User Guide

Carbon Dioxide
Ion Selective
Electrode

Thermo
SCIENTIFIC

CONTENTS

GENERAL INFORMATION

Introduction

This user guide contains information on the preparation, operation and maintenance for the carbon dioxide ion selective electrode (ISE). General analytical procedures, electrode characteristics and electrode theory are also included in this user guide. Carbon dioxide electrodes measure free carbon dioxide ions in aqueous solutions quickly, simply, accurately and economically.

Technical Support Chemists can be consulted for assistance and troubleshooting advice. Within the United States call 1.800.225.1480 and outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer.

Required Equipment

Meter– Thermo Scientific Orion ISE meter, such as the 4-Star pH/ISE meter or 5-Star pH/ISE/DO/conductivity meter. The 9502BNWP carbon dioxide electrode can be used on any ISE meter with a BNC connection. The electrode can also be used on meters with a variety of inputs when an adapter cable is used.

Stirrer– Magnetic stirrer or stir probe, Cat. No. 096019. The stir probe can be used with 3-Star, 4-Star and 5-Star benchtop meters.

Labware– Volumetric flasks, graduated cylinders and beakers.

Required Solutions

Distilled or Deionized Water – To prepare all solutions and standards.

Standard Solutions

0.1 M sodium bicarbonate standard solution, Cat. No. 950206

1000 ppm as $CaCO_3$ standard solution, Cat. No. 950207

1000 ppm as CO_2 standard solution – To prepare, dilute 22.7 mL of 0.1 M standard, Cat. No. 950206, to 100 mL in a volumetric flask

Carbon Dioxide Buffer Solution, Cat. No. 950210 – To adjust solution pH to the operating range of the electrode. 5 mL of carbon dioxide buffer must be added to each 50 mL sample and standard solution.

Storage Solution, Cat. No. 941706 – To store the electrode, 0.1 M sodium chloride (NaCl).

Internal Filling Solution, Cat. No. 950202 – To fill the electrode.

Solutions For inner Body Check

pH 4.01 buffer (with 0.1 M NaCl added) – For checking inner body operation. Use a 4.01 buffer, Cat. No. 910104. Add 1.16 g reagent-grade NaCl to 100 mL of the buffer solution. Dissolve solid and store the buffer for repeated use. Discard buffer if turbidity develops.

pH 7.00 buffer (with 0.1 M NaCl added) – For checking inner body operation. Use a 7.00 buffer, Cat. No. 910107. Add 1.16 g reagent-grade NaCl to 100 mL of the buffer solution. Dissolve solid and store the buffer for repeated use. Discard buffer if turbidity develops.

USING THE ELECTRODE

Setup

Electrode Assembly And Preparation

The electrode is shipped assembled, with a membrane in place for packing. Disassemble the electrode as shown in step 1 of **Figure 1,** and discard the membrane. Reassemble according to instructions in **Figure 1**. After assembly the membrane should be slightly distended by the inner body of the electrode. A membrane should last several months, depending on usage. Membrane failure is characterized by a shift in electrode potential, drift, and poor response. See **TROUBLESHOOTING.**

1. Remove top cap. Lift out inner body. Pour out old internal filling solution. Remove bottom cap.
2. Remove O-ring, old membrane and white spacer ring from cap.
3. Place the white membrane spacer ring in the bottom cap with the flat membrane down towards the sample solution.
4. Place O-ring on top of the white membrane spacer ring. Screw body into bottom cap.
5. Fill outer body with internal filling solution. Fill with about one inch of solution
6. Put inner body into outer body. Screw top cap on. Excess solution will vent.

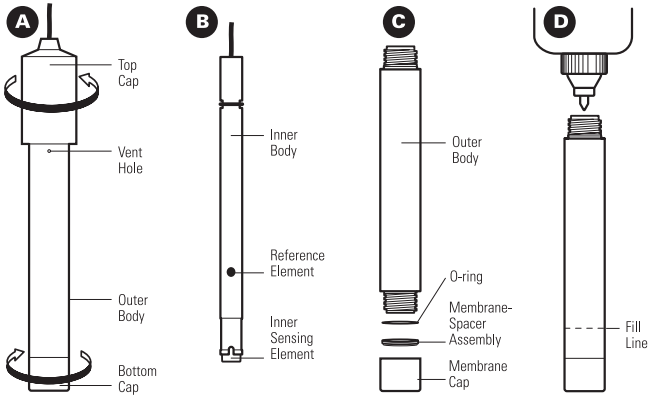

Figure 1 Electrode Assembly and Preparation

Checking Electrode Operation (Slope)

These are general instructions which can be used with most meters to check electrode operation. See the meter user guide for more specific information.

This procedure measures electrode slope. Slope is defined as the change in millivolts observed with every tenfold change in concentration. Obtaining the slope value provides the best means for checking electrode operation.

1. Connect the electrode to the meter.

   Certain meters may require special adapters. Consult your meter user guide.

