

User Guide

Nitrogen Oxide
Ion Selective
Electrode



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Introduction

This user guide contains information on the preparation, operation and maintenance for the nitrogen oxide ion selective electrode (ISE). General analytical procedures, electrode characteristics and electrode theory are also included in this user guide. Nitrogen oxide electrodes measure nitrogen oxide in aqueous solutions quickly, simply, accurately and economically. Step-by-step procedures are given for the conversion of nitrate to nitrite, the measurement of nitrogen dioxide in air, and the measurement of nitrite in meat processing brines and food.

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. For the most current contact information, visit www.thermo.com/contactwater.

For the latest application and technical resources for Thermo Scientific Orion products, visit www.thermo.com/waterapps.

Nitrogen Oxide Gas Sensing Combination ISE, Cat. No. 9546BN and 954600

The nitrogen oxide combination electrode has the sensing and reference half-cells built into one electrode, which decreases the amount of required solutions and reduces waste. The nitrogen oxide combination electrode is available with a BNC connector, Cat. No. 9546BN, or a U.S. standard connector, Cat. No. 954600.

The nitrogen oxide electrode includes the following:

- 20 loose membranes
- 1 reusable membrane cap
- 1 spare parts kit
- Tweezers for handling the membranes
- Bottle of electrode filling solution with dispensing cap

Required Equipment

1. Thermo Scientific Orion ISE meter, such as the 4-Star pH/ISE meter or 5-Star pH/ISE/DO/conductivity meter; equivalent ISE meter; or mV meter with a 0.1 mV resolution.

Nitrogen oxide electrodes can be used on any ISE or mV meter with a BNC or U.S. standard connection. The electrodes can also be used on meters with a variety of inputs when an adapter cable is used. Visit www.thermo.com/water for details.

2. Thermo Scientific Orion nitrogen oxide combination electrode, Cat. No. 9546BN or 954600.
3. Magnetic stirrer or Thermo Scientific Orion stirrer probe, Cat. No. 096019. The stirrer probe can be used with 3-Star, 4-Star and 5-Star benchtop meters.
4. Volumetric flasks, graduated cylinders and beakers.
5. Distilled or deionized water.
6. Nitrogen oxide electrode filling solution, Cat. No. 954602.
7. 0.1 M NaNO_2 nitrogen oxide calibration standard, Cat. No. 954606.

To prepare a 1000 ppm nitrogen oxide as nitrite standard, add 217 mL of the 0.1 M nitrogen oxide standard, Cat. No. 954606, to a 1 liter volumetric flask and dilute to the mark with distilled water.

To prepare a 1000 ppm nitrogen oxide as nitrogen (N) standard, add 714 mL of the 0.1 M nitrogen oxide standard, Cat. No. 954606, to a 1 liter volumetric flask and dilute to the mark with distilled water.

8. Nitrogen oxide acid buffer solution, Cat. No. 956410. The acid buffer solution adjusts the solution pH and provides a constant background ionic strength for samples and standards.
9. Nitrogen oxide storage solution – prepare by adding 10 mL of the acid buffer solution, Cat. No. 956410, to a 100 mL volumetric flask and dilute to the mark with distilled water.

Serial Dilutions

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

1. **To prepare a 10^{-2} M standard (460 ppm as NO_2^- and 140 ppm as N)** – Pipet 10 mL of the 0.1 M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.
2. **To prepare a 10^{-3} M standard (46.0 ppm as NO_2^- and 14.0 ppm as N)** – Pipet 10 mL of the 10^{-2} M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.
3. **To prepare a 10^{-4} M standard (4.60 ppm as NO_2^- and 1.40 ppm as N)** – Pipet 10 mL of the 10^{-3} M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

To prepare standards with a different concentration use the following formula:

$$C_1 * V_1 = C_2 * V_2$$

C_1 = concentration of original standard

V_1 = volume of original standard

C_2 = concentration of standard after dilution

V_2 = volume of standard after dilution

For example, to prepare 100 mL of a 100 ppm nitrogen oxide as nitrogen (N) standard from a 1400 ppm nitrogen oxide as nitrogen (N) standard:

$$C_1 = 1400 \text{ ppm nitrogen oxide}$$

$$V_1 = \text{unknown}$$

$$C_2 = 100 \text{ ppm nitrogen oxide}$$

$$V_2 = 100 \text{ mL}$$

$$1400 \text{ ppm} * V_1 = 100 \text{ ppm} * 100 \text{ mL}$$

$$V_1 = (100 \text{ ppm} * 100 \text{ mL}) / 1400 \text{ ppm} = 7.14 \text{ mL}$$

Electrode Setup

Nitrogen Oxide Electrode Preparation

A new electrode is shipped dry and without a membrane installed. Avoid excessive handling of the membrane during assembly; this may affect the hydrophobic properties of the membrane and shorten the membrane life. Use the tweezers when handling the membrane. A membrane will last from one week to several months, depending on usage.

Electrode Assembly

1. Hold the electrode vertically and unscrew the top cap from the outer body. See **Figure 1**.
2. Carefully lift the inner body out of the outer body. See **Figure 2**. Dispose of any electrode filling solution that is in the outer body.
3. Unscrew the membrane cap from the outer body. See **Figure 2**. Remove the O-ring, existing membrane (if a membrane was previously installed) and membrane spacer from the membrane cap.
4. Carefully separate a new membrane from the packing paper and discard the paper. Place the new membrane in the cap with the dull side towards the inner sensing element and the shiny side down towards the sample solution.
5. Ensure that the thin O-ring is firmly inserted into the membrane spacer and place the membrane spacer into the membrane cap on top of the new membrane with the O-ring towards the sample solution.
6. Place the medium O-ring on top of the membrane spacer. Screw the outer body into the membrane cap.
7. Fill the outer body with electrode filling solution. Fill it with approximately one inch of solution. See **Figure 3**.
8. Insert the inner body into the outer body and screw on the top cap. Excess electrode filling solution may come out of the vent hole. When the membrane is installed, it should be slightly distended by the inner body of the electrode.
9. Allow the assembled electrode to soak for 30 minutes in the nitrogen oxide electrode storage solution.

Figure 1

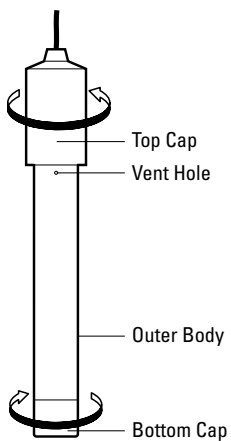


Figure 2

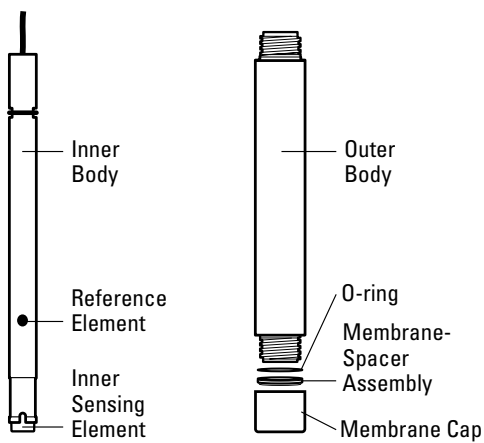
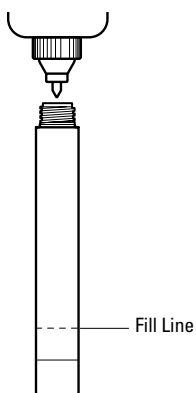


