

Instruction Manual

HI 4105

Carbon Dioxide

Ion

Selective Electrode



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HI 4105 Carbon Dioxide Electrode

I. Introduction:

The Hanna HI 4105 Carbon Dioxide gas sensing electrode is a combination electrode designed for the measurement of Carbon Dioxide in aqueous solutions such as water, soft drinks or wine, samples. Carbonate and Bicarbonate ions are also measured by conversion to Carbon Dioxide gas upon ISA addition.

II. Specifications

Type:	CO ₂ gas sensing electrode with glass pH internal, Ag/ AgCl reference and gas permeable membrane.
Species detected:	CO ₃ ²⁻ , HCO ₃ ⁻ , CO ₂
CO ₂ Measurement Range:	0.02 M to 4 x 10 ⁻⁴ M 880 to 17.6 ppm
Interfering ions:	SO ₂ /SO ₃ ²⁻ , H ₂ S/S ²⁻
Operating Temperature:	0 to 40°C
Operating pH:	4-5 pH
Dimensions:	12 mm (OD) X 120 mm (insertion) 0.47" x 4.72"
Wetted materials:	Delrin®, body and cap with PTFE membrane
Connection:	BNC

III. Theory of Operation:

The Carbon Dioxide electrode is a complete potentiometric cell that contains both a silver/silver chloride (Ag/AgCl) reference and a pH measurement element. These elements are housed within a thermoplastic body in a chloride ion-containing electrolyte, and are isolated from the sample by a PTFE membrane.

ISA addition changes the pH of the sample to approximately 4.7 pH and Bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions in the sample are converted to carbon dioxide (CO_2). The CO_2 in the sample solution diffuses through the PTFE membrane where it dissolves into the thin film of fill solution found between the membrane and the internal pH membrane. Here it converts back into bicarbonate and hydrogen ions. The pH changes proportionally with the concentration of dissolved gas in the sample solution. Diffusion of CO_2 continues until the partial pressures of the gas in the sample and thin film are equal.

The Nernst expression for an Carbon Dioxide sensor is expressed in the equation below. Note that the potential is a function of the Carbon Dioxide gas, which in turn is related to the hydrogen ion concentration. The glass internal, Ag/AgCl reference, equilibrium constant and Henry's law constant are rolled into the E' and E° terms. The Nernst equation for the sensor becomes the equation noted below:

$$E = E' + 2.3RT/nF \log [\text{CO}_2] = E^\circ + 0.059 \log [\text{H}^+]$$

E = observed potential

E' = Reference and fixed internal voltages

R = gas constant (8.314 J/K Mol)

n = Charge on ion (equivalents/mol)

