# OMEGA ENGINEERING
# ISE-8860 AND ISE-8862
# INSTRUCTION MANUAL

## General Instructions

### Introduction:

The Omega Sodium Ion Electrodes are used to quickly, simply, accurately, and economically measure Sodium ion in aqueous solutions. These Sodium ion electrodes are intended to measure sodium in the range of 1 to 1x10$_{-5}$M. For more concentrated sodium solutions and for solutions containing high levels of potassium and lithium, please contact Omega Engineering Inc.'s pH Engineering Department.

### 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. Magnetic stirrer
4. The ISE-8860 Sodium Ion Electrode or ISE-8862 Sodium Combination Ion Glass Electrode
5. Double Junction Reference Electrode, PHFS-A250 filling solution in the inner chamber and the PHFS-1041 filling solution in the outer chamber.

### Required Solutions

1) Deionized or distilled water for solution preparation.

2) Sodium Standard, 0.1M NaCl

To prepare this standard, add 5.85 grams of reagent grade sodium chloride to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.

3) Sodium Standard, 1000 ppm NA$^{+}$

To prepare this standard, add 1.65 grams of reagent grade sodium chloride to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.

## GENERAL PREPARATION

### Electrode Preparation

Remove the rubber cap(s) covering the electrode tip(s) and the rubber band covering the filling hole(s) of the reference electrode. Fill the combination electrode or the reference electrode salt bridge with the appropriate filling solution.

Soak the tip of the sodium electrode in distilled or deionized water for 10 minutes, followed by storage in standard sodium solution ($10^{-2}$) until ready to use and between measurements.

Connect the electrode(s) to the proper terminal(s) on the meter as recommended by the meter manufacturer.

### Electrode Storage

Between measurements and overnight, the electrode may be stored in $10^{-2}$M sodium solution. For longer periods of time (2-3 weeks), rinse the electrode well and store dry in the original electrode box, remembering to cover the filling hole of the reference portion of the ISE-8862 combination electrode in addition to replacing the protective cap on the sensing element. If using the **ISE-8860** mono probe, cover the sensing element with the protective cap and the filling hole of the separate reference electrode.

### Electrode Slope Check (with standard pH/mV meter)
(check electrode each day)

To a 150 ml beaker, add 100 ml of distilled water. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip(s) into the solution.

Using a pipet, add 1 ml of 0.1M or 1000 ppm sodium standard to the beaker. When the reading is stable, record the millivolt reading.

Using a pipet, add 10 ml of the standard used above to the beaker. When the reading has stabilized, record the millivolt reading.

Determine the difference between the two readings. A difference of 54 ± 2 mV indicates correct electrode operation, assuming the solution temperature is between 20° and 25°C. See the **Troubleshooting Guide** if the potential change is not within this range.

**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 electrode each day)

Prepare standard sodium solutions whose concentrations vary by tenfold. Use either the 0.1M NaCl or the 1000 ppm $NA^+$ standard stock solutions. Use the serial dilution method for this preparation.

To a 150 ml beaker, add 100 ml of the lower value standard. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip(s) into the solution.

Assure that the meter is in the concentration mode.

Adjust the meter to the concentration of the lower value standard and fix the value in the memory according to the meter manufacturer's instructions.

Rinse the electrode with distilled water and blot dry.

To a 150 ml beaker, add 100 ml of the higher value standard. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip(s) into the solution.

Adjust the meter to the concentration of the higher value standard and fix the value in the memory.

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 Guide** if the slope is not within this range.

## MEASUREMENT

### Measuring Hints

All samples and standards should be at the same temperature for precise measurement, preferably ambient temperature.

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.

Always rinse the electrode tip(s) with distilled water and blot dry with a fresh tissue between readings to prevent solution carryover. Do not rub or wipe the sensing membrane.

Check the sodium ion electrode for any bubbles on the membrane surface after immersion in the solution.

A sluggish responding sodium electrode may point to contaminants on the membrane. Soak the electrode in distilled water for 5 minutes to clean the membrane. Rinse the electrode and soak in a standard solution for about 5 minutes before use.

For high ionic strength samples, standards should be prepared with a composition similar to that of the sample.

Dilute concentrated (over 0.1M) samples before measurement.

### Sample Requirements

Make sure that the samples and standards are at the same temperature. About a 2% error will be introduced for a 1°C difference in temperature. Temperature should be less than 50°C.

All samples and standards must be aqueous. They must not contain organic solvents. Interferences found in Table 3 should be absent.

### Units of Measurement

Sodium concentrations are measured in units of parts per million, moles per liter, or any other convenient concentration unit. Table 1 indicates some of the concentration units.

TABLE 1: Concentration Unit Conversion Factors

| ppm as $Na^+$ | ppm as NaCl | moles/liter |
|---|---|---|
| 2.30 | 5.85 | $1 \times 10^{-4}$ |
| 23.00 | 58.50 | $1 \times 10^{-3}$ |
| 230.00 | 585.00 | $1 \times 10^{-2}$ |

## MEASUREMENT PROCEDURE

### Direct Measurement

A simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The temperature of both sample solution and of standard solutions should be the same.