Figure 3



Checking Electrode Operation (Slope)

These are general instructions that can be used with most meters to check the electrode operation. Refer to 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. If the electrode has been stored dry, prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to a meter with a mV mode. Set the meter to the mV mode.
3. Add 100 mL of distilled water and 10 mL of acid buffer solution, Cat. No. 956410, to a 150 mL beaker. Stir the solution thoroughly.
4. Rinse the electrode with distilled water and place the electrode into the solution prepared in step 3.
5. Select either a 0.1 M nitrogen oxide or 1000 ppm nitrogen oxide as nitrogen (N) standard. Pipet 1 mL of the standard into the beaker and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
6. Pipet 10 mL of the same standard into the same beaker and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
7. There should be a -54 to -60 mV difference between the two millivolt readings when the solution temperature is between 20 to 25 °C. If the millivolt potential is not within this range, refer to the **Troubleshooting** section.

Measurement Units

Nitrogen oxide concentration can be measured in moles per liter (M), parts per million (ppm) or any convenient concentration unit.

Table 1
Concentration Unit Conversion Factors

Moles/Liter (M)	ppm as NO ₂ ⁻	ppm as N
1.0	46000	14000
10 ⁻¹	4600	1400
10 ⁻²	460	140
10 ⁻³	46	14
10 ⁻⁴	4.6	1.4

Sample Requirements

All samples must be aqueous and must not contain organic solvents. Contact Technical Support for information on using the electrode for specific applications.

The solution temperature must be less than 50 °C. Samples and standards should be at the same temperature.

A 1 °C difference in temperature for a 10⁻³ M nitrogen oxide solution will give rise to about a 2% measurement error.

In all analytical procedures, acid buffer solution must be added to all samples and standards so they will have the proper osmotic strength and pH. After the addition of the acid buffer, all samples and standards should fall between pH 1.1 and 1.7, so that all the nitrous acid is converted to nitrogen oxide gases (NO, NO₂, N₂O₃ and N₂O₄). Since the buffering capacity of the acid buffer is limited, highly acidic or buffered samples must be adjusted to pH 1.1 to 1.7 before the acid buffer is added.

Samples and standards also must have a total level of dissolved species (osmotic strength, see the **Effect of Dissolved Species** and **Temperature** sections) less than 0.5 M. Solutions with an osmotic strength greater than 0.5 M should be diluted before the acid buffer is added. If the sample has a high osmotic strength, it will cause excessive drift. For example, an electrode placed in a 1.0 osmolal solution will have a drift rate of 0.1 to 0.2 mV per minute.

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. If a nitrite sample is at a concentration greater than 5×10^{-5} M and requires storage, make the sample slightly alkaline to avoid the loss of nitrogen oxide gases. Samples with levels of nitrite below 5×10^{-5} M should be made slightly acidic to prevent carbon dioxide absorption. To every 100 mL of low level sample (below 5×10^{-5} M), add 0.6 grams of sodium dihydrogen phosphate, NaH_2PO_4 , and 0.6 grams of sodium monohydrogen phosphate, Na_2HPO_4 , for a pH of 6.2.

Measuring Hints

- The rate of nitrous acid loss at 25 °C from a stirred 100 mL buffered solution in an open beaker is about 90% in 14 hours. Minimize the loss of nitrogen oxide from the sample by performing the following recommendations:
 - Store samples according to the procedure in the **Sample Storage** section.
 - Use beakers that minimize the ratio of surface area to volume.
 - Keep beakers that contain standards and samples covered between measurements.
- Add 10 mL of acid buffer solution, Cat. No. 956410, to every 100 mL of sample or standard immediately before making measurements.
- Stir all standards and samples at a uniform, moderate rate. Place a piece of insulating material, such as Styrofoam or cardboard, between the magnetic stir plate and beaker to prevent measurement errors from the transfer of heat to the sample.
- Always use freshly prepared standards for calibration.
- Always rinse the electrode with distilled water between measurements and shake the electrode to remove the water and prevent sample carryover. Do not wipe or rub the electrode membrane.
- Allow all standards and samples to reach the same temperature for precise measurements.
- Verify the electrode calibration every two hours by placing the electrode in a fresh aliquot of the least concentrated standard used for calibration. If the value has changed by more than 2%, recalibrate the electrode.
- After immersing the electrode in a solution, check the electrode membrane for air bubbles and remove air bubbles by reimmersing the electrode in the solution and gently tapping it.
- For high ionic strength samples, prepare standards with a background composition similar to the sample.

Nitrogen Oxide Electrode Storage

Short Term Storage

Between measurements, rinse the electrode thoroughly with distilled water and store it in the nitrogen oxide electrode storage solution. To prepare the electrode storage solution, add 10 mL of the acid buffer solution, Cat. No. 956410, to a 100 mL volumetric flask and dilute to the mark with distilled water.

Note: *Do not store the electrode in the air. If the electrode is accidentally left in the air and erratic results are obtained, the space between the inside of the membrane and the inner body may be dry. To make the electrode usable again, wet the membrane with internal filling solution by unscrewing the top cap of the electrode, lifting up the internal sensing element and reinserting it.*

Long Term Storage

For storage over one week or if the electrode is stored indefinitely, disassemble the electrode completely and rinse the inner body, outer body and membrane cap with distilled water. Dry and reassemble the electrode without filling solution or a membrane.

Nitrogen Oxide Electrode Maintenance

If the electrode response drifts or becomes sluggish, the membrane may contain a surface layer of contaminants. Restore the electrode performance by soaking the electrode in distilled water for about 5 minutes and then soaking the electrode in a 10 ppm nitrogen oxide standard solution for about 1 hour. If soaking the electrode does not restore normal electrode performance, replace the nitrogen oxide membrane.

A membrane will last from one week to several months depending on the usage. Membrane failure is characterized by a shift in the electrode potential, drift or poor response. Membrane failure may be apparent on visual inspection as dark spots or discoloration of the membrane.

Rinse the electrode with distilled water, obtain a new membrane and refer to the **Electrode Preparation** section for instructions on installing a new membrane on the electrode.

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 using a series of standards. The concentration of the samples is determined by comparison to the standards. The acid buffer solution is added to all solutions to ensure that samples and standards are in the correct pH range and have similar ionic strength. Direct measurements are most conveniently made in the 10^{-5} M to 5×10^{-3} M concentration range. Below 10^{-5} M, the rate of gas diffusion through the membrane is slow and response time is poor. Above 5×10^{-3} M, the partial pressure of gas in solution is sufficiently great to cause diffusion out of solution. Direct measurement can still be used to measure samples above 5×10^{-3} M if samples are diluted before adding acid buffer.

Incremental Techniques provide a useful method for measuring samples, since a calibration is not required. 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 to 100 times) excess of complexing agents. As in direct calibration, any convenient concentration unit can be used.

Known Addition is 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.

