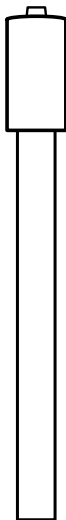


# User Guide

Thiocyanate  
Ion Selective  
Electrode



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This publication supersedes all previous publications on this subject.

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# Introduction

This user guide contains information on the preparation, operation and maintenance for the thiocyanate ion selective electrode (ISE). General analytical procedures, electrode characteristics and electrode theory are also included in this user guide. Thiocyanate electrodes measure free thiocyanate ions in aqueous solutions quickly, simply, accurately and economically.

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. For the most current contact information, visit [www.thermo.com/contactwater](http://www.thermo.com/contactwater).

For the latest application and technical resources for Thermo Scientific Orion products, visit [www.thermo.com/waterapps](http://www.thermo.com/waterapps).

## **Thiocyanate Solid State Half-Cell ISE, Cat. No. 9458BN**

The thiocyanate half-cell electrode must be used with the double junction reference electrode, Cat. No. 900200. The thiocyanate half-cell electrode is available with a BNC connector, Cat. No. 9458BN.

# Required Equipment

1. Thermo Scientific Orion ISE meter, such as the 4-Star pH/ISE meter or 5-Star pH/ISE/DO/conductivity meter; equivalent ISE meter; or mV meter with a 0.1 mV resolution.

Thiocyanate electrodes can be used on any ISE or mV meter with a BNC connection. The electrodes can also be used on meters with a variety of inputs when an adapter cable is used. Visit [www.thermo.com/water](http://www.thermo.com/water) for details.

2. Thermo Scientific Orion thiocyanate electrode, Cat. No. 9458BN
3. Thermo Scientific Orion double junction reference electrode, Cat. No. 900200.
4. Magnetic stirrer or Thermo Scientific Orion stirrer probe, Cat. No. 096019. The stirrer probe can be used with 3-Star, 4-Star and 5-Star benchtop meters.
5. Volumetric flasks, graduated cylinders and beakers.
6. Distilled or deionized water.
7. Double junction reference electrode filling solutions. Use the inner chamber filling solution, Cat. No. 900002, and outer chamber filling solution, Cat. No. 900003.
8. 0.1 M NaSCN calibration standard. To prepare the standard, place 8.107 grams of reagent-grade sodium thiocyanate in a one liter volumetric flask. Add about 500 mL of distilled water and swirl to dissolve the solids. Dilute to the mark with distilled water and mix the solution thoroughly.
9. Thiocyanate ionic strength adjuster (ISA), Cat. No. 940011. ISA provides a constant background ionic strength for samples and standards.

# Serial Dilutions

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

1. **To prepare a  $10^{-2}$  M NaSCN standard (581 ppm SCN<sup>-</sup>)** – Pipet 10 mL of the 0.1 M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.
2. **To prepare a  $10^{-3}$  M NaSCN standard (58.1 ppm SCN<sup>-</sup>)** – Pipet 10 mL of the  $10^{-2}$  M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.
3. **To prepare a  $10^{-4}$  M NaSCN standard (5.81 ppm SCN<sup>-</sup>)** – Pipet 10 mL of the  $10^{-3}$  M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

To prepare standards with a different concentration use the following formula:

$$C_1 * V_1 = C_2 * V_2$$

**C<sub>1</sub>** = concentration of original standard

**V<sub>1</sub>** = volume of original standard

**C<sub>2</sub>** = concentration of standard after dilution

**V<sub>2</sub>** = volume of standard after dilution

For example, to prepare 1000 mL of a 100 ppm thiocyanate standard from a 5810 ppm thiocyanate standard:

**C<sub>1</sub>** = 5810 ppm thiocyanate

**V<sub>1</sub>** = unknown

**C<sub>2</sub>** = 100 ppm thiocyanate

**V<sub>2</sub>** = 1000 mL

$5810 \text{ ppm} * V_1 = 100 \text{ ppm} * 1000 \text{ mL}$

$V_1 = (100 \text{ ppm} * 1000 \text{ mL}) / 5810 \text{ ppm} = 17.2 \text{ mL}$

# Electrode Setup

## Electrode Preparation

**9458BN Thiocyanate Half-Cell Electrode** – Remove the protective shipping cap from the sensing element and save the cap for storage.

**900200 Double Junction Reference Electrode** – Prepare the reference electrode according to the reference electrode user guide. Fill the reference electrode with inner chamber filling solution, Cat. No. 900002, and outer chamber filling solution, Cat. No. 900003.

