

## Nitrogen Oxide Electrode Instruction Manual

### GENERAL INSTRUCTIONS

The Nitrogen Oxide Electrode is used to quickly, simply, accurately, and economically measure nitrite in aqueous solutions and nitrate in aqueous solutions (after conversion to nitrite).

### **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 Nitrogen Oxide Electrode.

### **Required Solutions**

- 1) Deionized or distilled water for solution preparation.
- 2) Nitrogen Oxide Buffer Solution, Sodium Sulfate/Sulfuric Acid, Cat. No. WD-35803-57. To prepare acid buffer solution from your own stock, fill a 1 liter volumetric flask about half full with distilled water, add 322 grams of sodium sulfate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ ) and 10 ml glycerin. Dissolve by swirling the flask, and fill to the mark with distilled water. Adjust the pH of the solution to 1.3 with concentrated sulfuric acid under a fume hood. 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 acid buffer.
- 3) Nitrite Standard, 0.1M  $\text{NaNO}_2$ . To prepare this standard, add 6.91 grams of reagent grade sodium nitrite and 10 ml of 1 M NaOH to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.
- 4) Nitrite Standard, 1000 ppm  $\text{NO}_2^-$ . To prepare this standard, add 1.50 grams of reagent grade sodium nitrite and 10 ml of 1 M NaOH to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and

invert several times to mix the solution.

- 5) Nitrite Standard, 100 ppm  $\text{NO}_2^{-1}$  as N. To prepare this standard, add 0.49 grams of reagent grade sodium nitrite,  $\text{NaNO}_2$ , to a 1000 ml volumetric flask about half full of distilled water, swirl to dissolve the solid, fill to the mark, cap, and invert several times to mix the solution.
- 6) Internal Filling Solution,  $\text{NaNO}_2$ .
- 7) Nitrogen Oxide Electrode Storage Solution, for storing the electrode between use. Dilute 10 ml of the Acid Buffer Solution to 100 ml with distilled water.

## **ELECTRODE PREPARATION**

### **Electrode Assembly**

The electrode is shipped dry. Before using it, unscrew the large cap (see Figure 1 at end of manual), remove the inner glass electrode from the outer body, and soak the inner glass electrode tip in the internal filling solution for at least two hours. Fill the outer body half full of internal filling solution, place the inner glass electrode into the outer body, and screw on the large cap until fingertight. While using the electrode, 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 the breakage of the membrane causes failure of the electrode. It is recommended to check the membrane on every newly assembled electrode. A simple and effective way is available. Connect the newly assembled electrode to a pH/mV meter and place the electrode tip in deionized water for about 15 minutes. Add acid buffer solution (see **Required Solutions**) to the deionized water. A drastic change in the reading in a positive direction indicates damage to the membrane.

### **Changing Membrane (see Figure 4)**

1. Unscrew the top cap from the outer body and remove the inner glass body from the epoxy outer body. Carefully place the glass body aside.
2. Unscrew the small bottom cap from the outer body. Remove the old membrane cartridge from the small cap by pushing out the cartridge with the tool provided.

3. Insert the new membrane cartridge into the small cap by pushing in the cartridge until it seats using the tool provide. Screw the small bottom cap onto the outer body.
4. Using the syringe provided, fill the outer body with approximately 2 ml of inner filling solution.
5. Place glass inner body into epoxy outer body containing the internal filling solution and screw on the upper cap until fingertight.

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

Connect the electrode to the meter in the same manner as any other combination electrode. No external reference electrode is required. To prevent air entrapment, mount the electrode at a 20° angle from the vertical.

### **Electrode Standardization (with standard pH/mV meter) (check electrode each day)**

To a 150 ml beaker, add 90 ml of distilled water and 10 ml of acid buffer. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution. Remove any air bubbles on the electrode tip by redipping electrode.

Using a pipet, add 1 ml of 0.1M, or 1000 ppm nitrite, or 100 ppm nitrite as N standard to the beaker. When the reading is stable, record the millivolt reading.

Using a pipet, add 10 ml of the standard used above to the beaker. When the reading has stabilized, record the millivolt reading.