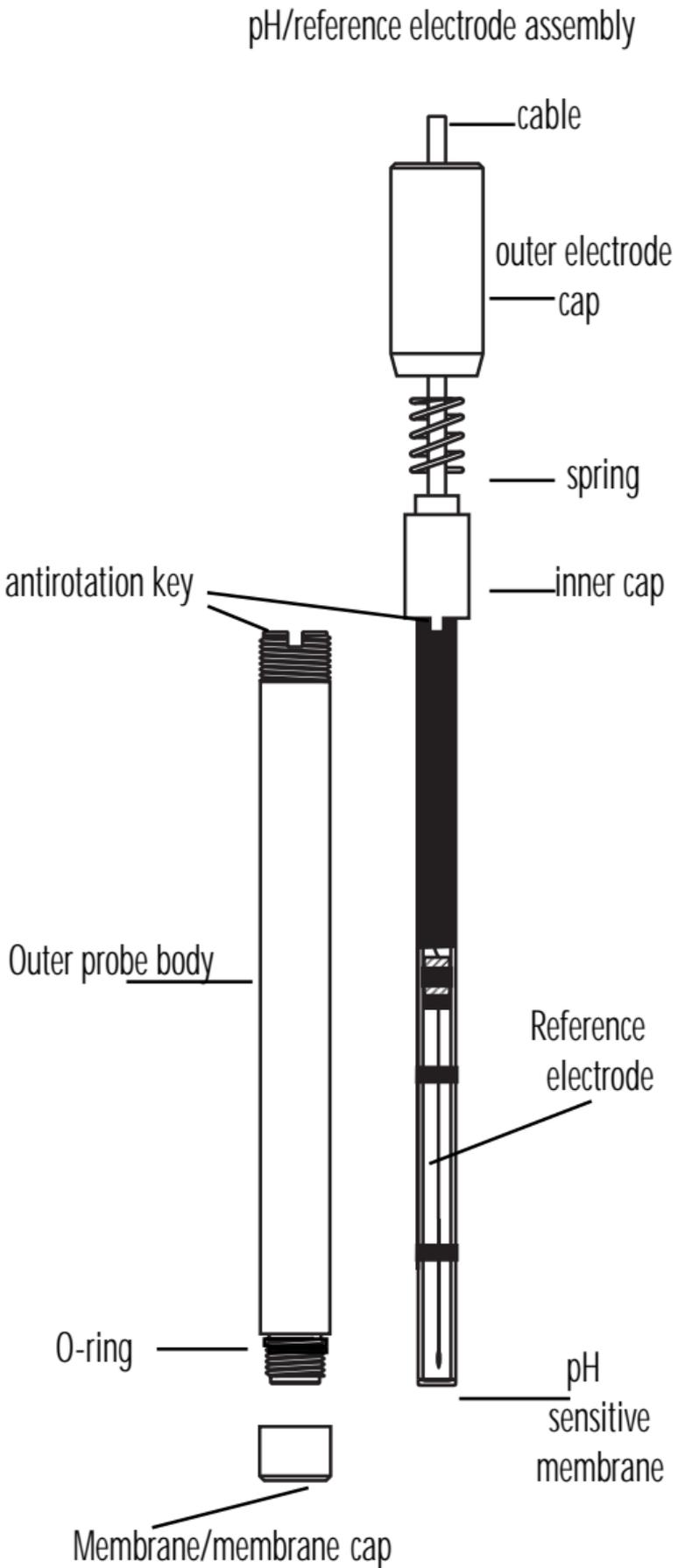
T = absolute temperature in K

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

The mV should increase in a Nernstian manner as the carbon dioxide partial pressure increases in the sample.

IV. Design Elements

The Hanna HI 4105 Carbon Dioxide gas sensor has 3 main parts. These are the membrane/membrane cap, outer probe body with antirotation key and the pH/reference assembly which includes the outer electrode cap, spring, inner cap and pH/reference electrode assembly.



V. Equipment Required:

- 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 meter is not available).
- Hanna HI 180 magnetic stirrer or equivalent with stirring bars. (Note: Isolate beakers from stirrer motor heat by placing insulating material such as foam or cork between them).
- Hanna HI 4000-71 gas sensor test vessel or Hanna HI 76404 electrode holder or equivalent with Beakers or other suitable measurement vessel with plastic sealing film or wrap.

VI. Solutions Required for Calibration:

Ionic Strength Adjuster (ISA), 500 mL: HI 4005-00

Hanna 0.1 M standard, 500 mL: HI 4005-01

Hanna 1000 ppm CO₂ standard, 500 mL: HI 4005-03*

*Please Note: This calibration standards is ppm as CaCO₃

See Section XVII for additional solutions and accessories used for maintenance.

Using volumetric pipettes and glassware prepare serial dilutions of the standard. Select concentrations that will approximately bracket the concentration of the samples to be measured. Standards with concentrations less than 10⁻³M should be prepared fresh daily. Store solution in a tightly sealed bottle without ISA added. 10 mL of HI 4005-00 ISA should be added to each 100 mL sample of standard and samples just prior to measurement. ISA adjusts the pH of the sample or standard to about pH 4.7 thus converting carbonate and bicarbonate ion to carbon dioxide. It also provides samples and standards a constant ionic strength background that stabilizes the solutions activity coefficient and permits concentration to be measured directly.