**Direct Measurement of Sodium** (using a standard pH/mV meter)

1) Prepare $10^{-2}$, $10^{-3}$, and $10^{-4}$M or 100, 10, and 1 ppm standards by serial dilution of the 0.1M or 1000 ppm standard. If samples have an ionic strength above 0.1M, prepare standards with a composition similar to samples.

2) Place the most dilute solution ($10^{-4}$M or 1 ppm) on the magnetic stirrer and begin stirring at a constant rate.

After assuring that the meter is in the mV mode, lower the electrode tip(s) into the solution. When the reading has stabilized, record the mV reading.

3) Place the midrange solution ($10^{-3}$M or 10 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode(s) with distilled water and blotting dry, immerse the electrode tip(s) in the solution. When the reading has stabilized, record the mV reading.

4) Place the most concentrated solution ($10^{-2}$M or 100 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode(s) with distilled water and blotting dry, immerse the electrode tip(s) 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). A typical calibration curve can be found in Figure 1. The calibration curve may be extrapolated down to about $1\times10^{-5}$M or 0.23 ppm as sodium.

6) To a clean, dry 150 ml beaker, add 100 ml of sample. Place the beaker on the magnetic stirrer and begin stirring. Place the electrode tip(s) in the solution. When the reading has stabilized, record the millivolt reading. Determine the concentration directly from the calibration curve.

7) The electrode should be recalibrated every 1-2 hours. Simply repeat steps 2-5 above.

**Direct Measurement of Sodium** (using an ion meter)

1) By serial dilution of the 0.1M or 1000 ppm sodium standard, prepare two sodium standards whose concentration is near the expected sample concentration. Measure out 100 ml of each standard into individual 150 ml beakers.

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.

3) Lower the electrode tip(s) into the solution.

4) Adjust the meter to the concentration of the sodium standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

5) Rinse the electrode tip(s) with distilled water and blot dry.

6) Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate.

7) Lower the electrode tip(s) into the solution.

8) Adjust the meter to the concentration of the sodium standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

9) For low level measurements, place the rinsed, dried electrode into a solution containing 100 ml of distilled water. After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.

10) Place 100 ml of the sample in a 150 ml beaker, place it on the magnetic stirrer, and begin stirring.

11) Immerse the electrode tip(s) in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.

12) The electrode should be recalibrated every 1-2 hours. Simply repeat Steps 2-8 (2-9) above.

## ELECTRODE CHARACTERISTICS

### Reproducibility

Direct electrode measurements reproducible to ± 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

If present at high enough levels, other cations like potassium or lithium interfere with electrode response and will result in measurement errors or electrode malfunction.

Soaking the sodium electrode in distilled or deionized water for an hour, followed by soaking for a few hours in dilute sodium standard, may be necessary if the electrode is exposed to high levels of interfering ion. This treatment is indicated if electrode response becomes sluggish and drifty.

## Temperature Influences

Samples and standards should be at the same temperature, since electrode potentials are influenced by changes in temperature.

Provided that temperature equilibria has occured, the sodium ion electrodes can be used at temperatures from 0°-50°C. Room temperature measurements are recommended, since measurements at temperatures markedly different from room temperature may require equilibrium times up to one hour.

Table 4 indicates the variation of theoretical slope with temperature.

TABLE 4: Temperature vs Value for the Electrode Slope

| Temp (°C) | "S" |
|---|---|
| 0 | 54.20 |
| 10 | 56.18 |
| 20 | 58.16 |
| 25 | 59.16 |
| 30 | 60.15 |
| 40 | 62.13 |
| 50 | 64.11 |

## Electrode Response

Plotting the electrode mV potential against the sodium concentration on semi-logarithmic paper results in a straight line with a slope of about 54mV per decade.

The time needed to reach 99% of the stable electrode potential reading, the electrode response time, varies from one minute or less for sodium concentration changes in samples $10^{-4}$M or higher to several minutes near the detection limit.

## Limits of Detection

The upper limit of detection in pure sodium chloride solution is 1M. If other ions are present, the upper limit of detection is above $10^{-1}$M sodium, 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 1 and $10^{-1}$M or calibrate the electrode at 4 or 5 intermediate points.

## ELECTRODE THEORY

### Electrode Operation

Sodium Ion Electrodes consist of an electrode body containing an ion exchanger in a sensing module. This sensing module contains a liquid internal filling solution in contact with a gelled organophilic membrane containing a sodium ion selective ion exchanger.