Titrations are quantitative analytical techniques for measuring the concentration of a species by incremental addition of a reagent (titrant) that reacts with the sample species. Sensing electrodes can be used for determination of the titration end point. Ion selective electrodes are useful as end point detectors, because they are unaffected by sample color or turbidity. Titrations are approximately 10 times more precise than direct calibration, but are more time-consuming.

A titration can be used as a cross-check for known addition or direct measurement. Potassium permanganate is used as the titrant. When added to a nitrite sample solution, potassium permanganate reacts with nitrite and reduces the measured potential. Potassium permanganate requires a highly acidic background to fully react with nitrite:



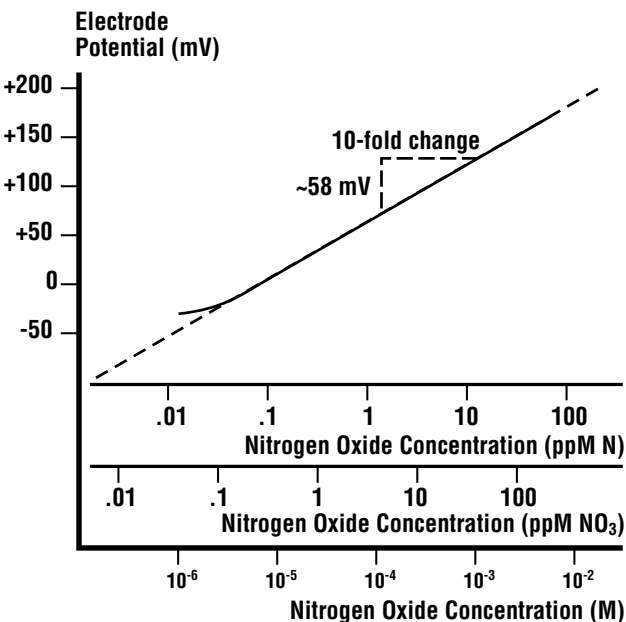
This reaction of permanganate and nitrite is slow, so response time will be slow. Also the titration end point may be in error if other oxidizable species are in the sample.

Direct Calibration Technique

Typical Direct Calibration Curve

In the direct calibration procedure, a calibration curve is constructed either in the meter memory or on semi-logarithmic paper. Electrode potentials of standard solutions are measured and plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only two standards are needed to determine a calibration curve. In non-linear regions, more points must be taken. Procedures are given in the **Direct Calibration Technique** section for sample concentrations in the linear region of electrode response. The **Low Level Calibration Technique** section provides procedures for measurements in the non-linear region of electrode response.

Figure 4
Typical Direct Calibration Curve



Direct Calibration Overview

The following direct measurement procedures are recommended for moderate to high level measurements. Samples must be in the linear range of the electrode – 10^{-5} M to 5×10^{-3} M. A two point calibration is sufficient, although more points can be used. When using an ISE meter, sample concentrations can be read directly from the meter. When using a mV meter, a calibration curve can be prepared on semi-logarithmic graph paper, or a linear regression (against logarithmic concentration values) can be performed using a spreadsheet or graphing program.

Calibration Hints

- Standard concentrations should bracket the expected sample concentrations.
- Always add 10 mL of acid buffer solution, Cat. No. 956410, per 100 mL of standard or sample.
- For high ionic strength samples that have an ionic strength of 0.5 M or greater, prepare standards with a background composition similar to that of the samples, or measure the samples using the known addition method.
- During calibration, measure the least concentrated standard first, and work up to the most concentrated standard.

Direct Calibration Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to the meter.
3. Prepare at least two standards that 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. See the **Serial Dilution** section for instructions on how to prepare standards. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to the **Temperature Effects** section.

Direct Calibration Procedure Using a Meter with an ISE Mode

Note: See the meter user guide for more specific information.

1. Add 100 mL of the less concentrated standard and 10 mL of acid buffer solution to a 150 mL beaker and stir the solution thoroughly.
2. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. Wait for a stable reading and adjust the meter to display the value of the standard, as described in the meter user guide.
3. Add 100 mL of the more concentrated standard and 10 mL of acid buffer solution to a second 150 mL beaker and stir the solution thoroughly.
4. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. Wait for a stable reading and adjust the meter to display the value of the second standard, as described in the meter user guide.
5. Record the resulting slope value. The slope should be between -54 and -60 mV when the standards are between 20 and 25 °C.
6. Add 100 mL of sample and 10 mL of acid buffer solution to a clean 150 mL beaker and stir the solution thoroughly.
7. Rinse the electrode with distilled water, blot it dry and place it into the sample. The concentration of the sample will be displayed on the meter.

Note: Other solution volumes may be used, as long as the ratio of solution to acid buffer solution remains 10:1.

Direct Calibration Procedure Using a Meter with a mV Mode

Note: See the meter user guide for more specific information.

1. Set the meter to the mV mode.
2. Add 100 mL of the less concentrated standard and 10 mL of acid buffer solution to a 150 mL beaker and stir the solution thoroughly.
3. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
4. Add 100 mL of the more concentrated standard and 10 mL of acid buffer solution to a second 150 mL beaker and stir the solution thoroughly.
5. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Using semi-logarithmic 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. Add 100 mL of sample and 10 mL of acid buffer solution to a clean 150 mL beaker and stir the solution thoroughly.
8. Rinse the electrode with distilled water, blot it dry and place it 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 of the sample.

Note: Other solution volumes may be used, as long as the ratio of solution to acid buffer solution remains 10:1.

Known Addition Technique

Known addition is a convenient technique for measuring samples in the linear range of the electrode because no calibration curve is required. 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. The total concentration of nitrite can be measured in the absence of complexing agents down to 4×10^{-6} M (0.18 ppm NO_2).

Accurate results require 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.
- 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.
- With double or multiple known addition, the final addition should be 10 to 100 times the sample concentration.
- Add 10 mL of acid buffer solution to every 100 mL of sample before analysis.

Known Addition Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to the meter.
3. Prepare a standard solution that will cause the nitrogen oxide concentration of the sample to double when added to the sample solution. Refer to **Table 2** for guidelines.
4. Determine the electrode slope by performing the procedure in the **Checking Electrode Operation (Slope)** section.
5. Rinse the electrode with distilled water.

Table 2
Guideline For Known Addition

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

* Most convenient volume to use

Known Addition Using a Meter with a Known Addition Mode

Note: See the meter user guide for more specific information.

1. Set the meter to measure in the known addition mode.
2. Measure 100 mL of sample and 10 mL of acid buffer solution and pour the solutions into a 150 mL beaker. Rinse the electrode with distilled water and place it into the sample solution. Stir the solution thoroughly.
3. When a stable reading is displayed, set the meter as described in the meter user guide, if required.
4. Pipet the appropriate amount of the standard solution into the beaker. Stir the solution thoroughly.
5. When a stable reading is displayed, record the sample concentration.

