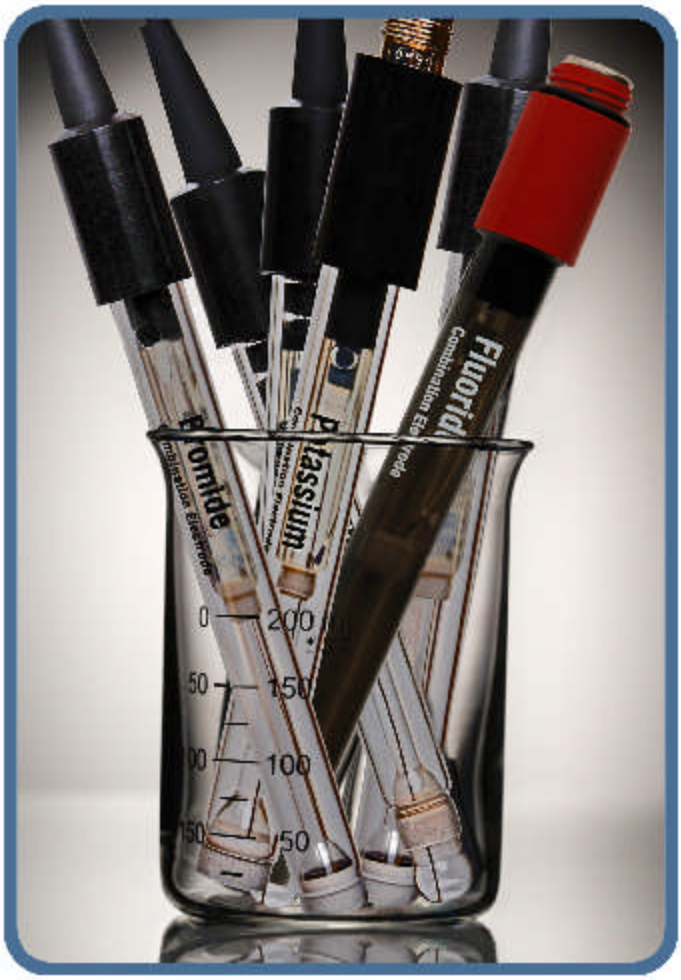
Van London Co.

"When Accuracy Matters"



Nitrogen Oxide Gas Sensing Electrode

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GENERAL INSTRUCTIONS

Introduction

The Van London Co. Nitrogen Oxide Gas-Sensing Electrode is used to measure nitrite in aqueous solutions. The measurement is not affected by sample color or turbidity.

Required Equipment

1. An ion meter
2. Nitrogen Oxide Gas Sensing Electrode
3. Nitrogen Oxide 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. Nitrogen Oxide Standard, 1000 ppm NO_2, Cat. No. NOXAS02.
3. Van London Co. Nitrogen Oxide Ionic Strength Adjuster (ISA), Cat. No. NOXIS01.
4. Van London Co. Nitrogen Oxide Electrode Filling Solution, Cat. No. N0XIF01.
5. Nitrogen Oxide Electrode Storage Solution, for storing the electrode between use. Dilute 10 ml of the Van London Co. Acid Buffer Solution to 100 ml with distilled water.

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 NOXIF01 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 Nitrogen Oxide 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°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 Nitrogen Oxide standard, prepare two Nitrogen Oxide 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 Nitrogen Oxide 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 Nitrogen Oxide 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 Nitrogen Oxide electrodes are used or stored for long periods, they will experience some deterioration in performance and slope errors will increase.

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. 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.

Nitrogen Oxide 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 $\pm$2% can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuation, drift, and noise limit reproducibility.

Interferences

Table 1 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, Sn^{+2} and Fe^{+2}, may react with nitrous acid, though ionic species cannot cross themembrane and interfere with electrode measurements. The glass internal sensing element will be damaged by prolonged use in solutions containing 10^{-3}M fluoride ion.

Low level nitrite measurements (below 10^{-5}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, $KC_8H_6O_4$. 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 course fritted gas dispersion tube. The loss of nitrite is less than 5%, since the bubbling is necessary for only about 5 minutes.

TABLE 1: Concentration of Possible Interferences Causing a 10% Error at Various Levels of $NaNO_2$.

