

# *ISE35LB*

*ISE Low Level Sodium*

*OPERATION MANUAL*

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**Consort**

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## General Instructions

### Introduction

The Consort ULTRA LOW LEVEL Sodium Ion Selective Electrode is designed to monitor sodium levels in the ppb range where conventional sodium electrodes are inaccurate. The monitoring of sodium at this level is essential in many applications especially in power plants where sodium impurities in the ppb range cause stress corrosion cracking in high pressure steam turbines and stainless-steel generators.

### Required Equipment

1. An ion meter
2. ULTRA LOW LEVEL Sodium Ion Sensing Electrode – ISE35LB
3. Plastic syringe, pipets, volumetric flasks, 150 ml beakers

### Required Solutions

1. Deionized or distilled water for solution preparation.
2. Consort Sodium Standard, 1000 ppb Na<sup>+</sup>, **ISC35**.
3. Consort Ionic Strength Adjuster (ISA35), 4M NH<sub>4</sub>Cl/4M NH<sub>4</sub>OH. 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 (NH<sub>4</sub>Cl). Under a hood, add 270 ml of concentrated ammonium hydroxide (NH<sub>4</sub>OH), 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. pipet 10 ml of the newly-made ISA into a 100 ml volumetric flask and dilute to volume with deionized water.
4. If one switches from ammonium hydroxide/ammonium chloride to a pinch of calcium hydroxide as an ISA, then the limit of detection can be readily extended down to 1 ppb on the bench. You need to add about 0.2 g Ca(OH)<sub>2</sub> per 100 ml of standard or sample.
5. Dilute Electrode Rinse Solution. To prepare this solution from your own laboratory stock, add 20 ml of ISA to a one litre 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.

### 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 re-dipping probe.
2. Using a pipet, add 1 ml of 1000 ppb standard into the solution. Stir moderately. After 1 minute, record the mV reading.
3. Using a pipet, add 10 ml of the 1000 ppb sodium 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 40-59 mV between 10 ppb and 100 ppb 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 ppb sodium standard, prepare two sodium standards whose concentration is near the expected sample concentration. (e.g 10 ppb and 100 ppb) For example, to make a 100 ppb standard, pipet 10 ml of the 1000 ppb standard into a 100 ml volumetric flask and dilute to volume with deionized water. Next to make a 10 ppb standard, A 1 ppb 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.
- The tests that were run with Ca(OH)<sub>2</sub> as ISA were used to measure the lowest limit of detection by estimation. In other words, there was a 183 mV difference negative below 2 ppm, which translates to a limit of detection around 1 ppb. There were no specific mV readings recorded for 1 ppb, 10 ppb, 100 ppb, 1000 ppb. The user will have to determine the slope between 1 ppb and 10 ppb by experimentation.

## 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 ( $\text{NH}_4^+$ ), 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>
$\text{Li}^+$	1.5ppm	15ppm	150ppm
$\text{K}^+$	17ppm	170ppm	1700ppm
$\text{Rb}^+$	$1.1 \times 10^4$ ppm	$1.1 \times 10^5$ ppm	-
$\text{NH}_4^+$	$1.8 \times 10^3$ ppm	$1.8 \times 10^4$ ppm	-
$\text{Ag}^+$	.0001ppm	.001ppm	.01ppm
$\text{Ti}^+$	$4.5 \times 10^3$ ppm	$4.5 \times 10^4$ 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  $\text{Na}^+$ , 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. Check also the use of  $\text{Ca}(\text{OH})_2$  as ISA to improve the limit of detection.

### 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.

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

Low Slope or No Slope (continued)	standard used as ISA  membrane failure (wet, perforation, discoloration)	use ISA  replace membrane/electrode
Incorrect Answer but calibration curve is good)	incorrect standards  wrong units used  ISA added to standards and not samples  sample carryover	prepare fresh standards  apply correct conversion factor: $10^{-9}\text{M} = 23 \text{ ppm as Na}^+$  add same proportions of ISA to standards and samples  rinse electrodes thoroughly between samples

## ***SPECIFICATIONS***

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



## ELECTRODE THEORY

The 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,  $C_i$ , by the activity coefficient,  $\gamma$ , by:

$$X = \gamma C_i$$

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

$$I = 1/2 \sum C_i Z_i^2$$

where

- $C_i$  = concentration of ion X
- $Z_i$  = charge of ion
- $\Sigma$  = 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,  $\gamma$ , 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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