**Note:** *Add filling solution each day before using the electrode. The filling solution level should be at least one inch above the level of sample in the beaker to ensure a proper flow rate. The fill hole should always be open when taking measurements.*



## Checking Electrode Operation (Slope)

These are general instructions that can be used with most meters to check the electrode operation. 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 has been stored dry, prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to a meter with a mV mode. Set the meter to the mV mode.
3. Add 100 mL of distilled water and 2 mL of ISA into a 150 mL beaker. Stir the solution thoroughly.
4. Rinse the electrode with distilled water and place the electrode into the solution prepared in step 3.
5. Select either a 0.1 M or 1000 ppm thiocyanate standard. Pipet 1 mL of the standard into the beaker and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
6. Pipet 10 mL of the same standard into the same beaker and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
7. There should be a -54 to -60 mV difference between the two millivolt readings when the solution temperature is between 20 to 25 °C. If the millivolt potential is not within this range, refer to the **Troubleshooting** section.

## Measurement Units

Thiocyanate concentration can be measured in moles per liter (M), parts per million (ppm) or any convenient concentration unit.

**Table 1**  
**Concentration Unit Conversion Factors**

Moles/Liter (M)	ppm
1.0	58100
$10^{-1}$	5810
$1.72 \times 10^{-2}$	1000
$10^{-2}$	581
$10^{-3}$	58.1
$10^{-4}$	5.81
$1.72 \times 10^{-5}$	1

## Sample Requirements

The epoxy body of the thiocyanate electrode is resistant to damage by aqueous solutions. The electrode may be used intermittently in solutions that contain methanol, benzene or acetone. Contact Technical Support for information on using the electrode for specific applications.

Samples and standards should be at the same temperature. A 1 °C difference in temperature for a  $10^{-3}$  M thiocyanate solution will give rise to about a 2% error.

The solution temperature must be less than 50 °C.

In all analytical procedures, ISA must be added to all samples and standards before measurements are taken.

## Measuring Hints

- Stir all standards and samples at a uniform, moderate rate. Place a piece of insulating material, such as Styrofoam or cardboard, between the magnetic stir plate and beaker to prevent measurement errors from the transfer of heat to the sample.
- Always use freshly prepared standards for calibration.
- Always rinse the electrode with distilled water between measurements and shake the electrode to remove the water and prevent sample carryover. Do not wipe or rub the electrode sensing element.
- Allow all standards and samples to reach the same temperature for precise measurements.
- Concentrated samples (greater than  $10^{-1}$  M thiocyanate) should be diluted before measurement.
- Verify the electrode calibration every two hours by placing the electrode in a fresh aliquot of the least concentrated standard used for calibration. If the value has changed by more than 2%, recalibrate the electrode.
- After immersing the electrode in a solution, check the electrode sensing surface for air bubbles and remove air bubbles by reimmersing the electrode in the solution and gently tapping it.
- For high ionic strength samples, prepare standards with a background composition similar to the sample.
- The fill hole cover must be open during measurements to ensure a uniform flow of filling solution.

# **Electrode Storage**

## **Thiocyanate Half-Cell Electrode Storage**

The thiocyanate half-cell electrode should be rinsed thoroughly with distilled water and stored dry in the air at all times. When storing the electrode for long periods of time, cover the sensing element with the protective shipping cap.

## **Double Junction Reference Electrode Storage**

The double junction reference electrode may be stored in the outer chamber filling solution, Cat. No. 900003, between sample measurements and up to one week. The filling solution inside the electrode should not be allowed to evaporate, as crystallization will result.

For storage longer than one week, drain the reference electrode, flush the inside with distilled water and store the electrode dry.

# Electrode Maintenance

## Polishing the Thiocyanate Half-Cell Electrode

The sensing surface of solid state electrodes can wear over time, which causes drift, poor reproducibility and loss of response in low level samples. The electrode can be restored by polishing the sensing surface with a polishing strip, Cat. No. 948201. The polishing strip can also be used if the sensing surface has been etched or chemically poisoned.

1. Cut off about an inch of the polishing strip.
2. Hold the electrode with the sensing surface facing up.
3. Place a few drops of distilled water on the sensing surface.
4. With the frosted side of the polishing strip facing down, use light finger pressure to place the polishing strip on top of the sensing surface.
5. Rotate the electrode for about 30 seconds.
6. Rinse the electrode with distilled water and soak the electrode in a 1 ppm or  $10^{-5}$  M thiocyanate standard for ten minutes.

## Double Junction Reference Electrode Flushing

If the area between the electrode sleeve and inner cone becomes clogged with sample or precipitate, flush the area with filling solution or distilled water.

1. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to drain the electrode. Push down on the cap until all the filling solution is drained from the chamber.
2. Fill the electrode with distilled water and then push down on the cap until all the water is drained from the chamber.
3. Fill the electrode with fresh filling solution up to the fill hole. Push down on the cap to allow a few drops of filling solution to drain out of the electrode and replenish the lost filling solution.

# Analytical Techniques

A variety of analytical techniques are available to the analyst. The following is a description of these techniques.

**Direct Calibration** is a simple procedure for measuring a large number of samples. Only one meter reading is required for each sample. Calibration is performed using 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.