   Note that gas-sensing electrodes are placed in the electrode holder so that they are at a 20° angle from the vertical. This avoids trapping air bubbles at the tip of the electrode.
2. Place 45 mL distilled water and 5 mL carbon dioxide buffer into a 100 mL beaker. Stir thoroughly. Set the meter to the mV mode.
3. Rinse electrode with distilled water and place in the solution prepared in step 2 above.
4. Select either 0.1 M or 1000 ppm standard. Pipet 0.5 mL of the standard into the beaker. Stir thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
5. Pipet 5 mL of the same standard into the same beaker. Stir thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
6. The difference between the first and second potential reading is defined as the slope of the electrode. The difference should be in the range of 54-60 mV/decade when the solution temperature is 25° C. If the potential is not within this range, refer to **TROUBLESHOOTING.**

Before Analysis

Units of Measurement

Carbon dioxide can be measured in units of moles per liter, parts per million as carbon dioxide, parts per million as calcium carbonate, or any other convenient concentration unit. See **Table 1** for conversion units.

Table 1
Concentration Unit Conversion Factors

Moles/Liter	ppm as CO_2	ppm as $CaCO_3$
10^{-4}	4.4	10.0
10^{-3}	44.0	100.0
10^{-2}	440.0	1000.0

Sample Requirements

Samples must be aqueous. Samples and standards should be at the same temperature. A 1°C difference in temperature will give rise to about a 2% measurement error.

In all analytical procedures, carbon dioxide buffer solutions must be added to samples and standards before measurement. After addition of the buffer solution, all samples and standards should fall within the pH 4.8 to 5.2 range so that all bicarbonate and carbonate is converted to carbon dioxide and so that possible interferences are minimized. Since the buffering capacity of the acid buffer is limited, highly basic, highly acidic, or buffered samples must be adjusted to pH 4.8 - 5.2 before the carbon dioxide buffer is added.

The addition of buffer solution also adjusts the total level of dissolved species in solution to 0.4 M. If the total level of dissolved species is greater than 1 M after the addition of carbon dioxide buffer, the sample should be diluted before measurement. See **Effects of Dissolved Species.**

Sample Storage

If possible, samples should be measured at once, waiting only a sufficient time for the sample to come to the temperature of the electrode. In an open 150 mL beaker at 25° C, carbon dioxide diffuses out of an acidic solution at a rate of about 3% per minute with stirring and 0.5% without stirring. At higher temperatures the rate of CO_2 loss increases. If solutions must be stored, make them slightly alkaline (pH 8-9) by adding 10 N NaOH* and storing them in a tightly capped vessel to prevent pick-up of CO_2 from the air. Just before measurement, acidify these stored samples with carbon dioxide buffer.

* The amount of NaOH needed to adjust the pH will depend upon the sample pH and buffering capacity. For unbuffered samples in the slightly acidic range, 1 mL of 10N NaOH per 100 mL of sample will be sufficient. NaOH should not be used to store samples containing less than 100 ppm CO_2 since carbonate is usually collected in a stoppered glass bottle. Fill the bottle completely and cap tightly to prevent loss of CO_2.

Measuring Hints

Minimize CO_2 loss from samples by:

- Measuring samples as soon as possible after collection.
- Storing samples according to **Sample Storage**.
- Minimizing the ratio of surface area to volume in the beaker.
- Keeping beakers containing standards and samples covered between measurements according to **Sample Storage**.
- Adding carbon dioxide buffer just before measurement.
- Stir all standards and samples at a uniform rate during measurement. Magnetic stirrers may generate sufficient heat to change solution temperature. Place a piece of insulating material such as cork, cardboard, or styrofoam between the stirrer and beaker.
- Verify calibration every two hours by placing electrode in the first standard solution used for calibration. If the value has changed, recalibrate.
- Always use fresh standards for calibration.

- Always rinse electrode with distilled water between measurements (see **Electrode Preparation**). Shake after rinsing to prevent solution carry over. Blot dry. Do not wipe or rub the sensing membrane.
- Allow all standards and samples to come to room temperature for precise measurement.
- After immersion in solution, check electrode for any air bubbles on membrane surface and remove.

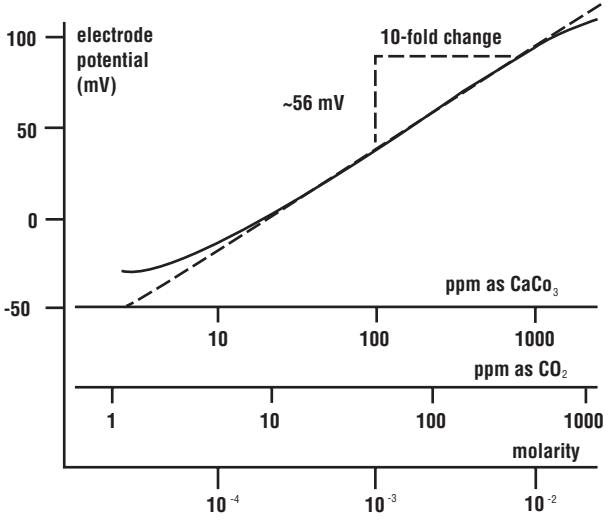

Figure 2
Typical Response Of The Carbon Dioxide Electrode

Analytical Procedures

Analytical Techniques

A variety of analytical techniques are available to the analyst. The following is a description of these techniques.