An electrode potential develops across the membrane when the membrane is in contact with a sodium solution. Measurement of this potential against a constant reference potential with a digital pH/mV meter or with a specific ion meter depends on the level of free sodium ion in the solution. The level of sodium ions, corresponding to the measured potential, is described by the Nernst equation:

$$E = E_{\circ} + S \log X$$

where:

$E$ = measured electrode potential
$E_{\circ}$ = 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 the ions in solution. Total sodium concentration, $C_t$, includes free sodium ions, $C_f$, plus bound or complexed sodium ions, $C_b$. Since the sodium ion electrodes only respond to free ion, the free ion concentration is:

$$C_f = C_t + C_b$$

The activity is related to the free ion concentration, $C_f$, by the activity coefficient, $\gamma$, by:

$$X = \gamma \, C_f$$

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

$$I = \tfrac{1}{2}\Sigma C_x Z_x^2$$

where:

$C_x$ = concentation of ion X
$Z_x$ = charge on 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.

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 interdiffusion of ions into 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 solution diffuse into the sample should be equitransferant. No junction potential can result if the rate at which the positive and negative charge carried into the sample is equal.

Strongly acidic (pH = 0-2) and strongly basic (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 an equitransferant salt. One must either calibrate the electrode(s) in the same pH range as the samples or use a known increment 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 glassware, the electrode(s), the reagents, the sample, and the technique.

### Meter

The meter is the easiest component to eliminate as a possible cause of error. Most meters are provided with an instrument check-out procedure in the instruction manual and a shorting strap for convenience in troubleshooting. Consult the manual for complete instructions and verify that the instrument operates as indicated and is stable in all steps.

### Glassware

Clean glassware will drain clean. That is, when rinsed with distilled or deionized water, the water does not bead on the inside walls of the glassware.

## Electrodes

The electrode(s) 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(s) fail to respond as expected, see the section **Measureing Hints.** Repeat the slope check.

3. If the electrode(s) still fail to respond as expected, substitute another sodium ion electrode that is known to be in good working order for the questionable electrode. If the problem persists and you are using an electrode pair, try the same routine with a working reference electrode.

4. If the problem persists, the reagents may be of poor quality, interferences in the sample may be present or the technique may be faulty. See **Reagents**, **Sample**, and **Technique** sections below.

5. If another electrode is not available for test purposes and if the electrode in use is suspect, review the instruction manual and be sure to:
   - clean and rinse the electrode(s) thoroughly
   - prepare the electrode(s) properly
   - use proper filling solution and standards
   - measure correctly and accurately
   - review **Troubleshooting Hints.**

## Standards

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! Error may result from contamination of prepared standards, accuracy of dilution, quality of distilled water, or a mathematical error in calculating the concentrations.

## Sample

If the electrode works properly in standards, but not in sample, look for possible interferences, complexing agents, or substances which could affect response or physically damage the sensing electrode or the reference electrode. If possible, determine the composition of the samples and check for problems. See **Measuring Hints, Sample Requirements**, and **Interferences.**

## Technique

Check the method of analysis for compatibility with your sample. Direct measurement may not always be the method of choice. If working at low levels, be sure to use low level measurement techniques.

Also, be sure that the expected concentration of the ion of interest is within the electrode's limits of detection.

If problems persist, review operational procedures and instruction manual to be sure that proper technique has been followed.

## Troubleshooting Hints

| Symptom | Possible Causes | Next Step |
|---|---|---|
| Out of Range Reading | defective meter | perform meter check-out procedure (see meter instruction manual) |
| | electrode(s) not plugged in properly | unplug electrode(s) and reseat |
| | reference filling solution not added | fill combination or reference electrode with proper level of electode filling solution |
| | air bubble on membrane | remove bubble by redipping electrode |
| "Incorrect Answer" (but calibration curve is good) | incorrect scaling of semilog paper | plot millivolts on the linear axis. On the log 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 | apply correct conversion factor: $10^{-3}$M = 23.0 ppm as NA$^{+}$ = 58.5 ppm as NaCl |
| | all solutions not at same temperature | all solutions must be at room temperature before measurement |
| Drift (reading slowly changing in one direction) | samples and standards at different temperatures | allow solutions to come to room temperature before measurement |
| | incorrect internal filling solution | fill outer body with recommended filling solution |
| | electrode exposed to interferences | see section on **Interferences** |
| Low Slope or No Slope | standards contaminated or incorrectly made | prepare fresh standards |
| | electrode exposed to interferences | see section on **Interferences** |
| Noisy or Unstable Readings (readings continuously or randomly changing) | defective meter | perform meter check-out procedure (see meter instruction manual) |
| | air bubble on membrane | remove bubble by redipping electrode |
| | meter or stirrer not grounded | ground meter or stirrer |
| | wrong reference electrode | do not use calomel or Ag/AgCl (frit or fiber-type reference electrode |

## SPECIFICATIONS

Concentration Range: $1 \times 10^{-5}$ to 1M
(0.2 to 23,000 ppm as $NA^+$)

pH Range: 5.0 to 10

Temperature Range: 0° to 50°C

Resistance: 1-5 Mohms

Reproducibility: ± 2%

Size: 110 mm length
12 mm diameter
1 m cable length

Sample: aqueous solutions only

Specifications subject to change without notice

M-3966