VII. General Guidelines

- Calibration standards and sample solutions should have the same ionic strength. ISA should be added to both samples and standards immediately before taking measurements.
- Calibration standards and sample solutions should be stirred at the same rate using identical sized stir bars. Stir thoroughly and continuously.
- Calibration standards and sample solutions should be at the same temperature. Thermally insulate solution vessel from magnetic stirrer with cork or other insulating medium.
- Wait until sensor value has stabilized before taking reading (at least 5 minutes when going from more dilute to more concentrated samples, longer when the order is reversed).
- Surface coating on the PTFE membrane will effect the response. Inspect sensor before using. Wash off with a jet of deionized water or mild detergent to remove film.
- Replace PTFE membrane if damage is evident or a droplet of internal electrolyte is seen.
- Rinse electrode with distilled or deionized water between samples and dab dry with lab wipe or other soft disposable absorbent toweling.
- Check calibration every 1-2 hours. Recalibrate if necessary.
- Position sensors at an angle of approximately 20° to 30° from verticle to reduce possibility of trapping gas bubbles on on the membrane cap. Gas bubbles also form from solution out-gassing due to temperature change. Gently tap body of sensor to dislodge them.
- Close container with plastic wrap or use HI 4000-71 gas sensor test vessel to prevent gas from leaving.
- If electrode was left out in air for a prolonged period, gently pulling cable will permit an exchange of fill solution at the membrane surface. Re-Calibration is required.

VIII. Inner Electrode Check

Prior to assembling the electrode for the **first time** or subsequently reactivating it after extended periods of dry storage, the inner electrode assembly should be hydrated and then tested as a pH electrode.

Prepare pH test solutions HI 4000-47-4 and HI 4000-47-7 by mixing and dissolving each buffer packet in separate containers with 50 mL deionized water. These pH solutions contain chloride ions and pH buffers that are used to verify the inner electrode (pH internal) is operational. See Section XVII for replacement accessories and maintenance items.

For a new sensor:

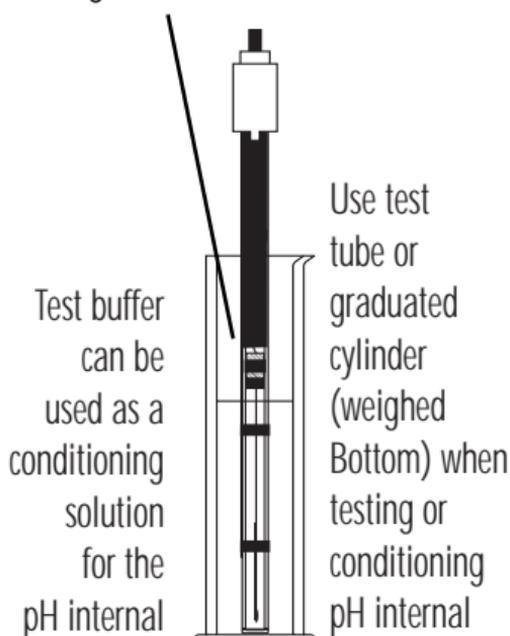
Remove the protective shipping cap from the glass inner electrode.



For existing sensor:

Unscrew the upper cap on the top of the electrode and carefully withdraw the internal pH/reference assembly.

For stable readings, glass should be covered to the bottom of the long black band.



- If sensor has been stored or shipped dry, it should be “conditioned” by soaking the pH/reference assembly 1 hour or more in one of the pH test solutions.
- Avoid touching the pH glass with your fingers.
- Attention: The pH/reference assembly is fragile! Support the upper portion of the internal cell while immersing the glass and reference assembly. A tall narrow container with weighted bottom is best. The pH test solution should cover the bottom of the large black band.

Test: Connect the BNC connector on the electrode cable to a pH/mV (mV or ORP mode) meter. Carefully immerse the sensor assembly into one of the buffers. When the measurement stabilizes record the mV generated. Rinse sensor tip in deionized water and dab dry between buffers to prevent solution carry-over. Do not rub the glass. Take a measurement in the second buffer and record mV. Pay attention to minus sign if present.

Calculate the difference in mV between the two solutions.

Example of typical values:

HI 4000-47-7 -90.2 mV

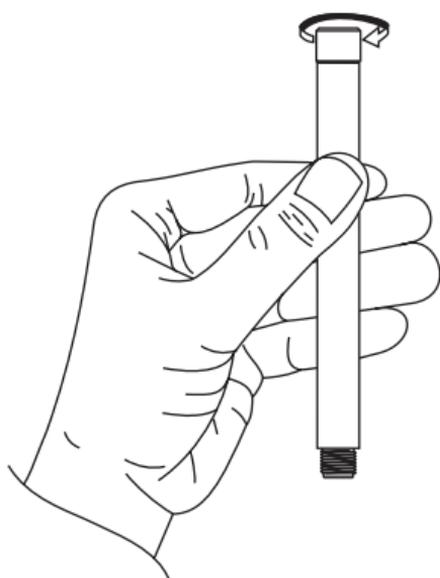
HI 4000-47-4 80.66 mV

Difference $170.8 \text{ mV} = 80.6 - (-90.2)$

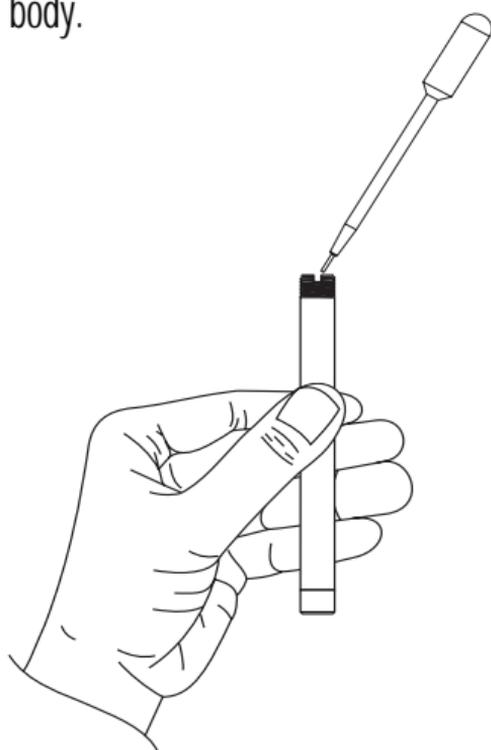
A calculated value equal or greater than 160 mV is acceptable for ambient temperatures between 20° and 25°C.

IX. Electrode Preparation

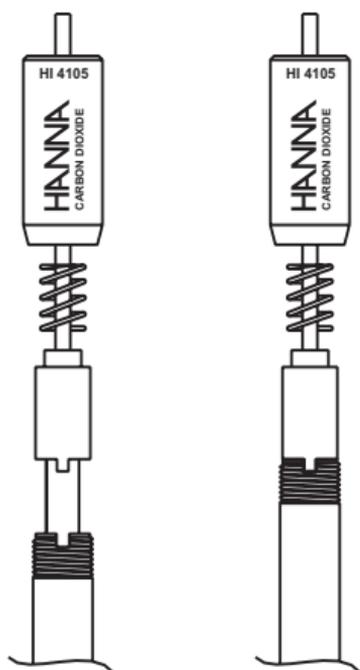
- 1) Remove glass internal from sensor body and perform inner electrode check. (See section VIII).
- 2) The HI 4105 sensor comes with three easily replaceable membrane caps (two which are spares). Remove a cap from membrane box and screw on to lower threads of outer probe body, compressing the o-ring seal. Avoid touching working area of membrane with your fingers as skin oil will change the membrane properties.



- 3.) Using dropper provided, add about 2 mL of carbon dioxide internal fill solution HI 4005-40 into outer probe body.



- 4) Insert and position the inner glass/reference assembly into the outer body so that the anti-rotation key sits in the cut out on the outer probe body.



- 5) Holding the electrode upright, slide spring and electrode cap down cable and screw cap on outer body until fully engaged. Do not invert electrode. Do not overtighten.
- 6) Install assembled electrode in gas sensor test vessel or in electrode holder and connect cable connector to pH/mV meter.

X. Quick Check of Electrode Slope

- Connect BNC (connector) to pH/mV/ISE meter.
- Place meter in mV mode.
- Place 100 mL of deionized water into a vessel with stir bar. Add 10 mL of ISA Hanna HI 4005-00.
- Place sensor into prepared sample.
- Add 1 mL of 1000 ppm or 0.1 M Carbon dioxide standard to beaker and stir sample. Wait approximately 5 minutes. Record the mV value when stable.
- Add an additional 10 mL of standard to the solution. Record the mV when reading has stabilized (approximately 5 minutes). 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 54 ± 4 mV at ambient temperatures between 20 and 25°C.

XI. Corrective action

- Verify standard has been properly added.
- Verify ISA has been added in the correct ratio to the standard (1 part ISA to 10 parts sample or standard).
- Verify that the upper cap has been screwed in all the way.
- Verify electrode is connected properly to meter and the meter is powered.
- Verify membrane cap is tightened securely to probe body.
- Examine the membrane for discoloration or perforations or for internal fill solution that might have leaked through the PTFE membrane. Replace membrane cap if damaged.