**Low Level Calibration** is similar to the direct calibration technique. This method is recommended when the expected sample concentration is less than  $5 \times 10^{-5}$  M thiocyanate. A minimum three point calibration is recommended to compensate for the electrode's non-linear response at these concentrations. A special calibration standard preparation procedure is the best means of preparing low level calibration standards.

**Incremental Techniques** provide a useful method for measuring samples, since a calibration is not required. The different incremental techniques are described below. They can be used to measure the total concentration of a specific ion in the presence of a large (50 to 100 times) excess of complexing agents. As in direct calibration, any convenient concentration unit can be used.

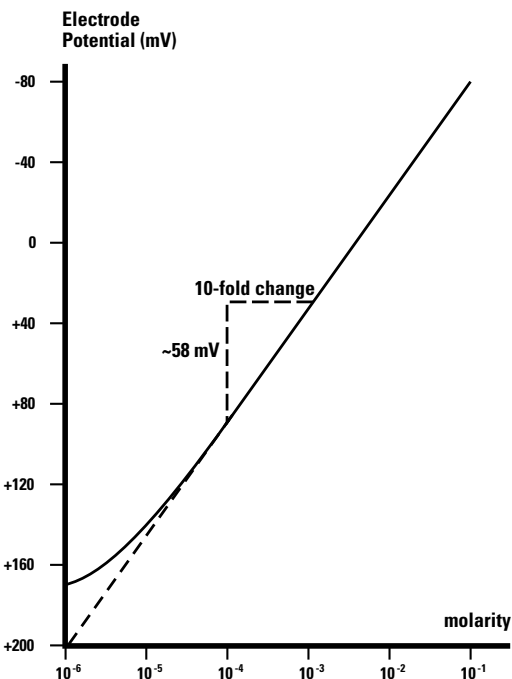
**Known Addition** is useful for measuring dilute samples, checking the results of direct calibration (when no complexing agents are present), or measuring the total concentration of an ion in the presence of an excess complexing agent. The electrode is immersed in the sample solution and an aliquot of a standard solution containing the measured species is added to the sample. From the change in potential before and after the addition, the original sample concentration is determined.

# Direct Calibration Technique

## Typical Direct Calibration Curve

In the direct calibration procedure, a calibration curve is constructed either in the meter memory or on semi-logarithmic paper. Electrode potentials of standard solutions are measured and plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only two standards are needed to determine a calibration curve. In non-linear regions, more points must be taken. These direct calibration procedures are given for concentrations in the region of linear electrode response. Low level measurement procedures are given in a following section for measurements in the non-linear electrode region.

**Figure 1**  
**Typical Direct Calibration Curve**



## Direct Calibration Overview

The following direct measurement procedures are recommended for moderate to high level measurements. Samples must be in the linear range of the electrode – greater than  $5 \times 10^{-5}$  M thiocyanate. A two point calibration is sufficient, although more points can be used. When using an ISE meter, sample concentrations can be read directly from the meter. When using a mV meter, a calibration curve can be prepared on semi-logarithmic graph paper, or a linear regression (against logarithmic concentration values) can be performed using a spreadsheet or graphing program.

### Calibration Hints

- Standard concentrations should bracket the expected sample concentrations.
- Always add 2 mL of ISA, Cat. No. 940011, per 100 mL of standard or sample.
- For high ionic strength samples that have an ionic strength of 0.1 M or greater, prepare standards with a background composition similar to that of the samples, or measure the samples using the known addition method.
- During calibration, measure the least concentrated standard first, and work up to the most concentrated standard.



## Direct Calibration Setup

1. Prepare the electrodes as described in the **Electrode Preparation** section.
2. Connect the electrodes to the meter.
3. Prepare at least two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. See the **Serial Dilution** section for instructions on how to prepare standards. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to the **Temperature Effects** section.

## Direct Calibration Procedure Using a Meter with an ISE Mode

**Note:** See the meter user guide for more specific information.

1. Add 100 mL of the less concentrated standard and 2 mL of ISA to a 150 mL beaker and stir the solution thoroughly.
2. Rinse the electrodes with distilled water, blot dry and place into the beaker with the less concentrated standard. Wait for a stable reading and adjust the meter to display the value of the standard, as described in the meter user guide.
3. Add 100 mL of the more concentrated standard and 2 mL of ISA to a second 150 mL beaker and stir the solution thoroughly.
4. Rinse the electrodes with distilled water, blot dry and place into the beaker with the more concentrated standard. Wait for a stable reading and adjust the meter to display the value of the second standard, as described in the meter user guide.
5. Record the resulting slope value. The slope should be between -54 and -60 mV when the standards are between 20 and 25 °C.
6. Add 100 mL of sample and 2 mL of ISA to a clean 150 mL beaker and stir the solution thoroughly.
7. Rinse the electrodes with distilled water, blot dry and place into the sample. The concentration of the sample will be displayed on the meter.

