

**PHOENIX ELECTRODE COMPANY  
CARBON DIOXIDE  
GAS-SENSING ELECTRODE  
INSTRUCTION MANUAL**

**GENERAL INSTRUCTIONS**

**Introduction**

The pHoenix Carbon Dioxide Gas-Sensing Electrode is used to quickly, simply, accurately, and economically measure carbon dioxide, carbonate, and bicarbonate in aqueous solutions. With a flow-through cap, the electrode can be used in flow-through applications.

**Required Equipment**

1. A pH/mV meter or an ion meter, either line operated or portable.
2. Semi-logarithmic 4-cycle graph paper for preparing calibration curves when using the meter in the mV mode.
3. A magnetic stirrer.
4. The pHoenix Carbon Dioxide Electrode, Cat. No. C021501.

**Required Solutions**

1. Deionized or distilled water for solution preparation.
2. pHoenix Carbon Dioxide Standard, 0.1M NaHCO<sub>3</sub>, Cat. No. C02AS01. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 8.40 grams of reagent-grade NaHCO<sub>3</sub>. Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled wafer, cap, and upend several times to mix the solution.
3. pHoenix Carbon Dioxide Standard, 1000 ppm NaHCO<sub>3</sub> as CO<sub>2</sub>, Cat. No. C02AS02. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 1.91 grams of reagent-grade NaHCO<sub>3</sub>. Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend several times to mix the solution.
4. pHoenix Carbon Dioxide Standard, 100 ppm NaHCO<sub>3</sub> as CaCO<sub>3</sub>, Cat. No. C02AS03. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 0.084 grams of reagent-grade

$\text{NaHCO}_3$ . Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend several times to mix the solution.

5. pHoenix Carbon Dioxide Buffer Solution, Cat. No. C02IS01. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water, add 294 grams of  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$  (sodium citrate dihydrate). Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water. Stir the solution and adjust the pH of the solution to 4.5 with concentrated HCl. This buffer is used to adjust the pH of the solution to the operating range of the electrode. To each 100 ml of sample and standard solution, add 10 ml of carbon dioxide buffer.
6. pHoenix Sodium Chloride Solution, 0.1M NaCl, Cat. No. NA0AS01. This solution is used to store the electrode. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water, add 5.8 grams reagent-grade sodium chloride. Swirl the flask to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.
7. pHoenix Carbon Dioxide Electrode Filling Solution, Cat. No. C02IF01.

## GENERAL PREPARATION

### **Electrode Preparation**

This electrode is shipped dry. Before using, unscrew the large cap (See Figure 5), and remove the inner glass electrode from the outer body. Fill the outer body with 2 to 3 ml of internal filling solution. Place inner glass electrode into the outer body, and screw on the large cap until finger tight. Place the assembled electrode in an electrode holder with a  $20^\circ$  angle from the vertical to avoid trapping air bubbles at the bottom of the electrode.

### **Checking Membrane**

A small hole of any size on the membrane or breakage of the membrane causes failure of the electrode. It is recommended to check the membrane on every newly assembled electrode.

1. Connect a newly assembled electrode to a pH/mV meter.
2. Lower the electrode tip in distilled water.

3. Record the reading after stirring the distilled water for about 15 minutes.
4. Add proper buffer solution (see Required Solutions) to the distilled water. A drastic change in the reading in a positive direction indicates damage of the membrane.

### **Changing the Membrane**

Unscrew the small cap from the outer body and remove the old membrane cartridge from the small cap. Insert the new membrane cartridge into place, and re-assemble the electrode. (See Figure 4.)

### **Connecting the Electrode to the Meter**

Connect the electrode to the meter according to the meter manufacturer's instructions. No external reference electrode is required. To prevent air entrapment, mount the electrode at a 20° angle from the vertical.

### **Electrode Slope Check (with pH/mV meter) (check electrodes each day)**

1. To a clean, dry, 150 ml beaker, add 90 ml of distilled water and 10 ml of carbon dioxide buffer. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the millivolt mode, lower the electrode tip into the solution. Remove air bubbles by redipping probe.
2. Using a pipet, add 1 ml of 0.1M or 1000 ppm standard into the solution. When the reading has stabilized, record the mV value.
3. Using a pipet, add 10 ml of the same CO<sub>2</sub> standard used above to the beaker. When the reading has stabilized, record the mV value.
4. Determine the difference between the two readings. The electrode is operating correctly if a difference of  $56 \pm 3$  mV is found, assuming the solution temperature is between 20° and 25°C. See the TROUBLESHOOTING section, if the change in potential is not within this range.

Slope is defined as the change in potential observed when the concentration changes by a factor of 10.

Electrode Slope Check (with ion meter)  
(check electrodes each **day**)

1. Prepare standard carbon dioxide solutions whose concentrations vary by tenfold. Use either the 0.1M or 1000 ppm carbon dioxide standard. Use the serial dilution method for this preparation.
2. To a 150 ml beaker, add 100 ml of the lower value standard and 1 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution. Assure that the meter is in the concentration mode.
3. Adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions.
4. Rinse the electrodes with distilled water and blot dry.
5. To another 150 ml beaker, add 100 ml of the higher value standard and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution.
6. Adjust the meter to the concentration of the standard and fix the value in the memory.
7. Read the electrode slope according to the meter manufacturer's instructions. Correct electrode operation is indicated by a slope of 90-100%. See the **TROUBLESHOOTING** section if the slope is not within this range.

**MEASUREMENT**

**Measuring Hints**

Samples should be measured immediately after collection. Samples should be stored according to the directions given in **Sample Storage** if immediate measurement is not possible.