If drift is seen:

- Verify electrode and standards are at same temperature.
- Verify electrode has adequate fill solution.
- Verify electrode was not left in air for prolonged period.

XII. Sample Handling

- For optimum results, allow samples and standards and the HI 4105 electrode to reach the same temperature.
- As CO_2 is volatile, measure samples immediately after collection.
- If sample must be stored: Completely fill collection bottle with dilute samples and tightly cap container to prevent carbon dioxide loss or contamination from other sources.
- If sample must be stored: For acetic samples, add sodium hydroxide (10N) to raise pH to 8-9 for storage. Tightly close collection bottle.
- If sample must be stored: keep sample at a lower temperature than it was collected at until time of measurement.
- Add Hanna HI 4005-00 ISA just prior to measurement to adjust standards and samples to a pH between 4.2-5.2 for measurement. ISA must mix thoroughly with solutions and time allowed to convert carbonate and bicarbonate species to CO_2 (dissolved).
- Covering sample and standards after adding ISA will minimize carbon dioxide loss from the solution.
- Calibration standards and samples must be the same ionic strength. The concentration for all dissolved species in a sample should not exceed 1M. Samples that exceed this should be diluted with CO_2 free deionized water. Do not reduce CO_2 below 10^{-4}M . Multiply the final result by the corresponding dilution factor.

XIII. Direct Calibration and Measurement

The direct measurement method is best used in the linear working regions of the sensor. (See figure for typical sensor response) and can be used when 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 measurement range of the unknowns. HI 4005-00 ISA is added prior to measurement and the solution is stirred thoroughly and continuously. Covering the vessel to prevent gas loss is advised.

A pH/mV meter in mV mode and semi-log graph paper may also be used. Two or freshly prepared standards that are in the measurement range of the unknowns (with ISA added), are measured in mV mode on the meter. These standards are plotted on semilog graph paper and their 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.

For both direct reading and mV conversion, ISA is added prior to measurement, the solution stirred thoroughly and continuously and the vessel should be covered to prevent gas loss.

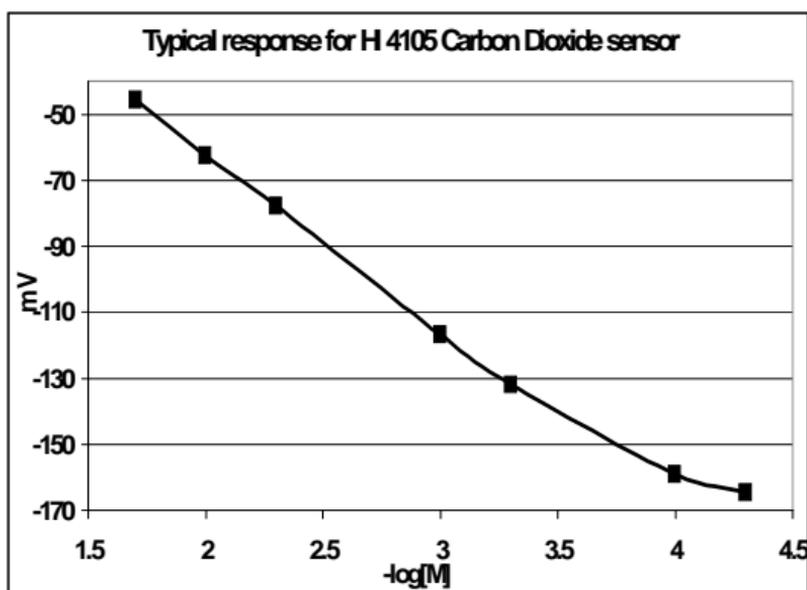
In the lower concentration ranges the electrode calibration becomes less linear, many more calibration points are needed, and calibration will need to be repeated more frequently. Known addition method may also be used in these regions provided the actual slope of the sensor has been determined.

Direct Measurement Procedure

1. Follow section IX to prepare sensor.
2. Follow section VI to prepare standards and solutions.
 - Standards should bracket the measurement range of interest and differ from each other by a factor of 10 in the linear regions.