Direct Calibration is a simple procedure for measuring a large number of samples. Only one meter reading is required for each sample. Calibration is performed in a series of standards. The concentration of the samples is determined by comparison to the standards. ISA is added to all solutions to ensure that samples and standards have similar ionic strength.

Incremental Techniques provide a useful method for measuring samples, since calibration is not required. As in direct calibration, any convenient concentration unit can be used. The different incremental techniques are described below. They can be used to measure the total concentration of a specific ion in the presence of a large (50-100 times) excess of complexing agents.

Known Addition is an alternate method useful for measuring dilute samples, checking the results of direct calibration (when no complexing agents are present), or measuring the total concentration of an ion in the presence of an excess complexing agent. The electrode is immersed in the sample solution and an aliquot of a standard solution containing the measured species is added to the sample. From the change in potential before and after the addition, the original sample concentration is determined.

Direct Calibration

Setup

1. Connect electrode to the meter.
2. Prepare two standards which bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. All standards should be at the same temperature as the samples. (For details on temperature effects on electrode performance, refer to **Temperature Effects**.)

If using a meter with direct concentration readout capability

See the meter user guide for more specific information.

1. Measure 50 mL of the more dilute standard into a 150 mL beaker. Add 5 mL carbon dioxide buffer. Stir thoroughly.
2. Rinse electrode with distilled water, blot dry and place into the beaker. Wait for a stable reading, then adjust the meter to display the value of the standard as described in the meter user guide.
3. Measure 50 mL of the more concentrated standard into a second 150 mL beaker. Add 5 mL carbon dioxide buffer. Stir thoroughly.
4. Rinse electrode with distilled water, blot dry and place into the beaker with more concentrated standard. Wait for a stable reading, then adjust the meter to display the value of the second standard, as described in the meter user guide.
5. Measure 50 mL of the sample into a 150 mL beaker. Add 5 mL carbon dioxide buffer. Stir thoroughly. Rinse electrode with distilled water, blot dry and place into sample. The concentration will be displayed on the meter.

If using a meter with millivolt readout only

1. Adjust the meter to measure mV.
2. Measure 50 mL of the more dilute standard into a 150 mL beaker. Add 5 mL carbon dioxide buffer. Stir thoroughly.
3. Rinse electrode with distilled water, blot dry and place into the beaker. When a stable reading is displayed, record the mV value and corresponding standard concentration.
4. Measure 50 mL of the more concentrated standard into a second 150 mL beaker. Add 5 mL carbon dioxide buffer. Stir thoroughly.
5. Rinse electrode with distilled water, blot dry and place into the second beaker. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Using semilogarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis.
7. Measure 50 mL of the sample into a 150 mL beaker. Add 5 mL carbon dioxide buffer. Stir thoroughly.
8. Rinse electrode with distilled water, blot dry and place into the beaker. When a stable reading is displayed, record the mV value.
9. Using the calibration curve prepared in step 6, determine the unknown concentration.

Known Addition

Known Addition is a convenient technique for measuring samples because no calibration curve is needed. It can be used to verify the results of a direct calibration or to measure the total concentration of an ion in the presence of a large excess of a complexing agent. The sample potential is measured before and after addition of a standard solution. Accurate measurement requires that the following conditions be met.

- Concentration should approximately double as a result of the addition.
- Sample concentration should be known to within a factor of three.
- In general, either no complexing agent or a large excess of the complexing agent may be present.
- The ratio of the uncomplexed ion to complexed ion must not be changed by addition of the standard.
- All samples and standards should be at the same temperature.

Setup

1. Connect electrode to the meter.
2. Prepare a standard solution which, upon addition to the sample, will cause the concentration of the carbon dioxide to double. Refer to **Table 2** as a guideline.
3. Determine the slope of the electrode by performing the procedure under Checking Electrode Operation (Slope).
4. Rinse electrode between solutions with distilled water.

Table 2

Volume of Addition	Concentration of Standard
1 mL	100 x sample concentration
5 mL	20 x sample concentration
10 mL*	10 x sample concentration

*Most convenient volume to use.