The ratio of surface area to volume in the beaker should be minimized. Beakers containing the samples or the standard should be kept covered between measurements.

Carbon dioxide buffer should be added just before measurement.

All samples and standards should be at the same temperature for precise measurement. A difference of 1°C in temperature will result in approximately a 2% error. All samples must be aqueous.

Always rinse the electrode with distilled water and blot dry between measurements. Use a clean, dry tissue to prevent cross-contamination.

Constant but not violent, stirring is necessary for accurate measurement. Magnetic stirrers can generate sufficient heat to change the solution temperature. To counteract this effect, place a piece of insulating material, such as gauze or Styrofoam, between the stirrer and the beaker.

Always check to see that the membrane is free from air bubbles after immersion into standard or sample.

### **sample Storage**

Samples should be measured immediately after preparation or collection, if possible. Wait only long enough for temperature equilibration between the sample and the electrode. At 25°C, in an open 150 ml beaker, carbon dioxide diffuses out of an acidic solution at a rate of about 3% per minute with stirring and at a rate of about 0.5% per minute without stirring. The loss of CO<sub>2</sub> increases with increasing temperature.

If the samples cannot be measured immediately, add 10M NaOH to make them slightly alkaline (pH 8-9) and store them in tightly capped vessels to prevent infusion of CO<sub>2</sub> from the air. The amount of 10M NaOH needed to adjust the pH to the alkaline range will depend on the sample's buffering capacity and the initial pH of the sample. If the samples contain less than 100 ppm CO<sub>2</sub>, collect in a stoppered glass bottle, filling completely and capping tightly to prevent CO<sub>2</sub> from escaping. Do not add NaOH, since carbonate is usually present in the base as a contaminant. If the sample contains more than 100 ppm CO<sub>2</sub>, is slightly acidic and un-buffered, adding 1 ml of 10M NaOH per 100 ml of sample will suffice. Prior to measurement, acidify these stored samples with carbon dioxide buffer.

### **Sample Requirements**

Carbon dioxide buffer must be added to standards and samples before measurement. When the buffer solution is added, all standards and samples should be in the range of pH 4.8 to 5.2. In this range, all bicarbonate and carbonate species are converted to carbon dioxide and all interferences are minimized. Highly basic, highly acidic, or buffered samples must be adjusted to pH 4.8 to 5.2 before the carbon dioxide buffer is added, since the buffering capacity of the acid buffer is limited.

Adding the buffer solution adjusts the total level of dissolved species in solution to 0.4M. The sample should be diluted before

measurement if the total level of dissolved species is greater than 1M after the addition of the carbon dioxide buffer. For a further explanation, see the section entitled **Effect of Dissolved Species**.

### Units of Measurement

Measurement of carbon dioxide can be expressed in units of moles/liter, ppm carbon dioxide, ppm calcium carbonate, or other convenient concentration unit. Table 1 lists conversion units.

TABLE 1: Concentration Unit Conversion Factors

| <u>moles/liter</u> | <u>ppm CO<sub>2</sub></u> | <u>ppm CaCO<sub>3</sub></u> |
|--------------------|---------------------------|-----------------------------|
| 10 <sup>-2</sup>   | 440.0                     | 1000.0                      |
| 10 <sup>-3</sup>   | 44.0                      | 100.0                       |
| 10 <sup>-4</sup>   | 4.4                       | 10.0                        |

### MEASUREMENT PROCEDURE

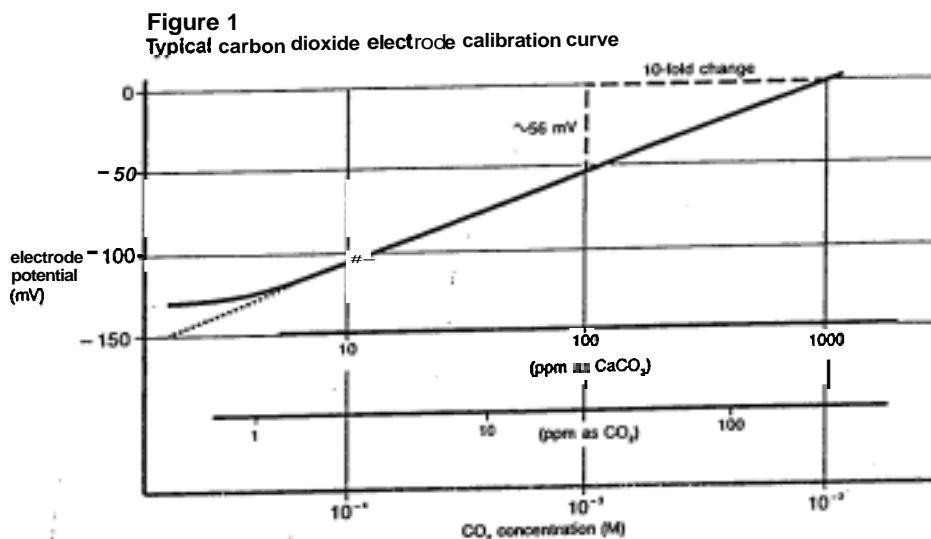
#### Direct Measurement

Direct measurement is a simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The ionic strength of samples and standards should be made the same by adjustment with ISA for all carbon dioxide solutions. The temperature of both sample solutions and standard solutions should be the same.

