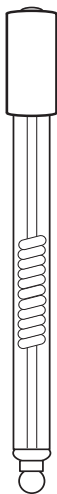


User Guide

ROSS® Sodium
Ion Selective
Electrode



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GENERAL INFORMATION

Introduction

This user guide contains information on the preparation, operation and maintenance for the ROSS sodium ion selective electrode (ISE). Sodium electrodes measure free sodium ions in aqueous solutions quickly, simply, accurately and economically. With their unique internal system, ROSS electrodes provide a faster response and greater stability and accuracy than conventional sodium electrodes. For the most consistent and fastest results, we recommend measuring sodium using the known addition procedure. Detailed instructions for performing this procedure are outlined in this user guide. General analytical procedures, electrode characteristics and electrode theory are also included in this user guide.

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.

ROSS® Sure-Flow® Sodium Combination ISE

The reference and sensing electrodes are built into one electrode, which decreases the amount of required solution and reduces waste. The built-in Sure-Flow reference junction prevents electrode clogging and provides fast and stable readings. The sodium combination ISE is available with a waterproof BNC connector, Cat.No. 8611BNWP.

ROSS® Sure-Flow® Sodium Half-Cell ISE

The sodium half-cell electrode must be used with the ROSS reference electrode, Cat. No. 800300, or ROSS Ultra reference electrode, Cat. No. 800500U. The sodium half-cell is available with a BNC connector, Cat. No. 8411BN.

Package Contents

The 8611BNWP and 8411BN ROSS sodium electrode kits contain the following:

ROSS sodium electrode filling solution, 50 mL, Cat. No. 900010
Sodium ionic strength adjustor (ISA), 475 mL, Cat. No. 841111
Sodium known addition standard, 475 mL, Cat. No. 841109
1000 ppm sodium standard with ISA, 475 mL, Cat. No.841109
1000 ppm sodium standard, 475 mL, Cat. No. 841108
Sodium reconditioning solution, 475 mL, Cat. No. 841113
Sodium electrode storage solution, 475 mL, Cat. No. 841101

Required Equipment

Meter– Thermo Scientific Orion ISE meter, such as the 4-Star pH/ISE meter or 5-Star pH/ISE/DO/conductivity meter. Sodium electrodes can be used on any ISE meter with a BNC connection. The electrodes can also be used on meters with a variety of inputs when an adapter cable is used.

Reference Electrode– The 8411BN sodium half-cell electrode requires the ROSS reference electrode, Cat. No. 800300 or the ROSS Ultra reference electrode, Cat. No. 800500U. Do not use the filling solution, Cat. No. 810007, that is shipped with the ROSS reference electrodes. Use the sodium electrode filling solution, Cat. No. 900010, that is shipped with the 8411BN electrode.

Stirrer– Magnetic stirrer or stir probe, Cat. No. 096019. The stir probe can be used with 3-Star, 4-Star and 5-Star benchtop meters.

Labware– Volumetric flasks, graduated cylinders and beakers. Plastic labware is recommended for low-level measurements.

Required Solutions

Known Addition Standard Solutions

1000 ppm sodium standard with ISA, Cat. No. 841109

1 M sodium standard with ISA, Cat. No. 650700

Standard Solutions

0.1 M sodium chloride standard, Cat. No. 941706

1000 ppm Sodium Standard, Cat. No. 841108*

100 ppm Sodium Standard, Cat. No. 941107

10 ppm Sodium Standard, Cat. No. 941105

Sodium Ionic Strength Adjustor (ISA), Cat. No. 841111

To keep a constant background ionic strength and adjust the pH, 4 M NH_4Cl and 4 M NH_4OH

Electrode Rinse Solution, Customer Prepared

For rinsing sodium electrodes between measurements. Make 1 liter of rinse solution by adding 10 mL of the ISA to a 1 liter squeeze bottle and filling it with distilled water

Sodium Reconditioning Solution, Cat. No. 841113

For restoring electrode response, 0.1 M NH_4HF_2

Sodium Electrode Storage Solution, Cat. No. 841101

For storing ROSS sodium electrode, 5 M NaCl , 0.08 M NH_4OH , and 0.08 M NH_4Cl

Reference Electrode Filling Solutions

Use for filling the ROSS sodium combination electrode, Cat. No. 8611BNWP, and the ROSS or ROSS Ultra reference electrode that is used in conjunction with the ROSS sodium half-cell electrode, Cat. No. 8411BN

Cat. No. 900010, 2 M NH_4Cl – For routine sodium measurements (sodium concentration greater than 10^{-5} M or 0.2 ppm)

Cat. No. 900012, 0.1 M NH_4Cl – For low-level sodium measurements (less than 10^{-5} M or 0.2 ppm)

Distilled or Deionized Water

USING THE ELECTRODE

Setup

Electrode Preparation

Note: Perform this procedure on new electrodes or electrodes that have been stored dry.

1. Remove the protective shipping cap from the ROSS sodium electrode sensing element and save it for electrode storage.
2. Clean any salt deposits from the exterior of the electrode by rinsing it with the sodium electrode rinse solution. Do not use water. (See **Required Solutions** for preparation instructions.)
3. **To Prepare the 8611BNWP:**
 - a. Uncover the fill hole by removing the fill hole plug (save for storage) and empty the electrode by pressing down on the electrode cap. See **Figure 1**.
 - b. Fill the electrode with the sodium electrode filling solution, Cat. No. 900010. See **Figure 2**. For low-level measurements (less than 10^{-5} M), Cat. No. 900012 is recommended. To function properly, the level of the filling solution must cover the coil and be at least one inch above the sample level on immersion. The electrode fill hole should be open whenever the electrode is in use.
 - c. Thoroughly wet the junction by pressing down on the electrode cap and allowing a small amount of filling solution to flow out. Replenish any lost filling solution.
4. **To Prepare the 8411BN and 800300/800500U:**

Fill the reference electrode according to the instructions in the reference electrode user guide. ROSS reference electrodes are shipped with a 3 M KCl filling solution, Cat. No. 810007, for use with pH electrodes. Do not use this filling solution for sodium measurements. Use the sodium electrode filling solution, Cat. No. 900010, that is provided with the 8411BN electrode. For low-level measurements, Cat. No. 900012 is recommended.
5. Soak the electrode for at least two hours in the sodium electrode storage solution, Cat. No. 841101.
6. After storage, refresh the junction by pressing down on the electrode cap and letting a small amount of solution flow out. Replenish any lost filling solution.

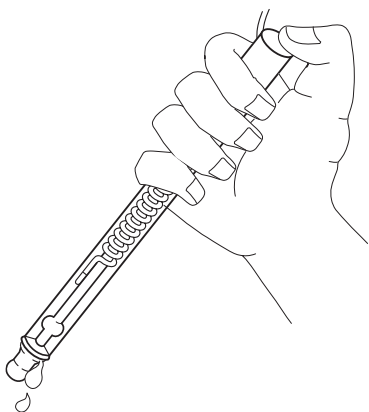


Figure 1
8611BNWP ROSS Sure-Flow Sodium Electrode Being Flushed

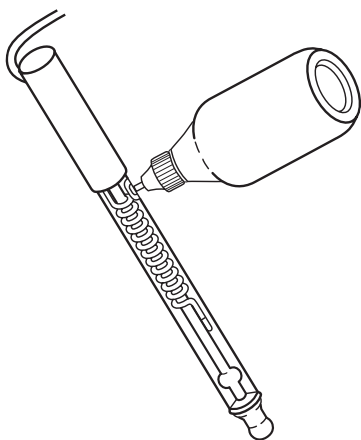


Figure 2
Filling the 8611BNWP ROSS Sure-Flow Sodium Electrode

Checking Electrode Operation (Slope)

These are general instructions, which can be used with most meters. 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(s) have been stored dry, condition the electrodes as described in the **Electrode Preparation** section.
2. Connect electrode(s) to the meter (refer to the meter user guide for assistance if needed).
3. Place 100 mL of distilled water into a 150 mL beaker. Add 10 mL of ISA, Cat. No. 841111. Stir the solution thoroughly. Set the meter to read in the mV mode.
4. Rinse the electrode(s) with sodium electrode rinse solution (see the **Required Solutions** section) and place in the solution prepared in step 3.
5. Select any standard from **Table 1**. Pipette 1 mL of this standard solution into the beaker. Stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
6. Pipette 10 mL of the same standard into the same beaker. Stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
7. The difference between the first and second potential readings is the slope of the electrode. The difference should be in the range of 54 to 60 mV, assuming the solution temperature is between 20 and 25 °C. If the potential is not within this range, recondition the electrode as described in the **Electrode Reconditioning** section. For other troubleshooting techniques, refer to the **Troubleshooting Checklist** section.

