

VAN LONDON
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pHoenix Co.



Sodium Ion Selective Electrode



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GENERAL INSTRUCTIONS

Introduction

The Van London-pHoenix Company Sodium Ion Selective Electrode is used to measure dissolved sodium ion in aqueous solutions.

Required Equipment

1. An ion meter
2. Sodium Ion Sensing Electrode
3. Plastic syringe, pipets, volumetric flasks, 150 ml beakers

Required Solutions

1. Deionized or distilled water for solution preparation.
2. Van London-pHoenix Company Sodium Standard, 1000 ppm Na⁺, Cat.# NAOAS02.
3. Van London-pHoenix Company Ionic Strength Adjuster (ISA), 4M NH₄Cl/4M NH₄OH. To prepare this solution from your own laboratory stock, half fill a 1000 ml volumetric flask with distilled water and add 214 grams of reagent-grade ammonium chloride (NH₄Cl). Under a hood, add 270 ml of concentrated ammonium hydroxide (NH₄OH), swirl the flask gently to dissolve the solid, and allow to cool. Fill the flask to the mark with distilled water, cap, and upend several times to mix the solution.
4. Van London-pHoenix Company Sodium Electrode Storage Solution, Cat.# NAOES01.
5. Dilute Electrode Rinse Solution. To prepare this solution from your own laboratory stock, add 20 ml of ISA to a one liter volumetric flask and fill to the mark with distilled water. Use this solution to rinse the electrode between measurements. DO NOT RINSE WITH DISTILLED WATER.

GENERAL PREPARATION

Electrode Preparation

Remove the rubber cap covering the electrode tip and the rubber insert covering the filling hole of the reference electrode. Fill the combination electrode with the filling solution shipped with the electrode to a level just below the fill hole. No preparation is required with a sealed reference electrode. Connect the electrode to the proper terminals of the meter as recommended by the meter manufacturer. Store the black shipping cap for later use. Soak the sodium electrode tip overnight in the electrode storage solution.

Electrode Slope Check (for Ion meters which display mV)

1. To a clean, dry, 150 ml beaker, add 100 ml of distilled water and 2 ml of ISA. After assuring that the meter is in the millivolt mode, lower the electrode tip into the solution. Stir moderately. Remove air bubbles on the clear glass membrane by redipping probe.
2. Using a pipet, add 1 ml of 1000 ppm standard into the solution. Stir moderately. After 1 minute, record the mV reading.
3. Using a pipet, add 10 ml of the 1000 ppm ammonia standard to the beaker. Stir moderately. After 1 minute, record the mV reading.
4. Determine the difference between the two readings. The electrode is operating correctly if a slope difference of 52-59 mV between 10 ppm and 100 ppm at 25°C is found, assuming the solution temperature is 25°C. Slope is defined as the change in mV observed when the concentration changes by a factor of 10.

Measurement using an Ion Meter (in the Concentration Mode)

1. By serial dilution of the 1000 ppm sodium standard, prepare two sodium standards whose concentration is near the expected sample concentration. (e.g 10 ppm and 100 ppm) For example, to make a 100 ppm standard, pipet 10 ml of the 1000 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. Next to make a 10 ppm standard, pipet 10 ml of the newly-made 100 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. A 1 ppm standard is made by further dilution of the 10 ppm standard. Measure out 100 ml of each standard into individual 150 ml beakers.

2. Assure that the meter is in the concentration mode and set for a 2-point calibration.
3. Lower the electrode tip into the least concentrated solution. Begin stirring at a constant rate. Add 2 ml of ISA to the solution and continue stirring.
4. After 1 minute, adjust the meter to the concentration of the more dilute sodium standard and fix the value in the memory according to the meter manufacturer's instructions.
5. Rinse the electrode tip with distilled water and blot dry.
6. Lower the electrode tip into the more concentrated solution. Begin stirring at a constant rate. Add 2 ml of ISA to the solution and continue stirring.
7. After 1 minute, adjust the meter to the concentration of the more concentrated sodium standard and fix the value in the memory according to the meter manufacturer's instructions.
8. Add 100 ml of the sample and 2 ml of ISA in a 150 ml beaker. Lower the electrode tip into the solution. Begin stirring at a constant rate. Ensure that the meter is in sample mode.
9. After 1 minute, read the concentration directly from the meter display.
10. The electrode should be re-calibrated every 2-3 hours. Simply repeat Steps 2-7 above.

Measuring Hints

As sodium electrodes are used or stored for long periods, they will experience some deterioration in performance and slope errors will increase. By using the meter's calibration controls this error can be corrected. If an electrode is able to be calibrated and is stable and responsive, it is still a functional electrode and may be used in service even though it no longer meets "new" electrode specifications.

All samples and standards should be at the same temperature for precise measurement. A difference of 1°C in temperature will result in approximately a 2% error.

Always rinse the electrodes with electrode rinse solution from a wash bottle between measurements. Use a clean, dry tissue to prevent cross contamination. Never use distilled water.

