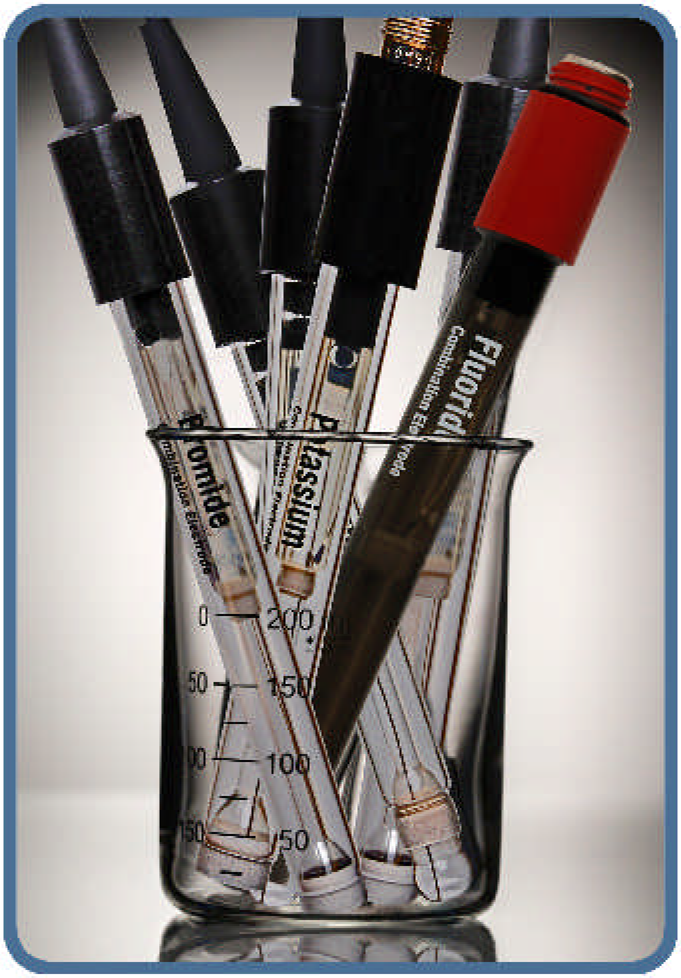
Van London Co.

"When Accuracy Matters"



Carbon Dioxide Gas Sensing Electrode

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GENERAL INSTRUCTIONS

Introduction

The Van London Co. Carbon Dioxide Gas-Sensing Electrode is used to measure dissolved carbon dioxide, carbonate, and bicarbonate in aqueous solutions. The measurement is not affected by sample color or turbidity.

Required Equipment

1. An ion meter
2. Carbon Dioxide Gas Sensing Electrode
3. Carbon Dioxide Membranes
4. Tweezers, plastic syringe, pipets, volumetric flasks, 150 ml beakers

Required Solutions

1. Deionized or distilled water for solution preparation.
2. Van London Co. Carbon Dioxide Standard, 1000 ppm Cat.# CO2AS02.
3. Van London Co. Carbon Dioxide Ionic Strength Adjuster (ISA), Cat. No. C02IS01.
4. Van London Co. Carbon Dioxide Electrode Filling Solution, Cat. No. C02IF01.
5. Sodium Chloride Solution, 0.1M NaCl. 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.

GENERAL PREPARATION

Electrode Preparation

Remove the small black shipping cap from the bottom of the electrode. Before using, grasp the black outer body with one hand and unscrew the cap at the top of the electrode with the other hand. Remove the inner pH glass electrode from the outer body. Rinse the glass electrode with deionized water to remove any KCl crystals. Store the black shipping cap for later use.

Fill the outer body with 2 to 3 ml of Electrode Filling Solution Cat.# CO2IF01 using the plastic syringe provided. **While holding the black outer body** insert the inner glass electrode back into the outer black body, and screw on the large cap until finger tight.
Note: Twisting of the black outer body after the glass inner body is inserted could result in the membrane being damaged. Be sure to screw the cap onto the body instead of screwing the body into the cap.

Connect the electrode to the meter with the BNC connector at the end of the cable as recommended by the meter manufacturer. To prevent air entrapment, place the electrode at a 20° angle from the vertical.