Determine the difference between the two readings. A difference of 56 ± 3 mV indicates correct electrode operation, assuming the solution temperature is between 20° and 25°C. See the **TROUBLESHOOTING** section if the potential change is not within this range.

### **Electrode Standardization (with ion meter) (check electrode each day)**

Prepare standard nitrite or N solutions whose concentrations vary by tenfold. Use either the 0.1M NaNO<sub>2</sub>, the 1000 ppm NO<sub>2</sub>, or 100 ppm NO<sub>2</sub> as N standard stock solutions. Use the serial dilution method for this preparation.

To a 150 ml beaker, add 100 ml of the lower value standard and 10 ml of acid buffer. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into

the solution.

Assure that the meter is in the concentration mode.

Adjust the meter to the concentration of the lower value standard and fix the value in the memory according to the meter manufacturer's instructions.

Rinse the electrode with distilled water and blot dry.

To a 150 ml beaker, add 100 ml of the higher value standard and 10 ml of acid buffer. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution.

Adjust the meter to the concentration of the higher value standard and fix the value in the memory.

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**

To minimize the loss of nitrous oxide from your solutions during measurement, samples should be measured immediately after collection. At room temperature, the rate of nitrous oxide loss from a stirred, 100 ml, acid buffered solution in an open beaker is about 90% in 14 hours. Between measurements, keep beakers containing samples and standards covered. Choose beakers with a low ratio of surface area to volume.

All samples and standards should be at the same temperature for precise measurement, preferably ambient temperature.

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 styrofoam sheet between the stirrer and beaker.

Always rinse the electrode tip with distilled water and blot dry with a fresh tissue between readings to prevent solution carryover. Do not rub or wipe the sensing membrane.

Follow the procedure under **Sample Storage** when storing samples.

Just before measurement, remember to add 10 ml of acid buffer to 100 ml of sample or standard.

Check the electrode for air bubbles adhering to the membrane surface after immersion in solution. Agitate the electrode gently to remove the air bubbles.

### **Sample Storage**

Samples should be measured immediately after the samples have come to the same temperature as the electrode. Nitrite concentrations greater than  $5 \times 10^{-5}M$  that require storage should be made slightly alkaline to avoid nitrogen oxide gas loss. Samples with nitrite concentrations below  $5 \times 10^{-5}M$  should be made slightly acidic to prevent carbon dioxide absorption. Add 0.6 grams sodium dihydrogen phosphate,  $NaH_2PO_4$ , to every 100 ml of low level sample (below  $5 \times 10^{-5}M$ ) and 0.6 grams sodium monohydrogen phosphate,  $Na_2HPO_4$ , for a pH of 6.2.

### **Sample Requirements**

Make sure that the samples and standards are at the same temperature. About a 2% error will be introduced for a  $1^\circ C$  difference in temperature. Temperature should be less than  $50^\circ C$ . All samples and standards must be aqueous. They must not contain organic solvents. Interferences found in Table 3 should be absent.

Acid buffer solution 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 1.0 to 1.5. In this range, all interferences are minimized.

### **Units of Measurement**

Nitrite concentrations are measured in units of parts per million as nitrite (or nitrogen dioxide), parts per million as nitrogen, moles per liter, or any other convenient concentration unit. Table 1 indicates some of the concentration units.

TABLE 1: Concentration Unit Conversion Factors

| <u>ppm <math>NO_2^{-1}</math></u> | <u>ppm N</u> | <u>moles/liter <math>NO_2^{-1}</math></u> |
|-----------------------------------|--------------|---|
| 4.6                               | 1.40         | $1 \times 10^{-4}$                        |
| 46.0                              | 14.00        | $1 \times 10^{-3}$                        |
| 460.0                             | 140.00       | $1 \times 10^{-2}$                        |

### **MEASUREMENT PROCEDURE**

#### **Direct Measurement**

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 acid buffer for all nitrite samples. The temperature of both sample solution and of standard solutions should be the same.

Direct measurements are most conveniently made in the concentration range of  $10^{-5}$  to  $5 \times 10^{-3}$ M. Below  $10^{-5}$ M, the rate of gas diffusion through the membrane is slow and response time is poor. The partial pressure of gas in solution is sufficiently great above  $5 \times 10^{-3}$ M to cause diffusion out of the solution. If samples are diluted before adding acid buffer, direct measurement can still be used to measure samples above  $5 \times 10^{-3}$ M.