#### Direct Measurement of Carbon Dioxide (using a pH/mV meter)

1. By serial dilution, prepare three standard solutions from the 0.1M or 1000 ppm stock standard. The resultant concentrations should be 10<sup>-2</sup>M, 10<sup>-3</sup>M, and 10<sup>-4</sup>M or 1000 ppm, 100 ppm, and 10 ppm.
2. Place 100 ml of the 10<sup>-4</sup>M (10 ppm) standard into a 150 ml beaker on the magnetic stirrer, add 10 ml of carbon dioxide buffer, and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution. After the reading has stabilized, record the mV reading.
3. Place 100 ml of the 10<sup>-3</sup>M (100 ppm) standard into a 150 ml beaker on the magnetic stirrer, add 10 ml of carbon dioxide buffer, and begin stirring at a constant rate. After rinsing the electrode with distilled water, blot dry, and immerse the tip in the solution. After the reading has stabilized, record the mV value.

4. Place 100 ml of the  $10^{-2}M$  (1000 ppm) standard into a 150 ml beaker on the magnetic stirrer, add 10 ml of carbon dioxide buffer, and begin stirring at a constant rate. After rinsing the electrode with distilled water, blot dry, and immerse the tip in the solution. After the reading has stabilized record the mV value.
5. Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis). A typical calibration curve appears in Figure 1.



A calibration curve is constructed on semi-logarithmic paper when using the pH/mV meter in the millivolt mode. The measured electrode potential in mV (linear axis) is plotted against the standard concentration (log axis). In the linear region of the curve, only three standards are necessary to determine a calibration curve. In the non-linear region, additional points must be measured. The direct measurement procedures given are for the linear portion of the curve.

6. To a clean, dry, 150 ml beaker add 100 ml of sample and add 10 ml of carbon dioxide buffer. Place the beaker on the magnetic stirrer and begin stirring. Rinse the electrode with distilled water, blot dry, and lower the tip in the solution. When the reading has stabilized record the mV value. Using the calibration curve, determine the sample concentration.
7. The calibration should be checked every 1-2 hours. Assuming no change in ambient temperature, place the

electrode tips in the mid-range standard. After the reading has stabilized, compare it to the original reading recorded in Step 3 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of Steps 2-5 above. A new calibration curve should be prepared daily.

#### **Direct Measurement of Carbon Dioxide (using an ion meter)**

1. By serial dilution of the 0.1M or the 1000 ppm standards, prepare two standards whose concentration is near the expected sample concentration. Add 10 ml of carbon dioxide buffer to each 100 ml of standard. When calibrating, assume that the added buffer has no effect on the standard concentration.
2. Place the more dilute standard on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode.
3. Lower the electrode tip into the solution.
4. Adjust the meter to the concentration of the CO<sub>2</sub> standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
5. Rinse the electrode with distilled water and blot dry.
6. Place the more concentrated standard on the magnetic stirrer and begin stirring at a constant rate.
7. Lower the electrode tip into the solution.
8. Adjust the meter to the concentration of the carbon dioxide standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
9. After rinsing the electrode and blotting dry, place the electrode tip into 100 ml of the sample and 10 ml of carbon dioxide buffer. After stabilization, read the concentration directly from the meter display.
10. The calibration should be checked every 2 hours. Assuming no change in ambient temperature, place the electrode tip in the first carbon dioxide standard. After the reading has stabilized, compare it to the original reading in Step 4 above. A reading differing by more than 0.5 mV or a change in ambient temperature will necessitate the repetition of Step 2-8 above. The meter should be re-calibrated daily.



## ELECTRODE CHARACTERISTICS

### Reproducibility

Electrode measurements reproducible to +2% can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuation, drift, and noise limit reproducibility. Reproducibility is independent of concentration within the electrode's operating range.

### Interferences

Certain volatile weak acids are potential electrode interferences. Concentrations of these interfering species that cause a 10% error at  $10^{-3}M$   $CO_2$  (100 ppm  $CaCO_3$  or 44 ppm  $CO_2$ ), at pH 4 and 5, are listed in Table 2.

TABLE 2: Interference Levels - 10% Error at  $10^{-3}M$   $CO_2$ ,

| <u>Interferences</u>  | <u>pH 4</u>                        |                                     |
|---|------------------------------------|-------------------------------------|
| HCOOH<br>(formic acid)  | $7.5 \times 10^{-3}M$<br>(345 ppm) | $2.0 \times 10^{-2}M$<br>(1840 ppm) |
| CH <sub>3</sub> COOH<br>(acetic acid)                                 | $3.6 \times 10^{-3}M$<br>(216 ppm) | $6.2 \times 10^{-3}M$<br>(372 ppm)  |
| HSO <sub>3</sub> <sup>-</sup> (SO <sub>2</sub> )<br>(sulfur dioxide)  | $7.5 \times 10^{-4}M$<br>(48 ppm)  | $5.0 \times 10^{-3}M$<br>(320 ppm)  |
| NO <sub>2</sub> <sup>-</sup> (NO <sub>2</sub> )<br>(nitrogen dioxide) | $5.3 \times 10^{-4}M$<br>(24 ppm)  | $3.5 \times 10^{-3}M$<br>(160 ppm)  |

### Effect of Dissolved Species

One common substance that is a potential electrode interference is water vapor. The concentration of the internal filling solution under the membrane is changed when water, in the form of water vapor, moves across the electrode membrane. These changes will be seen as electrode drift. If the total level of dissolved species in solution - the osmotic strength - is approximately **equal** to that of the internal filling solution and the sample and electrode temperatures are the same, water vapor transport is not a problem.