Known Addition Using a Meter with a Millivolt Mode

1. Set the meter to the relative millivolt mode. If a relative millivolt mode is not available, use the millivolt mode.
2. Measure 100 mL of sample and 10 mL of acid buffer solution and pour the solutions into a 150 mL beaker. Stir the solution thoroughly.
3. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker. When a stable reading is displayed, set the meter to read 0.0 mV. If the reading cannot be adjusted to 0.0 mV, record the actual mV value.
4. Pipet the appropriate amount of standard solution into the beaker. Stir the solution thoroughly.
5. When a stable reading is displayed, record the mV value. If the meter could not be set to 0.0 mV in step 3, subtract the first reading from the second reading to calculate ΔE .
6. Use **Table 4** to find the Q value that corresponds to the change in potential, ΔE . To determine the original sample concentration, multiply Q by the concentration of the added standard:

$$C_{\text{sample}} = Q * C_{\text{standard}}$$

C_{standard} = standard concentration

C_{sample} = sample concentration

Q = value from **Table 4**

The table of Q values is calculated for a 10% volume change. The equation for the calculation of Q for different slopes and volume changes is given below.

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

Q = value from **Table 4**

$\Delta E = E_2 - E_1$

S = slope of the electrode

p = volume of standard / volume of sample and acid buffer

r = volume of sample and acid buffer / volume of sample

Calculating Known Addition for Samples using Lotus, Excel, or Quattro Spreadsheets

If it is more convenient, a simple spreadsheet can be set up to calculate the known addition results, using any ratio of sample to addition. A typical worksheet is shown in **Table 3**. The numbers shown are examples, but the formulas and their locations should be copied exactly.

Table 3
Known Addition Calculations using Lotus, Excel, or Quattro Spreadsheets

A	B	C
1		Enter Value
2	Volume of sample and acid buffer solution (mL)	110
3	Volume of addition (mL)	10
4	Concentration of addition	10
5	Volume of sample	100
6	Initial mV reading	45.3
7	Final mV reading	63.7
8	Electrode slope	-59.2
9		
10		Derived Values
11	Delta E	+C7 - C6
12	Solution volume ratio	+C3/C2
13	Antilog term	+10 [^] (C11/C8)
14	Sample volume ratio	+C2/C5
15	Q term	+C12*C14/ (((1+C12)*C13)-1)
16	Calculated initial concentration in same units as addition	+C15*C4

Note: For Excel, use = instead of + at start of formulas.

Table 4
Q Values for a 10% volume change
(slope of -58.2 mV/decade)

ΔE	Q Value	ΔE	Q Value	ΔE	Q Value
5.0	0.303	8.3	0.194	13.4	0.117
5.1	0.299	8.4	0.192	13.6	0.115
5.2	0.294	8.5	0.190	13.8	0.113
5.3	0.289	8.6	0.188	14.0	0.111
5.4	0.285	8.7	0.185	14.2	0.109
5.5	0.281	8.8	0.183	14.4	0.108
5.6	0.277	8.9	0.181	14.6	0.106
5.7	0.272	9.0	0.179	14.8	0.104
5.8	0.269	9.1	0.177	15.0	0.103
5.9	0.265	9.2	0.175	15.2	0.101
6.0	0.261	9.5	0.170	15.4	0.0993
6.1	0.257	9.6	0.168	15.6	0.0977
6.2	0.254	9.7	0.166	15.8	0.0962
6.3	0.250	9.8	0.165	16.0	0.0948
6.4	0.247	9.9	0.163	16.2	0.0933
6.5	0.243	10.0	0.161	16.4	0.0919
6.6	0.240	10.2	0.158	16.6	0.0905
6.7	0.237	10.4	0.155	16.8	0.0892
6.8	0.234	10.6	0.152	17.0	0.0878
6.9	0.231	10.8	0.149	17.2	0.0866
7.0	0.228	11.0	0.146	17.4	0.0853
7.1	0.225	11.2	0.143	17.6	0.0841
7.2	0.222	11.4	0.140	17.8	0.0828
7.3	0.219	11.6	0.138	18.0	0.0817
7.4	0.216	11.8	0.135	18.2	0.0805
7.5	0.214	12.0	0.133	18.4	0.0794
7.6	0.211	12.2	0.130	18.6	0.0782
7.7	0.209	12.4	0.128	18.8	0.0771
7.8	0.206	12.6	0.126	19.0	0.0761
7.9	0.204	12.8	0.123	19.2	0.0750
8.0	0.201	13.0	0.121	19.4	0.0740
8.1	0.199	13.2	0.119	19.6	0.0730
8.2	0.196				

ΔE	Q Value	ΔE	Q Value	ΔE	Q Value
19.8	0.0720	26.2	0.0481	32.6	0.0337
20.0	0.0710	26.4	0.0476	32.8	0.0334
20.2	0.0701	26.6	0.0470	33.0	0.0330
20.4	0.0691	26.8	0.0465	33.2	0.0327
20.6	0.0639	27.0	0.0459	33.4	0.0323
20.8	0.0631	27.2	0.0454	33.6	0.0320
21.0	0.0664	27.4	0.0449	33.8	0.0317
21.2	0.0656	27.6	0.0444	34.0	0.0313
21.4	0.0647	27.8	0.0439	34.2	0.0310
21.6	0.0639	28.0	0.0434	34.4	0.0307
21.8	0.0631	28.2	0.0429	34.6	0.0304
22.0	0.0623	28.4	0.0424	34.8	0.0301
22.2	0.0615	28.6	0.0419	35.0	0.0298
22.4	0.0607	28.8	0.0415	36.0	0.0283
22.6	0.0599	29.0	0.0410	37.0	0.0267
22.8	0.0592	29.2	0.0406	38.0	0.0256
23.0	0.0584	29.4	0.0401	39.0	0.0243
23.2	0.0577	29.6	0.0397	40.0	0.0232
23.4	0.0570	29.8	0.0392	41.0	0.0221
23.6	0.0563	30.0	0.0388	42.0	0.0210
23.8	0.0556	30.2	0.0384	43.0	0.0201
24.0	0.0549	30.4	0.0380	44.0	0.0191
24.2	0.0542	30.6	0.0375	45.0	0.0183
24.4	0.0536	30.8	0.0371	46.0	0.0174
24.6	0.0529	31.0	0.0367	47.0	0.0166
24.8	0.0523	31.2	0.0630	48.0	0.0159
25.0	0.517	31.4	0.0360	50.0	0.0145
25.2	0.0511	31.6	0.0356	52.0	0.0133
25.4	0.0505	31.8	0.0352	54.0	0.0121
25.6	0.0499	32.0	0.0348	56.0	0.0111
25.8	0.0493	32.2	0.0344	58.0	0.0102
26.0	0.0487	32.4	0.0341	60.0	0.0092

Titration Technique

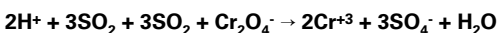
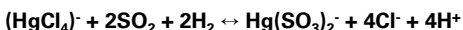
Nitrite can be quantitatively titrated with potassium permanganate if the nitrite sample is made 0.25 M in perchloric or nitric acid. Permanganate requires this high acidity to fully react with nitrite. Add increments of potassium permanganate to an acidified nitrite sample and plot millivolt readings (vertical axis) against the volume of titrant added (horizontal axis) on linear graph paper. Compute the sample nitrite concentration using the volume and molarity of permanganate added to the sample. Remember that two moles of permanganate react with five moles of nitrite.

