

COLE-PARMER REPLACEABLE MEMBRANE NITRATE ION ELECTRODES INSTRUCTION MANUAL

GENERAL INSTRUCTIONS

Introduction

The Cole-Parmer Combination Nitrate Ion Electrodes are used to quickly, simply, accurately, and economically measure nitrate in aqueous solutions. The primary advantage of combination ion-selective probes with replaceable sensing membranes is that when the sensing membrane fails or loses performance for whatever cause, it can be immediately replaced without discarding any other portion of the combination electrode. This results in time and cost savings.

Another distinct advantage of this replaceable membrane design is that when the sensing membrane fails or loses performance for whatever cause, membrane replacement has no unfortunate side effects on the performance of the reference electrode. There is no danger of reference electrolyte leakage upon replacing the membrane. The membrane replacement assembly is separated from the reference electrolyte/reference junction so that the membrane may be replaced without disturbing the reference electrolyte solution.

Yet another advantage of these ISE probes is the option of interchangeable sensing membranes, where one can select a membrane for a particular analytical ion. A single combination ISE body can be used to measure a variety of analytical ions by simple replacement of the membrane cartridge. This offers benefits in multiple ion analysis whereby an electrode kit containing various replaceable membranes can be made available for the analysis of different ions done on an occasional basis.

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 Cole-Parmer Replaceable Membrane Combination Nitrate Ion Electrode, Cat. No. 27505-12.

Required Solutions

1. Deionized or distilled water for solution and standard preparation.
2. Cole-Parmer Ionic Strength Adjuster (ISA), 2M (NH₄)₂SO₄, Cat. No. 27503-60. To prepare this solution from your own laboratory stock, half fill a 1000 ml volumetric

flask with distilled water and add 264 grams of reagent-grade ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$. Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend several times to mix the contents. ISA is added at the rate of 2 ml of ISA to each 100 ml of standard or sample to adjust the ionic strength to about 0.12M.

3. Cole-Parmer Nitrate Standard, 1000 ppm NO_3^{-1} , Cat. No. 27503-24. To prepare this solution from your own laboratory stock, add 1.37 grams of reagent-grade sodium nitrate to a one liter volumetric flask about half full with distilled water. Swirl the flask gently to dissolve the solid. Fill to the mark with distilled water, cap and upend several times to mix the solution.

GENERAL PREPARATION

Electrode Preparation

Remove the black protective cap covering the electrode tip and lower the rubber sleeve covering the filling hole of the reference chamber to expose the fill hole. Fill the combination electrode with the reference filling solution shipped with the electrode to a level just below the fill hole. Gently shake the electrode downward in the same manner as a clinical thermometer to remove any air bubbles which might be trapped behind the nitrate membrane. Prior to first usage, or after long-term storage, immerse the nitrate membrane in nitrate standard for thirty minutes. The electrode is now ready for use.

Connecting the Electrode to the Meter

Connect the electrode to the meter according to the meter manufacturer's instructions. No external reference electrode is required. To prevent air entrapment, mount the electrode at a 20° angle from the vertical.

Electrode Slope Check (with pH/mV meter) (check electrodes each day)

A small hole of any size around the membrane seal or breakage of the membrane causes failure of the electrode. It is recommended to check the membrane on every newly assembled electrode.

1. To a 150 ml beaker, add 100 ml of distilled water and two ml of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the millivolt mode, lower the electrode tips into the solution.
2. Using a pipet, add 1 ml of 1000 ppm nitrate standard to the beaker. When the reading has stabilized, record the mV reading.
3. Using a pipet, add 10 ml of the same nitrate standard used above to the beaker. When the reading has stabilized, record the mV reading.

4. Determine the difference between the two readings. The electrode is operating correctly if the millivolt potential has changed by 56 ± 2 mV, assuming the solution temperature is between 20° and 25°C. See the **TROUBLESHOOTING** sections if the potential change is not within this range.
5. Slope is defined as the change in potential observed when the concentration changes by a factor of 10.

Electrode Slope Check (with ion meter) (check electrodes each day)

A small hole of any size around the membrane seal or breakage of the membrane causes failure of the electrode. It is recommended to check the membrane on every newly assembled electrode.