Samples of low osmotic strength are automatically adjusted to the correct level through addition of carbon dioxide buffer. If samples have osmotic strengths greater than 1M, they should be diluted before measurement. However, this dilution should not reduce the carbon dioxide level below  $10^{-4}M$ . If dilution is not possible, for the reason mentioned, the sample can be measured by adjusting the osmotic strength of the electrode filling solution. The total level of dissolved species in the electrode filling solution may be adjusted by adding 0.425 grams of reagent-grade sodium nitrate (NaNO<sub>3</sub>) to 10 ml of electrode filling solution.

## Temperature Influences

Samples and standards should be within  $\pm 1^\circ\text{C}$  of each other, since electrode potentials are influenced by changes in temperature. Because of solubility equilibria on which the electrode depends, the absolute potential of the reference electrode changes slowly with temperature. The slope of the electrode, as indicated by the factor "S" in the Nernst equation, also varies with temperature. Table 3 gives values for the "S" factor in the Nernst equation for the carbon dioxide ion. Gases are expelled from a solution at a faster rate as the temperature increases.

**TABLE 3: Temperature vs. Values for the Electrode Slope**

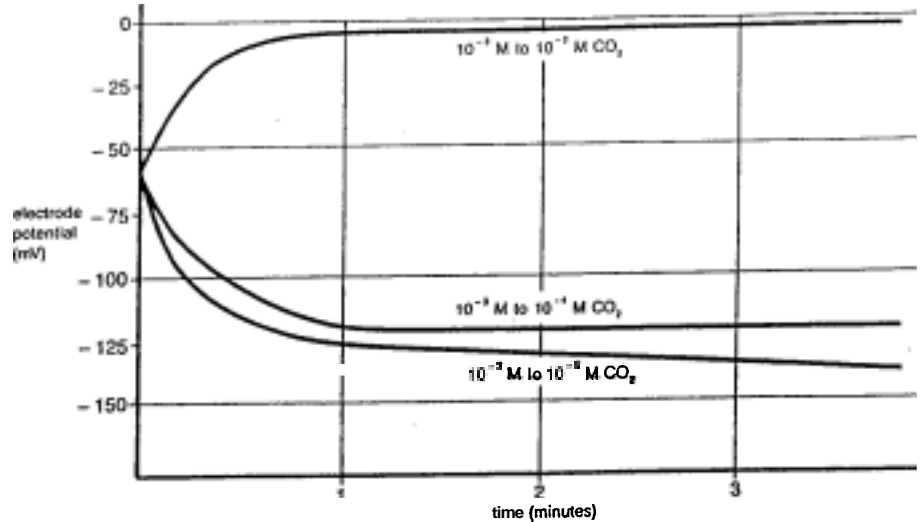
| <u>Temp. (<math>^\circ\text{C}</math>)</u> | <u>"S"</u> |
|--|------------|
| 0  | 54.20      |
| 5  | 55.20      |
| 10   | 56.18      |
| 15   | 57.17      |
| 20   | 58.16      |
| 25   | 59.16      |
| 30   | 60.15      |
| 35   | 61.14      |
| 40   | 62.13      |

## Electrode Response

Plotting the electrode mV potential against the carbon dioxide concentration on semi-logarithmic paper results in a straight line with a slope of about 56 mV per decade over the range  $1 \times 10^{-4}\text{M}$  to  $1 \times 10^{-2}\text{M}$ . (Refer to Figure 1.)

For carbon dioxide concentrations above  $1 \times 10^{-4}\text{M}$ , the electrode exhibits good time response (95% of total mV reading in two minutes or less). Response times are longer below this value and carbon dioxide loss to air may become a source of error. Samples above  $1 \times 10^{-2}\text{M}$  must be diluted before measurement. Figure 2 indicates the time response of the carbon dioxide electrode to changes in the carbon dioxide concentration.

**Figure 2**  
 Typical electrode time response to step changes in CO<sub>2</sub>



### Limits of Detection

The upper limit of detection in pure carbon dioxide solutions is  $1 \times 10^{-2} \text{ M}$ . Carbon dioxide is rapidly lost to the air above a concentration of  $1 \times 10^{-2} \text{ M}$ . Dilution may be used if carbon dioxide concentrations are above  $1 \text{ M}$ . Also dilute samples between  $1 \text{ M}$  and  $10^{-2} \text{ M}$  or calibrate the electrode at 4 or 5 intermediate points.

The lower limit of detection is around  $1 \times 10^{-4} \text{ M}$ . Refer to Figure 1 for a comparison of the theoretical response to the actual response at low levels of carbon dioxide. Carbon dioxide measurements below  $10^{-4} \text{ M CO}_2$  should employ low level procedures.

### pH Effects

The carbon dioxide electrode can be used over the pH range 4.8 to 5.2. It is necessary to adjust the sample pH using the recommended ISA to convert all carbonate and bicarbonate species in solution to carbon dioxide.

### Electrode Life

The carbon dioxide electrode will last six months in normal laboratory use. On-line measurements might shorten operational lifetime to several months. In time, the response time will increase and the calibration slope will decrease to the point calibration is difficult and membrane replacement is required.

### Electrode Storage

If storing the carbon dioxide electrode overnight or over the weekend, immerse the tip of the electrode in the  $0.1 \text{ M NaCl}$  storage solution. For longer periods of time, completely disassemble the electrode, rinse the inner body, the outer body, and the cap with distilled water. After drying, reassemble the electrode without filling solution.