#### **Direct Measurement of Nitrite (using a pH/mV meter)**

- 1) Prepare  $10^{-3}$ ,  $10^{-4}$ , and  $10^{-5}$ M or 100, 10, and 1 ppm standards by serial dilution of the 0.1M, 1000 ppm, or 100 ppm standard. Add 10 ml of acid buffer per 100 ml standard. If samples have an ionic strength above 0.1M, prepare standards with a composition similar to samples.
- 2) Place the most dilute solution ( $10^{-5}$ M or 1 ppm) on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution. When the reading has stabilized, record the mV reading.
- 3) Place the midrange solution ( $10^{-4}$ M or 10 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode with distilled water and blotting dry, immerse the electrode tip in the solution. When the reading has stabilized, record the mV reading.
- 4) Place the most concentrated solution ( $10^{-3}$ M or 100 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode with distilled water and blotting dry, immerse the electrode tip in the solution. When the reading has stabilized, record the mV reading.
- 5) Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis). A typical calibration curve can be found in Figure 3. The calibration curve may be extrapolated down to about  $10^{-6}$ M or 0.1 ppm.

A calibration curve is constructed on semi-logarithmic paper when using a 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. The non-linear portion of the curve requires the use of low level procedures.

- 6) To a clean, dry 150 ml beaker, add 100 ml of sample and 10 ml of acid buffer. Place the beaker on the magnetic stirrer and begin stirring. Place the electrode tip in the solution. When the reading has stabilized, record the millivolt reading. Determine the concentration directly from the calibration curve.
- 7) The electrode should be recalibrated every 1-2 hours. Simply repeat steps 2-5 above.

### Direct Measurement of Nitrite (using an ion meter)

- 1) By serial dilution of the 0.1M, 1000 ppm, or 100 ppm standard, prepare two nitrite standards whose concentration is near the expected sample concentration. Measure out 100 ml of each standard into individual 150 ml beakers and add 10 ml of acid buffer to each. When calibrating, assume that the added buffer has no effect on the standard concentration.
- 2) Place the more dilute solution 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 nitrite or N standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
- 5) Rinse the electrode tip with distilled water and blot dry.
- 6) Place the more concentrated solution 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 nitrite or N standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
- 9) For low level measurements, place the rinsed, dried electrode into a solution containing 100 ml of distilled water and 10 ml of acid buffer. After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.
- 10) Place 100 ml of the sample and 10 ml of acid buffer in a 150 ml beaker, place it on the magnetic stirrer, and begin stirring.
- 11) Immerse the electrode tip in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.
- 12) The electrode should be recalibrated every 1-2 hours. Simply repeat Steps 2-8 (2-9) above.



### Low Level Nitrite Determination (using a standard pH/mV meter)

This procedure is recommended for solutions with a nitrite concentration less than  $1.0 \times 10^{-5} \text{M}$  (1 ppm N). If the solution is high in ionic strength, but low in nitrite, use the same procedure, but prepare a calibration solution with a composition similar to the sample.

- 1) Using 20 ml of stock acid buffer, dilute to 100 ml with distilled water.
- 2) Dilute 1 ml of the 0.1M standard to 100 ml to prepare a  $1.0 \times 10^{-3} \text{M}$  standard solution for measurements in moles per liter. Dilute 10 ml of the 1000 ppm standard to prepare a 100 ppm standard solution for measurements in ppm.
- 3) To a 150 ml beaker, add 100 ml of distilled water and 1 ml of low level acid buffer. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.
- 4) Place the electrode tip in the solution. Assure that the meter is in the mV mode.
- 5) Add increments of the  $1.0 \times 10^{-3} \text{M}$  or 100 ppm standard as given in Table 2 below.
- 6) After the reading has stabilized, record the mV reading after each addition.