Constant, but not violent, stirring is necessary for accurate measurement.

Store the electrodes in electrode storage solution between measurements. Do not store in air or distilled water. Always soak new electrodes overnight in electrode storage solution prior to first use. When making low level sodium measurements, use a dilute sodium chloride storage solution. Add 1 ml of ISA to 100 ml of dilute storage solution.

Plastic lab-ware should be used for low level measurements (<1 ppm).

All measurements should be made in basic solution. All samples and standards should be adjusted to a pH>9 with ISA.

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

Dilute concentrated samples (over 5000 ppm) before measurement.

Use fresh standards for calibration. Re-calibrate every few hours for routine measurement.

The glass electrode sensing bulb will not be attacked by most organic solvents.

The sample measuring range is pH 9-12. Use the ISA recommended to adjust the pH for best accuracy.

Low Level Sodium Determination (using a pH/mV meter)

This procedure is recommended for solutions with a sodium concentration less than 1 ppm. If the solution is high in ionic strength, but low in sodium, use the same procedure, but prepare a calibration solution with a composition similar to the sample. Use plastic lab-ware for low sodium measurements.

- Using 20 ml of standard ISA, dilute to 100 ml with distilled water.
- Dilute 20 ml of the outer chamber filling solution to 100 ml with distilled water and fill the reference electrode if using a double junction reference electrode.
- Dilute 10 ml of the 1000 ppm standard solution to 100 ml to prepare a 100 ppm standard solution. Add 1 ml of low level ISA to each 100 ml of standard. Standards should be prepared fresh daily.
- Using a 150 ml plastic beaker, add 100 ml of distilled water and 1 ml of low level ISA. Add NH_4OH , if necessary, to adjust the pH above 9. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.
- Place the electrode tips in the solution. Assure that the meter is in the mV mode.
- Add increments of the 100 ppm standard as given in Table 1 below.
- After the reading has stabilized, record the mV reading after each addition.

TABLE 1: Step-wise Calibration for Low Level Sodium Measurements

<u>Step</u>	<u>Pipet</u>	<u>Added Volume (ml)</u>	<u>Concentration ppm</u>
1	A	0.1	0.10
2	A	0.1	0.20
3	A	0.2	0.40
4	A	0.2	0.60
5	A	0.4	0.99
6	B	2.0	2.91
7	B	2.0	4.76

Pipet A = 1 ml graduated pipet

Pipet B = 2 ml pipet

Solutions: additions of 100 ppm standard to 100 ml of distilled water and 1 ml of low level ISA.

- Using the appropriate computer program or semi-logarithmic graph paper, plot the millivolt reading (linear axis) against the concentration (log axis).
- Rinse the electrodes with electrode rinse solution and blot dry.
- To a 150 ml plastic beaker add 100 ml of sample and 1 ml of low level ISA. Place the beaker on the magnetic stirrer and begin stirring. Adjust the pH, if necessary, to above 9. 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.
- Prepare a new low level calibration curve daily. Check the calibration curve every two hours by repeating Steps 3-8.

ELECTRODE CHARACTERISTICS

Reproducibility

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

Interferences

Table 3 lists some common cations that, if present in high enough levels, will cause electrode interferences and measurement errors or electrode drift when using the sodium ion electrodes.

Most samples do not contain or contain very little of the cations shown in Table 2. The ammonium ion (NH_4^+), found in the recommended ISA, will not result in an error if all samples and standards have the same level of ISA present.

Electrode drift and slow response could indicate the presence of high interference from the ions listed. Soak the electrodes in electrode storage solution when this happens to restore proper response.

TABLE 2: Levels of Interfering Ions Resulting in a 10% Error at Specified Levels of Sodium

<u>Interference</u>	<u>1 ppm</u>	<u>10ppm</u>	<u>100ppm</u>
Li ⁺	1.5ppm	15ppm	150ppm
K ⁺	17ppm	170ppm	1700ppm
Rb ⁺	1.1X10 ⁴ ppm	1.1X10 ⁵ ppm	--
NH ₄ ⁺	1.8X10 ³ ppm	1.8X10 ⁴ ppm	--
Ag ⁺	.0001ppm	.001ppm	.01ppm
Tl ⁺	4.5X10 ³ ppm	4.5X10 ⁴ ppm	--

Temperature Influences

The electrode response will shift and change slope with change in temperature. Standards and samples should be at the same temperature. A 2% error results with a 1°C temperature change for a 10 ppm solution.

The electrode can be used at temperatures from 0° - 80°C. Room temperature measurements are recommended, since measurements at temperatures quite different from room temperature may require equilibrium times up to one hour.

Electrode Response

Plotting the electrode mV potential against the sodium concentration results in a straight line with a slope of about 56 mV between 10 ppm and 100 ppm at 25°C.

For sodium concentrations above 10 ppm Na⁺, the electrode exhibits good time response (95% of total mV reading in one minute or less). Response times are longer below this value.