Table 1– Standards For Checking Electrode Slope

Cat. No.	Description
941706	0.1 M sodium chloride standard
841108	1000 ppm sodium standard

Before Analysis

Units of Measurement

Sodium can be measured in units of moles per liter, parts per million, % salt, mg/serving, or any other convenient unit depending on the concentration units used for standard solutions. A list of some conversion factors can be found in **Table 2**.

Table 2– Concentration Unit Conversion Factors

To Convert From:	To:	Multiply By:
Moles/Liter NaCl or Moles/Liter Na	ppm Na	23,000
	ppm NaCl	58,500
	% Na	2.3
	% NaCl	5.85
	mg Na/100 g, mg Na/100 mL	2,300
	mg NaCl/100 g, mg NaCl/100 mL	5,850
	ppm Na	moles/liter Na
moles/liter NaCl		0.0000171
% Na		0.0001
% NaCl		0.000254
ppm NaCl		2.54
mg NaCl/100 g, mg Na/100 mL		0.100
mg NaCl/100 g, mg NaCl/100 mL		0.254

Concentration Unit Conversion Factors (cont.)

To Convert From:	To:	Multiply By:
% NaCl, % salt	moles/liter Na	0.434
	moles/liter NaCl	0.171
	ppm Na	3,932
	% Na	0.3932
	ppm NaCl	10,000
	mg Na/100 g, mg Na/100 mL	393
	mg NaCl/100 g, mg NaCl/100 mL	1,000

Sample Requirements

Samples must fall in the pH range of 6 to 12 after pH adjustment, depending on sample concentration. For best accuracy, use the recommended ISA to adjust the pH to between 9 to 10. Refer to **Figure 3**.

The sodium electrode glass body is resistant to attack by most organic solvents, however, the response of the sensing bulb may become sluggish and measurements may drift when used in organic solvents. Contact our Technical Support Chemists for information on using the electrode in unusual applications such as non-aqueous samples.

One of the benefits of the ROSS sodium electrode is that the electrode responds rapidly to temperature changes. If the meter has an adjustable isopotential point and an automatic temperature compensator probe, it is possible to perform temperature compensated sodium measurements. Refer to the **Temperature Effects** section for more information. If these features are unavailable, samples and standards should be at the same temperature.

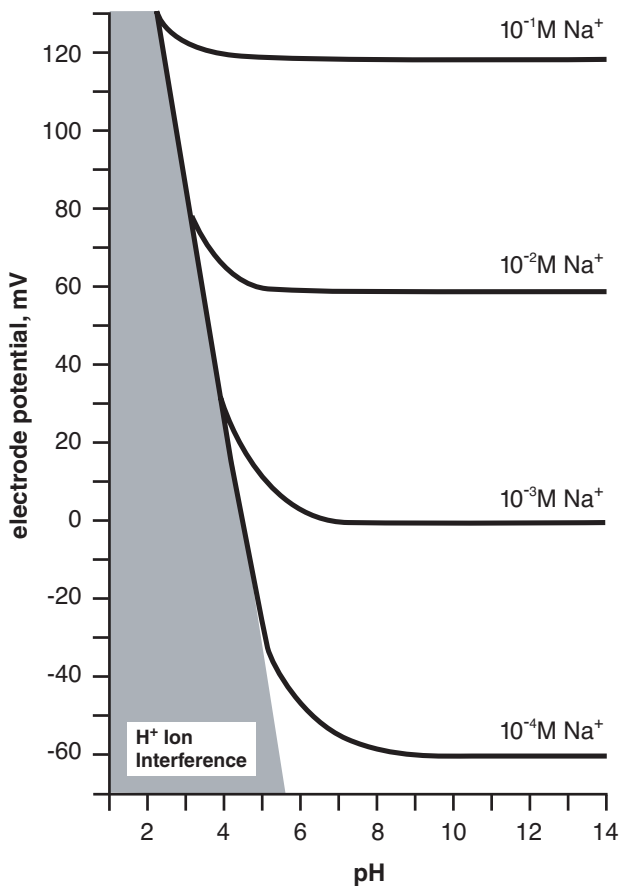


Figure 3
 Electrode Potential Behavior Vs. Solution pH in Pure NaCl
 Solution at 25 °C

Measuring Hints

- For the fastest, most consistent results, use a known addition procedure.
- Add ISA to all standards and samples. Use ratio of 10 mL of ISA per 100 mL sample or standard.
- Stir all standards and samples at a uniform rate during measurement. Magnetic stirrers may generate sufficient heat to change solution temperature. Place a piece of insulating material such as cork, cardboard, or styrofoam between the stirrer and beaker.
- If using direct calibration, verify calibration every two hours by placing electrodes in the first standard solution used for calibration and if necessary recalibrate.
- Always use fresh standards for calibration and measurement.
- Check the electrode slope daily. See the **Electrode Operation** section.
- Always rinse electrodes with sodium electrode rinse solution between measurements. (See the Required Solutions section for preparation.) Shake the electrode after use of rinse solution to prevent solution carryover. ***Do not wipe or rub the sensing element.***
- Adjust all samples and standards to between pH 9 to 10 with the sodium ionic strength adjustor, Cat. No. 841111. Be sure to add same proportion of ISA to samples and standards.
- Use plastic labware for low-level measurements.
- If the electrode response becomes sluggish, treat the sodium electrode with sodium reconditioning solution, Cat. No. 841113. See the **Electrode Reconditioning** section.
- Store the sodium electrode in sodium electrode storage solution, Cat. No. 841101, when the electrode is not in use. For low-level measurements, use a more dilute storage solution, 1 part storage solution to 100 parts of distilled water.
- Do not store the electrode in or rinse with distilled water.
- For high ionic strength samples, prepare standards with composition similar to that of the sample.

Analytical Procedures

Analytical Techniques

A variety of analytical techniques are available to the analyst.

Incremental Techniques

Useful methods since calibration is not required. These methods include a variety of spiking procedures – adding a standard solution to the sample, or sample to a standard solution. Advantages of incremental techniques are speed and ease of measurement, and ability to analyze samples containing complexing agents, concentrated samples, those varying widely in temperature, or dry soluble samples. The incremental techniques which are useful for sodium analysis are described below.

Known Addition provides the fastest, most consistent results when performing sodium measurements. The electrodes are immersed in the sample solution and an aliquot of a standard solution containing sodium is added to the sample. From the change in potential before and after the addition, the original sample concentration is determined. There are three types of known addition procedures: multiple known addition, double known addition, and single known addition.

Multiple Known Addition can be performed by the Thermo Scientific Orion 960 Autochemistry System and provides the most accurate results of any of these techniques. A series of additions of a sodium known addition standard solution are automatically dispensed into the sample and the original sodium concentration is calculated and reported by the instrument.

Double Known Addition can be performed by the Thermo Scientific Orion 960 Autochemistry System. Two aliquots of sodium standard solution are added to the sample, resulting in the automatic determination of the original sodium concentration of the sample and the slope of the electrode. Both double known addition and multiple known addition measure electrode slope during analysis, thus eliminating the need for a separate slope check.