Electrode Slope Check (for Ion meters which display mV)

1. To a clean, dry, 150 ml beaker, add 100 ml of distilled water and 10 ml of ISA. After assuring that the meter is in the millivolt mode, lower the electrode tip into the solution. Stir moderately. Remove air bubbles on the white Teflon membrane by redipping probe.
2. Using a pipet, add 1 ml of 1000 ppm standard into the solution. Stir moderately. After 1 minute, record the mV reading.
3. Using a pipet, add 10 ml of the 1000 ppm ammonia standard to the beaker. Stir moderately. After 1 minute, record the mV reading.
4. Determine the difference between the two readings. The electrode is operating correctly if a slope difference of 56±3 mV is found, assuming the solution temperature is 25^{o}C. Slope is defined as the change in mV observed when the concentration changes by a factor of 10.
5. See the following **Checking Membrane** section if the slope is not within the 56±3 mV range. Otherwise, skip to the **Direct Measurement** section if the slope is correct.

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 an Ion meter. Set meter to Concentration mode.
2. Lower the electrode tip in distilled water.
3. Record the reading after stirring the distilled water for about 15 minutes.
4. Add 10 ml ISA solution to the distilled water. A drastic change in the ppm reading in a positive direction (>100 ppm) indicates damage of the membrane.
5. See the following **Changing Membrane** section if there is a drastic change in the ppm reading.
6. If no damage to the membrane is indicated, consult the **TROUBLESHOOTING** section in the back of this manual and repeat the Electrode Slope Check.

Changing Membrane (if damage of membrane has occurred)

1. Grasp the black outer body with one hand. Unscrew the cap at the top of the electrode with the other hand. Remove the inner pH glass body from the epoxy outer body. Carefully place the glass body aside.
2. Unscrew the bottom cap from the outer body and remove the old membrane cartridge from the small cap. Insert the new membrane cartridge into place. Place the bottom cap gently onto the threads and screw the bottom cap on until finger tight. Check that the membrane is free of wrinkles and holes or else repeat the above steps.
3. Using the syringe provided, fill the outer body with approximately 2-3 ml of Electrode Filling Solution.
4. While holding the black outer body, insert glass inner body into black outer body containing the electrode filling solution and screw on the upper cap until finger tight.
   Note: Twisting of the black outer body after the glass inner body is inserted could result in the membrane being damaged. Be sure to screw the cap onto the body instead of screwing the body into the cap.
5. Repeat the **Electrode Slope Check** above. Consult the **TROUBLESHOOTING** Section if the slope is not 56±3 mV after changing the membrane. Otherwise, proceed to the Measurement section which follows.

Measurement using an Ion Meter (in the Concentration Mode)

1. By serial dilution of the 1000 ppm carbon dioxide standard, prepare two ammonia standards whose concentration is near the expected sample concentration. (e.g 10 ppm and 100 ppm) For example, to make a 100 ppm standard, pipet 10 ml of the 1000 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. Next to make a 10 ppm standard, pipet 10 ml of the newly-made 100 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. A 1 ppm standard is made by further dilution of the 10 ppm standard. Measure out 100 ml of each standard into individual 150 ml beakers.
2. Assure that the meter is in the concentration mode and set for a 2-point calibration.
3. Lower the electrode tip into the least concentrated solution. Begin stirring at a constant rate. Add 10 ml of ISA to the solution and continue stirring.
4. After 1 minute, adjust the meter to the concentration of the more dilute carbon dioxide standard and fix the value in the memory according to the meter manufacturer's instructions.
5. Rinse the electrode tip with distilled water and blot dry.
6. Lower the electrode tip into the more concentrated solution. Begin stirring at a constant rate. Add 10 ml of ISA to the solution and continue stirring.
7. After 1 minute, adjust the meter to the concentration of the more concentrated carbon dioxide standard and fix the value in the memory according to the meter manufacturer's instructions.
8. Add 100 ml of the sample and 10 ml of ISA in a 150 ml beaker. Lower the electrode tip into the solution. Begin stirring at a constant rate. Ensure that the meter is in sample mode.
9. After 1 minute, read the concentration directly from the meter display.