1. Prepare standard nitrate solutions whose concentrations vary by ten fold. Use the 1000 ppm nitrate standard. Use the serial dilution method for this preparation.
2. To a 150 ml beaker, add 100 ml of the lower value standard and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution. Assure that the meter is in the concentration mode.
3. Adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions.
4. Rinse the electrodes with distilled water and blot dry.
5. To another 150 ml beaker, add 100 ml of the higher value standard and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution.
6. Adjust the meter to the concentration of the standard and fix the value in the memory.
7. 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** sections if the slope is not within this range.

Changing the Membrane Cartridge (when necessary)

1. Unscrew the bottom cap from the outer body. Remove the old membrane cartridge from the bottom cap by pushing out the cartridge with the tool provided with the electrode.

2. Insert the new membrane cartridge into the bottom cap by pushing in the cartridge using the opposite end of the tool until it seats.
3. Invert the outer body and check that there is inner filling solution inside the center chamber. Using the syringe provided, fill the outer body with inner filling solution if necessary.
4. Place the bottom cap onto the outer body threads and screw the bottom cap onto the outer body until fingertight. Check that the assembled cap is not leaking at the bottom of the electrode or else repeat the above steps.
5. Gently shake the electrode downward in the same manner as a clinical thermometer to remove any air bubbles which might be trapped behind the nitrate membrane. Immerse the nitrate electrode in nitrate standard for thirty minutes. The electrode is now ready for use.
6. Connect the electrode to the meter and repeat the electrode slope check.

MEASUREMENT

Measuring Hints

1. All samples and standards should be at the same temperature for precise measurement. A difference of 1°C in temperature will result in a 2% measurement error.
2. The sensing membrane is normally subject to water uptake and might appear milky. This has no effect on performance.
3. 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.
4. Always rinse the electrodes with distilled water and blot dry between measurements. Use a clean, dry tissue to prevent cross-contamination.
5. For samples with high ionic strength, prepare standards whose composition is similar to the sample.
6. Use fresh standards for calibration.
7. Use 2 ml of ISA for each 100 ml of sample or standard.
8. Always check to see that the membrane is free from air bubbles after immersion into standard or sample.

9. A slow responding electrode may be caused by interferences to the electrode. To restore proper performance, soak the electrode in distilled water for about 5 minutes to clean the membrane, rinse, and soak in standard solution for about 5 minutes.

Sample Requirements

* All samples must be aqueous and not contain organics which can dissolve in the membrane or extract out the liquid ion exchanger.

* The temperature of the standard solutions and of the sample solutions should be the same and below 40°C. About a 2% error will be introduced for a 1°C difference in temperature.

* Interferences should be absent. If they are present, use the procedures found in the **Interferences** section to remove them.

* The pH range for the nitrate ion electrode is 2.5-11. Neutralize samples outside this range with acid or base to bring them in range.

Units of Measurement

Nitrate concentrations are measured in units of ppm as sodium nitrate, ppm as nitrate, 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 NaNO₃</u>	<u>ppm NO₃⁻¹</u>	<u>moles/liter</u>
850.0	620.0	1.0 X 10 ⁻²
85.0	62.0	1.0 X 10 ⁻³
8.5	6.2	1.0 X 10 ⁻⁴

MEASUREMENT PROCEDURE

Direct Measurement

Direct measurement is 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 ISA for all nitrate solutions. The temperature of both sample solution and standard solutions should be the same.