Single Known Addition can be most conveniently performed on an advanced Thermo Scientific Orion ISE meter. This technique involves the addition of an aliquot of sodium standard. Electrode slope should be measured as a preliminary step using the procedure described in the meter user guide or in the **Checking Electrode Operation (Slope)** section.

Analate Addition is often used to measure soluble solid samples, viscous samples, small or very concentrated samples, to diminish the effects of complex sample matrices, or to diminish the effects of varying sample temperatures. This method is not suitable for dilute or low concentration samples. The electrodes are immersed in a standard solution containing the ion to be measured and an aliquot of the sample is added to the standard. The original sample concentration is determined from the change in potential before and after the addition.

Direct Calibration

A procedure used for measuring a large number of samples whose concentration varies over a wide range. Calibration is performed in a series of standards. The concentration of the samples is determined by comparison to the standards. ISA is added to all solutions to ensure that samples and standards have similar ionic strength.

Detailed instructions for double and single known addition are found in this user guide. For the multiple known addition procedure, refer to the meter user guide. General instructions for direct calibration are also described in this user guide.

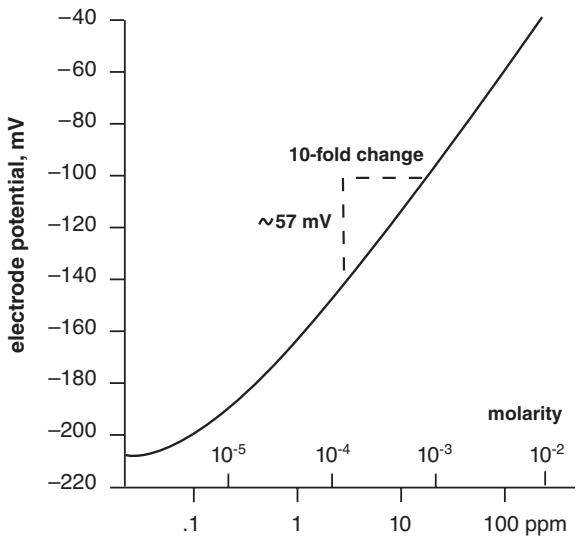


Figure 4
Typical ROSS Sodium Electrode Calibration Curve

A calibration curve of a typical ROSS sodium electrode demonstrates the log/linear response of the electrode using a pH/mV meter. The calibration curve is constructed on semilogarithmic paper. Electrode potentials (mV) of standard solutions are measured and plotted on the linear axis against their concentrations on the log axis. When measuring in the non-linear region of the curve, special procedures are recommended. See the **Low-Level Measurements** section.

Known Addition

General Preparation

Known addition has been found to be the best technique for measuring sodium, providing the fastest, most consistent results. It is especially convenient since no calibration is required. The electrodes are immersed in the sample, an aliquot of sodium standard is added, and the original sodium concentration is measured.

For optimal results, total concentration of the sample solution should double upon the addition of an aliquot of sodium standard solution. Therefore, the sample concentration must be known to within a factor of three. The most commonly used volume addition is 10 mL of standard to 100 mL of sample, using a standard which is ten times more concentrated than the sample.

For double known addition, two additions are required, thus the most convenient method is to make a 1 mL and a 10 mL addition of a standard whose concentration is 100 times the sample concentration. These size aliquot are most convenient and minimize volume change.

To minimize changes in ionic strength, ISA is added to all sodium standards in the same ratio as it is added to the samples. All samples should be stirred throughout measurements.

1. Prepare the electrode(s) according to instructions in the **Electrode Preparation** section.
2. Connect electrode(s) to the meter.
3. If using the single known addition technique, measure the electrode slope according to the instructions in the **Checking Electrode Operation (Slope)** section or the meter user guide.

Solution Preparation

1. Prepare 1 liter of sodium electrode rinse solution by adding 10 mL of ISA, Cat. No. 841111, to a 1 liter squeeze bottle and filling it with distilled water.
2. Prepare the sodium standard solution. Add 10 mL of ISA to every 100 mL of sodium standard. Mix the solution thoroughly. Use for known addition technique.

If more dilute standards are required than those available, dilute standard and then add 10 mL of ISA to every 100 mL of standard.

Standard Preparation For Single Known Addition

Prepare a sodium standard whose concentration is ten times the sample concentration (if concentration is unknown see note below). For example, if the sample is about 1 ppm sodium, prepare a sodium standard whose concentration is 10 ppm sodium, then add ISA.

Standard Preparation For Double Known Addition

Prepare a sodium standard whose concentration is 100 times the sample concentration. For example, if sample is about 1 ppm sodium, prepare a sodium standard whose concentration is 100 ppm and then add ISA.

Notes On Known Addition

For sodium analysis the ratio of addition of ISA to samples and standards is 10:100. This represents a 10% dilution and must be taken into consideration when calculating the results of the analysis. The procedures in this user guide when followed exactly will yield the correct answer. If you modify the procedures to better suit your analysis, remember to take the dilution into account.

For known addition the basic equation is as follows:

$$C_{\text{sam}} = \frac{p}{[(1 + p)10^{\Delta E/S}] - 1} \cdot C_{\text{std}}$$

where:

C_{sam} = concentration of the sample

C_{std} = concentration of the standard

E = change in millivolts

S = slope of the electrode

$$p = \frac{\text{volume of standard}}{\text{volume of sample}}$$

By keeping the proportion of ISA added to samples and standards the same, the dilution factor cancels in the equation as shown:

$$C_{\text{sam}} \cdot \frac{100 \text{ mL}}{110 \text{ mL}} = \frac{p}{[(1 + p)10^{\Delta E/S}] - 1} \cdot C_{\text{std}} \cdot \frac{100 \text{ mL}}{110 \text{ mL}}$$

$$C_{\text{sam}} = \frac{p}{[(1 + p)10^{\Delta E/S}] - 1} \cdot C_{\text{std}} \cdot \frac{100 \text{ mL}}{110 \text{ mL}} \cdot \frac{110 \text{ mL}}{100 \text{ mL}}$$

If any of the terms are changed the dilution must be taken into consideration. For example, using the known addition standard prepared in a background of 10% ISA, such as Cat. No. 841109, changes the equation:

$$C_{\text{sam}} \cdot \frac{100 \text{ mL}}{110 \text{ mL}} = \frac{p}{[(1 + p)10^{\Delta E/S}] - 1} \cdot C_{\text{std}}$$

$$C_{\text{sam}} = \frac{p}{[(1 + p)10^{\Delta E/S}] - 1} \cdot C_{\text{std}} \cdot \frac{100 \text{ mL}}{110 \text{ mL}}$$

$$C_{\text{sam}} = \frac{p}{[(1 + p)10^{\Delta E/S}] - 1} \cdot C_{\text{std}} \cdot 1.1$$

In conclusion, follow the procedures recommended in this user guide for the easiest method. When changing anything in these procedures, make sure to take the dilution factor into account. If using a meter which calculates the answer, be certain that your procedure is in agreement with the requirements of that particular meter technique.

Note: If sample concentration is unknown, obtain a millivolt reading on the sample with ISA added. Using the typical electrode calibration curve in **Figure 4**, read the approximate concentration from the graph, and use this value as a guideline in preparing the sodium standard.

Calibration and Measurement

Double Known Addition Using the EA940 / 960 Titrator

For most double known addition analysis, it is recommended that:

- Sample volume be 100 mL
- The concentration of the standard added be 100 times the expected sample concentration
- The volume of the first addition of standard be 1 mL
- The volume of the second addition of standard be 10 mL

Before Analysis: Press **SPEED**, then **2**, to proceed through the **OPERATOR MENU** steps listed below.

Display	Action
1. OPERATOR MENU?	Press yes .
2. CHANGE THE ELECTRODE ID?	Select Na ⁺ .
3. Na⁺ ISO = 1.0000	Press yes .
4. SET NUMBER OF SIGNIFICANT DIGITS?	Select 3.