TABLE 2: Stepwise Calibration for Low Level Nitrite Measurements

| <u>Step</u> | <u>Pipet</u> | <u>Added<br/>Volume (ml)</u> | <u>Concentration<br/>M</u> | <u>ppm</u> |
|-------------|--------------|------------------------------|----------------------------|------------|
| 1           | A            | 0.1                          | $1.0 \times 10^{-6}$       | 0.1        |
| 2           | A            | 0.1                          | $2.0 \times 10^{-6}$       | 0.2        |
| 3           | A            | 0.2                          | $4.0 \times 10^{-6}$       | 0.4        |
| 4           | A            | 0.2                          | $6.0 \times 10^{-6}$       | 0.6        |
| 5           | A            | 0.4                          | $9.9 \times 10^{-6}$       | 1.0        |
| 6           | B            | 2                            | $2.9 \times 10^{-5}$       | 2.9        |
| 7           | B            | 2                            | $4.8 \times 10^{-5}$       | 4.8        |

Pipet A = 1 ml graduated pipet

Pipet B = 2 ml pipet

Solutions: Additions of  $1.0 \times 10^{-3}M$  or 100 ppm standard to 100 ml of distilled water and 1 ml of low level acid buffer.

- 7) On semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis) as in Figure 1.
- 8) Rinse the electrode in distilled water and blot dry.
- 9) Measure out 100 ml of the sample into a 150 ml beaker, add 1 ml of low level acid buffer, and place the beaker on the magnetic stirrer. Begin stirring. Lower the electrode tip into the solution.
- 10) After the reading has stabilized, record the mV reading and determine the concentration from the low level calibration curve.
- 11) Prepare a new low level calibration curve daily. Check the calibration curve every 1-2 hours by repeating Steps 3-7 above.

#### **Low Level Nitrite Determination (using an ion meter)**

Follow the procedure given for normal nitrite determination using an ion meter and the blank correction procedure.

#### **Titration**

If the nitrite sample is diluted in 0.25M perchloric or nitric acid, nitrite can be quantitatively titrated with potassium permanganate, which requires high acidity to fully react with nitrite. Increments of potassium permanganate are added to an acidified nitrite sample and the millivolt readings plotted (vertical axis) against the volume of titrant added (horizontal axis) on linear graph paper. The sharpest slope change is taken as the endpoint of the reaction and the sample's nitrite concentration is computed using the volume of titrant, the titrant concentration, and the volume of sample used. Keep in mind that 2 moles of permanganate react with 5 moles of nitrite.

#### **ELECTRODE CHARACTERISTICS**

##### **Reproducibility**

Direct electrode measurements reproducible to 2% can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuations, drift, and noise limit reproducibility.

Reproducibility is independent of concentration within the electrode's operating range.

### **Interferences**

Table 3 lists some common interfering species that, if present in high enough levels, will cause electrode interferences and measurement errors or electrode drift when using the nitrite ion electrode. The main interfering species are volatile weak acids, gases that react with water to form acid solutions.

The rate of the interfering species diffusion across the electrode membrane, the presence of other interferences, and the time of exposure to the sample must also be taken into consideration. If sample exposure is brief and the rate of interfering species diffusion across the membrane is slow, measurements of nitrous acid are possible. Certain acids (lactic, pyruvic, and hydrofluoric) may cause interference with long term exposure (30 minutes), but exhibit negligible interference with short term exposure (5 minutes).

Irreversible changes in the electrode's internal filling solution can take place slowly when the electrode is exposed to sulfur dioxide. Potassium dichromate should be added to the sample to remove sulfur dioxide.

The halogens--chlorine, bromine, and iodine--also react with nitrous acid. The stannous and ferrous ions,  $\text{Sn}^{+2}$  and  $\text{Fe}^{+2}$ , may react with nitrous acid, though ionic species cannot cross the membrane and interfere with electrode measurements. The glass internal sensing element will be damaged by prolonged use in solutions containing  $10^{-3}\text{M}$  fluoride ion.