Nitrogen Oxide Measurement Methods

Measurement of Nitrogen Dioxide in Air

Combining the high sensitivity of the nitrogen oxide electrode with an efficient nitrogen dioxide absorption method allows the measurement of as little as 10 ppb nitrogen dioxide in integrated air samples. Ambient nitrogen dioxide is efficiently absorbed in a neutral buffered, aqueous collection solution. The solution is acidified, and the resulting nitrite level is determined by the known addition technique.

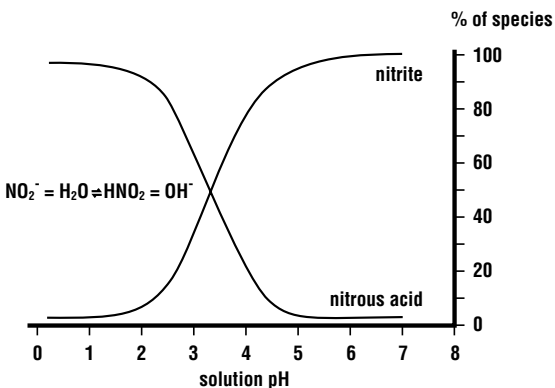
Absorbed sulfur dioxide is a potential interference, as it reacts with absorbed nitrogen dioxide. The sulfur dioxide interference can be eliminated by adding tetrachloromercurate (TCM) and potassium dichromate to the absorbing solution. TCM will complex any free sulfur dioxide and upon acidification, dichromate will react with sulfur dioxide as the TCM complex is broken:



Carbon dioxide is not an interference in this method as it is not appreciably absorbed in solutions of pH 6.2 or lower.

Two procedures are described for the measurement of nitrogen dioxide in air. The first procedure is faster and allows variable air sample size but requires a special gas impinger apparatus. In both procedures, the same absorbing solution, acid buffer and standardizing solutions are used.

Figure 5
Fraction of Nitrous Acid and Nitrite Ion as a Function of pH



Required Equipment for the Nitrogen Dioxide in Air Method

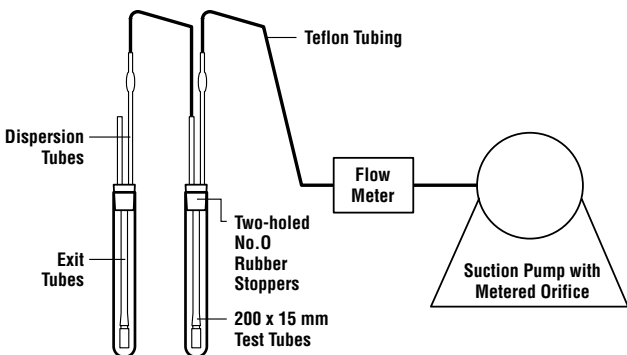
In addition to the items listed in the **Required Equipment** section, the following items are needed for this method:

1. Gas impinger apparatus – see **Figure 6**. A Rockwell 1255 dry test meter can be substituted for the flow meter and suction pump for better control of sample collection.
2. Glassware – a 2 liter, one-necked, round bottom flask.
3. Absorbing solution – to prepare 1 liter of absorbing solution, add the following to a 1 liter volumetric flask:
 - 3.7 grams of sodium dihydrogen phosphate, NaH_2PO_4
 - 3.3 grams of sodium monohydrogen phosphate, Na_2HPO_2
 - 10.86 grams of mercuric chloride, HgCl_2
 - 5.9 grams of potassium chloride, KCl
 - 2.9 grams of potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$

Once all of the items listed above are added to the 1 liter volumetric flask, dilute to the mark with distilled water.

Caution: HgCl_2 is very poisonous.

Figure 6
Gas Impinger Apparatus



Measurement Procedure for the Nitrogen Dioxide in Air Method

Using Gas Impinger Apparatus:

1. Place 20 mL of the absorbing solution in the first impinger and 10 mL in the second. Draw 2 liters of air sample at STP through absorbing solution. A collection rate of 2 to 5 liters per hour is recommended for 98 to 99% efficiency. Ten liters per hour shows 92 to 94% efficiency. If the nitrogen dioxide levels are expected to be higher than 8 ppm, a lower volume of air can be collected.
2. After sample collection, transfer the absorbing solutions from both impingers to a 150 mL beaker. Add 3 mL of the acid buffer solution and stir the solution thoroughly.
3. Place the nitrogen oxide electrode into the solution. Set the meter to the mV mode.
4. Add 3 mL of a ppm nitrite standard that is about 10 times the expected nitrite level in the absorbing solution and gently stir the solution. When a stable reading is displayed, record the mV value.
5. Find the concentration ratio, Q, from Table 4. Calculate the nitrogen dioxide concentration (ppm v/v) in the air sample:

$$[\text{NO}_2] \text{ ppm} = 0.487 \text{ VQA} / \text{FT}$$

where:

A = concentration of added standard (ppm nitrite)

V = volume of absorbing solution (mL)

F = gas flow rate (liters per hour)

T = time of sample collection (hours)

Using Standard Glassware:

1. Place 30 mL of the absorbing solution into the 2 liter, one-necked, round bottom flask containing the air to be analyzed. Close the flask for one hour to allow nitrogen dioxide absorption to take place.
2. Transfer the absorbing solution to a 150 mL beaker. Add 3 mL of the acid buffer and gently stir the solution.
3. Place the nitrogen oxide electrode into the solution. Set the meter to the mV mode.
4. Add 3 mL of a ppm nitrite standard that is about 10 times as concentrated as the expected nitrite level in the absorbing solution and gently stir the solution. When a stable reading is displayed, record the mV value.
5. Find the concentration ratio, Q , from Table 4. Calculate the nitrogen dioxide concentration (ppm v/v) in the air sample using $FT = 2$ liters.

Measurement of Nitrite/Nitrate

Nitrate can be converted to nitrite by copperized cadmium with efficiencies of 97% or better over the concentration range 10^{-5} M to 10^{-2} M (0.1 to 140 ppm N). The reduction can be carried out using a reduction column described below. The column can be regenerated.

This method measures total nitrite and nitrate nitrogen. If nitrate nitrogen alone is to be measured, nitrite in an unreduced portion of sample is measured according to the procedure, see the **Direct Measurement Technique** section. The result is then subtracted from the nitrite/nitrate total.

Required Equipment for the Measurement of Nitrite/Nitrate Method

In addition to the items listed in the **Required Equipment** section, the following items are needed for this method:

1. Reduction column – a 25 mL buret, prepared as follows:
 - a. Wash the column with 1 M HCl to clean the surface. Rinse well with distilled water.
 - b. Place 30 grams of cadmium powder and 100 mL of cupric sulfate solution into a 150 mL beaker and stir for 10 minutes. Filter and wash well with distilled water. Do not let the copperized cadmium dry out.
 - c. Place a 1 cm layer of glass wool in the stopcock end of a 25 mL buret. Add the copperized cadmium, tapping for even packing. Place a second 1 cm layer of glass wool on top. Pour about 10 mL of distilled water through the column to further settle the packing. The prepared column should be about 6 cm long, excluding the glass wool, and liquids should flow through at about 1 to 2 mL per minute.
2. Cadmium powder – Alfa Inorganics 100 mesh m2N5.
3. Cupric sulfate solution – dissolved 7.8 grams of reagent-grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in one liter of water.