**Note:** Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.

## Direct Calibration Procedure Using a Meter with a mV Mode

**Note:** See the meter user guide for more specific information.

1. Set the meter to the mV mode.
2. Add 100 mL of the less concentrated standard and 2 mL of ISA to a 150 mL beaker and stir the solution thoroughly.
3. Rinse the electrodes with distilled water, blot dry and place into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
4. Add 100 mL of the more concentrated standard and 2 mL of ISA to a second 150 mL beaker and stir the solution thoroughly.
5. Rinse the electrodes with distilled water, blot dry and place into the beaker with the more concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis.
7. Add 100 mL of sample and 2 mL of ISA to a clean 150 mL beaker and stir the solution thoroughly.
8. Rinse the electrodes with distilled water, blot dry and place into the beaker. When a stable reading is displayed, record the mV value.
9. Using the calibration curve prepared in step 6, determine the unknown concentration of the sample.

**Note:** Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.

# Low Level Calibration Technique

These procedures are for solutions that have a thiocyanate concentration of less than  $5 \times 10^{-5}$  M thiocyanate. For solutions low in thiocyanate but high in total ionic strength (greater than  $10^{-1}$  M), perform the same procedure by preparing a calibrating solution with a composition similar to the sample.

Accurate results require that the following conditions be met:

- Prepare at least three calibration standards that bracket the expected sample concentration.
- Always use low level ISA for standards and samples.
- Adequate time must be allowed for electrode stabilization. Longer response time will be needed at low level measurements.
- Stir all standards and samples at a uniform rate.

## Low Level Setup

1. Prepare the electrodes as described in the **Electrode Preparation** section.
2. Connect the electrodes to the meter. Set the meter to the mV mode.
3. Prepare the low level ISA by pipeting 20 mL of the ISA, Cat. No. 940011, into a 100 mL volumetric flask and diluting to the mark with distilled water. Use low level ISA for low level measurements only.
4. Prepare a  $10^{-3}$  M thiocyanate standard by pipeting 1 mL of the 0.1 M NaSCN calibration standard and 1 mL of the low level ISA into a 100 mL volumetric flask and diluting to the mark with distilled water.

## Low Level Calibration and Measurement

1. Add 100 mL of distilled water and 1 mL of low level ISA to a 150 mL beaker.
2. Rinse the electrodes with distilled water, blot dry and place into the beaker. Stir the solution thoroughly.
3. Add increments of the  $10^{-3}$  M thiocyanate standard mixed with low level ISA to the beaker using the steps outlined in **Table 2**. Record the stable millivolt reading after each increment.
4. On semi-logarithmic paper, plot the concentration (log axis) against the millivolt potential (linear axis). Prepare a new calibration curve with fresh standards each day.
5. Measure 100 mL of sample and 1 mL of low level ISA and pour the solutions into a clean 150 mL beaker. Rinse the electrodes with distilled water, blot dry and place into the sample.
6. Stir the solution thoroughly. When a stable reading is displayed, record the mV value.
7. Determine the sample concentration corresponding to the measured potential from the low level calibration curve.

**Table 2**  
**Calibration Curve For Low Level Calibrations**

Additions of standard (with low level ISA) to 100 mL distilled water and 1 mL low level ISA solution.

Step	Pipet Size	Volume Added	Concentration (M)
1	1 mL	0.1 mL	$1.0 \times 10^{-6}$
2	1 mL	0.1 mL	$2.0 \times 10^{-6}$
3	1 mL	0.2 mL	$4.0 \times 10^{-6}$
4	1 mL	0.2 mL	$6.0 \times 10^{-6}$
5	1 mL	0.4 mL	$9.9 \times 10^{-6}$
6	2 mL	2.0 mL	$2.9 \times 10^{-5}$
7	2 mL	2.0 mL	$4.8 \times 10^{-5}$

# Known Addition Technique

Known addition is a convenient technique for measuring samples in the linear range of the electrode (greater than  $5 \times 10^{-5}$  M thiocyanate) because no calibration curve is required. It can be used to verify the results of a direct calibration or to measure the total concentration of an ion in the presence of a large excess of a complexing agent. The sample potential is measured before and after addition of a standard solution.

Accurate results require that the following conditions be met:

- Concentration should approximately double as a result of the addition.
- Sample concentration should be known to within a factor of three.
- Either no complexing agent or a large excess of the complexing agent may be present.
- The ratio of the uncomplexed ion to complexed ion must not be changed by addition of the standard.
- All samples and standards should be at the same temperature.
- With double or multiple known addition, the final addition should be 10 to 100 times the sample concentration.
- Add 2 mL of ISA to every 100 mL of sample before analysis.