- Standards and solutions should be at the same temperature. 10 mL of ISA is added to each 100 mL of sample and standard.
 - Protect these solutions from loss of dissolved gas by covering and using promptly.
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 (approximately 5 minutes).
 5. To prevent carry over and contamination of samples, rinse sensors with deionized water and dab dry between samples.
 6. Between measurements suspend sensor tip in a small sample of CO₂ Conditioning solution; HI 4005-45. Rinse body with deionized water and dab dry before placing in next sample.
 7. Check HI 4105 electrode calibration every 2 hours by verification of at least one calibration point.

Typical calibration curve for HI 4105 Carbon Dioxide ISE



XIV. Other Measurement Techniques

Known Addition

An unknown concentration of carbon dioxide can be determined by adding a known amount (volume and concentration) of carbon dioxide standard to a known volume of the sample. This technique is extremely useful for carbon dioxide because changes in the sensor calibration are corrected for continuously because, the standard and sample are measured within minutes of one another. The technique can use an ideal sensor slope, but actual slopes at the temperature of measurement should be determined and used if possible. This will improve accuracy.

1. The volume of the unknown sample (V_{Sample}) is measured accurately and placed into the closed sample vessel. The sensor is secured in the vessel and then the vessel is placed on a stirrer.
2. ISA is added at 1 part per 10 parts sample.
3. When the measurement is stable the mV value is noted.
4. A known amount, volume (V_{Standard}) and concentration (C_{Standard}), of CO_2 standard is then added to the sample. mV values are again noted when the measurement is stable.
5. The mV change is then calculated (ΔE).
6. Using the measured and calculated values, the sample concentration (C_{Sample}) can be determined.

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

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

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

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

Note:

This method is preprogrammed in the Hanna HI 4222pH/ISE/mV meter, which simplifies the method greatly and permits repeated determinations easily.

Example:

Carbon Dioxide determination with known addition:

1. A 50 mL sample of unknown (V_{SAMPLE}) is placed in a clean vessel with an electrode. 5 mL of ISA is added to the sample. The sample is covered and permitted to mix thoroughly and continuously. The mV is then recorded when the sensor has stabilized.
2. 5 mL (V_{STANDARD}) of 0.1 M (C_{STANDARD}) standard is then added to the vessel and is permitted to mix. The mV value increases as the concentration increases. (Note: for other concentration samples, add a known volume and concentration of standard to produce a 30 mV change or greater.
3. The unknown carbon dioxide concentration in the original sample (C_{SAMPLE}) can then be determined by using the equation provided.

XV. Storage and Care of the HI 4105 sensor

The HI 4105 sensor can be stored assembled and ready to use in HI 4005-45 Conditioning solution overnight or between measurements. After overnight storage, gently pull on the cable to compress the spring mechanism thus permitting electrolyte to exchange from the bulk to the thin film between the membrane and glass. Calibration is required after doing this.

For longer term storage (over a week), disassemble the sensor completely and rinse off the internal pH/reference assembly, the outer body and the membrane cap. It is advised the membrane cap be discarded to prevent possible problems associated with reuse. Cover the glass tip with the protective shipping cap and store parts securely in the original shipping box. When reassembling the sensor follow section IX.

XVI. Conversion Tables

For CO₂

Multiply by

Moles/L (M) CO₂ to ppm CO₂ (mg/L)

4.4×10^4

ppm CO₂ (mg/L) to M (Moles/L)

2.273×10^{-3}

For CaCO₃ (ppm)

Multiply by

Moles/L (M) CO₂ to ppm CaCO₃ (mg/L)

1.00×10^5

XVII. HI 4105 Accessories and Replacement Parts

For Calibration :

Code

HI 4005-00	Ionic Strength Adjuster (500 mL)
HI 4005-01	Hanna 0.1 M CO ₂ Standard (500 mL)
HI 4005-03*	Hanna 1000 ppm CO ₂ Standard (500 mL)

*Please Note: This calibration standard is ppm as CaCO₃

For Maintenance:

HI 4005-40	Hanna Carbon Dioxide Fill Solution (4 X 30 mL)
HI 4005-45	Hanna Carbon Dioxide Conditioning Solution (500 mL)
HI 4000-47	Bulk package of 10 each HI 4000-47-4 and HI 4000-47-7 Buffer Packets
HI 4005-53	Replacement Membranes Caps (3 Membrane Caps)
HI 4000-54	Replacement pH/reference Electrode Assembly for CO ₂
HI 4000-71	Gas Sensor test vessel
HI 740155P	Capillary Pipettes (20 piece)

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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