Note: Since ISA is added to the standards and samples in the same ratio it is unnecessary to correct for the dilution which occurs when adding ISA. Make sure to follow instructions exactly. Enter the value of the standard before the addition of the ISA and enter the volume of the sample plus ISA.

Analysis: Following is the sequence of messages displayed when performing a double known addition measurement. Press **SPEED**, then **0** to begin.

Display	Action
1. CALIBRATE 1:Na⁺ 10:24 12-07-86	Press yes .
2. CALIBRATE BY DIRECT MEASUREMENT?	Press no .
3. USE INCREMENTAL TECHNIQUES?	Press yes .

Display	Action
4. 1 = KA 2 = KS 3 = AA 4 = AS	Press 1 to choose known addition.
5. 1 = SINGLE INCREMENT 2 = DOUBLE INCREMENT	Press 2 to choose double known addition.
6. 1:NA⁺ ELECTRODE IN SAMPLE?	Add 10 mL ISA to 100 mL sample and place electrode in sample. Stir moderately throughout measurement. Then press yes .
7. SAMPLE VOL = 100.00 IS THIS CORRECT?	Press yes if sample plus ISA volume is correct. Use numeric keys to change sample volume if it is incorrect, then press yes . (If 10 mL were added to 100 mL, change to 110.)
8. EMF = -182.3 mV NOT READY	None required. Electrode response is unstable, wait for a stable reading. NOTE: <i>EA 940's internal stability criteria may be overridden and current stability accepted for measurement by pressing yes.</i>
9. EMF = -171.3 YES TO CONTINUE	Electrode response is stable, press yes to continue with known addition.
10. STD ADDED TO SAMPLE?	Add first addition of sodium standard to sample (usually 1 mL), then press yes .
11. STD CONC N = 1.0000 IS THIS CORRECT?	Press yes if standard concentration is correct. Enter the concentration the standard would have had before addition of ISA. Use numeric keys to change standard concentration if it is incorrect, then press yes .
12. STD VOL = 1.0000 IS THIS CORRECT?	Press yes if volume of standard added is correct. Use numeric keys to change standard volume if it is incorrect, then press yes .

Display	Action
13. EMF = -155.6 NOT READY	None required. Electrode response is unstable, wait for a stable reading. NOTE: EA 940's internal stability criteria may be overridden and current stability accepted for measurement by pressing yes .
14. EMF = -154.3 YES TO CONTINUE	Electrode response is stable, press yes to continue with known addition.
15. STD ADDED TO SAMPLE + STD	Add second addition of same standard to sample containing first addition (usually 10 mL), then press yes .
16. STD VOL = 10.000 IS THIS CORRECT?	Press yes if volume of standard added is correct. Enter volume of second addition. Use numeric keys to change standard volume if it is incorrect, then press yes .
17. EMF = -139.4 NOT READY	None required. Electrode response is unstable, wait for a stable reading. NOTE: EA 940's internal stability criteria may be overridden and current stability accepted for measurement by pressing yes .
18. EMF = -137.2 YES TO CONTINUE	Electrode response is stable, press yes to continue with known addition.
19. 1:NA+ CONCN=1.00 REPEAT TECHNIQUE?	Sodium concentration of sample is displayed. Press yes to do another double known addition measurement. Press no to select a different technique. Electrode slope may be checked by pressing 2nd Function , then 4 .

Single Known Addition Using the EA940 / 960 Titrator

Before Analysis: Press **SPEED**, then **2**, to proceed through the **OPERATOR MENU** steps listed below.

Display	Action
1. OPERATOR MENU?	Press yes .
2. CHANGE THE ELECTRODE ID?	Select Na ⁺ .
3. Na ⁺ ISO = 1.0000	Press yes .
4. SET NUMBER OF SIGNIFICANT DIGITS?	Select 3.

Analysis: Following is the sequence of messages displayed when performing a single known addition. Press **SPEED**, then **0** to begin.

Display	Action
1. CALIBRATE 1: Na ⁺ 10:24 12-07-86	Press yes .
2. CALIBRATE BY DIRECT MEASUREMENT?	Press no .
3. USE INCREMENTAL TECHNIQUES?	Press yes .
4. 1 = KA 2 = KS 3 = AA 4 = AS	Press 1 to choose known addition.
5. 1 = SINGLE INCREMENT 2 = DOUBLE INCREMENT	Press 1 to choose single known addition.
6. NA ⁺ ELECTRODE IN SAMPLE?	Add 10 mL ISA and place electrode in sample. Stir moderately throughout measurement. Then press yes .
7. SAMPLE VOL = 100.00 IS THIS CORRECT?	Press yes if sample plus ISA volume is correct. (If 10 mL ISA were added to 100 mL samples, change to 110.) Use numeric keys to change sample volume if it is incorrect, then press yes .

Display	Action
8. SLOPE = +59.2 mV/DEC IS THIS CORRECT?	Press yes if slope value and polarity sign are correct. Use numeric keys to change slope value if it is incorrect, then press yes . If actual slope is unknown, enter +59 mV/DEC, or perform slope check in Checking Electrode Operation (Slope) or according to EA 940 user guide.
9. EMF = -182.3 mV NOT READY	None required. Electrode response is unstable, wait for a stable reading. <i>NOTE: EA 40's internal stability criteria may be overridden and current stability accepted for measurement by pressing yes.</i>
10. EMF = -171.3 YES TO CONTINUE	Electrode response is stable, press yes to continue with known addition.
11. STD ADDED TO SAMPLE?	Add sodium standard to sample, then press yes .
12. STD CONC = 1.0000 IS THIS CORRECT?	Press yes if sodium standard concentration is correct. Enter volume of standard before addition of ISA. Use numeric keys to change standard concentration if it is incorrect, then press yes .
13. STD VOL = 10.000 IS THIS CORRECT?	Press yes if volume of sodium standard added is correct. Use numeric keys to change standard if it is incorrect, then press yes .
14. EMF = -155.6 NOT READY	None required. Electrode response is unstable, wait for a stable reading. <i>NOTE: EA 940's internal stability criteria may be overridden and current stability accepted for measurement by pressing yes.</i>

Display	Action
15. EMF = -154.3 YES TO CONTINUE	Electrode response is stable, press yes to continue with known addition.
16. 1:NA+ CONCN=1.00 REPEAT TECHNIQUE?	Sodium concentration of sample is displayed. Press yes to do another known addition measurement. Press no to select a different technique.

Table 3– Q Tables for ROSS Sodium Known Addition

Dilution: 10 mL to 110 mL 0.090909
 Mixture: Sample 100 mL, ISA = 10 mL, KA = 10 mL

Na+ ΔE	Slope				
	55.0	57.0	58.0	59.0	60.0
5.0	0.2636	0.2713	0.2751	0.2789	0.2826
5.2	0.2552	0.2628	0.2666	0.2703	0.2739
5.4	0.2473	0.2548	0.2585	0.2621	0.2657
5.6	0.2398	0.2471	0.2508	0.2544	0.2579
5.8	0.2327	0.2399	0.2435	0.2470	0.2505
6.0	0.2259	0.2330	0.2365	0.2400	0.2435
6.2	0.2195	0.2265	0.2299	0.2334	0.2368
6.4	0.2133	0.2202	0.2236	0.2270	0.2304
6.6	0.2075	0.2143	0.2176	0.2210	0.2243
6.8	0.2019	0.2086	0.2119	0.2152	0.2184
7.0	0.1966	0.2032	0.2064	0.2097	0.2129
7.2	0.1915	0.1980	0.2012	0.2044	0.2075
7.4	0.1866	0.1930	0.1962	0.1993	0.2024
7.6	0.1820	0.1882	0.1913	0.1944	0.1975
7.8	0.1775	0.1837	0.1867	0.1898	0.1928
8.0	0.1732	0.1793	0.1823	0.1853	0.1882
8.2	0.1691	0.1751	0.1780	0.1810	0.1839
8.4	0.1651	0.1710	0.1739	0.1768	0.1797
8.6	0.1613	0.1671	0.1700	0.1728	0.1757
8.8	0.1576	0.1633	0.1662	0.1690	0.1718
9.0	0.1541	0.1597	0.1625	0.1653	0.1681
9.2	0.1506	0.1562	0.1590	0.1617	0.1644
9.4	0.1474	0.1528	0.1556	0.1583	0.1610
9.6	0.1442	0.1496	0.1523	0.1549	0.1576
9.8	0.1411	0.1464	0.1491	0.1517	0.1543
10.0	0.1381	0.1434	0.1460	0.1486	0.1512
10.2	0.1353	0.1405	0.1431	0.1456	0.1482
10.4	0.1325	0.1376	0.1402	0.1427	0.1452
10.6	0.1298	0.1349	0.1374	0.1399	0.1424
10.8	0.1272	0.1322	0.1347	0.1372	0.1396
11.0	0.1247	0.1296	0.1321	0.1345	0.1369
11.2	0.1223	0.1271	0.1295	0.1320	0.1343
11.4	0.1199	0.1247	0.1271	0.1295	0.1318
11.6	0.1176	0.1224	0.1247	0.1271	0.1294
11.8	0.1154	0.1201	0.1224	0.1247	0.1270