Sample Reduction and Measurement Procedures for the Measurement of Nitrite/Nitrate Method

1. Prepare sodium nitrite standards by serial dilution of 1000 ppm as N standard. Draw a calibration curve or calibrate an ISE meter per the **Direct Measurement Technique** section.
2. Add 25 mL of sample to the prepared column and discard the effluent.
3. Add 25 mL of sample to the column and collect the effluent in 5 mL portions.
4. Place 5 mL of the acid buffer and 45 mL of distilled water in a 150 mL beaker and immerse the electrode in the solution. Add the first 5 mL of sample effluent and stir gently. Wait for a stable reading and record.
5. Determine the concentration of the diluted sample from the calibration curve or directly from the ISE meter. To find the total nitrite/nitrate sample concentration in ppm as N, multiply the result by 10 (this takes account of the 10 fold dilution of the effluent).
6. Repeat the measurement with successive 5 mL increments of sample effluent until results are reproducible.
7. To determine the nitrate concentration alone, measure the nitrite before sample reduction and subtract the nitrite result from the total nitrite/nitrate measurement after reduction.

Nitrite in Meat Processing Brines

Nitrate added to meat is best controlled by measuring nitrite in the processing brine, rather than in the meat itself. Ascorbic acid is not an interference for the method.

Required Equipment for the Nitrite in Meat Processing Brines Method

All items are listed in the **Required Equipment** section.

Measurement Procedure for the Nitrite in Meat Processing Brines Method

Measure the brine nitrite concentration using the procedure in the **Known Addition Technique** section, using a 1000 ppm nitrite standard. If the brine nitrite level is too high (a potential change of less than 5 mV), add 10 mL of the brine to a 100 mL volumetric flask and dilute to volume with distilled water. Measure the diluted brine concentration by known addition, using the 1000 ppm nitrite standard, and multiply the result by 10 to find the nitrite level in the brine.

Nitrite in Foods

The importance of measuring nitrite levels in food has increased as a result of research suggesting adverse health effects from nitrite activities. The known addition method given below for nitrite analysis is simple and accurate for nitrite levels above 1 ppm. If the sample contains significant amounts of fat, the membrane lifetime will be shortened.

Required Equipment for the Nitrite in Foods Method

All items are listed in the **Required Equipment** section.

Measurement Procedure for the Nitrite in Foods Method

1. Prepare a nitrite standard approximately equal to the sample level by dilution of the 1000 ppm standard.
2. Add 10 grams of finely divided food sample and 100 mL of distilled water to a 250 mL beaker. Stir the solution thoroughly. Add 10 mL of the acid buffer.
3. Determine the level of nitrite in the waste-dispersed food sample using the procedure in the **Known Addition Technique** section. Multiply result by 10 to find the nitrite level in the food sample.

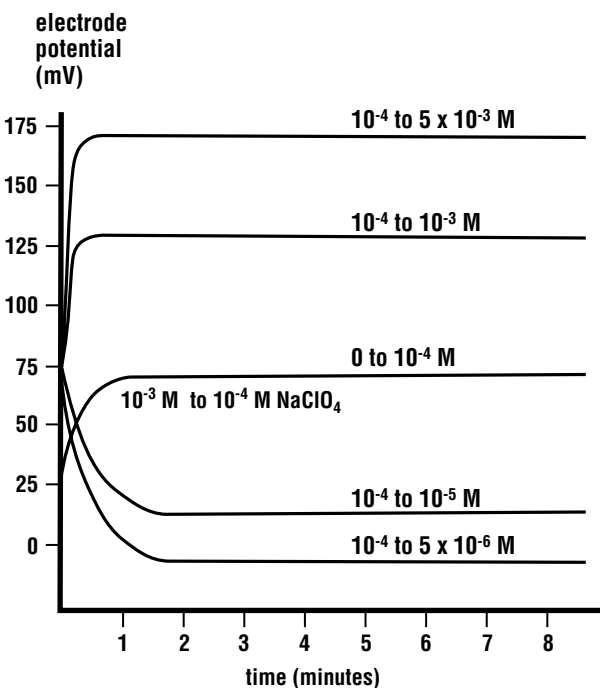
Electrode Characteristics

Electrode Response

The electrode potential plotted against concentration on semi-logarithmic paper results in a straight line with a slope of about -54 to -60 mV per decade change in concentration.

The electrode exhibits good time response (99% of response in one minute or less) for nitrous acid concentrations above 10^{-5} M nitrogen oxide. See **Figure 7**.

Figure 7
Typical Electrode Response to Nitrogen Oxide Concentrations



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 hourly calibrations, direct electrode measurements reproducible to $\pm 2\%$ can be obtained.

Effect of Dissolved Species

Water vapor is a potential electrode interference. Water can move across the membrane as water vapor, increasing or decreasing the concentration of the internal filling solution under the membrane. Any such changes will be seen as electrode drift. Water vapor transport across the membrane is not a problem if the osmotic strength of the sample is adjusted to equal that of the internal filling solution (0.5 osmolal) and if the electrode and sample temperatures are the same. Samples must be allowed to reach room temperature before adding the acid buffer solution and measuring.

The addition of the recommended acid buffer solution to samples of low osmotic strength will automatically adjust them to the correct osmotic strength. Samples with higher osmotic strengths should be diluted before measurement. Dilution should not reduce the nitrogen oxide level to below 4×10^{-6} M. Samples with osmotic strengths greater than 0.5 M that cannot be diluted can be measured by adjusting the osmotic strength of the internal filling solution. To adjust the internal filling solution, add 1.2 grams of reagent-grade KNO_3 to 25 mL of internal filling solution and dissolve completely.

Temperature Effects

A change in temperature will cause electrode response to shift and change slope. **Table 5** 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 faster the nitrogen oxide loss from solution.

Table 5
Theoretical Slope vs. Temperature Values

Temperature (°C)	Slope (mV)
0	-54.20
10	-56.18
20	-58.16
25	-59.16
30	-60.15
40	-62.13

Interferences

Volatile weak acids interfere with electrode measurements.

Volatile weak acids are gases that react with water to form acidic solutions. Concentrations of these interfering species that cause a 10% error at various nitrite levels are listed in **Table 6**.

The rate of interfering species diffusion across the electrode membrane, time of exposure to the sample and presence of other interferences are not accounted for in the simplified expression in **Table 6**. If the rate of interfering species diffusion across the membrane is slow, measurements of nitrous acid are possible if sample exposure is brief. For example, hydrofluoric, lactic and pyruvic acids may cause interference with long-term (30 minutes) exposure, but have negligible interference with short-term exposure (five minutes or less).

Sulfur dioxide is an interference and can slowly cause irreversible changes in the electrode internal filling solution. To remove sulfur dioxide, potassium dichromate should be added to the sample. Chlorine, bromine and iodine also react with nitrous acid. While ionic species cannot cross the membrane and interfere with electrode measurements, some, such as the stannous and ferrous ions, Sn^{+2} and Fe^{+2} , may react with nitrous acid. Prolonged use in solutions containing 10^{-3} M fluoride will result in damage to the glass internal sensing element.