Known Addition Table for an added volume one-tenth the sample volume. Slopes (in the column headings) are units of mV/decade

ΔE	Q_1 Concentration Ratio			
Monovalent	(57.2)	(58.2)	(59.2)	(60.1)
5.0	0.2894	0.2933	0.2972	0.3011
5.2	0.2806	0.2844	0.2883	0.2921
5.4	0.2722	0.2760	0.2798	0.2835
5.6	0.2642	0.2680	0.2717	0.2754
5.8	0.2567	0.2604	0.2640	0.2677
6.0	0.2495	0.2531	0.2567	0.2603
6.2	0.2426	0.2462	0.2498	0.2533
6.4	0.2361	0.2396	0.2431	0.2466
6.6	0.2298	0.2333	0.2368	0.2402
6.8	0.2239	0.2273	0.2307	0.2341
7.0	0.2181	0.2215	0.2249	0.2282
7.2	0.2127	0.2160	0.2193	0.2226
7.4	0.2074	0.2107	0.2140	0.2172
7.6	0.2024	0.2056	0.2088	0.2120
7.8	0.1975	0.2007	0.2039	0.2071
8.0	0.1929	0.1961	0.1992	0.2023
8.2	0.1884	0.1915	0.1946	0.1977
8.4	0.1841	0.1872	0.1902	0.1933
8.6	0.1800	0.1830	0.1860	0.1890
8.8	0.1760	0.1790	0.1820	0.1849
9.0	0.1722	0.1751	0.1780	0.1809
9.2	0.1685	0.1714	0.1742	0.1771
9.4	0.1649	0.1677	0.1706	0.1734
9.6	0.1614	0.1642	0.1671	0.1698
9.8	0.1581	0.1609	0.1636	0.1664
10.0	0.1548	0.1576	0.1603	0.1631
10.2	0.1517	0.1544	0.1571	0.1598
10.4	0.1487	0.1514	0.1540	0.1567
10.6	0.1458	0.1484	0.1510	0.1537
10.8	0.1429	0.1455	0.1481	0.1507
11.0	0.1402	0.1427	0.1453	0.1479
11.2	0.1375	0.1400	0.1426	0.1451
11.4	0.1349	0.1374	0.1399	0.1424
11.6	0.1324	0.1349	0.1373	0.1398
11.8	0.1299	0.1324	0.1348	0.1373
12.0	0.1276	0.1300	0.1324	0.1348
12.2	0.1253	0.1277	0.1301	0.1324
12.4	0.1230	0.1254	0.1278	0.1301
12.6	0.1208	0.1232	0.1255	0.1278
12.8	0.1187	0.1210	0.1233	0.1256
13.0	0.1167	0.1189	0.1212	0.1235
13.2	0.1146	0.1169	0.1192	0.1214
13.4	0.1127	0.1149	0.1172	0.1194
13.6	0.1108	0.1130	0.1152	0.1174
13.8	0.1089	0.1111	0.1133	0.1155
14.0	0.1071	0.1093	0.1114	0.1136
14.2	0.1053	0.1075	0.1096	0.1118
14.4	0.1036	0.1057	0.1079	0.1100
14.6	0.1019	0.1040	0.1061	0.1082
14.8	0.1003	0.1024	0.1045	0.1065
15.0	0.0987	0.1008	0.1028	0.1048
15.5	0.0949	0.0969	0.0989	0.1009
16.0	0.0913	0.0932	0.0951	0.0971
16.5	0.0878	0.0897	0.0916	0.0935
17.0	0.0846	0.0865	0.0883	0.0901
17.5	0.0815	0.0833	0.0852	0.0870