## Known Addition Setup

1. Prepare the electrodes as described in the **Electrode Preparation** section.
2. Connect the electrodes to the meter.
3. Prepare a standard solution that will cause the thiocyanate concentration of the sample to double when added to the sample solution. Refer to **Table 3** for guidelines.
4. Determine the electrode slope by performing the procedure in the **Checking Electrode Operation (Slope)** section.
5. Rinse the electrodes with distilled water and blot dry.

**Table 3**  
**Guideline For Known Addition**

<b>Volume of Addition</b>	<b>Concentration of Standard</b>
1 mL	100 times sample concentration
5 mL	20 times sample concentration
10 mL*	10 times sample concentration

\* Most convenient volume to use

## Known Addition Using a Meter with a Known Addition Mode

**Note:** See the meter user guide for more specific information.

1. Set the meter to measure in the known addition mode.
2. Measure 100 mL of the sample and 2 mL of ISA and pour the solutions into a beaker. Rinse the electrodes with distilled water and place into the sample solution. Stir the solution thoroughly.
3. When a stable reading is displayed, set the meter as described in the meter user guide, if required.
4. Pipet the appropriate amount of the standard solution into the beaker. Stir the solution thoroughly.
5. When a stable reading is displayed, record the sample concentration.



## Known Addition Using a Meter with a Millivolt Mode

1. Set the meter to the relative millivolt mode. If a relative millivolt mode is not available, use the millivolt mode.
2. Measure 100 mL of sample and 2 mL of ISA and pour the solutions into a 150 mL beaker. Stir the solution thoroughly.
3. Rinse the electrodes with distilled water, blot dry and place into the beaker. When a stable reading is displayed, set the meter to read 0.0 mV. If the reading cannot be adjusted to 0.0 mV, record the actual mV value.
4. Pipet the appropriate amount of standard solution into the beaker. Stir the solution thoroughly.
5. When a stable reading is displayed, record the mV value. If the meter could not be set to 0.0 mV in step 3, subtract the first reading from the second reading to calculate  $\Delta E$ .
6. Use **Table 5** to find the Q value that corresponds to the change in potential,  $\Delta E$ . To determine the original sample concentration, multiply Q by the concentration of the added standard:

$$C_{\text{sample}} = Q * C_{\text{standard}}$$

$C_{\text{standard}}$  = standard concentration

$C_{\text{sample}}$  = sample concentration

Q = value from **Table 5**

The table of Q values is calculated for a 10% volume change. The equation for the calculation of Q for different slopes and volume changes is given below.

$$Q = (p * r) / \{(1 + p) * 10^{\Delta E/S} - 1\}$$

Q = value from **Table 5**

$\Delta E = E_2 - E_1$

S = slope of the electrode

p = volume of standard / volume of sample and ISA

r = volume of sample and ISA / volume of sample

## Calculating Known Addition for Samples using Lotus, Excel, or Quattro Spreadsheets

If it is more convenient, a simple spreadsheet can be set up to calculate the known addition results, using any ratio of sample to addition. A typical worksheet is shown in **Table 4**. The numbers shown are examples, but the formulas and their locations should be copied exactly.

**Table 4**  
**Known Addition Calculations using Lotus, Excel, or Quattro Spreadsheets**

A	B	C
1		Enter Value
2	Volume of sample and ISA (mL)	102
3	Volume of addition (mL)	10
4	Concentration of addition	10
5	Volume of sample	100
6	Initial mV reading	-45.3
7	Final mV reading	-63.7
8	Electrode slope	-59.2
9		
10		Derived Values
11	Delta E	+C7 - C6
12	Solution volume ratio	+C3/C2
13	Antilog term	+10 <sup>^</sup> (C11/C8)
14	Sample volume ratio	+C2/C5
15	Q term	+C12*C14/ (((1+C12)*C13)-1)
16	Calculated initial concentration in same units as addition	+C15*C4