## ELECTRODE THEORY

### **Electrode Operation**

A gas-permeable membrane is used to separate the sample solution from the electrode's internal filling solution in the Phoenix Carbon Dioxide Gas-Sensing Electrode. Dissolved carbon dioxide in the sample solution permeates the membrane until an equilibrium is reached between the partial pressure of the CO<sub>2</sub> in the internal filling solution and the partial pressure of the CO<sub>2</sub> in the sample solution. The partial pressure of carbon dioxide in any given sample will be proportional to the concentration of carbon dioxide.

Diffusion across the membrane affects the level of hydrogen ions in the internal filling solution:



The relationship between the hydrogen ion, the bicarbonate ion, carbon dioxide, and water is given by the equation:

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = \text{constant}$$

The bicarbonate ion level can be considered constant since the internal filling solution contains a high level of sodium bicarbonate:

$$[\text{H}^+] = [\text{CO}_2] \times \text{constant}$$

The electrode sensing element's potential, with respect to the internal reference element, varies in a Nernstian manner with changes in the hydrogen level.

The Nernst equation shows the relationship between the potential of the pH internal element and the hydrogen ion concentration:

$$E = E_0 + S \log [\text{H}^+]$$

where:

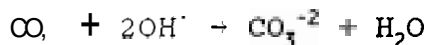
- E = measured electrode potential
- E<sub>0</sub> = reference potential (a constant)
- [H<sup>+</sup>] = hydrogen ion concentration
- S = electrode slope (-56mV/decade)

Because the hydrogen ion concentration is directly related to the carbon dioxide concentration, electrode response to carbon dioxide is also Nernstian:

$$E = E_0 + S \log [\text{CO}_2]$$

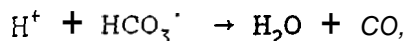
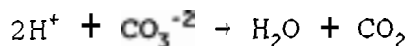
## Carbon Dioxide Chemistry

Carbon dioxide exists as bicarbonate and carbonate in basic solutions:



The solution's pH governs the amount of carbon dioxide present in the form of carbonate and bicarbonate ions. At a pH of 5, essentially all the carbon dioxide in solution is in the  $\text{CO}_2$  form.

The pH is held between 4.8 and 5.2 by the carbon dioxide buffer used in carbon dioxide determinations and converts the carbonate and bicarbonate to the  $\text{CO}_2$  form:



The total amount of carbon dioxide, carbonate, and bicarbonate is then measurable in the solution.

### ELECTRODE APPLICATION

#### Carbon Dioxide Content of Wines and Carbonated Beverages

Wines and carbonated beverages have a high (greater than  $2 \times 10^{-2} \text{M}$  or 880 ppm) carbon dioxide concentration. As a result, samples are measured after dilution. When samples are collected, they must be made basic immediately or  $\text{CO}_2$  will escape into the atmosphere (see Sample Storage section). After diluting the sample, it must be acidified with carbon dioxide buffer. The carbon dioxide concentration is determined by direct measurement (see MEASUREMENT section). Finally, the original carbon dioxide concentration is calculated, taking the dilution factor into account.

The required equipment and solutions are found in Required Equipment and Required Solutions. In addition, pH Adjustment Solution, 10M NaOH, is required.

To measure a sample:

1. Calibrate the meter according to the directions in the MEASUREMENT section.
2. Add enough 10M NaOH solution to adjust the pH of the sample above 10 immediately when the sample container is opened.

3. To a 100 ml volumetric flask, quantitatively transfer 10 ml of the alkaline sample to the flask and fill to the mark with distilled water. After agitating the flask to mix the contents, transfer the solution to a 150 ml beaker.
4. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Add 10 ml of carbon dioxide buffer. Lower the tip of the electrode in the solution. Record the mV reading when stable. Determine the measured concentration from the calibration curve.
5. Using the following formula, determine the carbon dioxide sample concentration:

$$C_s = 10 \times \frac{V_s + V_{\text{NaOH}}}{V_s} \times C_m$$

where:

- $C_s$  = sample concentration
- $V_s$  = sample volume before adding NaOH
- $V_{\text{NaOH}}$  = volume of NaOH added to sample
- $C_m$  = measured concentration

Example: Assume 12 ml of 10M NaOH was added to 360 ml of sample. The total volume would then be 372 ml. Add 10 ml of this mixture to a 100 ml volumetric flask. Dilute to the mark with distilled water. By taking into account the addition of base to the sample and the sample dilution, the measured concentration is related to the actual sample concentration:

$$C_m = 10 \times \frac{360+12}{360} C_s$$

$$C_s = 10.33 C_m$$

### Carbonate Content in Groundwater

Free CO<sub>2</sub>, bicarbonate, and carbonate - the total amount of carbonate - in ground water or seawater, will depend on location, temperature, depth, and pH. Using the measurement procedure in the **MEASUREMENT** section, the carbonate level in groundwater or seawater can be measured. Grab samples taken in the field or ocean can be preserved for laboratory testing by following the procedures given in the **Sample Storage** section.

### Carbonate Measurements in Concentrated Ammonium Hydroxide

Since carbon dioxide is easily absorbed by highly basic solutions, concentrated ammonium hydroxide often contains carbonate as an impurity. By a variation of the direct measurement procedure, the amount of carbonate in concentrated ammonium hydroxide can be

measured. By adding increments of a 10,000 ppm standard to an acid reagent, a calibration curve is constructed, the sample concentration is determined from the calibration curve, taking the dilution factor into account.

The required equipment is found in the **Required** Equipment section. You will also need a 1 ml graduated pipet and a 10 ml pipet.