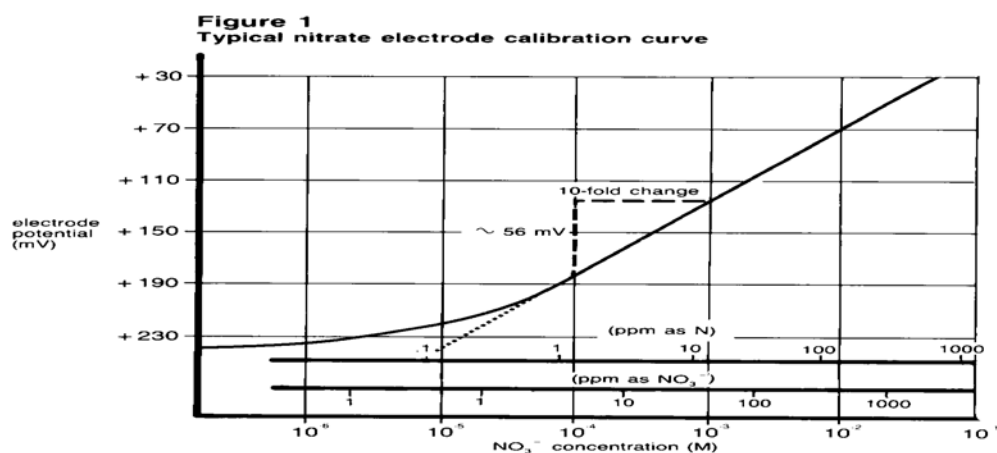
Direct Measurement of Nitrate (using a pH/mV meter)

1. By serial dilution, prepare three standard solutions from the 1000 ppm stock standard. The resultant concentrations should be 1000, 100 and 10 ppm nitrate

standards. Add 2 ml of ISA to each 100 ml of standard. Prepare standards with a composition similar to the samples if the samples have an ionic strength above 0.1M.

2. Place the most dilute solution (10 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tips into the solution. After the reading has stabilized, record the mV reading.
3. Place the mid-range solution (100 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring. After rinsing the electrodes with distilled water, blot dry and immerse the electrode tips in the solution. When the reading has stabilized, record the mV value.
4. Place the most concentrated solution (1000 ppm) in a 150 ml beaker on the magnetic stirrer and begin stirring. After rinsing the electrodes in distilled water, blot dry, and immerse the electrode tips 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). Extrapolate the calibration curve down to about 1.0 ppm NO_3^- . A typical calibration curve can be found in Figure 1.

A calibration curve is constructed on semi-logarithmic paper when using the 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 the sample and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Rinse the electrode tips with distilled water, blot dry, and lower the electrode tips into the solution. When the reading has stabilized, record the mV reading. Using the calibration curve, determine the sample concentration.
7. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tips in the mid-range standard. After the reading has stabilized, compare it to the original reading recorded in Step 3 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of Steps 2-5 above. A new calibration curve should be prepared daily.

Direct Measurement of Nitrate (using an ion meter)

1. By serial dilution of the 1000 ppm nitrate standard, prepare two nitrate standards whose concentration is near the expected sample concentration. Measure out 100 ml of each standard into individual 150 ml beakers and add 2 ml of ISA to each.
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. Lower the electrode tips into the solution.
3. Adjust the meter to the concentration of the nitrate standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
4. Rinse the electrodes with distilled water and blot dry.
5. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution.
6. Adjust the meter to the concentration of the nitrate standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
7. For low level measurements, place the rinsed, dried electrodes into a solution containing 100 ml of distilled water and 2 ml of ISA. After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.
8. Place 100 ml of the sample and 2 ml of ISA in a 150 ml beaker. Place the beaker on the magnetic stirrer and begin stirring.

9. Immerse the electrode tips in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.
10. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tips in the first nitrate standard. After the reading has stabilized, compare it to the original reading in Step 3 above. A reading differing by more than 0.5 mV or a change in ambient temperature will necessitate the repetition of Steps 2-6 above. The meter should be re-calibrated daily.

Low Level Nitrate Measurements (using a pH/mV meter)

This procedure is recommended for solutions with ionic strengths less than 0.2 ppm. If the solution is high in ionic strength, but low in nitrate, use the same procedure, but prepare a calibration solution with a composition similar to the sample.

1. Using 20 ml of standard ISA, dilute to 100 ml with distilled water. This low level ISA [0.4M (NH₄)₂SO₄] is added at the rate of 1 ml low level ISA to each 100 ml of sample. The background ionic strength will be 4.0X 10⁻³M.
2. Use the 1000 ppm standard for preparing a 100 ppm NO₃⁻¹ standard by diluting 10 ml of the 1000 ppm standard to 100 ml. Standards should be prepared fresh daily.
3. Add 1 ml of the low level ISA to a 100 ml volumetric flask and fill to the mark with distilled water. Pour this solution into a 150 ml beaker and place the beaker on the magnetic stirrer. Begin stirring at a constant rate.
4. Place the electrode tips in the solution. Assure that the meter is in the mV mode.
5. Add increments of the 100 ppm standard as given in Table 2 below.
6. After the reading has stabilized, record the mV reading after each addition.