**Note:** For Excel, use = instead of + at start of formulas.



**Table 5**  
**Q Values for a 10% volume change**

$\Delta E$	Q	$\Delta E$	Q	$\Delta E$	Q
5.0	0.297	8.5	0.188	14.0	0.112
5.1	0.293	8.6	0.186	14.2	0.110
5.2	0.288	8.7	0.184	14.4	0.108
5.3	0.284	8.8	0.182	14.6	0.106
5.4	0.280	8.9	0.180	14.8	0.105
5.5	0.276	9.0	0.178	15.0	0.103
5.6	0.272	9.1	0.176	15.2	0.1013
5.7	0.268	9.2	0.174	15.4	0.0997
5.8	0.264	9.3	0.173	15.6	0.0982
5.9	0.260	9.4	0.171	15.8	0.0967
6.0	0.257	9.5	0.169	16.0	0.0952
6.1	0.253	9.6	0.167	16.2	0.0938
6.2	0.250	9.7	0.165	16.4	0.0924
6.3	0.247	9.8	0.164	16.6	0.0910
6.4	0.243	9.9	0.162	16.8	0.0897
6.5	0.240	10.0	0.160	17.0	0.0884
6.6	0.237	10.2	0.157	17.2	0.0871
6.7	0.234	10.4	0.154	17.4	0.0858
6.8	0.231	10.6	0.151	17.6	0.0846
6.9	0.228	10.8	0.148	17.8	0.0834
7.0	0.225	11.0	0.145	18.0	0.0822
7.1	0.222	11.2	0.143	18.2	0.0811
7.2	0.219	11.4	0.140	18.4	0.0799
7.3	0.217	11.6	0.137	18.6	0.0788
7.4	0.214	11.8	0.135	18.8	0.0777
7.5	0.212	12.0	0.133	19.0	0.0767
7.6	0.209	12.2	0.130	19.2	0.0756
7.7	0.207	12.4	0.128	19.4	0.0746
7.8	0.204	12.6	0.126	19.6	0.0736
7.9	0.202	12.8	0.123	19.8	0.0726
8.0	0.199	13.0	0.121	20.0	0.0716
8.1	0.197	13.2	0.119	20.2	0.0707
8.2	0.195	13.4	0.117	20.4	0.0698
8.3	0.193	13.6	0.115	20.6	0.0689
8.4	0.190	13.8	0.113	20.8	0.0680

$\Delta E$	$Q$	$\Delta E$	$Q$	$\Delta E$	$Q$
21.0	0.0671	28.0	0.0440	35.0	0.0304
21.2	0.0662	28.2	0.0435	36.0	0.0289
21.4	0.0654	28.4	0.0431	37.0	0.0275
21.6	0.0645	28.6	0.0426	38.0	0.0261
21.8	0.0637	28.8	0.0421	39.0	0.0249
22.0	0.0629	29.0	0.0417	40.0	0.0237
22.2	0.0621	29.2	0.0412	41.0	0.0226
22.4	0.0613	29.4	0.0408	42.0	0.0216
22.6	0.0606	29.6	0.0403	43.0	0.0206
22.8	0.0598	29.8	0.0399	44.0	0.0196
23.0	0.0591	30.0	0.0394	45.0	0.0187
23.2	0.0584	30.2	0.0390	46.0	0.0179
23.4	0.0576	30.4	0.0386	47.0	0.0171
23.6	0.0569	30.6	0.0382	48.0	0.0163
23.8	0.0563	30.8	0.0378	49.0	0.0156
24.0	0.0556	31.0	0.0374	50.0	0.0149
24.2	0.0549	31.2	0.0370	51.0	0.0143
24.4	0.0543	31.4	0.0366	52.0	0.0137
24.6	0.0536	31.6	0.0362	53.0	0.0131
24.8	0.0530	31.8	0.0358	54.0	0.0125
25.0	0.0523	32.0	0.0354	55.0	0.0120
25.2	0.0517	32.2	0.0351	56.0	0.0115
25.4	0.0511	32.4	0.0347	57.0	0.0110
25.6	0.0505	32.6	0.0343	58.0	0.0105
25.8	0.0499	32.8	0.0340	59.0	0.0101
26.0	0.0494	33.0	0.0336		
26.2	0.0488	33.2	0.0333		
26.4	0.0482	33.4	0.0329		
26.6	0.0477	33.6	0.0326		
26.8	0.0471	33.8	0.0323		
27.0	0.0466	34.0	0.0319		
27.2	0.0461	34.2	0.0316		
27.4	0.0456	34.4	0.0313		
27.6	0.0450	34.6	0.0310		
27.8	0.0445	34.8	0.0307		

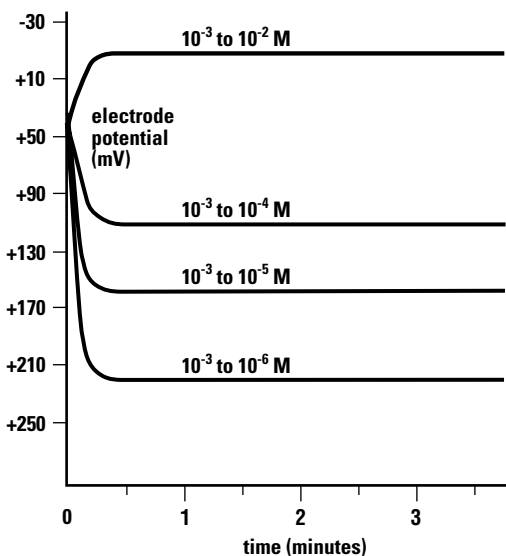
# Electrode Characteristics

## Electrode Response

The electrode potential plotted against concentration on semi-logarithmic paper results in a straight line with a slope of about -54 to -60 mV per decade change in concentration.