In addition to the solutions found in the **Required** Solutions section prepare the following:

1. A standard solution of 10,000 ppm carbonate,  $\text{CO}_3^{2-}$ . To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water, add 14.0 grams of reagent-grade sodium bicarbonate ( $\text{NaHCO}_3$ ). Swirl the flask to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution.
2. 3M sulfuric acid reagent., To prepare this solution from your own laboratory stock, add approximately 500 ml of distilled water to a one liter volumetric flask. Using a hood and protective safety equipment and extreme caution, add 167 ml of concentrated sulfuric acid (18M  $\text{H}_2\text{SO}_4$ ) to the flask. Swirl the flask slowly after small additions to mix the acid and dissipate the heat. Finally, add remaining distilled water to the mark. Allow the solution to cool to room temperature. Upend the stoppered flask several times to mix the solution.

TO measure a sample:

1. To a clean, dry 150 ml beaker, add 100 ml of 3 M sulfuric acid to a 150 ml beaker.. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip in the solution. Add the standard solution (10,000 ppm), using the steps given in Table 4 below. Record the mV reading after each addition. Plot the concentration (log axis) against the mV potential (linear axis) on semi-logarithmic paper. The plotted concentration is eleven times the actual concentration due to sample dilution.
2. To another 150 ml beaker, add 100 ml of the acid reagent. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the tip of the electrode in the solution. Add 10 ml of the sample to the beaker and record the mV reading. Determine the concentration from the calibration curve.

TABLE 4: Step-wise Calibration for Measurement

| <u>Step</u> | <u>Pipet</u> | <u>Added Volume</u> | <u>Concentration</u> |
|-------------|--------------|---------------------|----------------------|
| 1           | A            | 0.1 ml              | 109.9 ppm            |
| 2           | A            | 0.9 ml              | 1089 ppm             |
| 3           | B            | 10.0 ml             | 10900 ppm            |

A = 1 ml graduated pipet

B = 10 ml volumetric pipet

### TROUBLESHOOTING      GUIDE

The goal of troubleshooting is the isolation of a problem through checking each of the system components in turn: the meter, the glassware, the electrodes, the standards, the sample, and the technique.

#### Meter

The meter is the easiest component to eliminate as a possible cause of error. Most meters are provided with an instrument check-out procedure in the instruction manual and a shorting strap for convenience in troubleshooting. Consult the manual for complete instructions and verify that the instrument operates as indicated and is stable in all steps.

#### Glassware

Clean glassware is essential for good measurement. Be sure to wash the glassware well with a mild detergent and rinse very well with distilled or deionized water. Clean glassware will drain without leaving water droplets behind.

#### Electrodes

The electrodes may be checked by using the procedure found in the sections entitled Electrode Slope Check.

1. Be sure to use distilled or deionized water when following the procedures given in Electrode Slope Check.
2. If the electrode fails to respond as expected, see the sections Measuring Hints and Electrode Response. Repeat the slope check.
3. If the electrode still does not perform as described, determine whether the carbon dioxide inner body is working properly as directed in Checking the Electrode Inner **Body**.



4. If the stability and the slope check out properly, but measurement problems persist, the standards may be of poor quality, the sample may contain interferences or the technique may be in error. (See **Standard**, **Sample** and **Technique** sections below.)
5. Before replacing a "faulty" electrode, review the instruction manual and be sure to:
  - Clean and rinse the electrode thoroughly.
  - Prepare the electrode properly.
  - Use proper filling solution, buffer, and standards.
  - Measure correctly and accurately.
  - Review **TROUBLESHOOTING HINTS**.

### **Standards**

The quality of results depends greatly upon the quality of the standards. ALWAYS prepare fresh standards when problems arise. It could save hours of frustrating troubleshooting! Error may result from contamination of prepared standards, accuracy of dilution, quality of distilled water, or a mathematical error in calculating the concentrations.

The best method for preparation of standards is by serial dilution. This means that an **initial** standard is diluted, using volumetric glassware, to prepare a second standard solution. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

### **Sample**

If the electrode works properly in standards but not in sample, look for possible interferences, complexing agents, or substances which could affect response or physically damage the sensing electrode or the reference electrode. If possible, determine the composition of the samples and check for problems. See **Sample Requirements** and **Interferences**.

### **Technique**

Be sure that the electrode's limit of detection has not been exceeded. Be sure that the analysis method is clearly understood and is compatible with the sample.

Refer to the instruction manual again. Reread **GENERAL PREPARATION** and **ELECTRODE CHARACTERISTICS**.

If trouble still persists, call pHOenix Electrode Company at 1-800-522-7920 and ask for the Technical Services Department.

## TROUBLESHOOTING HINTS

| Symptom   | Possible Causes                        | Next Step  |
|---|--|--|
| Out of Range Reading  | defective meter                        | perform meter checkout procedure (see meter instruction manual)                            |
|   | defective inner body                   | refer to Checking the <b>Electrode Inner Body</b>  |
|   | electrode not plugged in properly      | unplug electrode and reseat  |
|   | internal filling solution not added    | fill outer body of electrode with proper amount of internal filling solution               |
|   | air bubble on membrane                 | remove bubble by re-dipping electrode  |
|   | electrode not in solution              | put electrode in solution  |
| Noisy or Unstable Reading (readings continuously or random changing.) | insufficient internal filling solution | fill outer body of electrode with proper amount of internal filling solution               |
|   | defective meter                        | perform meter checkout procedure (see meter instruction manual)                            |
|   | bottom cap loose                       | ensure that bottom cap is screwed on tight enough to close gap between bottom cap and body |