Carbon dioxide is a significant factor in low level (below 10^{-5} M or 0.5 ppm) nitrite measurements. For low level measurements, standard solutions should be prepared with fresh, deionized water. Carbon dioxide should be removed from standards and samples by the following procedure:

1. Add 2 mL of 0.25 M potassium hydrogen phthalate, $\text{KC}_8\text{H}_5\text{O}_4$, to a 100 mL sample. This provides some buffering capacity as the solution tends to become less acidic as carbon dioxide is removed.
2. Adjust pH to 5.5 with 2.5 M perchloric acid.
3. Bubble nitrogen through solution at a rate of one liter per minute for about five minutes through a coarse fretted gas dispersion tube. Since only five minutes of bubbling is necessary, the loss of nitrite is less than 5%.

Table 6
Levels of Interference that will Cause 10% Error at Various
Levels of Nitrite

	10⁻⁴ M Nitrite	10⁻³ M Nitrite	10⁻² M Nitrite
Acetic Acid	3 x 10 ⁻⁴	3 x 10 ⁻³	3 x 10 ⁻²
Carbon Dioxide	3 x 10 ⁻³	3 x 10 ⁻²	0.3
Formic Acid	2 x 10 ⁻⁵	2 x 10 ⁻⁴	2 x 10 ⁻³
Hydrofluoric Acid	1 x 10 ⁻⁴	1 x 10 ⁻³	1 x 10 ⁻²
Lactic Acid	2 x 10 ⁻⁵	2 x 10 ⁻⁴	2 x 10 ⁻³
Pyruvic Acid	1 x 10 ⁻⁵	1 x 10 ⁻⁴	1 x 10 ⁻³
Sulfur Dioxide	1 x 10 ⁻⁶	1 x 10 ⁻⁵	1 x 10 ⁻⁴

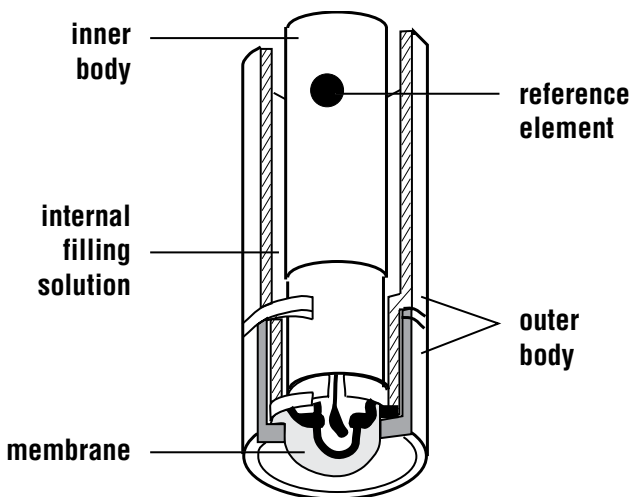
Membrane Life

A membrane will last from one week to several months, depending on usage. Membrane failure is characterized by a shift in electrode potential, drift or poor response. Refer to the **Electrode Maintenance** section for instructions on changing the membrane. Before replacement, refer to the **Troubleshooting** section to make sure that the difficulties are caused by the membrane.

Theory of Operation

The nitrogen oxide electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode filling solution. The gaseous anhydrides of nitrous acid, from an acidified nitrite-containing sample, diffuse through the membrane until the partial pressures of the nitrogen oxides (NO , NO_2 , N_2O_3 and N_2O_4) are the same on both sides of the membrane. In any given sample, the partial pressure of the gaseous anhydrides will be proportional to their concentration.

Figure 8
Nitrogen Oxide Electrode Construction



Nitrogen oxides affect the level of nitrous acid, HNO_2 , in the internal filling solution:



When nitrogen oxides have equilibrated across the gas-permeable membrane, a relationship between nitrous acid, nitrite and hydrogen ion is established in the internal filling solution of the electrode:

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

The internal filling solution contains a sufficiently high level of sodium nitrite for the entire concentration to be considered constant. Hydrogen ion concentration becomes proportional to the nitrous acid concentration:

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

This expression for hydrogen ion concentration can be substituted into the Nernst equation which relates the pH electrode potential to the hydrogen ion concentration:

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{S} \log [\text{H}^+]$$

where:

- E** = measured electrode potential
- E₀** = reference potential
- H⁺** = hydrogen concentration in solution
- S** = electrode slope (-59.2 mV/decade)

Substitution in the above equation shows that the electrode response to nitrous acid is Nernstian:

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{S} \log [\text{HNO}_2]$$

The reference potential, E₀, is partly determined by the internal reference element that responds to the fixed level of chloride in the filling solution.

Chemistry of Nitrogen Oxides

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

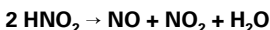
Many common oxidizing agents such as hydrogen peroxide, permanganate, chlorine, bromine, ozone, etc., are reduced by nitrous acid. Dichromate is not reduced in nitrite solutions if the pH is 1 or greater. In general:



Many reducing agents, including sulfur dioxide, stannous ion, ferrous ion, and iodine are oxidized in nitrite solution:



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



In acid solution, nitrous acid is slowly decomposed according to the following equation:



The loss of nitrite through decomposition is less than a few percent an hour. More nitric acid is lost as nitric oxide and nitrogen dioxide on exposure to air or even through the walls of plastic containers. If a nitrous acid solution is stirred rapidly at 25 °C, 90% loss of nitrous acid is observed in 14 hours.

The fraction of free nitrite in aqueous solution as a function of pH is shown in Figure 6. The relationship between nitrous acid and nitrite is given by the following equation:

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

The $\text{p}K_1$ for nitrite varies with temperature and ionic strength. In dilute solutions, $\text{p}K_1 = 3.49$ at 0 °C, 3.34 at 30 °C. Likewise at 25 °C, $\text{p}K_1 = 3.29$ in 0.07 M sodium perchlorate, NaClO_4 , and 2.8 in 1 M sodium perchlorate.

Troubleshooting

Follow a systematic procedure to isolate the problem. The measuring system can be divided into four components for ease in troubleshooting: meter, electrode, sample/application and technique.

Meter

The meter is the easiest component to eliminate as a possible cause of error. Thermo Scientific Orion meters include an instrument checkout procedure and shorting cap for convenience in troubleshooting. Consult the meter user guide for directions.

Electrode

1. Rinse the electrode thoroughly with distilled water.
2. Verify the electrode performance by performing the procedure in the **Checking Electrode Operation (Slope)** section.
3. If the electrode fails this procedure, review the **Measuring Hints** section. Clean the electrode thoroughly as directed in the **Electrode Maintenance** section. Drain and refill the electrode with fresh filling solution.
4. Repeat the procedure in the **Checking Electrode Operation (Slope)** section.
5. If the electrode still does not perform correctly, perform the procedure in the **Checking the Inner Body** section to determine if the inner body is working properly.
6. If the electrode passes the procedure in the **Checking the Inner Body** section, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error.
7. Before replacing a faulty electrode, review this user guide and be sure to thoroughly clean the electrode; correctly prepare the electrode; use the proper filling solution, acid buffer solution and standards; correctly measure the samples and review the **Troubleshooting Checklist** section.

Sample/Application

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! Errors 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 serial dilution. Refer to the **Serial Dilution** section. The electrode and meter may operate with standards, but not with the sample. In this case, check the sample composition for interferences, incompatibilities or temperature effects. Refer to the **Sample Requirements, Temperature Effects** and **Interferences** sections.