Low level nitrite measurements (below  $10^{-5}\text{M}$  or 0.5 ppm) are affected by carbon dioxide. Standard solutions for low level nitrite measurements should be prepared with fresh, deionized water. Remove carbon dioxide from standards and samples by the following steps:

1. To a 100 ml sample, add 2 ml of 0.25M potassium hydrogen phthalate,  $\text{KC}_8\text{H}_6\text{O}_4$ . This provides the solution with some buffering capacity as it becomes less acidic as the carbon dioxide is removed.
2. Use 2.5M perchloric acid to adjust the pH to 5.5.
3. At the rate of 1 liter per minute, bubble nitrogen gas through the solution for about 5 minutes through a coarse fritted gas dispersion tube. The loss of nitrite is less than 5%, since the bubbling is necessary for only about 5

minutes.

**TABLE 3:** Concentration of Possible Interferences Causing a 10% Error at Various Levels of  $\text{NaNO}_2$ .

| <u>Interferences</u><br>(moles/liter) | <u><math>10^{-2}\text{M NO}_2^{-1}</math></u> | <u><math>10^{-3}\text{M NO}_2^{-1}</math></u> | <u><math>10^{-4}\text{M NO}_2^{-1}</math></u> |
|---------------------------------------|---|---|---|
| acetic acid                           | $3 \times 10^{-2}$                            | $3 \times 10^{-3}$                            | $3 \times 10^{-4}$                            |
| carbon dioxide                        | $3 \times 10^{-1}$                            | $3 \times 10^{-2}$                            | $3 \times 10^{-3}$                            |
| formic acid                           | $2 \times 10^{-3}$                            | $2 \times 10^{-4}$                            | $2 \times 10^{-5}$                            |
| hydrofluoric acid                     | $1 \times 10^{-2}$                            | $1 \times 10^{-3}$                            | $1 \times 10^{-4}$                            |
| lactic acid                           | $2 \times 10^{-3}$                            | $2 \times 10^{-4}$                            | $2 \times 10^{-5}$                            |
| pyruvic acid                          | $1 \times 10^{-3}$                            | $1 \times 10^{-4}$                            | $1 \times 10^{-5}$                            |
| sulfur dioxide                        | $1 \times 10^{-4}$                            | $1 \times 10^{-5}$                            | $1 \times 10^{-6}$                            |

### Temperature Influences

Samples and standards should be at the same temperature, since electrode potentials are influenced by changes in temperature.

Provided that temperature equilibria has occurred, the nitrite ion electrode can be used at temperatures from  $0^\circ$ - $50^\circ\text{C}$ . Room temperature measurements are recommended, since measurements at temperatures markedly different from room temperature may require equilibrium times up to one hour.

Table 4 indicates the variation of theoretical slope with temperature.

**TABLE 4:** Temperature vs Value for the Electrode Slope

| <u>Temp (<math>^\circ\text{C}</math>)</u> | <u>"S"</u> |
|---|------------|
| 0   | 54.20      |
| 10  | 56.18      |
| 20  | 58.16      |
| 25  | 59.16      |
| 30  | 60.15      |
| 40  | 62.13      |
| 50  | 64.11      |

### 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 1) the total level of dissolved species in solution--the osmotic strength--is below 1M and 2) the sample and electrode temperature 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 acid buffer. If samples have osmotic strengths greater than 1M, they should be diluted before measurement. However, this dilution should not reduce the nitrogen oxide level below  $4 \times 10^{-6}$ M. If dilution is not possible for the reason mentioned above, 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 1.2 grams reagent grade potassium nitrate,  $\text{KNO}_3$ , to 25 ml of internal filling solution, dissolving completely, and filling the salt bridge with this adjusted solution.

### **Electrode Response**

Plotting the electrode mV potential against the nitrogen oxide concentration (from about  $5 \times 10^{-6}$  to  $5 \times 10^{-3}$ M) on semi-logarithmic paper results in a straight line (over 3-4 decades) with a slope of about 56 mV per decade. Refer to Figure 3.

The time needed to reach 95% of the stable electrode potential reading, the electrode response time, varies from two minute or less for nitrous acid concentration changes in samples  $10^{-6}$ M or higher to several minutes near the detection limit. Refer to Figure 4. Samples above  $10^{-3}$ M must be diluted before measurement.

### **Electrode Storage**

The electrode should be kept in electrode storage solution between

measurements, never in air.

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.