|  |  |  |
|--|--|--|
|  | defective inner body                               | refer to Checking the Electrode Inner Body   |
|  | air bubbles on membrane                            | remove bubbles by redipping electrode  |
|  | meter or stirrer improperly grounded               | check meter and stirrer for grounding  |
| Drift (reading slowly changing in one direction) | internal filling solution leakage                  | ensure that membrane is installed properly   |
|  | incorrect internal filling solution                | refill outer body of electrode using filling solution shipped with electrode             |
|  | total sample level of dissolved species above 1M   | dilute sample  |
|  | electrode in sample too long; CO, <b>loss</b>      | reduce surface area-to-volume ratio, slow down rate of stirring, avoid high temperatures |
|  | membrane failure (wet, perforation, discoloration) | replace membrane   |
|  | samples and standards not at constant temperature  | allow samples and standards to come to room temperature before use                       |
|  | heat generated by magnetic stirrer                 | place insulating material between stirrer and beaker                                     |
|  | defective inner body                               | refer to Checking the Electrode Inner Body   |

|  |  |  |
|--|--|--|
|  | electrode exposed to air for extended period       | hold electrode by outer body and pull on electrode cable. Internal filling solution will flow under membrane and restore electrode response        |
| Low Slope or No Slope                              | standards contaminated or incorrectly made         | prepare fresh standards  |
|  | buffer not used                                    | use recommended buffer   |
|  | standard used as buffer                            | use buffer   |
|  | electrode exposed to air for extended period       | hold electrode by outer body and pull on electrode cable. Internal filling solution will flow under membrane and restore electrode response        |
|  | membrane failure (wet, perforation, discoloration) | replace membrane   |
|  | defective inner body                               | refer to <b>Checking the Electrode Inner Body</b>  |
| "Incorrect Answer" (but calibration curve is good) | incorrect scaling of semi-log paper                | plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration |
|  | incorrect sign                                     | be sure to note sign of millivolt value correctly  |

|   |  |
|---|--|
| incorrect standards                       | prepare fresh standards  |
| wrong units used                          | apply correct conversionfactor:<br>$10^{-3}M = 44 \text{ ppm as } CO_2 = 100 \text{ ppm as } CaCO_3$ |
| buffer added to standards and not samples | add same proportions of buffer to standards and samples  |
| sample carryover                          | rinse electrodes thoroughly between samples  |

### Checking the Electrode Inner Body

If the electrode slope is found to be low during operation, the following solutions will be necessary to check the inner body:

- pH 4 Buffer (0.1M NaCl added)

Add 2.9 grams of reagent-grade NaCl to 500 ml of pH 4 buffer. Dissolve the solid. The solution may be **stored** for repeated use.

- pH 7 Buffer (0.1M NaCl added)

Add 2.9 grams of reagent-grade NaCl to 500 ml of pH 7 buffer. Dissolve the solid. The solution may be stored for repeated use.

Disassemble the carbon dioxide electrode. If the electrode is dry, soak the glass tip of the inner body in pHoenix Carbon Dioxide Electrode Filling Solution, Cat. No. C02IF01 for two hours.

Rinse the electrode thoroughly with distilled water. Put 100 ml of pH 7 buffer (0.1M NaCl added) in a 150 ml beaker. Place the beaker on the magnetic stirrer, and begin stirring. Immerse the tip of the inner body in the solution so that the reference element is covered. Make sure that the meter is in the mV mode. Record the meter reading when stable.

Rinse the inner body thoroughly in distilled water. Put 100 ml of pH 4 buffer (0.1M NaCl added) in a 150 ml beaker, place the beaker on the magnetic stirrer, and begin stirring. Immerse the tip of the inner body in the solution so that the reference element is covered. Observe the change in the meter reading carefully. In less than 30 seconds after immersion, the reading should change 100 mV. The meter reading should stabilize in 3-4 minutes, with a difference greater than 150 mV if the inner body sensing elements are operating properly.

### SPECIFICATIONS

Concentration Range:  $1 \times 10^{-2}M$  to  $1 \times 10^{-4}M$  CO,  
(440 ppm to 4.4 ppm CO,)

pH Range: 4.8 to 5.2

Temperature Range: 0° to 50°C

Inner Body Resistance: -1000 Mohm

Reproducibility:  $\pm 2\%$

Size: 110 mm length  
12 mm diameter  
1 m cable length

Storage: store electrodes in 0.1M NaCl

### ORDERING INFORMATION

| P/N            | DESCRIPTION  |
|----------------|--|
| C021501        | Carbon Dioxide Gas Sensing Electrode   |
| C02MK02        | Carbon Dioxide Membrane Cartridge Kit,<br>box of 3 membrane cartridges and spare o-rings |
| C02IF01        | Carbon Dioxide Electrode Filling Solution  |
| C02AS01        | Carbon Dioxide Standard, 0.1M NaHCO <sub>3</sub>   |
| C02AS02        | Carbon Dioxide Standard, 1000 ppm as CO,   |
| <b>C02AS03</b> | Carbon Dioxide Standard, 100 ppm as <b>CaCO<sub>3</sub></b>                              |
| c02IS01        | Carbon Dioxide Buffer Solution, 0.1M Citrate Buffer                                      |
| NA0AS01        | Carbon Dioxide Electrode Storage Solution, 0.1M <b>NaCl</b>                              |