Na⁺ ΔE	Slope				
	55.0	57.0	58.0	59.0	60.0
12.0	0.1132	0.1179	0.1201	0.1224	0.1247
12.2	0.1111	0.1157	0.1180	0.1202	0.1225
12.4	0.1091	0.1136	0.1158	0.1181	0.1203
12.6	0.1071	0.1116	0.1138	0.1160	0.1182
12.8	0.1052	0.1096	0.1118	0.1140	0.1161
13.0	0.1033	0.1077	0.1098	0.1120	0.1141
13.2	0.1015	0.1058	0.1079	0.1101	0.1122
13.4	0.0997	0.1040	0.1061	0.1082	0.1103
13.6	0.0980	0.1022	0.1043	0.1064	0.1084
13.8	0.0963	0.1005	0.1025	0.1046	0.1066
14.0	0.0947	0.0988	0.1008	0.1028	0.1049
14.2	0.0931	0.0971	0.0991	0.1012	0.1032
14.4	0.0915	0.0955	0.0975	0.0995	0.1015
14.6	0.0900	0.0940	0.0959	0.0979	0.0999
14.8	0.0885	0.0924	0.0944	0.0963	0.0983
15.0	0.0871	0.0909	0.0929	0.0948	0.0967
15.2	0.0857	0.0895	0.0914	0.0933	0.0952
15.4	0.0843	0.0881	0.0900	0.0918	0.0937
15.6	0.0829	0.0867	0.0886	0.0904	0.0923
15.8	0.0816	0.0853	0.0872	0.0890	0.0909
16.0	0.0803	0.0840	0.0858	0.0877	0.0895
16.2	0.0791	0.0827	0.0845	0.0863	0.0881
16.4	0.0779	0.0815	0.0833	0.0850	0.0868
16.6	0.0767	0.0802	0.0820	0.0838	0.0855
16.8	0.0755	0.0790	0.0808	0.0825	0.0843
17.0	0.0744	0.0778	0.0796	0.0813	0.0830
17.2	0.0732	0.0767	0.0784	0.0801	0.0818
17.4	0.0721	0.0756	0.0773	0.0790	0.0807
17.6	0.0711	0.0745	0.0761	0.0778	0.0795
17.8	0.0700	0.0734	0.0750	0.0767	0.0784
18.0	0.0690	0.0723	0.0740	0.0756	0.0773
18.5	0.0665	0.0698	0.0714	0.0730	0.0746
19.0	0.0642	0.0673	0.0689	0.0705	0.0720
19.5	0.0619	0.0650	0.0666	0.0681	0.0696
20.0	0.0598	0.0628	0.0643	0.0658	0.0673

Na+ ΔE	Slope 55.0	57.0	58.0	59.0	60.0
20.5	0.0578	0.0607	0.0622	0.0637	0.0651
21.0	0.0558	0.0587	0.0602	0.0616	0.0630
21.5	0.0540	0.0568	0.0582	0.0596	0.0610
22.0	0.0522	0.0550	0.0564	0.0577	0.0591
22.5	0.0506	0.0532	0.0546	0.0559	0.0573
23.0	0.0489	0.0516	0.0529	0.0542	0.0555
23.5	0.0474	0.0500	0.0513	0.0526	0.0539
24.0	0.0459	0.0485	0.0497	0.0510	0.0522
24.5	0.0445	0.0470	0.0482	0.0495	0.0507
25.0	0.0431	0.0456	0.0468	0.0480	0.0492
25.5	0.0418	0.0442	0.0454	0.0466	0.0478
26.0	0.0406	0.0429	0.0441	0.0452	0.0464
26.5	0.0394	0.0417	0.0428	0.0439	0.0451
27.0	0.0382	0.0405	0.0416	0.0427	0.0438
27.5	0.0371	0.0393	0.0404	0.0415	0.0426
28.0	0.0360	0.0382	0.0393	0.0403	0.0414
28.5	0.0350	0.0371	0.0382	0.0392	0.0403
29.0	0.0340	0.0361	0.0371	0.0381	0.0392
29.5	0.0330	0.0351	0.0361	0.0371	0.0381
30.0	0.0321	0.0341	0.0351	0.0361	0.0371
31.0	0.0304	0.0323	0.0332	0.0342	0.0352
32.0	0.0287	0.0306	0.0315	0.0324	0.0334
33.0	0.0272	0.0290	0.0299	0.0308	0.0317
34.0	0.0258	0.0275	0.0283	0.0292	0.0301
35.0	0.0244	0.0261	0.0269	0.0278	0.0286
36.0	0.0232	0.0248	0.0256	0.0264	0.0272
37.0	0.0220	0.0235	0.0243	0.0251	0.0259
38.0	0.0209	0.0224	0.0231	0.0239	0.0246
39.0	0.0198	0.0213	0.0220	0.0227	0.0235
40.0	0.0189	0.0202	0.0210	0.0217	0.0224
41.0	0.0179	0.0193	0.0200	0.0206	0.0213
42.0	0.0171	0.0184	0.0190	0.0197	0.0203
43.0	0.0162	0.0175	0.0181	0.0188	0.0194
44.0	0.0155	0.0167	0.0173	0.0179	0.0185
45.0	0.0147	0.0159	0.0165	0.0171	0.0177

Na+ ΔE	Slope 55.0	57.0	58.0	59.0	60.0
46.0	0.0140	0.0152	0.0157	0.0163	0.0169
47.0	0.0134	0.0145	0.0150	0.0156	0.0162
48.0	0.0127	0.0138	0.0144	0.0149	0.0155
49.0	0.0121	0.0132	0.0137	0.0142	0.0148
50.0	0.0116	0.0126	0.0131	0.0136	0.0141
51.0	0.0111	0.0120	0.0125	0.0130	0.0135
52.0	0.0105	0.0115	0.0120	0.0125	0.0129
53.0	0.0101	0.0110	0.0114	0.0119	0.0124
54.0	0.0096	0.0105	0.0109	0.0114	0.0119
55.0	0.0092	0.0100	0.0105	0.0109	0.0114
56.0	0.0088	0.0096	0.0100	0.0104	0.0109
57.0	0.0084	0.0092	0.0096	0.0100	0.0104
58.0	0.0080	0.0088	0.0092	0.0096	0.0100
59.0	0.0076	0.0084	0.0088	0.0092	0.0096
60.0	0.0073	0.0080	0.0084	0.0088	0.0092
61.0	0.0070	0.0077	0.0081	0.0084	0.0088
62.0	0.0067	0.0074	0.0077	0.0081	0.0084

Direct Calibration

For new electrodes, or those which have been stored dry, follow the procedure in the **Electrode Preparation** section.

