) should be diluted before measurement. Multiply the final result by the corresponding dilution factor.
- For high ionic strength samples, prepare standards with similar ionic strength by increasing the ISA addiiton.
- Calibration standards and sample solutions should be at same temperature.
- 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 bromide sensor in a dilute standard will optimize response. Use concentrations approximately 10^{-3}M or less.
- 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 membrane surface.

HI 4002

- 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 4102

- 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.

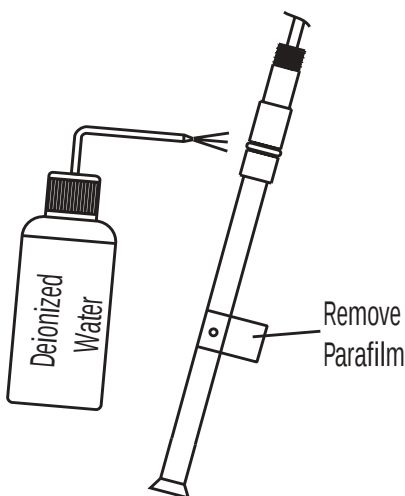
VIII. Electrode Preparation

HI 4002

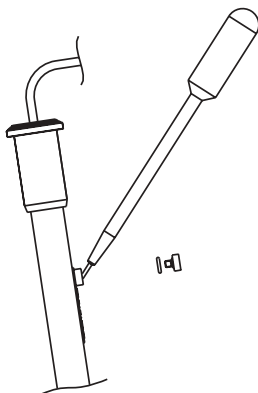
1. Remove protective cover from sensor tip.
2. Prepare reference electrode by filling outer electrolyte reservoir with HI 7072.
3. Place sensor and reference electrodes into electrode holder and connect cable connectors to meter.

HI 4102

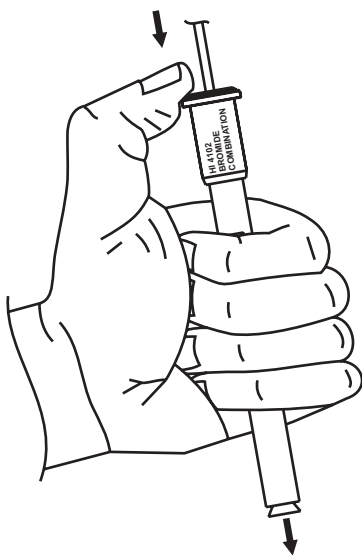
1. Unwrap plastic film seal found over ceramic junction on inner stem and discard. This is only used for shipping and long term storage.
2. Rinse inner stem with deionized water making certain to wet the o-ring found on the inner stem.



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

- Connect sensors to pH/mV/ISE meter
- Place meter in mV mode.
- Place 100 mL of DIW into a beaker with stir bar.
- Place 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 ± 4 mV.

X. Corrective action

- Verify protective cap has been removed (HI 4002).
- Verify plastic film has been removed from inner stem (HI 4102).
- 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 bromide or <80 ppm 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 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

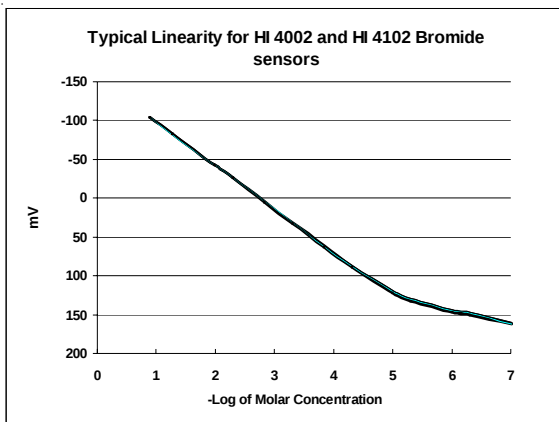
This method is a simple procedure for measuring many samples. A direct reading ISE meter (HI 4222 or equivalent) determines concentration of the unknown by a direct reading after calibrating the meter with the standards. The meter is calibrated with two or more freshly made standards that are in the linear measurement range of the unknowns. More calibration standards are required in non-linear regions. Unknowns are read directly. At very low levels of bromide, special precautions must be employed for reproducible measurements. Water used for standards must be bromide free and sensors and glassware must be rinsed repeatedly with this water to prevent carry over. In the region where the electrode response appears curved, more calibration points are needed, and calibration will need to be repeated more frequently.

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.
Two mL HI 4000-00 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 DIW and dap dry between samples.



XII. Other Measurement Techniques

Known Addition (for Br⁻)

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.

Example: Bromide ion determination with known addition.

1. A 50 mL sample of unknown (V_{sample}) is placed in a clean plastic beaker with a bromide sensor. Add 2 mL of HI 4000-00 ISA (V_{ISA}), mix well and record the stable mV value (mV 1).
2. 5 mL (V_{std}) of 10^{-1}M (C_{std}) standard is added to the beaker and the mV value decreases. The unknown bromide concentration in the original sample (C_{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 bromide electrode may be used as an indicator to follow the progress of a bromide 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 bromide concentration while small additions of silver nitrate titrant are added. The silver reacts with the bromide ions forming a precipitate of silver bromide. At the stoichiometric end point, a large change in mV occurs. Measurements may be automated by use of the Hanna Titrator HI 901 or titrated manually.

XIII. pH

The HI 4102 and HI 4002 electrodes may be used in solutions with pH values between 2 and 12.5. Samples that fall beyond this range should be adjusted.

XIV. Storage and Care of the HI 4002 and HI 4102 sensors

The HI 4002 sensor can be stored in very dilute standards ($< 10^{-3}M$) for short periods of time and should be stored dry with the protective cap on when not in use.

The model HI 4102 combination electrode can be left in dilute standards ($< 10^{-3} M$) 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 Br⁻

Multiply by

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

7.99×10^4

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

1.252×10^{-5}