Interferences (moles/liter)	10^{-2}M NO_2^{-1}	10^{-3}M NO_2^{-1}	10^{-4}M NO_2^{-1}
acetic acid	3×10^{-2}	3×10^{-3}	3×10^{-4}
carbon dioxide	3×10^{-1}	3×10^{-2}	3×10^{-3}
formic acid	2×10^{-3}	2×10^{-4}	2×10^{-5}
hydrofluoric acid	1×10^{-2}	1×10^{-3}	1×10^{-4}
lactic acid	2×10^{-3}	2×10^{-4}	2×10^{-5}
pyruvic acid	1×10^{-3}	1×10^{-4}	1×10^{-5}
sulfur dioxide	1×10^{-4}	1×10^{-5}	1×10^{-6}

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^{o}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 Nitrogen Oxide concentration results in a straight line with a slope of 56±3 mV between 10 ppm and 100 ppm at 25°C.

For Nitrogen Oxide concentrations above 0.2 ppm, the electrode exhibits good time response (95% of total mV reading in 30 seconds or less). Response times are longer below this value and Nitrogen Oxide loss to air may become a source of error. Samples above 220 ppm must be diluted before measurement.

Limits of Detection
The upper limit of detection in pure Nitrogen Oxide solutions is 220 ppm. Nitrogen Oxide is rapidly lost to the air above a concentration of 220 ppm. Dilution may be used if Nitrogen Oxide concentrations are above 220 ppm. The lower limit of detection is around 0.2 ppm.

pH Effects
The Nitrogen Oxide electrode can be used over the pH range 1.1 to 1.7. It is necessary to adjust the sample pH using the recommended ISA to convert nitrite in solution to Nitrogen Oxide.

Electrode Life
The Nitrogen Oxide 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 Nitrogen Oxide 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 Nitrogen Oxide electrode overnight or over the weekend, immerse the tip in the storage solution.

For longer periods of time, completely disassemble the electrode, rinse the inner body, the outer body, and the cap with distilled water. After drying, reassemble the electrode without filling solution. **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 Nitrogen Oxide 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 redipping electrode
	meter or stirrer improperly grounded	check meter and stirrer for grounding
Drift (reading slowly changing in one direction)	internal filling solution leakage	ensure that membrane is installed properly
	incorrect internal filling solution	refill outer body of electrode using filling solution shipped with electrode
	total sample level of dissolved species above 1M	dilute sample
	electrode in sample too long; CO_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 Inner Body** following this section
	electrode exposed to air for extended period	hold electrode by outer body and pull 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	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 Inner Body** 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 = 46 ppm as NO_2^{-1} = 14 ppm as N
	ISA added to standards and not samples	add same proportions of ISA to standards 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 Nitrogen Oxide 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 Nitrogen Oxide 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:	220 ppm to 0.2 ppm NO_2
pH Range:	1.1 to 1.7
Slope:	56±3 mV between 10 ppm and 100 ppm at 25°C
Temperature Range:	0° to 50°C
Interferences:	SO2, HF, Acetic acid
Reproducibility:	± 2%
Size:	110 mm length
	12 mm diameter
	1 m cable length

ELECTRODE THEORY

Electrode Operation

The Van London Co. 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 (NO, NO_2, N_2O_3, and N_2O_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, HNO_2, in the internal filling solution, is affected by the nitrogen oxides:

$$2\ H^+ + 2\ NO_2^- \leftrightarrow 2\ HNO_2 \leftrightarrow NO + NO_2 + H_2O \leftrightarrow N_2O_3 + H_2O$$

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

$$\text{constant} = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

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

$$[H^+] = [HNO_2] \times \text{constant}$$

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

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

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:

$$E = E_o{}^1 + S \log[HNO_2]$$

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:

$$HNO_2 + \text{oxidizing agents} \rightarrow HNO_3$$

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

$$HNO_2 + \text{reducing agents} \rightarrow 2\ NO$$

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

$$2\ HNO_2 \leftrightarrow NO + NO_2 + H_2O$$

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

$$3\ HNO_2 \rightarrow H^+ + NO_3^- + 2\ NO + H_2O$$

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 though 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 3 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:

$$\frac{[NO_2^-]}{[HNO_2]} = \frac{K_1}{H^+} \quad \text{or} \quad \log \frac{[NO_2^-]}{[HNO_2]} = pH - pK_1$$

the solution.