If the electrode is not to be used for a long period 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**

The Nitrogen Oxide Electrode uses a hydrophobic gas-permeable membrane to separate the electrode's internal solution from the sample solution. The sample diffuses dissolved gaseous anhydrides of nitrous acid, from an acidified nitrite-containing sample, through the membrane until the partial pressure of the nitrogen oxides ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ , and  $\text{N}_2\text{O}_4$ ) is the same on both sides of the membrane. The partial pressure of the gaseous anhydrides is proportional to their concentration.

The level of nitrous acid,  $\text{HNO}_2$ , in the internal filling solution, is affected by the nitrogen oxides:



The equilibrium equation gives rise to the equilibrium constant in the following equation:

$$\text{constant} = \frac{[\text{H}^+] [\text{NO}_2^-]}{[\text{HNO}_2]}$$

The nitrite ion concentration can be considered fixed, since the internal filling solution contains sodium nitrite at a sufficiently high level. As a result:

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

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

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

where: E = measured electrode potential  
 $E_o$  = reference potential (a constant)  
 $[H^+]$  = hydrogen ion concentration  
 S = electrode slope (~56 mV)

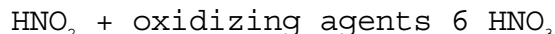
Because the hydrogen concentration is proportional to the nitrous acid concentration, electrode response to nitrous acid is also Nernstian:

$$E = E_o + S \log [HNO_2]$$

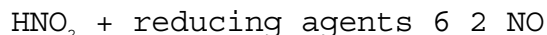
### NITROGEN OXIDE CHEMISTRY

Nitrite is the anion of nitrous acid, a weak acid. Nitrous acid and nitrite are reactive species which can be either oxidized or reduced in aqueous solutions. Nitrite is more reactive in acid media, in general.

Nitrous acid can reduce many common oxidizing agents such as hydrogen peroxide, permanganate, ozone, chlorine, and bromine. If the pH is 1 or greater, dichromate is not reduced in nitrite solutions. In general:



Reducing agents, such as iodine, ferrous ion, sulfur dioxide, and stannous ion, are oxidized in nitrite solution:



Nitrous acid reacts with amines, including relatively unreactive tertiary amines, giving nitrogen, diazonium salts and nitroso amines. Sulfamic acid reacts selectively and very rapidly with nitrous acid to form nitroso sulfamic acid. Nitrous acid is in equilibrium in solution with nitric oxide and nitrogen dioxide:



Nitrous acid is slowly decomposed, in acid solution, according to the following equation:



Less than a few percent per hour nitrite is lost through decomposition. More nitric acid is lost as nitric oxide and nitrogen dioxide on exposure to air or even through the walls of plastic containers. Stirring a nitrous acid solution rapidly at

25°C for 14 hours shows a loss of 90% nitrous acid.

Figure 5 shows the fraction of free nitrite in aqueous solution as a function of pH. The relationship between nitrous acid and nitrite is given by the following:

$$\frac{[\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{K_1}{\text{H}^+} \quad \text{or} \quad \log \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} = \text{pH} - \text{p}K_1$$

## **TROUBLESHOOTING**

### **Troubleshooting Guide**

The most important principal 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. 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.

#### **Electrode**

1. Rinse electrode thoroughly with distilled water.
2. Perform **Electrode Slope Check**.



3. If electrode fails this procedure, re-soak nitrogen oxide electrode as directed in **Electrode Assembly** and **Checking Membrane**.

4. Repeat **Electrode Slope Check**.

5. If the electrode still does not perform as described, determine whether the nitrogen oxide inner body is working properly as directed in **Checking the Electrode Inner Body**.

6. If the stability and the slope check out properly, but measurement problems persist, the standards may be of poor quality, the sample may contain interference or complexing agents, or the technique may be in error. See **Standard, Sample** and **Technique** sections below.

7. 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
- review **Troubleshooting Hints**

### **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 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**

Check the method of analysis for compatibility with your sample. Direct measurement may not always be the method of choice. If working at low levels, be sure to use low level measurement techniques.

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 instruction manual to be sure that proper technique has been followed. Call your distributor and ask for the Technical Services Department to answer any questions.