TABLE 2: Step-wise Calibration for Low Level Nitrate Measurements

<u>Step</u>	<u>Pipet</u>	<u>Added Volume (ml)</u>	<u>Concentration</u>	
			<u>M NO₃⁻¹</u>	<u>ppm NO₃⁻¹</u>

1	A	0.1	1.0×10^{-6}	0.1
2	A	0.1	2.0×10^{-6}	0.2
3	A	0.2	4.0×10^{-6}	0.4
4	A	0.2	6.0×10^{-6}	0.6
5	A	0.4	9.9×10^{-6}	1.0
6	B	2.0	2.9×10^{-5}	2.9
7	B	2.0	4.8×10^{-5}	4.8

Pipet A = 1 ml graduated pipet

Pipet B = 2 ml pipet

Solutions: additions of 100 ppm standard to 100 ml of ISA as prepared in Step 3 above.

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

Low Level Nitrate Determination (using an ion meter)

Follow the procedure given for normal nitrate determinations using an ion meter and the blank correction procedure.

ELECTRODE CHARACTERISTICS

Reproducibility

Electrode measurements reproducible to $\pm 2\%$ 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

Certain anions are electrode interferences and will cause electrode malfunction, drift or measurement errors if present in high enough levels. The level of interfering common anions that will cause a 10% error at three levels of nitrate is given in Table 3.

TABLE 3: Concentration of Possible Interferences Causing a 10% Error at Various Levels of Nitrate; Background Ionic Strength of 0.12M (NH₄)₂SO₄.

Interferences (moles/liter)	<u>10⁻²M</u>	<u>10⁻³M</u>	<u>10⁻⁴M NO₃⁻¹</u>
Cl ⁻¹	3.0X10 ⁻¹	3.0X10 ⁻²	3.0X10 ⁻³
NO ₂ ⁻¹	7.0X10 ⁻³	7.0X10 ⁻⁴	7.0X10 ⁻⁵
Br ⁻¹	7.0X10 ⁻³	7.0X10 ⁻⁴	7.0X10 ⁻⁵
CN ⁻¹	1.0X10 ⁻³	1.0X10 ⁻⁴	1.0X10 ⁻⁵
ClO ₃ ⁻¹	5.0X10 ⁻⁴	5.0X10 ⁻⁵	5.0X10 ⁻⁶
I ⁻¹	5.0X10 ⁻⁵	5.0X10 ⁻⁶	5.0X10 ⁻⁷
ClO ₄ ⁻¹	1.0X10 ⁻⁶	1.0X10 ⁻⁷	1.0X10 ⁻⁸

Interferences (ppm)	<u>100 ppm N</u>	<u>10 ppm N</u>	<u>1 ppm N</u>
Cl ⁻¹	7600	760	76.0
NO ₂ ⁻¹	230	23.0	2.30
Br ⁻¹	400	40.0	4.00
CN ⁻¹	20.0	2.00	0.20
ClO ₃ ⁻¹	30.0	3.00	0.30
I ⁻¹	4.00	0.40	0.04
ClO ₄ ⁻¹	0.07	0.007	0.0007

Interferences such as chloride, bromide, iodide and cyanide can be removed by precipitation with 0.5 grams of silver sulfate added to 100 ml of sample. Nitrite interference can be removed by adding 0.3 grams of sulfamic acid to 100 ml of sample. Carbonate and bicarbonate, which are weak interferences, can be removed by acidifying the sample to pH 4.5 with sulfuric acid. Organic (carboxylic) anions hinder the nitrate electrode response and can be removed by adding 10 grams of aluminum sulfate to 100 ml of sample.

The above interference removal procedures require similar treatment of standards as well as

samples.