ΔE	Q_1 Concentration Ratio			
Monovalent	(57.2)	(58.2)	(59.2)	(60.1)
18.0	0.0786	0.0804	0.0822	0.0839
18.5	0.0759	0.0776	0.0793	0.0810
19.0	0.0733	0.0749	0.0766	0.0783
19.5	0.0708	0.0724	0.0740	0.0757
20.0	0.0684	0.0700	0.0716	0.0732
20.5	0.0661	0.0677	0.0693	0.0708
21.0	0.0640	0.0655	0.0670	0.0686
21.5	0.0619	0.0634	0.0649	0.0664
22.0	0.0599	0.0614	0.0629	0.0643
22.5	0.0580	0.0595	0.0609	0.0624
23.0	0.0562	0.0576	0.0590	0.0605
23.5	0.0545	0.0559	0.0573	0.0586
24.0	0.0528	0.0542	0.0555	0.0569
24.5	0.0512	0.0526	0.0539	0.0552
25.0	0.0497	0.0510	0.0523	0.0536
25.5	0.0482	0.0495	0.0508	0.0521
26.0	0.0468	0.0481	0.0493	0.0506
26.5	0.0455	0.0467	0.0479	0.0491
27.0	0.0442	0.0454	0.0466	0.0478
27.5	0.0429	0.0441	0.0453	0.0464
28.0	0.0417	0.0428	0.0440	0.0452
28.5	0.0405	0.0417	0.0428	0.0439
29.0	0.0394	0.0405	0.0416	0.0427
29.5	0.0383	0.0394	0.0405	0.0416
30.0	0.0373	0.0383	0.0394	0.0405
31.0	0.0353	0.0363	0.0373	0.0384
32.0	0.0334	0.0344	0.0354	0.0364
33.0	0.0317	0.0326	0.0336	0.0346
34.0	0.0300	0.0310	0.0319	0.0328
35.0	0.0285	0.0294	0.0303	0.0312
36.0	0.0271	0.0280	0.0288	0.0297
37.0	0.0257	0.0266	0.0274	0.0283
38.0	0.0245	0.0253	0.0261	0.0269
39.0	0.0233	0.0241	0.0249	0.0257
40.0	0.0222	0.0229	0.0237	0.0245
41.0	0.0211	0.0218	0.0226	0.0233
42.0	0.0201	0.0208	0.0215	0.0223
43.0	0.0192	0.0199	0.0205	0.0212
44.0	0.0183	0.0189	0.0196	0.0203
45.0	0.0174	0.0181	0.0187	0.0194
46.0	0.0166	0.0172	0.0179	0.0185
47.0	0.0159	0.0165	0.0171	0.0177
48.0	0.0151	0.0157	0.0163	0.0169
49.0	0.0145	0.0150	0.0156	0.0162
50.0	0.0138	0.0144	0.0149	0.0155
51.0	0.0132	0.0137	0.0143	0.0148
52.0	0.0126	0.0131	0.0136	0.0142
53.0	0.0120	0.0125	0.0131	0.0136
54.0	0.0115	0.0120	0.0125	0.0130
55.0	0.0110	0.0115	0.0120	0.0124
56.0	0.0105	0.0110	0.0115	0.0119
57.0	0.0101	0.0105	0.0110	0.0114
58.0	0.0096	0.0101	0.0105	0.0109
59.0	0.0092	0.0096	0.0101	0.0105
60.0	0.0088	0.0092	0.0096	0.0101

If using an instrument with direct known addition readout capability

See the meter user guide for more specific information.

1. Set up meter to measure in the known addition mode.
2. Measure 50 mL of the sample into a beaker. Rinse electrode with distilled water, place in sample solution. Add 5 mL carbon dioxide buffer. Stir thoroughly.
3. When a stable reading is displayed, calibrate the meter as described in the meter user guide.
4. Pipet the appropriate amount of the standard solution into the beaker. Stir thoroughly.
5. When a stable reading is displayed, record the sample concentration.

Analysis using a meter with millivolt readout only

Use this procedure when no instructions for known addition are available in the meter user guide.

1. Set the meter to relative millivolt mode.
2. Measure 50 mL of the sample into a 100 mL beaker. Add 5 mL carbon dioxide buffer. Stir thoroughly.
3. Rinse electrode with distilled water, blot dry and place into beaker. When a stable reading is displayed, set the reading to 000.0. If the reading cannot be set to 000.0, record the mV value.
4. Pipet the appropriate amount of standard solution into the beaker. Stir thoroughly.
5. When a stable reading is displayed, record the mV value. If the meter could not be zeroed in step 3, subtract the first reading from the second to find ΔE.

6. From **Table 3**, find the value, Q, that corresponds to the change in potential, ΔE. To determine the original sample concentration, multiply Q by the concentration of the added standard:

$$C_{sam} = QC_{std}$$

where:

C_{std} = standard concentration

C_{sam} = sample concentration

Q = reading from known addition table

The table of Q values is calculated for a 10% volume change for electrodes with slopes between 57.2 to 60.1 mV/decade. The equation for the calculation of Q for different slopes and volume changes is given below:

$$Q = \frac{p}{(1+p)10^{\Delta E/S} - 1}$$

where:

Q = reading from known addition table

$\Delta E = E_2 - E_1$

S = slope of the electrode

$$p = \frac{\text{volume of standard}}{\text{volume of sample}}$$

Electrode Storage

To store the electrode between samples, overnight or over a weekend, immerse the electrode tip in a 0.1M NaCl storage solution. If the electrode is not to be used for longer periods of time, completely disassemble and rinse inner body, outer body, and cap with distilled water. Dry and reassemble electrode without filling solution.

TROUBLESHOOTING

Troubleshooting checklist

Symptom	Possible cause
Off Scale or Over-range reading	Defective meter
	Defective inner body
	Electrode not plugged in properly
	Internal filling solution not added
	Air bubble on membrane
	Electrode not in solution
Noisy or unstable readings (erratic-rapidly changing)	Insufficient internal filling solution
	Defective meter
	Bottom cap loose
	Defective inner body
	Carbon dioxide buffer not used
	Meter stirrer improperly grounded
Drift (reading slowly changing in one direction)	Internal filling solution leakage
	Incorrect internal filling solution
	Total level of dissolved species above 1M
	Electrode in sample too long; CO_2 loss
	Membrane failure (wet, perforation, discoloration)
	Solutions not at constant temperature
	Heat generated by magnetic stirrer

Next Step

Perform meter checkout procedure

Refer to **Troubleshooting Guide** (check inner body operation)