1. Connect the electrode(s) to the meter.
2. Prepare standards with a ten-fold difference in concentration in the range of the expected sample concentration. Standards can be prepared in any concentration unit to suit the particular analysis requirement. Use **Table 4** as a guide for diluting standards. All standards should be at the same temperature as the samples. (For details on temperature effects on electrode performance, refer to **Temperature Effects**.)
3. Prepare 1 liter of sodium electrode rinse solution by adding 10 mL of ISA, Cat. No. 841111, to a 1 liter squeeze bottle and filling it with distilled water.

Table 4– Standards Table

A. Salt as Sodium Chloride (NaCl)

Units	Stock Solution	Dilution	Dilution	Dilution
percent (%)	10% NaCl, Cat. No. 841105	1% NaCl 1:10 diln of 10%	0.1% NaCl 1:10 diln of 1%	
ppm (parts per million, mg/L)	1000 ppm NaCl, use 0.1%, Cat. No. 841106	100 ppm NaCl, 1:10 diln of 1000 ppm	10 ppm NaCl, 1:10 diln of 100 ppm	
mg/100 g or mg/100 mL	100 mg/100 g NaCl, use 0.1%, Cat. No. 841106	10 mg/100 g NaCl, 1:10 diln of 100 mg/100	1 mg/100 g NaCl, 1:10 diln of 10 mg/100	
molarity (M)	0.1 M, Cat. No. 941706	0.01 M 1:10 diln of 0.1 M	0.001 M 1:10 diln of 0.01 M	0.0001 M 1:10 diln of 0.001 M

B. Sodium (Na⁺)

Units	Stock Solution	Dilution	Dilution	Dilution
percent (%)	10% sodium Cat. No. 841107	1% sodium 1:10 diln of 10%	0.1% sodium 1:10 diln of 1%	
ppm (parts per million, mg/L)	1000 ppm Na, Cat. No. 841108	100 ppm Na, Cat. No. 941107	10 ppm Na, Cat. No. 941105	1 ppm Na 1:10 diln of 10 ppm
mg/100 g or mg/100 mL	mg/100 g or mg/100 mL 100 g/100 g Na, Cat. No. 841108	10 mg/100 g Na, 1:10 diln of 100 mg/100 g	1 mg/100 g Na, 1:10 diln of 10 mg/100 g	
molarity (M)	0.1 M, Cat. No. 941706	0.01 M 1:10 diln of 0.1 M	0.001 M 1:10 diln of 0.01 M	0.0001 M 1:10 diln of 0.001 M

If using a meter with direct concentration readout capability:

1. Measure 100 mL of the more dilute standard into a 150 mL beaker. Add 10 mL of ISA. Stir the solution thoroughly.
2. Rinse the electrode(s) with sodium electrode rinse solution and place into beaker. Wait for a stable reading, and then calibrate the meter to display the value of the standard as described in the meter user guide.
3. Measure 100 mL of the more concentrated standard into a second 150 mL beaker. Add 10 mL of ISA. Stir thoroughly.
4. Rinse the electrode(s) with sodium electrode rinse solution and place in more concentrated standard. Wait for a stable reading, then adjust the meter to display the value of the second standard as described in the meter user guide.
5. Measure 100 mL of the sample into a 150 mL beaker. Add 10 mL ISA. Stir thoroughly. Rinse electrode(s) with sodium electrode rinse solution and place into sample. The concentration will be displayed on the meter.

If your meter does not have a concentration mode, use a calibration curve and read millivolts:

1. Adjust the meter to measure absolute mV.
2. Measure 100 mL of the more dilute standard into a 150 mL beaker. Add 10 mL ISA. Stir thoroughly.
3. Rinse electrode(s) with sodium electrode rinse solution and place into beaker. When a stable reading is displayed, record the mV value and corresponding standard concentration.
4. Measure 100 mL of the more concentrated standard into a second 150 mL beaker. Add 10 mL ISA. Stir thoroughly.
5. Rinse electrode(s) with sodium electrode rinse solution and place into beaker. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Using semilogarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the concentration value of the standards on the logarithmic axis. An example of a graph can be found in **Figure 3**.
7. Measure 100 mL sample into a 150 mL beaker. Add 10 mL ISA. Stir thoroughly.
8. Rinse electrode(s) with sodium electrode rinse solution and place into beaker. When a stable reading is displayed, record the mV value.
9. Using the calibration curve prepared in step 6, determine the concentration of the unknown.

Low-Level Measurement

The lower limit of detection for the ROSS sodium electrode is specified as 0.02 ppm (10^{-6} M). This is considered the lowest concentration which can be reasonably measured under laboratory conditions.

Below 1 ppm, the apparent slope of the electrode decreases as a result of a number of problems encountered in normal laboratory measurements. These include absorption of sodium ions onto the walls of beakers and solution containers; contamination from the air, reagents, skin, and distilled water; long time response; and interferences, which become a larger problem at lower concentrations of sodium. To minimize these problems, follow the recommendations below, using careful technique to afford greater accuracy and reproducibility.

- Use plastic or teflon labware.
- Be sure all labware is thoroughly rinsed with sodium-free distilled water.
- Reduce the concentration of ISA from 10 mL per 100 mL sample and standard to 1 mL per 100 mL sample and standard.
- Use the known addition technique to increase the measured concentration. Prepare known addition standards with the same ratio of ISA as used in the samples.
- If the meter has a blank correction, use according to instructions in meter user guide.
- If measuring by direct measurement, measure dilute solutions before concentrated solutions.
- Check distilled water to be sure it is sodium free. Add 1 mL ISA to 100 mL distilled water, place electrodes in solution and record the millivolt reading after two minutes. It will be unstable. Use the calibration curve in the user guide to determine the sodium concentration of the water.
- Allow up to 5 to 10 minutes for stable readings.
- Minimize sample contact with the atmosphere.
- Wear gloves to keep sodium from the skin from coming in contact with solutions.
- pH must be greater than 7 to prevent hydrogen ion interference.
- Store electrodes in diluted storage solution. Dilute the sodium electrode storage solution, Cat. No. 841101, 1 part per 100 parts of distilled water.

Electrode Maintenance and Storage

Cleaning the Sure-Flow® Junction

1. Press the electrode cap and let filling solution drain from the electrode carrying away any contamination. Refill the electrode with fresh filling solution.
2. For particularly dirty electrodes, the junction can be held open and flushed with sodium rinse solution. Refill the electrode with fresh filling solution.

8411BN and 800300/800500U

Routine Storage (1 week or less)

Soak the sodium electrode in sodium electrode storage solution, Cat. No. 841101. Replace with fresh storage solution weekly or sooner if crystallization occurs or solution becomes contaminated.

Soak the reference electrode in reference electrode filling solution. Distilled water is also an acceptable storage solution. Do not soak the reference electrode in sodium electrode storage solution. If this should occur, change the filling solution before use.

Long Term Storage (over 1 week)

Rinse the sodium electrode well with sodium electrode rinse solution and cover the sensing element with its protective cap containing a few drops of storage solution.

The reference electrode should be filled and the fill hole securely covered. Cover reference junction with its protective cap containing a few drops of filling solution.

8611BNWP

Routine Storage (1 week or less)

Soak the electrode in sodium electrode storage solution, Cat. No. 841101. Immerse both the tip of the electrode and the reference junction. Replace storage solution weekly or sooner if crystallization or contamination occur. Maintain sodium electrode filling solution at a level which covers the coil.

After storage, refresh the junction by pressing on the cap and letting a small amount of filling solution drain out. Replenish lost filling solution.

Long Term Storage (over 1 week)

Rinse exterior of the electrode well with sodium electrode rinse solution. Fill reference chamber and replace the fill hole plug. Cover the sensing element and reference junction with the protective cap containing a few drops of storage solution. Before returning to use, prepare as for new electrode.