If the electrode is exposed to high levels of interfering ions which cannot be removed, the electrode reading may drift and the response may become sluggish. Restore performance by soaking in distilled water for 30 minutes followed by soaking in nitrate standard for 30 minutes.

Temperature Influences

Samples and standards should be at the same temperature, since electrode potentials are influenced by changes in temperature. A 1°C difference in temperature results in a 2% error at the 10^{-3}M level. Because of the solubility equilibria on which the electrode depends, the absolute potential of the reference electrode changes slowly with temperature. The slope of the nitrate electrode, as indicated by the factor "S" in the Nernst equation, also varies with temperature. Table 4 gives values for the "S" factor in the Nernst equation for the nitrate ion.

The operating range of the nitrate ion electrode is 0°-40°C, provided that temperature equilibrium has occurred.

If the temperature varies substantially from room temperature, equilibrium times up to one hour are recommended.

TABLE 4: Temperature vs. Values for the Electrode Slope

<u>Temp (Oc)</u>	<u>S"</u>
0	54.20
10	56.18
20	58.18
25	59.16
30	60.15
40	62.13
50	64.11

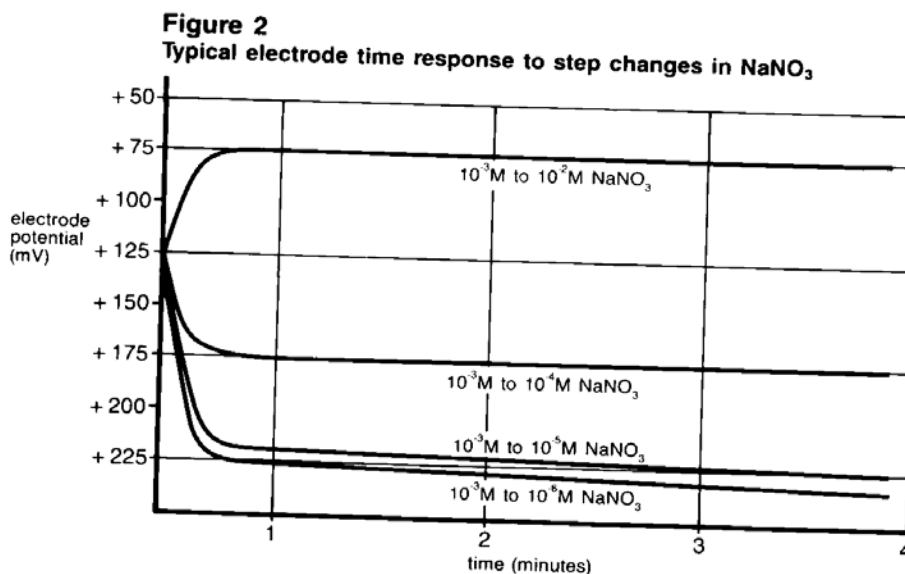
Electrode Response

Plotting the mV potential against the nitrate concentration on semi-logarithmic paper results in a straight line with a slope of about 56 mV per decade. (Refer to Figure 1.)

The time needed to reach 99% of the stable electrode potential reading, the electrode response time, varies from one minute or less in highly concentrated solutions to several minutes near the detection limit. (Refer to Figure 2.)

Limits of Detection

The upper limit of detection in pure sodium nitrate solutions is 1M. In the presence of other



ions, the upper limit of detection is above 10^{-1}M nitrate, but two factors influence this upper limit. Both the possibility of a liquid junction potential developing at the reference electrode and the salt extraction effect influence this upper limit. Some salts may infuse into the electrode membrane at high salt concentrations, causing deviation from the theoretical response. Either dilute samples between 1M and 10^{-1}M or calibrate the electrode at 4 or 5 intermediate points.

The lower limit of detection is influenced by the slight water solubility of the ion exchanger used in the sensing portion of the

electrode. Refer to Figure 1 for a comparison of the theoretical response to the actual response at low levels of nitrate. Nitrate measurements below 10^{-5}M NO_3^{-1} ($0.6\text{ ppm as NO}_3^{-1}$) should employ low level procedures.

pH Effects

The operating range of the nitrate electrode is from pH 2.5 to pH 11.