Technique

If trouble persists, review operating procedures. Review calibration and measurement sections to be sure proper technique has been followed. Verify that the expected concentration of the ion of interest is within the limit of detection of the electrode.

Check the method of analysis for compatibility with your sample. Direct measurement may not always be the method of choice. If a large amount of complexing agents are present, known addition may be the best method.

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/contactwater.

For the latest application and technical resources for Thermo Scientific Orion products, visit www.thermo.com/waterapps.

Warranty

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

Checking the Inner Body

1. Prepare a pH 4.01 buffer with 0.1 M NH_4Cl or 0.1 M NaCl – Combine 100 mL of pH 4.01 buffer, Cat. No. 910104, and 0.54 grams of reagent-grade NH_4Cl or 0.58 grams of reagent-grade NaCl . Thoroughly stir the solution and label the bottle as Solution 1. Store the buffer for repeated use. Discard the buffer if turbidity develops.
2. Prepare a pH 7.00 buffer with 0.1 M NH_4Cl or 0.1 M NaCl – Combine 100 mL of pH 7.00 buffer, Cat. No. 910107, and 0.54 grams of reagent-grade NH_4Cl or 0.58 grams of reagent-grade NaCl . Thoroughly stir the solution and label the bottle as Solution 2. Store the buffer for repeated use. Discard the buffer if turbidity develops.

Note: *The temperature of the buffers and distilled water must be $25\text{ }^\circ\text{C} \pm 4\text{ }^\circ\text{C}$ and all solutions should be at same temperature within $\pm 1\text{ }^\circ\text{C}$.*

3. Disassemble the nitrogen oxide electrode. If the electrode is dry, soak the glass tip of the inner body in filling solution for at least two hours.
4. Connect the electrode to a meter with a mV mode. Set the meter to the mV mode.
5. Rinse the inner body with distilled water and place it in the pH 7 buffer with 0.1 M NH_4Cl or 0.1 M NaCl added. Make sure that the coiled reference wire is completely covered. Stir the solution throughout the procedure. Record the millivolt reading after two minutes.
6. Rinse the inner body in distilled water and place it in the pH 4 buffer with 0.1 M NH_4Cl or 0.1 M NaCl added. Watch the change in the meter reading carefully. The reading should change by 100 mV in less than 30 seconds after immersion in the pH 4 buffer. After three minutes, the mV difference between pH 7 and pH 4 should be greater than 150 mV if the inner body is operating correctly.

Troubleshooting Checklist

Symptom: Off-scale or over-range reading

Membrane failure – Replace the membrane. Refer to the **Electrode Preparation** section for instructions.

Inner body not properly conditioned – Soak the inner body in electrode filling solution for at least two hours. For best results, soak the inner body overnight.

Inner body defective – Refer to the **Troubleshooting** section and perform the checking the inner body procedure.

Electrode filling solution not added – Fill the electrode up to the fill line with electrode filling solution.

Air bubble on the membrane – Remove bubbles by gently tapping the side of the electrode.

Electrode not in solution – Insert the electrode in solution.

Electrode not plugged into the meter properly – Unplug and reconnect the electrode.

Defective meter – Perform the meter checkout procedure (refer to the meter user guide).

Symptom: Low slope or no slope

Membrane failure – Replace the membrane. Refer to the **Electrode Preparation** section for instructions.

Inner body defective – Refer to the **Troubleshooting** section and perform the checking the inner body procedure.

Standards contaminated or made incorrectly – Prepare fresh standards, refer to the **Serial Dilution** section.

Acid buffer solution not used or incorrect acid buffer solution used – Add acid buffer, Cat. No. 956410, to all standards and samples immediately before taking measurements.

Electrode exposed to air for extended period – Replace the membrane. Refer to the **Electrode Preparation** section for instructions.

Symptom: Noisy or unstable readings (erratic, rapidly changing)

Insufficient electrode filling solution – Fill the electrode up to the fill line with electrode filling solution.

Membrane cap loose – Ensure that the membrane cap is on tight enough to close the gap between the cap and body.

Inner body defective – Refer to the **Troubleshooting** section and perform the checking the inner body procedure.

Acid buffer solution not used – Use the recommended acid buffer solution, Cat. No. 956410.

Defective meter – Perform the meter checkout procedure (refer to the meter user guide).

Symptom: Wrong answer but calibration curve is correct

Standards contaminated or made incorrectly – Prepare fresh standards, refer to the **Serial Dilution** section.

Incorrect scaling of semi-logarithmic paper – Refer to the **Direct Calibration Technique** section.

Incorrect millivolt sign used – Make sure to correctly record the sign of mV values.

Incorrect units used – Apply the correct conversion factor:
 $10^{-3} \text{ M} = 46 \text{ ppm as } \text{NO}_2^- = 14 \text{ ppm as N}$

Complexing agents in sample – Use known addition, titration techniques or a decomplexing procedure.

Acid buffer solution added to standards, but not samples – Add the same proportion of acid buffer solution to all standards and samples.

Symptom: Drift (reading slowly changing in one direction)

Membrane failure – Replace the membrane. Refer to the **Electrode Preparation** section for instructions.

Inner body defective – Refer to the **Troubleshooting** section and perform the checking the inner body procedure.

Nitrogen oxide loss from sample sitting too long – Reduce the surface area to volume ratio, slow the rate of stirring and avoid high temperatures.

Filling solution leaking – Ensure that the membrane is installed properly. Refer to the **Electrode Preparation** section.

Electrode not assembled properly – Ensure that the inner body is fully inserted in the top of the outer body when assembling the electrode. Refer to the **Electrode Preparation** section.

Samples and standards at different temperatures – Allow solutions to come to room temperature before measurement.

Incorrect electrode filling solution used – Fill the electrode using the correct electrode filling solution, Cat. No. 954602.

Total level of dissolved species above 1 M – Dilute solutions.

Meter or stirrer improperly grounded – Check meter and stirrer for grounding issues.

Solutions not at constant temperature – Allow solutions to come to room temperature before use.

Magnetic stirrer generating heat – Place insulating material between the magnetic stirrer and beaker.

Electrode exposed to air for extended period – Replace the membrane. Refer to the **Electrode Preparation** section for instructions.

Ordering Information

Cat. No.	Description
9546BN	Nitrogen oxide electrode with BNC connector
954600	Nitrogen oxide electrode with U.S. standard connector
954604	Loose membranes, box of 20
950015	Spare parts kit for nitrogen oxide electrode
956410	Acid buffer solution, 475 mL bottle
954602	Electrode filling solution, 60 mL bottle
954606	0.1 M NaNO ₂ standard, 475 mL bottle

Specifications

Concentration Range

4×10^{-6} M to 5×10^{-3} M

0.18 ppm to 230 ppm as NO_2

pH Range

1.1 to 1.7 pH

Temperature Range

0 to 50 °C

Electrode Resistance

1,000 megohms

Reproducibility

$\pm 2\%$

Size

Body Diameter: 17 mm

Body Length: 150 mm

Cap Diameter: 22 mm

Cable Length: 1 meter

** Specifications are subject to change without notice*

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254818-001 Rev. A 10-08

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