Limits of Detection

The upper limit of detection in pure sodium solutions is 20,000 ppm.

Free sodium ion concentration down to 0.1 ppm can be measured in basic solutions. For measurements below 1 ppm, use plastic lab-ware (and low level procedures) since a significant pickup of sodium may occur from glassware due to removal from container walls.

pH Effects

The electrode response to sodium ions is greatly influenced by the pH of the solution. Hydrogen ion interferes with measurements of low level sodium ion measurements, although the electrode can be used over a wide pH range

The pH should be adjusted to a pH greater than 9 by the addition of ISA to all standards and samples for optimal results over the entire concentration range of sodium. Additional ammonium hydroxide may be necessary to adjust the pH to the desired level in some cases.

Electrode Life

The sodium electrode will last one year in normal laboratory use. On-line measurements might shorten operational lifetime to several months. In time, the response time will increase and the calibration slope will decrease to the point calibration is difficult and electrode replacement is required.

Since sodium electrodes have a limited shelf life, it is important to have a backup electrode which is in working condition when required.

Electrode Storage

The sodium ion electrode should be stored in the sodium electrode storage solution, never in air or in distilled water. A more dilute sodium chloride solution (with pH adjusted through the use of ISA) may be used for storage before low level measurements. For longer storage (longer than two weeks), rinse and dry the sensing glass and cover the glass tip with any protective cap shipped with the electrode. The reference portion of the combination electrode (or the outer chamber of the reference electrode) should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

TROUBLESHOOTING HINTS

*Remember to remove the black protective shipping cap on the bottom of the electrode and expose the fill hole underneath the electrode cap. Fill the electrode with the Reference Filling Solution shipped with the electrode to a level just below the fill hole.

<u>Symptom</u>	<u>Possible Causes</u>	<u>Next Step</u>
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction manual)
	defective electrode	check electrode operation
	electrode not plugged in properly	unplug electrode from meter and reset
	electrode reference chamber not filled	fill reference chamber as instructed in <u>Electrode Preparation</u>
	air bubble on membrane	remove air bubble by re-dipping electrode
	electrode not in solution	put electrode in solution
Noisy or Unstable Reading (readings continuously or randomly changing.)	insufficient reference filling solution	fill outer body of electrode with proper amount of reference filling solution
	defective meter	check meter with shorting strap (see meter instruction manual)
	defective electrode	check electrode operation
	air bubble on membrane	remove air bubble by re-dipping electrode
	meter or stirrer improperly grounded	check meter and stirrer for grounding
	Drift (reading slowly changing in one direction)	electrode exposed to interferences
incorrect reference filling solution		refill outer body of electrode using filling solution shipped with electrode
total sample level of dissolved species above 1M		dilute sample
membrane failure (wet, perforation, discoloration)		replace electrode
samples and standards at different temperatures		allow samples and standards to come to same temperature before measurement
Low Slope or No Slope		standards contaminated or incorrectly made
	ISA not used	use recommended ISA

	standard used as ISA	use ISA
	membrane failure (wet, perforation, discoloration)	replace electrode
"Incorrect Answer" but calibration curve is good)	incorrect standards	prepare fresh standards
	wrong units used	apply correct conversion factor: $10^{-3}\text{M} = 23 \text{ ppm as Na}^+$
	ISA added to standards and not samples	add same proportions of ISA to standards and samples
	sample carryover	rinse electrodes thoroughly between samples

SPECIFICATIONS

Concentration Range:	saturated solutions to 0.02 ppm
pH Range:	5 to 12 (depending on Na^+ level)
Slope:	52 – 59 mV between 10 ppm and 100 ppm at 25°C
Temperature Range:	-5° to 70°C
Interferences:	H^+ , K^+ , Li^+ , Ag^+ , Cs^+ , Tl^+
Reproducibility:	$\pm 2\%$
Size:	110 mm length 12 mm diameter 1 m cable length
Storage:	store in 5M NaCl with added ISA

ELECTRODE THEORY

The pHoenix Sodium Ion Electrodes are composed of a sodium-selective glass membrane bonded to a glass body. When the membrane is in contact with a solution containing sodium ions, an electrode potential develops across the membrane. This electrode potential is measured against a constant reference potential, using a pH/mV meter or an ion meter. The level of sodium ions, corresponding to the measured potential, is described by the Nernst equation.

$$E = E_0 + S \log X$$

where:

- E = measured electrode potential
- E_0 = reference potential (a constant)
- S = electrode slope (.56 mV/decade)
- X = level of sodium ions in solution

The activity, X, represents the effective concentration of free sodium ions in the solution. The activity is related to the free ion concentration, C_f , by the activity coefficient, γ , by:

$$X = \gamma C_f$$

Activity coefficients may vary, depending on the total ionic strength, I, determined as:

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

where:

- C_x = concentration of ion X

Z_x = charge of ion

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 is added to samples and standards. The recommended ISA for sodium is an ammonium chloride/ammonium hydroxide buffer. 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 sodium ions.

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