Electrode Life

The nitrate electrode will last six months in normal laboratory use. On-line measurement 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 cartridge replacement is required.

Electrode Storage

The Cole-Parmer Nitrate Ion Electrodes may be stored for short periods of time in 100 ppm nitrate solution. For longer storage (longer than two weeks), rinse and dry the nitrate membrane and cover the tip with any protective cap shipped with the electrodes. The reference portion of the combination electrode should be drained of filling solution and the rubber sleeve placed over the filling hole.

ELECTRODE THEORY

Electrode Operation

The nitrate electrode consists of an electrode body containing a liquid fill solution in contact with a membrane cartridge. This membrane cartridge contains a gelled organophilic membrane containing a nitrate ion exchanger.

When the membrane is in contact with a solution containing free nitrate ions, an electrode potential develops across the membrane. This electrode potential is measured against a constant reference potential, using a standard pH/mV meter or an ion meter. The level of nitrate ions, corresponding to the measured potential, is described by the Nernst equation:

$$E = E^{\sim} - S \log X$$

where: E = measured electrode potential
E[~] = reference potential (a constant)
S = electrode slope (~56 mV/decade)
X = level of nitrate ions in
solution

The activity, X, represents the effective concentration of the ions in solution. The total nitrate ion concentration, C_t, is the sum of free nitrate ion, C_f, and complexed or bound perchlorate ion, C_b.

The electrode is able to respond to only the free ions, whose concentration is :

$$C_f = C_t - C_b$$

Since nitrate ions form very few stable complexes, the free ion concentration may be equated to the total ion concentration.

The activity is related to the free ion concentration, C_f , by the activity coefficient, γ , by:

$$X = \gamma C_f$$

Activity coefficients vary, depending on total ions strength, I , defined as:

$$I = 1/2 \sum C_x Z_x^2$$

where: C_x = concentration of ion X

Z_x = charge of ion X

Σ = sum of all of the types of ions in the solution

In the case of high and constant ionic strength relative to the sensed ion concentration, the activity coefficient, γ , is constant and the activity, X , is directly proportional to the concentration.

To adjust the background ionic strength to a high and constant value, ionic strength adjuster (ISA) is added to samples and standards. The recommended ISA for nitrate is $(\text{NH}_4)_2\text{SO}_4$. Solutions other than this may be used as ionic strength adjusters as long as ions that they contain do not interfere with the electrode's response to nitrate ions.

The reference electrode must also be considered. When two solutions of different composition are brought into contact with one another, liquid junction potentials arise. Millivolt potentials occur from the inter-diffusion of ions in the two solutions. Electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions, since ions diffuse at different rates. When making measurements, it is important to remember that this potential be the same when the reference is in the standardizing solution as well as in the sample solution or the change in liquid junction potential will appear as an error in the measured electrode potential.

The composition of the liquid junction filling solution in the reference electrode is most important. The speed with which the positive and negative ions in the filling solutions diffuse into the samples should be as nearly equal as possible, that is, the filling solution should be equitransferent. No junction potential can result if the rate at which positive and negative charge carried into the sample is equal.

Strongly acidic ($\text{pH} = 0-2$) and strongly basic ($\text{pH} = 12-14$) solutions are particularly

troublesome to measure. The high mobility of hydrogen and hydroxide ions in samples make it impossible to mask their effect on the junction potential with any concentration of equitransferent salt. One must either calibrate the electrodes in the same pH range as the sample or use a known incremental method for ion measurement.

TROUBLESHOOTING GUIDE

The goal of troubleshooting is the isolation of a problem through checking each of the system components in turn: the meter, the plastic-ware, the electrodes, the standards & reagents, the sample, and the technique.

Meter

The meter may be checked by following the check-out procedure in the instrument instruction manual.

Plastic-ware

Clean plastic-ware is essential for good measurement. Be sure to wash the plastic-ware well with a mild detergent and rinse very well with distilled or deionized water.

Electrodes

The electrodes may be checked by using the procedure found in the sections entitled **Electrode Slope Check**.