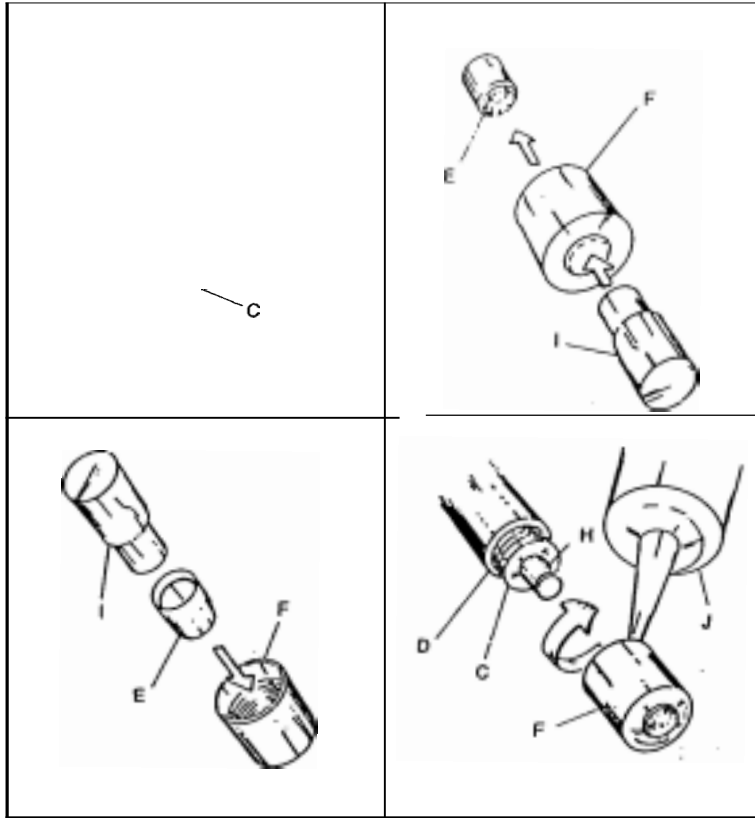


Figure 4 —Membrane Cartridge Replacement

- A. Large cap
- B. O-ring
- C. Outer body
- D. O-ring
- E. Membrane Cartridge
- F. Small cap
- G. Inner glass electrode
- H. Gas sensing electrode
- I. Cartridge tool
- J. Filling dispenser
- K. Filling solution

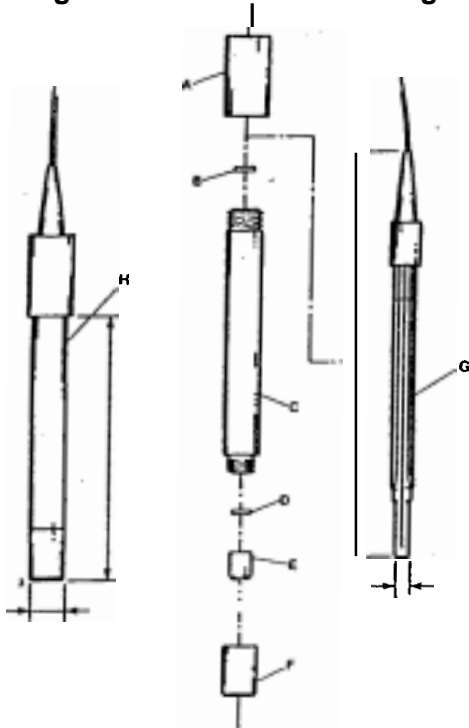


Figure 5 —Electrode Ass'embly



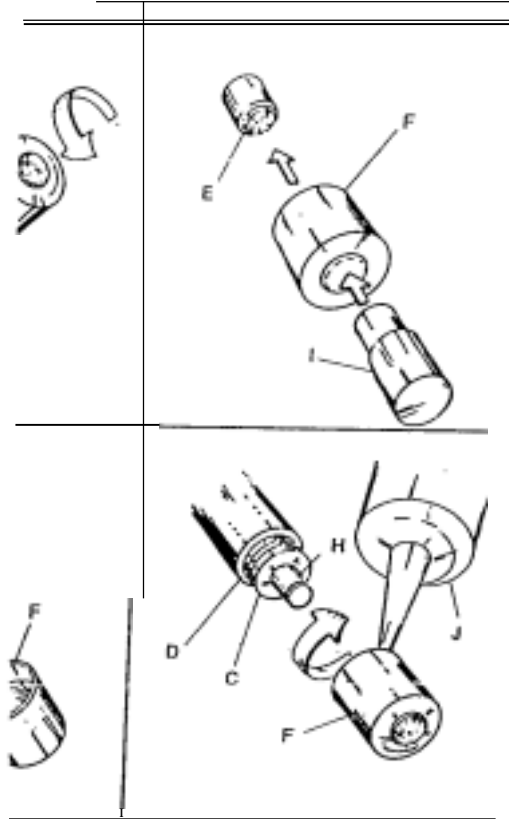
Figure 6 —Assembly Kit

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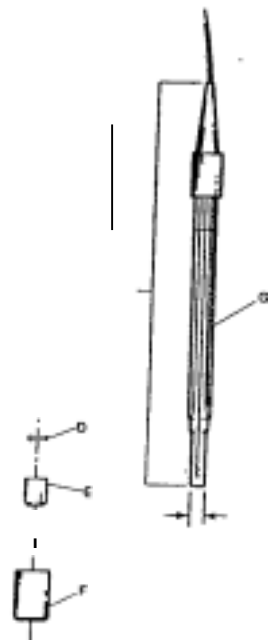


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- C. Outer body
- D. O-ring
- E. Membrane Cartridge
- F. Small cap
- G. Inner glass electrode
- H. Gas sensing electrode
- I. Cartridge tool
- J. Filling dispenser
- K. Filling solution

**Membrane Cartridge Replacement**



**Electrode Assembly**



**Figure 6—Assembly Kit**