TROUBLESHOOTING

Troubleshooting Checklist

Symptom	Possible Causes
Off-scale or Over-range reading	Defective meter Electrode(s) not plugged in properly No reference electrode or reference electrode not filled Electrode(s) not in solution Defective electrode
Noisy or unstable readings	Defective meter Meter or stirrer improperly grounded Defective electrode Blocked reference junction
Drift	Electrode rinsed with distilled water Membrane exposed to interferences Defective electrode Insufficient flow from reference electrode Incorrect reference electrode fill solution
Low slope or No slope	Standards contaminated or incorrectly made ISA not used pH too low Membrane needs reconditioning Blocked reference junction Defective electrode
Wrong Answer	Contaminated standards Sample pH too low Meter calibrated incorrectly Interferences present

Next Step

Perform meter checkout (see meter user guide)
Check meter user guide for correct electrode connection
Reference electrode is required; see **Required Equipment**
or **Required Solutions**
Put electrode(s) in standard solution
See electrode section in **Troubleshooting Guide**

Perform meter checkout procedure (see meter user guide)
Check meter and stirrer for grounding
See electrode section in **Troubleshooting Guide**
Clean reference electrode as described in reference electrode user
guide

Use sodium electrode rinse solution
Recondition sodium electrode
See electrode section in **Troubleshooting Guide**
Suspend electrode in air and let filling solution flow
for fifteen minutes
Check that electrode is filled with correct solution

Prepare fresh standards

Use recommended ISA
Use recommended ISA
Recondition sodium electrode
Clean reference electrode as described in reference electrode
user guide
See electrode section in **Troubleshooting Guide**

Prepare fresh standards
Use recommended ISA
Check **Troubleshooting Guide** of meter user guide
See section on **Interferences**

Troubleshooting Guide

The most important principle in troubleshooting is to isolate the components of the system and check each in turn. The components of the system are: the meter, electrodes, standard, sample, and technique.

Meter

The meter is the easiest component to eliminate as a possible cause of error. Thermo Scientific Orion meters are provided with an instrument checkout procedure in the user guide and a shorting strap cap for convenience in troubleshooting. Consult the user guide for complete instructions and verify that the instrument operates as indicated and is stable in all steps.

Electrodes

1. Rinse electrode(s) thoroughly with sodium rinse solution.
2. Perform the procedure in the **Checking Electrode Operation (Slope)** section.
3. If electrode fails this procedure, restore sodium electrode response as directed in **Electrode Reconditioning**. Clean the reference electrode per the reference electrode user guide.
4. Repeat the procedure in the **Checking Electrode Operation (Slope)** section.
5. If the electrode(s) still do not perform as described, and the 8411BN ROSS half-cell sodium electrode is being used, determine whether the sodium or reference electrode is at fault. To do this, substitute a known working ROSS electrode for the electrode in question and repeat the procedure in the **Checking Electrode Operation (Slope)** section.
6. If the stability and slope check out properly, but measurement problems persist, the sample may contain interferences or the technique may be in error. See the **Standard, Sample, and Technique** sections.
7. Before replacing a faulty electrode, or if another electrode is not available for test purposes, review this user guide and be sure to:
 - Clean the electrode thoroughly
 - Condition the electrode properly
 - Use proper filling solutions, ISA, and standards
 - Measure correctly
 - Review the **Troubleshooting Checklist** section

Standard

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, inaccuracy of dilution, quality of distilled water, or a mathematical error in calculating the concentrations.

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

Sample

If the electrode(s) work properly in standards but not in sample, look for possible interferences 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 the **Sample Requirements, Interferences, and pH Requirements** sections.

Technique

Check the method of analysis for compatibility with your sample. Known addition is usually the method of choice for this electrode. If the sample is viscous, alternate addition may solve the problem. Check your meter user guide for information on this technique. If working at low levels, be sure to follow the low-level measurement technique.

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 user guides to be sure that proper technique has been followed. Review the **Measuring Hints** and **Analytical Procedures** sections.

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/water.

Warranty

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

ELECTRODE CHARACTERISTICS

Electrode Response

The electrode potential plotted against concentration on semilogarithmic paper results in a straight line with a slope of about 57 mV per decade. See **Figure 4**.

The electrode exhibits good time response (99% response in one minute or less) for concentrations above 10^{-5} M. Electrode response time is also a function of temperature. The response times will be faster at temperatures above room temperature; it may become increasingly longer at lower temperatures. For normal use, operation below 15 °C should be avoided. Below this concentration or temperature, response times are considerably longer. See **Figure 4**.

Polarization of the sodium electrode glass membrane may occur from wiping the bulb or repeatedly moving the electrode from solution to solution. This build-up of static electrical charge is common to sodium electrodes in general. This can be overcome by using Known Addition as the analytical technique, as concentration is calculated based on a change in mV, not comparison to an absolute mV value.

If your electrode becomes polarized and you prefer to use direct measurement techniques, allow the electrode to discharge by soaking in storage solution for several hours.

After prolonged use, a hydrated layer forms on the surface of the sodium-sensitive glass, which causes slower response times. This layer may be removed by briefly exposing the electrode to the sodium reconditioning solution, Cat. No. 841113.

See the **Electrode Reconditioning** section.

Limit of Detection

The sodium concentration in basic solutions can be measured under normal laboratory conditions down to 5×10^{-6} M. Measurements below 10^{-5} M sodium must be made with extreme care as significant pickup of sodium ion may occur due to desorption from container walls as well as from dust and other contamination. Ordinary glass will dissolve sufficiently to produce spurious results at low levels. Plastic laboratory ware is recommended. See the **Low-Level Measurements** section.

Reproducibility

Reproducibility is limited by factors such as drift and noise. Within the electrode's operating range, reproducibility is independent of concentration. Known addition measurements reproducible to $\pm 2\%$ can be obtained.

Temperature Effects

In traditional reference and sensing electrodes, the potential of the internal cells is based on a slightly soluble, metal/metal salt reference system, most commonly calomel/mercury or silver/silver chloride. These cells have two distinct disadvantages when temperature fluctuations are encountered. First, the internal cell potential will change because the salt solubility changes with temperature. The internal cell potentials of the sensing and the reference electrode may not change in the same way, nor at the same rate. This results in a potential error which will be interpreted as an error in concentration of the ion being measured. Second, longer equilibrium times are required to compensate for varying solubilities that occur with temperature changes. Slow response and drift are often seen when such electrodes are used with temperature variation.

The internal cell design of the ROSS sodium electrodes and the ROSS reference electrodes eliminates these shortcomings. Since there is little change due to temperature, the internal equilibration time is no longer a factor.

The slope term S , in the Nernst equation is actually $2.3 RT/nF$, where R and F are constants, n is the charge on the measured species, and T is the temperature in degrees Kelvin. This means that the slope of the electrode, like all electrodes, will change with changes in temperature. Calibration curves generated at varying temperatures are shown in **Figure 5**.

These curves intersect at the isopotential point, which is the concentration at which the potential of the electrode does not vary with temperature. If the isopotential point is known or can be measured experimentally, and if the meter has a means of adjusting the isopotential point, temperature compensation for the ROSS sodium electrode is possible. If this correction is not possible for the meter in use, all standards and samples should be kept at the same temperature for utmost accuracy. Whichever the case, the performance of the ROSS sodium electrode will be far superior to that of conventional sodium probes because of its unique ability to resist many complications of temperature variation.

The typical isopotential point for the ROSS sodium electrode is 5×10^{-3} M (114 ppm as Na^+). This value may vary and will change as the electrode ages, the typical range is 5×10^{-3} M to 5×10^{-1} M. For greatest temperature accuracy, the isopotential of each electrode can be determined as outlined.

Determining An Isopotential Point

1. Prepare two standards whose concentration range brackets the isopotential point. For the ROSS sodium electrode, prepare 10^{-2} M and 10^{-3} M or 100 ppm and 1000 ppm standards.
2. Measure the millivolt value of the standards at room temperature, 20-25 °C.
3. Measure the millivolt value of the standards at a different room temperature; 75 °C is recommended.
4. On semilogarithmic graph paper, plot the concentration values on the log axis versus the millivolt values on the linear axis, as any calibration curve would be drawn (see **Figure 5**).
5. The lines will intersect at the isopotential point. Read the concentration off the graph for this point from the log axis.