1. Be sure to use distilled or deionized water when following the procedures given in **Electrode Slope Check**.
2. If the electrode fails to respond as expected, see the section **Measuring Hints**. Repeat the slope check.
3. If the electrodes still fail to respond as expected, replace the membrane cartridge (**See Changing the Membrane Cartridge section**).
4. If the measurement problems still exist, the standards maybe of poor quality, the sample may contain interferences or complexing agents, or the technique maybe in error (See Standard sample and Technique sections below).
5. Review the instruction manual and be sure to:
 - Clean and rinse the electrodes thoroughly.
 - Prepare the electrodes properly.
 - Use the proper filling solution.

- Adjust the pH and the ionic strength of the solution by the use of the proper ISA.
- Measure correctly and accurately.
- Review **TROUBLESHOOTING HINTS**.

Standards & Reagents

Whenever problems arise with the measuring procedure that has been used successfully in the past, be sure to check the standard and reagent solutions. If in doubt about the credibility of any of the solutions, prepare them again. Errors may result from contamination of the ISA, incorrect dilution of standards, poor quality distilled/deionized water, or a simple mathematical miscalculation.

Sample

Look for possible interferences, complexing agents, or substances which could affect the response or physically damage the sensing electrode (or the reference electrode) if the electrodes work perfectly in the standard, but not in the sample.

Try to determine the composition of the samples prior to testing to eliminate a problem before it starts. (See **Measuring Hints**, **Sample Requirements**, and **Interferences**.)

Technique

Be sure that the electrode's limit of detection has not been exceeded. Be sure that the analysis method is clearly understood and is compatible with the sample. Refer to the instruction manual again. Reread **GENERAL PREPARATION** and **ELECTRODE CHARACTERISTICS**.

If trouble still persists, call Cole-Parmer and ask for the Technical Services Department.

TROUBLESHOOTING HINTS

SYMPTOM	POSSIBLE CAUSES	NEXT STEP
Out of Range Reading	defective meter	check meter with shorting strap(see meter instruction manual)
	electrode(s) not plugged in properly	unplug electrode(s) and reseal
filled	reference electrode not filled	be sure reference is filled
	air bubbles on membrane	remove bubble by re-dipping electrode
	electrodes not in solution	put electrode(s) in solution

“Incorrect answer ”(but calibrate is)	incorrect scaling of semilog paper	Plot millivolts linear axis. On the log curve 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 in conversion	apply correct factor: 10-3M = 18 ppm NH ₄ ⁺ = 14ppm as N
	sample carryover	rinse electrodes thoroughly between samples
Drift (reading changing in one direction)	samples and standards at different temperatures	allow solutions slowly to come to room temperature before measurement
	electrode exposed to interferences	soak electrode ammonium standard
	incorrect reference filling solution	use recommended filling solution
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
	defective electrode	replace membrane cartridge
	electrode exposed to interferences	soak electrode in ammonium standard
	air bubble on membrane	remove bubble by re-dipping probe
Noisy or unstable readings (readings continuously or randomly changing)	defective meter	check meter with shorting strap
	air bubble on membrane	remove bubble by re-dipping electrode

defective electrode	replace membrane cartridge
electrode exposed to interferences	soak electrode in ammonium standard
meter or stirrer not grounded	ground meter or stirrer
outer filling solution level too low	fill electrode to level just below fill hole

SPECIFICATIONS

Concentration Range:	1M to 7×10^{-6} M (6.2×10^4 to 0.5 ppm as NO_3^{-1})
pH Range:	2.5 to 11
Temperature Range:	0° to 40°C
Resistance:	100 Mohms
Reproducibility:	±2%
Samples:	aqueous solutions only no organic solvents
Size:	110 mm in length 12 mm in diameter 1 m cable length
Storage:	Store in dilute nitrate solution

ORDERING INFORMATION

P/N	DESCRIPTION
27505-12	Nitrate Ion Electrode, combination, pvc body, replaceable membrane
27503-24	Nitrate Standard, 1000 ppm NO_3^{-1}
27503-06	Nitrate ISA (Ionic Strength Adjustor), 2 M $(\text{NH}_4)_2\text{SO}_4$
27505-62	Replacement Membrane Kit containing 3 membrane cartridges, o-rings, inner filling solution and reference filling solution

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