10. The electrode should be re-calibrated every 2-3 hours. Simply repeat Steps 2-7 above.

Measuring Hints

As carbon dioxide electrodes are used or stored for long periods, they will experience some deterioration in performance and slope errors will increase. By using the meter's calibration controls this error can be corrected. If an electrode is able to be calibrated and is stable and responsive, it is still a functional electrode and may be used in service even though it no longer meets "new" electrode specifications.

Samples should be measured immediately after collection. Samples should be stored in sealed containers if immediate measurement is not possible.

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 $1^{o}C$ in temperature will result in approximately a 2% error.

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.

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

Dilute concentrated samples (over 5000 ppm) before measurement.

Use fresh standards for calibration. Re-calibrate every few hours for routine measurement.

All samples and standards must be aqueous. They must not contain organic solvents.

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.

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 1.

TABLE 1: Interference Levels - 10% Error at 10^{-3}M CO_2

Interferences	pH 4	pH 5
HCOOH (formic acid)	7.5×10^{-3}M (345 ppm)	2.0×10^{-2}M (1840 ppm)
CH_3COOH (acetic acid)	3.6×10^{-3}M (216 ppm)	6.2×10^{-3}M (372 ppm)
$HSO_3^-(SO_2)$ (sulfur dioxide)	7.5×10^{-4}M (48 ppm)	5.0×10^{-3}M (320 ppm)

NO_2^-(NO_2) (nitrogen dioxide)	5.3 x 10^{-4}M (24 ppm)	3.5 x 10^{-3}M (160 ppm)

The level of ions in solution can change the solubility of ammonia, though ionic species cannot cross the gas-permeable membrane and are not considered direct electrode interferences. The level of ions in sample solution and standards do not interfere, given that they are equal. The same holds true for dissolved species. Electrode drift and slow response could indicate the presence of high interferences. Soak the electrode in distilled water for five minutes, then soak for five minutes in 100 ppm standard solution with ISA added, to restore proper response.

Temperature Influences

The electrode response will shift and change slope with change in temperature. Standards and samples should be at the same temperature. A 2% error results with a 1°C temperature change for a 10 ppm solution. Gases like CO_2 are expelled from a solution at a faster rate as the temperature increases.

The electrodes can be used at temperatures from 0° - 50°C. Room temperature measurements are recommended, since measurements at temperatures quite different from room temperature may require equilibrium times up to one hour.

Electrode Response

Plotting the electrode mV potential against the carbon dioxide concentration results in a straight line with a slope of 56±3 mV between 10 ppm and 100 ppm at 25°C.

For carbon dioxide concentrations above 4.4 ppm (1X10^{-4}M), the electrode exhibits good time response (95% of total mV reading in 30 seconds or less). Response times are longer below this value and carbon dioxide loss to air may become a source of error. Samples above 440 ppm (1X10^{-2}M) must be diluted before measurement.

Limits of Detection

The upper limit of detection in pure carbon dioxide solutions is 440 ppm (1X10^{-2}M). Carbon dioxide is rapidly lost to the air above a concentration of 440 ppm (1X10^{-2}M). Dilution may be used if carbon dioxide concentrations are above 1M. Also dilute samples between 1M and 10^{-2}M or calibrate the electrode at 4 or 5 intermediate points. The lower limit of detection is around 4.4 ppm (1X10^{-4}M).

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 one year 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.

Since carbon dioxide electrodes have a limited shelf life, it is important to have a backup electrode which is in working condition when required.

Electrode Storage

If erratic results are obtained from accidentally leaving the electrode in air, the space between the sensing element and the inside of the membrane may be dry. To remedy this situation and allow new filling solution to flow into the space, withdraw the glass electrode from the membrane by pulling the cable slightly.

For normal range measurements, keep the electrode tip immersed in a 10 ppm standard with added ISA between measurements. If storing the carbon dioxide electrode overnight or over the weekend, immerse the tip in the 0.1M NaCl storage solution without added ISA.

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. **See Electrode Preparation**.

TROUBLESHOOTING HINTS

*Remember to remove the black protective shipping cap on the bottom of the electrode and fill the outer body with Carbon Dioxide Electrode Filling Solution prior to first use.