## Troubleshooting Hints

| Symptom  | Possible Causes                      | Next Step  |
|--|--------------------------------------|--|
| Out of Range Reading                               | defective meter                      | perform meter check-out procedure (see meter instruction manual)   |
|  | electrode not plugged in properly    | unplug electrode and reseat  |
|  | electrode filling solution not added | fill outer body with proper level of electrode filling solution  |
|  | air bubbles on membrane              | remove bubbles by redipping electrode  |
|  | inner electrode body defective       | refer to <b>Checking the Electrode Inner Body</b>  |
|  | electrode not in solution            | put electrode in solution  |
| "Incorrect Answer" (but calibration curve is good) | incorrect scaling of semilog 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 number correctly   |
|  | incorrect standards                  | prepare fresh standards  |
|  | wrong units used                     | apply correct conversion factor:<br>$10^{-3}\text{M} = 46 \text{ ppm as NO}_2^{-1}$<br>$= 14 \text{ ppm as N}$                                     |

|  |  |   |
|--|--|---|
|  | incorrect addition of acid buffer                  | same proportion of acid buffer must be added to all samples and standards                                 |
|  | all solutions not at same temperature              | all solutions must be at room temperature before measurement  |
|  | sample carryover                                   | rinse electrodes thoroughly between samples   |
| Drift (reading slowly changing in one direction) | samples and standards at different temperatures    | allow solutions to come to room temperature before measurement  |
|  | electrode exposed to air for extended period       | unscrew electrode cap, lift the inner body slightly, and reinsert it to reestablish the electrolyte layer |
|  | incorrect internal filling solution                | fill outer body with recommended filling solution supplied with electrode                                 |
|  | leakage of internal filling solution               | check that membrane and o-rings are installed correctly   |
|  | membrane failure (wet, perforation, discoloration) | replace membrane  |
|  | defective electrode inner body                     | refer to <b>Checking Electrode Inner Body</b>   |
|  | total level of dissolved species above 1M          | dilute solution   |
| Low Slope or                                     | standards contaminated                             | prepare fresh   |

|   |   |   |
|---|---|---|
| No Slope  | or incorrectly made<br>acid buffer not used<br><br>electrode exposed to<br>air for extended<br>period of time<br><br>membrane failure<br>(wet, perforation,<br>discoloration)<br><br>defective electrode<br>inner body              | standards<br><br>use recommended acid<br>buffer<br><br>unscrew electrode<br>cap, lift inner<br>body slightly, and<br>reinsert it to<br>reestablish the<br>electrolyte layer<br><br>replace membrane<br><br>refer to <b>Checking<br/>Electrode Inner<br/>Body</b>  |
| Noisy or<br>Unstable Readings<br>(readings<br>continuously or<br>randomly changing) | defective meter<br><br>air bubble on membrane<br><br>acid buffer not used<br><br>meter or stirrer not<br>grounded<br><br>electrode inner body<br>defective<br><br>internal filling<br>solution insufficient<br><br>bottom cap loose | perform meter check-<br>out procedure (see<br>meter instruction<br>manual)<br><br>remove bubble by<br>redipping electrode<br><br>use recommended acid<br>buffer<br><br>ground meter or<br>stirrer<br><br>refer to <b>Checking<br/>the Electrode Inner<br/>Body</b><br><br>fill electrode with<br>proper amount of<br>internal filling<br>solution<br><br>make sure bottom<br>cap is on tight<br>enough to close gap<br>between cap and body |

### 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 nitrogen oxide electrode. IF the electrode is dry, soak the glass tip of the inner body in Nitrogen Oxide Electrode Filling Solution (Cat. No WD-35803-72) for at least 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:   | $5 \times 10^{-6}$ to $5 \times 10^{-3}$ M<br>(0.18 to 230 ppm)                           |
| pH Range:              | 1.1 to 1.7  |
| Temperature Range:     | 0° to 50°C  |
| Inner Body Resistance: | ~1000 megohms   |
| Reproducibility:       | " 2%  |
| Size:                  | 110 mm length<br>12 mm diameter<br>1 m cable length                                       |
| Storage:               | electrode should be stored in 10<br>ml acid buffer mixed with 90 ml<br>of deionized water |

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