The time response of the electrode (the time required to reach 99% of the stable potential reading) varies from several seconds in concentrated solutions to several minutes near the limit of detection.

**Figure 2**  
**Typical Electrode Response to Step Changes in Thiocyanate Concentration**



## Reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift and noise. Within the operating range of the electrode, reproducibility is independent of concentration. With hourly calibrations, direct electrode measurements reproducible to  $\pm 2\%$  can be obtained.

## Limits of Detection

The lower limit of detection is determined by the very slight water solubility of the sensing element. At low levels the electrode responds to thiocyanate in the sample as well as to ions dissolved from the sensing element. The discrepancy between the theoretical linear response in comparison with the actual response (full line) curves is due to the response to dissolved ions from the sensing element. For low levels, samples below  $5 \times 10^{-5}$  M thiocyanate, refer to the **Low Level Calibration** procedure. Allow longer stabilization time prior to reading meter to assure best results.

## Temperature Effects

Since electrode potentials are affected by changes in temperature, samples and standard solutions should be within  $\pm 1$  °C ( $\pm 2$  °F) of each other. At the  $10^{-3}$  M level, a 1 °C difference in temperature results in errors greater than 2%. The absolute potential of the reference electrode changes slowly with temperature because of the solubility equilibria on which the electrode depends. The slope of the electrode also varies with temperature, as indicated by the factor S in the Nernst equation. Theoretical values of the slope at different temperatures are given in **Table 6**. If the temperature changes, the meter and electrode should be recalibrated.

**Table 6**  
**Theoretical Slope vs. Temperature Values**

Temperature (°C)	Slope (mV)
0	- 54.20
10	- 56.18
20	- 58.16
25	- 59.16
30	- 60.15
40	- 62.13
50	- 64.11

## Interferences

The electrode will malfunction if the ions listed in **Table 7**, which form insoluble salts, are present at sufficiently high concentrations to form a layer of the salt on the sensing element surface. In addition, the electrode must not be placed in strong reducing solutions, which form a layer of metal on the electrode sensing element. If the surface of the sensing element becomes contaminated, restore the electrode performance by polishing the sensing surface. Mercury should be absent from all samples.

**Table 7** gives the maximum allowable concentration of common interfering ions expressed as the ratio of the interfering ion concentration to the sample thiocyanate concentration. If the ratio is exceeded, the electrode will malfunction. If the ratio is less than the value listed in the table, neither the accuracy of the measurement nor the sensing element surface will be affected.

**Table 7**  
**Thiocyanate Electrode Interferences**

Interferences	Maximum Ratio (moles/L)
(a) S <sup>2-</sup>	1 x 10 <sup>-6</sup>
I <sup>-</sup>	1 x 10 <sup>-6</sup>
Br <sup>-</sup>	3 x 10 <sup>-3</sup>
(a) CN <sup>-</sup>	7 x 10 <sup>-3</sup>
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	0.13
Cl <sup>-</sup>	20
(b) OH <sup>-</sup>	100

(a) Sulfide and cyanide may be removed by adding a nickel (+2) solution.

(b) Hydroxide interference can be removed by acidifying to pH 4 with 1 M HNO<sub>3</sub>.

### Example

What is the maximum level of bromide tolerable in a sample whose thiocyanate concentration is 10<sup>-3</sup> M? From **Table 7**, the maximum ratio is [Br<sup>-</sup>] / [SCN<sup>-</sup>] = 3 x 10<sup>-3</sup>.

$$[\text{Br}^-] = 3 \times 10^{-3} * [\text{SCN}^-] = 3 \times 10^{-3} * 10^{-3} =$$

3 x 10<sup>-6</sup> M maximum bromide concentration



## Complexation

Thiocyanate ions form complexes with some metal ions. Since the electrode responds only to free thiocyanate ions, the presence of any complexing agents lowers the measured concentration. **Table 8** lists the levels of complexing metals causing a 10% error.

Total concentration in the presence of a large excess (by a factor of at least 50 to 100) of complexing agent can be measured by the known addition method.

**Table 8**  
**Complexing Metals**

<b>Complexing Agent</b>	<b>10<sup>-4</sup> M Thiocyanate</b>	<b>10<sup>-3</sup> M Thiocyanate</b>	<b>10<sup>-2</sup> M Thiocyanate</b>
Ag <sup>+</sup>	1 x 10 <sup>-4</sup> M	1 x 10 <sup>-3</sup> M	1 x 10 <sup>-2</sup> M
Cu <sup>+</sup>	1 x 10 <sup>-4</sup> M	1 x 10 <sup>-3</sup> M	1 x 10 <sup>-2</sup> M
Cu <sup>+2</sup>	2 x 10 <sup>-2</sup> M	2 x 10 <sup>-2</sup> M	3 x 10 <sup>-2</sup> M
Fe <sup>+2</sup>	5 x 10 <sup>-3</sup> M	5 x 10 <sup>-3</sup> M	8 x 10 <sup>-3</sup> M