Unplug electrode and reseat

Fill outer body of electrode with proper amount of internal filling solution

Remove bubble by redipping electrode

Put electrode in solution

Fill outer body of electrode with proper amount of internal filling solution, see **Electrode Preparation**

Perform meter checkout procedure (see meter user guide)

Ensure that bottom cap is screwed on tight enough to close gap between bottom cap and body

Check inner body operation

Use recommended carbon dioxide buffer, Cat. No. 950210

Check meter and stirrer for grounding

Ensure that membrane is installed properly

Refill outer body of electrode using filling solution shipped with electrode, Cat. No. 950202

Dilute solution

Reduce surface-area-to-volume ratio, slow rate of stirring, avoid high temperatures

Replace membrane

Allow solutions to come to same temperature constant temperature before use

Place insulating material between stirrer and beaker

Symptom	Possible Causes
Drift (readings changing slowly in one direction)	Defective inner body
	Electrode exposed to air for extended period
	Samples and standards at different temperatures
Low slope or No slope	Standards contaminated or incorrectly made
	CO_2 buffer not used
	Standard used as CO_2 buffer
	Electrode exposed to air
	Membrane failure (wet, perforation, discoloration)
	Defective inner body
"Wrong Answer" (But calibration curve is OK)	Incorrect scaling of semilog paper
	Incorrect sign
	Incorrect standards
	Wrong units used
	CO_2 buffer added to standards and not samples

Next Step

Check inner body operation

Hold electrode by outer body and pull up on electrode cable. Internal filling solution will flow under membrane and restore electrode response

Allow solutions to come to same temperature before measurement

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Prepare fresh standards

Use recommended CO_2 buffer, Cat. No. 950210

Used CO_2 buffer!

Hold electrode by outer body and pull up on electrode for extended period cable. Internal filling solution will flow under membrane and restore electrode response.

Replace membrane

Check inner body operation

Plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration

Be sure to note sign of millivolt value correctly

Prepare fresh standards

Apply correct conversion factor:
10^{-3} M = 44 ppm as CO_2 = 100 ppm as $CaCO_3$

Add same proportion to standards and samples

Troubleshooting Guide

The most important principle in troubleshooting is to isolate the components of the system and check each in turn. The components of the system are: 1) Meter, 2) Electrode, 3) Standard, 4) Sample, and 5) Technique.

Meter

The meter is the easiest component to eliminate as a possible cause of error. Thermo Scientific Orion meters are provided with an instrument checkout procedure in the user guide and a shorting strap for convenience in troubleshooting. Consult the user guide for complete instructions and verify that the instrument operates as indicated and is stable in all steps.

Electrode

1. Rinse electrode thoroughly with distilled water.
2. Check electrode operation (slope).
3. If electrode fails in this procedure, check inner body as follows:

   NOTE: This is a troubleshooting procedure. If electrode slope is found to be low during operation, disassemble electrode and check inner body.

   Disassemble the electrode. If the electrode is dry, first soak the glass tip of the inner body in filling solution for at least 2 hours. Rinse the inner body with distilled water and immerse it in the pH 7 buffer with 0.1 M Cl^- added so that the reference element is covered. Stir throughout the procedure. Record electrode potential in millivolts.

   Rinse the inner body in distilled water and place in the pH 4 buffer with 0.1M Cl^- added. Watch the change in meter reading carefully. The reading should be greater than + 100 mV in less than 30 seconds after immersion in the pH 4 buffer. The meter reading should stabilize in 3 to 4 minutes in the range of + 150 to + 190 absolute millivolts. The millivolt difference between pH 7 and pH 4 should be greater than 150 mV if the inner body sensing elements are operating correctly.
4. Repeat step 2. **Checking Electrode Operation.**
5. If the stability and slope check out properly, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error. See **Standard**, **Sample**, and **Technique** sections.

6. Before replacing a “faulty” electrode, review the user guide and be sure to:
    -Clean the electrode thoroughly
    -Prepare the electrode properly
    -Use proper filling solutions, CO_2 buffer, and standards
    -Measure correctly
    -Review **Troubleshooting Checklist**

Standard

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 samples, 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, Interferences,** and **pH Requirements.**

Technique

Check the method of analysis for compatibility with your sample. Direct measurement is usually the method of choice for this electrode. However, known addition may be better for low level work. If the sample is viscous, analate addition may solve the problem.

Also, be sure that the expected concentration of the ion of interest is within the electrode’s limits of detection.

If problems persist, review operational procedures and user guides to be sure that proper technique has been followed. Reread **Measuring Hints** and **Analytical Procedures**.

Assistance

After troubleshooting all components of your measurement system, contact Technical Support. Within the United States call 1.800.225.1480 and outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer. For the most current contact information, visit www.thermo.com/water.

Warranty

For the most current warranty information, visit www.thermo.com/water.