Symptom	**Possible Causes**	**Next Step**
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction manual)
	defective inner pH glass body	refer to **Checking the Electrode Inner Body** following this section
	electrode not plugged in properly	unplug electrode from meter and reseat
	electrode outer body not filled	fill black outer body as instructed in **Electrode Preparation**
	air bubble on membrane	remove air bubble by re-dipping electrode
	electrode not in solution	put electrode in solution
Noisy or Unstable Reading (readings continuously or randomly changing)	insufficient internal filling solution	fill outer body of electrode with proper amount of internal filling solution
	defective meter	check meter with shorting strap (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 pH glass body	refer to **Checking the Electrode Inner Body** following this section
	air bubble on membrane	remove air bubble by re-dipping 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	dilute sample

	dissolved species above 1M	
	electrode in sample too long; CO_2 loss	reduce surface area to volume ratio, slow down rate of stirring, avoid high temperatures
	membrane failure(wet, perforation, discoloration)	replace membrane
	samples and standards at different temperatures	allow samples and standards to come to same temperature before measurement
	heat generated by magnetic stirrer	place insulating material between stirrer and beaker
	defective inner pH glass body	refer to **Checking the Electrode InnerBody** following this section
	electrode exposed to air for extended period	hold electrode by outer body and pull gently 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
	ISA not used	use recommended ISA
	standard used as ISA	use ISA
	electrode exposed to air for extended period period	hold electrode by outer body and gently pull on electrode cable. Internal filling solution will flow under membrane and restore electrode response.
	membrane failure (wet, perforation, discoloration)	replace membrane
	defective inner pH glass body	refer to **Checking the Electrode InnerBody** following this section
"Incorrect Answer" but calibration curve is good)	incorrect standards	prepare fresh standards
	wrong units used	apply correct conversion factor: 10^{-3}M = 44 ppm as CO_2 = 100 ppm as $CaCO_3$
	ISA added to standards and not samples	add same proportions of ISA to standards and samples
	sample carryover	rinse electrodes thoroughly between samples

Checking the Electrode Inner Body (Glass pH electrode)

If the electrode slope is found to be low during operation, disassemble the ammonia electrode. Grasp the black outer body with one hand and unscrew the cap at the top of the electrode with the other hand. Remove the inner pH glass electrode from the outer body. Rinse the glass electrode with deionized water to remove any KCl crystals. If the glass pH electrode is dry, soak the glass tip of the inner body in Ammonia Electrode Filling Solution for at least two hours.

Rinse the glass pH electrode thoroughly with distilled water. Put 100 ml of pH 7 buffer in a 150 ml beaker. Place the beaker on the magnetic stirrer, and begin stirring. Immerse the tip of the glass pH electrode 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 glass pH electrode 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 glass pH electrode 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 glass pH electrode sensing element is operating properly.

SPECIFICATIONS

Concentration Range:	1 x 10^{-2}M to 1 x 10^{-4}M CO_2 (440 ppm to 4.4 ppm CO_2)
pH Range:	4.8 to 5.2
Slope:	56±3 mV between 10 ppm and 100 ppm at 25°C
Temperature Range:	0° to 50°C
Interferences:	Volatile acids
Reproducibility:	± 2%
Size:	110 mm length 12 mm diameter 1 m cable length
Storage:	store electrodes in 0.1M NaCl

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_2 in the internal filling solution and the partial pressure of the CO_2 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:

$$CO_2 + H_2O\ \mathbf{6}\ H^+ + HCO_3\text{-}$$

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

$$\frac{[H^+]\ [HCO_3^-]}{[CO_2]} = \text{constant}$$

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

$$[H^+] = [CO_2] \text{ X constant}$$

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:

$$E = E_o + S \log [H^+]$$

where:

E = measured electrode potential
E_o = reference potential (a constant)
$[H^+]$ = hydrogen ion concentration
S = electrode slope ($\sim$56mV/decade)

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

$$E = E_1 + S \log [CO_2]$$

<u>Carbon Dioxide Chemistry</u>

Carbon dioxide exists as bicarbonate and carbonate in basic solutions:

$$CO_2 + OH^- \rightarrow HCO_3^-$$

$$CO_2 + 2OH^- \rightarrow CO_3^{-2} + H_2O$$

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 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 CO_2 form:

$$2H^+ + CO_3^{-2} \rightarrow H_2O + CO_2$$

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2$$

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