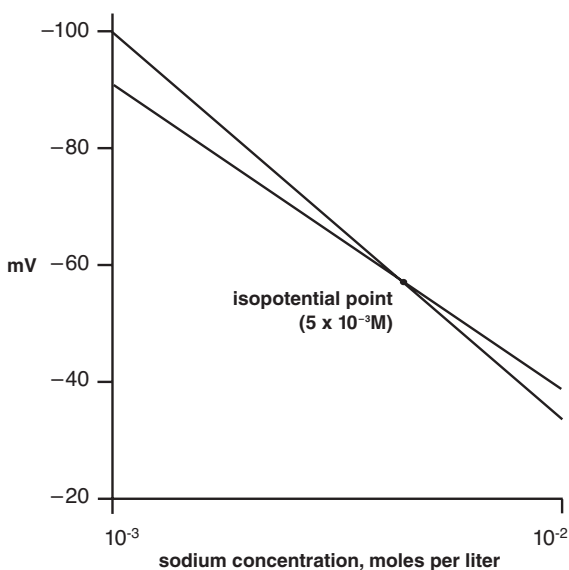


Figure 5
Isopotential Point

To determine the isopotential point of a sodium electrode, two standard solutions are measured at two different temperatures. The observed millivolt values are plotted on the linear axis and concentration is plotted on the log axis. The point of intersection is the isopotential point.

Interferences

Other cations, if present at high enough levels are measurement interferences and will cause errors. **Table 5** indicates levels of common cations that will cause 10% error at various concentrations of sodium.

In practically all samples, most cations listed in **Table 5** are absent or insignificantly low. Using the ammonium ion in the recommended ISA does not result in an error, provided that there is not a large amount of ammonium ion in the sample, and that all standards and samples have the same level of ISA added.

Table 5
Levels of Possible Interferences
Causing a 10% Error at Various Levels of Sodium

Interferences (Moles/Liter)	10⁻⁴M Na⁺	10⁻³M Na⁺	10⁻²M Na⁺
Li ⁺	4 x 10 ⁻³	4 x 10 ⁻²	0.4
K ⁺	1 x 10 ⁻²	0.1	1
Rb ⁺	0.3	3	–
NH ₄ ⁺	0.3	3	–
Ag ⁺	1 x 10 ⁻⁷	1 x 10 ⁻⁶	1 x 10 ⁻⁵
Tl ⁺	5 x 10 ⁻²	0.5	–

Interferences (ppm)	1 ppm Na⁺	10 ppm Na⁺	100 ppm Na⁺
Li ⁺	12	121	1,206
K ⁺	170	1,700	17,000
Rb ⁺	11,000	110,000	–
NH ₄ ⁺ as N	1,800	18,000	–
Ag ⁺	0.004	0.04	0.4
Tl ⁺	4,500	45,000	–

pH Effects

The electrode response to sodium ion in solutions at various pH is shown in **Figure 1**. Although the electrode can be used over a wide pH range, hydrogen ion interferes with measurements of low levels of sodium ion. The edge of the shaded area to the left of **Figure 1** indicates a minimum pH at which dilute sodium measurements can be made without hydrogen ion interference.

Electrode Life

The ROSS sodium electrode should last at least one year under normal laboratory use. In time, electrode slope will decrease and readings will drift, indicating that the electrode should be reconditioned. Refer to the **Troubleshooting Guide** section for more information.

Electrode Reconditioning

Use this procedure when electrode slope is low, or electrode experiences drift, and performance cannot be restored by soaking in sodium electrode storage solution.

Immerse the ROSS sodium electrode in sodium reconditioning solution, Cat. No. 841113 for 30 seconds. Rinse with sodium electrode rinse solution and store in sodium electrode storage solution, Cat. No. 841101 for 15 minutes before returning to use.

Theory Of Operation

In sodium measurement, the potential developed at a sodium selective membrane is measured through the use of two internal electrochemical cells. The membrane potential is added in series, to the potential of the sensing reference cell, and their sum is measured against the potential of the second (reference) cell. Since the potentials of the two internal reference cells remain constant, changes in potential are due to changes in sodium concentration.

The measured potential corresponding to the level of sodium ion in solution is described by the Nernst equation:

$$E = E_0 + S \log (A)$$

where:

E = measured electrode potential

E₀ = constant potential largely dependent on the reference electrode

A = sodium ion activity or “effective concentration of sodium”

S = electrode slope

Most analytical measurements are made to determine not the sodium activity, but the total concentration of sodium ion in solution.

The sodium ion activity is related to sodium concentration by the activity coefficient, x :

$$A = xC$$

Ionic activity coefficients are variable and largely depend on total ionic strength.

Ionic strength is defined as:

$$\text{Ionic strength} = 1/2 \sum C_i Z_i^2$$

where:

C_j = concentration of ion j

Z_j = charge of ion j

If background ionic strength is high and constant relative to the sensed ion concentration, then the activity coefficient is constant and activity is proportional to concentration. The electrode can then be used to measure concentration.

Ionic strength adjustor (ISA) is added to all sodium standards and samples so that the background ionic strength is high and constant relative to the variable concentrations of the sodium ion, and activity effects can be ignored in concentration measurements. A mixture of ammonium chloride and ammonium hydroxide is used with the sodium electrode as the ionic strength adjustor.

The reference electrode must also be considered. Liquid junction potentials arise any time two solutions of different composition are brought into contact. The potential results from the interdiffusion of ions in the two solutions. Since ions diffuse at different rates, ionic charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions. In making electrode measurements it is important that this potential be the same when the reference is in the standardizing solution as well as in the sample solution; otherwise, the change in liquid junction potential will appear as an error in the measured electrode potential.

To control this, the composition of the reference electrode filling solution is carefully chosen to be equitransferent. That is, the speed with which the positive and negative ions in the filling solution diffuse into the sample should be as nearly equal as possible. If the rate at which positive and negative charge is carried into the sample solution is equal, then no junction potential can result. The recommended filling solution, 2M NH_4Cl , very nearly meets these requirements.

ORDERING INFORMATION

Cat. No.	Description
8611BNWP	ROSS sodium combination electrode with waterproof BNC connection
8411BN	ROSS sodium half-cell electrode with BNC connection
800300	ROSS reference electrode
800500U	ROSS Ultra reference electrode
900010	ROSS sodium electrode and reference electrode filling solution, 5 x 50 mL bottles
841111	Sodium ISA, 475 mL bottle
841113	Sodium electrode reconditioning solution, 475 mL bottle
841101	Sodium electrode storage solution, 475 mL bottle
941706	0.1 M NaCl sodium standard solution, 475 mL bottle
841108	1000 ppm sodium standard solution, 475 mL bottle
941107	100 ppm sodium standard solution, 475 mL bottle
941105	10 ppm sodium standard solution, 475 mL bottle
900012	ROSS sodium electrode and reference electrode filling solution for low-level measurements, 5 x 50 mL bottles
841109	Sodium known addition standard, 1000 ppm with ISA, 475 mL bottle
650700	Sodium known addition standard, 1 M with ISA, 475 mL bottle

SPECIFICATIONS

Concentration Range

10⁻⁶ M to saturated
0.02 ppm to saturated

pH Range

6 to 12 pH
Use at recommended pH

Temperature Range

0 to 80 °C continuous use;
80 to 100 °C intermittent use

Electrode Resistance

Less than 300 megohms

Reproducibility

±2%

Isopotential Point

Approximately 114 ppm Na (0.005 M)

Minimum Sample Size

3 mL in a 50 mL beaker

Size

Electrode Length: 120 mm
Diameter: 12 mm
Cap Diameter: 16 mm
Cable Length: 1 meter

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Water Analysis Instruments

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