ELECTRODE CHARACTERISTICS

Electrode Response

When plotted on semilogarithmic paper, electrode potential response to carbon dioxide concentration is a straight line over two decades of concentration (5×10^{-4} M to 2×10^{-2} M) with a slope of about 54 to 60 mV per decade. See **Figure 2.**

The electrode exhibits good time response (95% of total mV reading in 1 minute or less) for carbon dioxide concentrations above 5×10^{-4} M. Below this value response times are longer, and carbon dioxide loss to air may become a source of error. Above 2×10^{-2} M, the partial pressure of carbon dioxide in solution is greater than normal atmospheric partial pressure of carbon dioxide, resulting in a loss of carbon dioxide to air. Samples above 2×10^{-2} M in carbon dioxide concentration should be diluted before measurement. **Figure 3** shows the time response of the carbon dioxide electrode to step changes in carbon dioxide concentration.

Reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift, and noise. Within the operating range of the electrode, reproducibility is independent of concentration. With calibration every hour, electrode measurements to 2% can be obtained.

Temperature Effects

A change in temperature will cause electrode response to shift and change slope. **Table 4** lists the variation of theoretical response with temperature. At 10^{-3} M, a 1°C temperature change gives rise to a 2% error. Samples and standards should be at the same temperature. Note that the higher the temperature, the greater the carbon dioxide loss from solution.

Table 4
Values of Theoretical Slope vs. Temperature

Temperature (˚C)	Slope (mV)
0	54.20
5	55.20
10	56.19
15	57.18
20	58.17
25	59.16
30	60.16
35	61.15
40	62.14

Interferences

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

Effects Of Dissolved Species

Water vapor is a potential electrode interference. Water can move across the membrane as water vapor, changing the concentration of the internal filling solution under the membrane. Such changes will be seen as electrode drift. Water vapor transport is not a problem if 1) the total level of dissolved species in solution (osmotic strength) is approximately equal to that of the internal filling solution and 2) electrode and sample temperatures are the same. Addition of carbon dioxide buffer to samples of low osmotic strength automatically adjusts them to the correct level. Samples with osmotic strengths greater than 1 M should be diluted before measurement. Dilution should not reduce the carbon dioxide level below 10^{-4} M. Samples with osmotic strengths above 1 M that cannot be diluted can be measured by adjusting the osmotic strength of the internal filling solution. To adjust the total level of dissolved species in the internal filling solution, add 0.425 g reagent grade $NaNO_3$ to 10 mL internal filling solution.

Table 5
Levels of Interferences Causing A 10% Error At 10^{-3} M CO_2

Interferences	pH 5	pH 4
NO_2- (NO_2)	3.5 x 10^{-3} M (160 ppm)	5.3 x 10^{-4} M (24 ppm)
HSO_3- (SO_2)	5 x 10^{-3} M (320 ppm)	7.5 x 10^{-4} M (48 ppm)
HOAc (Acetic acid)	6.2 x 10^{-3} M (0.37 g/100 mL)	3.6 x 10^{-3} M (0.22 g/100 mL)
HCOOH (Formic acid)	2.0 x 10^{-2} M	7.5 x 10^{-3} M

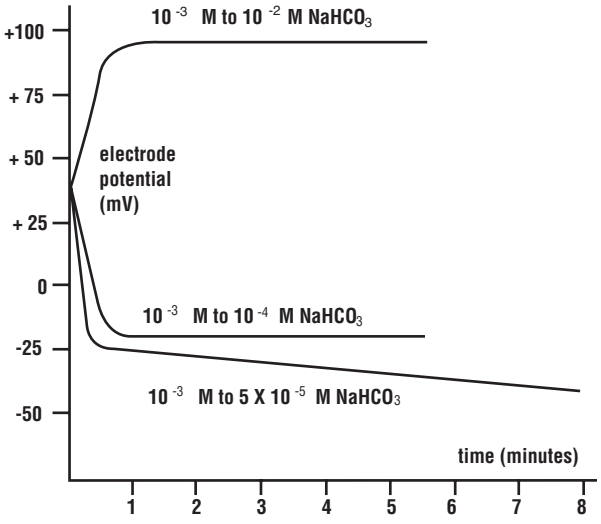

Figure 3
Typical Electrode Response
To Step Changes in Carbon Dioxide

Theory of Operation

The carbon dioxide electrode uses a gas-permeable membrane to separate the sample solution from the electrode internal solution. Dissolved carbon dioxide in the sample solution diffuses through the membrane until an equilibrium is reached between the partial pressure of CO_2 in the sample solution and the CO_2 in the internal filling solution. In any given sample the partial pressure of carbon dioxide will be proportional to the concentration of carbon dioxide.

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

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

The hydrogen level of the internal filling solution is measured by the pH electrode (inner body) located behind the membrane.

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

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

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

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

The potential of the pH sensing element is related to the hydrogen ion concentration by the Nersnst equation:

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

where:

E = measured electrode potential

E_0 = reference potential (a constant)

$[H^+]$ = hydrogen ion concentration

S = electrode slope

Since the hydrogen ion concentration is directly related to carbon dioxide concentration, electrode response to carbon dioxide is also Nernstian.

$$E = E_0 + S \log [CO_2]$$

The reference potential, E_0 is partly determined by the internal reference element that responds to the fixed level of chloride in the internal filling solution.

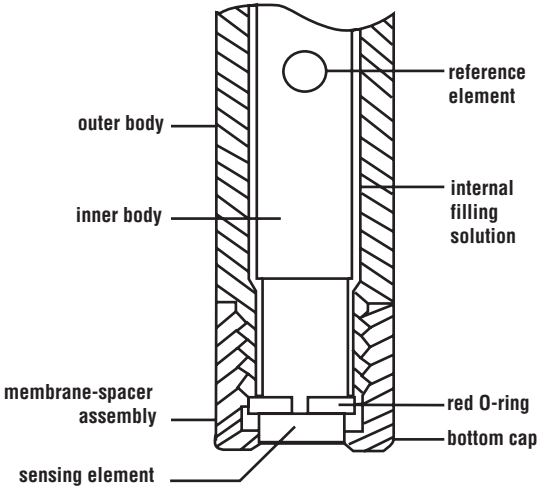

Figure 4
Construction Of The Carbon Dixoide Electrode

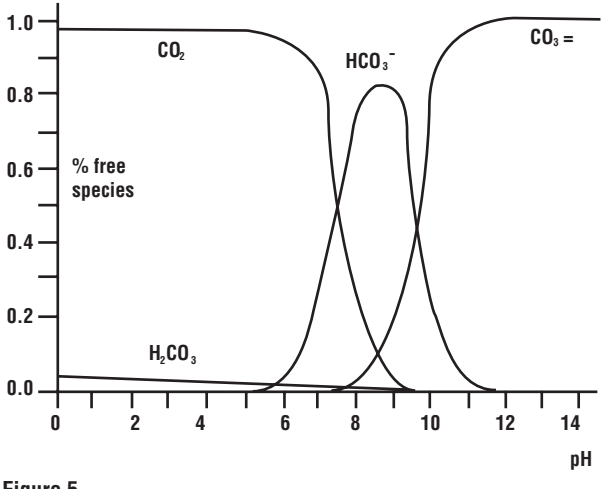

Figure 5
Fraction of Carbonate, Bicarbonate, and Carbon Dixoide Ion As A Function Of pH

Chemistry of Carbon Dioxide

Carbon dioxide reacts with water to form a weak carbonic acid solution:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

In basic solutions carbon dioxide exists as bicarbonate and carbonate:

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

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

The amount of carbon dioxide in the form of carbonate and bicarbonate depends on the pH of the solution. See **Figure 5.**

At pH 5, virtually all the carbon dioxide in the solution is in the CO_2 form. Below pH 5 carbon dioxide exists in the CO_2 form, but acetic acid, formic acid, nitrogen dioxide, and sulfur dioxide interfere significantly with the electrode measurement.

The carbon dioxide buffer used in carbon dioxide determinations keeps the pH between 4.8 and 5.2 and converts the carbonate and bicarbonate to the CO_2 form:

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

$$2H^+ + CO_3^{=} \rightleftharpoons H_2O + CO_2$$

The electrode then can be used to measure the total amount of carbon dioxide in solution.

The concentration of carbon dioxide in solution is directly proportional to the partial pressure of carbon dioxide over the solution. This relationship is described by Henry's law:

Henry Law Constant for CO_2

$$Kh = 1.25 \times 106 = \frac{PCO_2 \text{ in mmHg}}{[CO_2] \text{ in mole fractions}} \text{ at } 25°C$$

*Daniels & Alberty, Physical Chemistry, 2nd Ed. Wiley

Where:

$[CO_2]$ is the concentration of CO_2 in solution, PCO_2 is the partial pressure of CO_2, and Kh is Henry's constant, which varies with solution temperature.

ORDERING INFORMATION

Cat. No.	Description
9502BNWP	Carbon dioxide combination electrode, waterproof BNC connector
950202	Electrode filling solution, 50 mL bottle
950204	Membranes (4) with O-rings
950206	0.1 M $NaHCO_3$ standard solution, 475 mL bottle
950207	1000 ppm as $CaCO_3$ standard solution, 475 mL bottle
950210	Carbon dioxide buffer solution

SPECIFICATIONS

Concentration Range

10^{-4} M to 10^{-2} M CO_2
4.4 ppm to 400 ppm CO_2

pH Range

4.8 to 5.2 pH

Temperature Range

0˚ to 50˚C

Electrode Resistance

1000 megohms

Reproducibility

± 2%

Sample

Aqueous solutions only

Size

Electrode Length	151 mm
Body Diameter	17 mm
Cap Diameter	22 mm
Cable	75 cm

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Environmental Instruments
Water Analysis Instruments

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Toll Free: 800-225-1480
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