## Theory of Operation

The thiocyanate electrode consists of a sensing element bonded into an epoxy body. When the sensing element is in contact with a solution containing thiocyanate ions, an electrode potential develops across the sensing element. This potential, which depends on the level of free thiocyanate ion in solution, is measured against a constant reference potential with a digital pH/mV meter or ISE (concentration) meter. The measured potential corresponding to the level of thiocyanate ion in solution is described by the Nernst equation.

$$E = E_o + S * \log (A)$$

E = measured electrode potential

$E_o$  = reference potential (a constant)

A = thiocyanate ion activity level in solution

S = electrode slope (about -57 mV per decade)

$S = (2.3 RT) / nF$

R and F are constants, T = temperature in degrees K and

n = ionic charge

The level of thiocyanate ions, A, is the activity or “effective concentration” of free thiocyanate ions in solution. The thiocyanate ion activity is related to free thiocyanate ion concentration,  $C_f$ , by the activity coefficient,  $\gamma$ .

$$A = \gamma * C_f$$

Ionic activity coefficients are variable and largely depend on total ionic strength. The ionic strength of a solution is determined by all of the ions present. It is calculated by multiplying the concentration of each individual ion by the square of its charge, adding all these values up and then dividing by two.

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

$C_i$  = concentration of ion i

$Z_i$  = charge of ion i

$\sum$  symbolizes the sum of all the types of ions in solutions

If background ionic strength is high and constant relative to the sensed ion concentration, the activity coefficient is constant and activity is directly proportional to concentration. Ionic strength adjustor (ISA) is added to all thiocyanate standards and samples so that the background ionic strength is high and constant relative to variable concentrations of thiocyanate. For thiocyanate, the recommended ISA is 5 M  $\text{NaNO}_3$ . Other solutions can be used as long as they do not contain ions that would interfere with the electrode response to thiocyanate.

If samples have a high ionic strength (above 0.1 M), standards should be prepared with a composition similar to the samples.

Reference electrode conditions must also be considered. Liquid junction potentials arise any time when 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, the electrode 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 is the same when the reference is in the standardizing solution as well as in the same solution; otherwise, the change in liquid junction potential will appear as an error in the measured specific ion electrode potential.

The most important variable that analysts have under their control is the composition of the liquid junction filling solution. The filling solution should be equitransferent. That is, the speed with which the positive and negative ions in the filling solution diffuse into the sample should be nearly as 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.

# Troubleshooting

Follow a systematic procedure to isolate the problem. The measuring system can be divided into four components for ease in troubleshooting: meter, electrode, sample/application and technique.

## Meter

The meter is the easiest component to eliminate as a possible cause of error. Thermo Scientific Orion meters include an instrument checkout procedure and shorting cap for convenience in troubleshooting. Consult the meter user guide for directions.

## Electrode

1. Rinse the electrode thoroughly with distilled water.
2. Verify the electrode performance by performing the procedure in the **Checking Electrode Operation (Slope)** section.
3. If the electrode fails this procedure, review the **Measuring Hints** section. Clean the electrode thoroughly as directed in the **Electrode Maintenance** section. Drain and refill the reference electrode with fresh filling solution.
4. Repeat the procedure in the **Checking Electrode Operation (Slope)** section.
5. If the electrode fails this procedure again, determine whether the thiocyanate or reference electrode is at fault. To do this, substitute a known working electrode for the electrode in question and repeat the procedure in the **Checking Electrode Operation (Slope)** section.
6. If the electrode passes the procedure, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error.
7. Before replacing a faulty electrode, review this user guide and be sure to thoroughly clean the electrode; correctly prepare the electrode; use the proper filling solution, ISA, and standards; correctly measure the samples and review the **Troubleshooting Checklist** section.

## Sample/Application

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

The best method for preparation of standards is serial dilution. Refer to the **Serial Dilution** section. The electrode and meter may operate with standards, but not with the sample. In this case, check the sample composition for interferences, incompatibilities or temperature effects. Refer to the **Sample Requirements, Temperature Effects, Interferences** and **Complexation** sections.

## Technique

If trouble persists, review operating procedures. Review calibration and measurement sections to be sure proper technique has been followed. Verify that the expected concentration of the ion of interest is within the limit of detection of the electrode.

Check the method of analysis for compatibility with your sample. Direct measurement may not always be the method of choice. If a large amount of complexing agents are present, known addition may be the best method. If working with low level samples, follow the procedure in the **Low Level Calibration** section.

## 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/contactwater](http://www.thermo.com/contactwater).

For the latest application and technical resources for Thermo Scientific Orion products, visit [www.thermo.com/waterapps](http://www.thermo.com/waterapps).

## Warranty

For the most current warranty information, visit [www.thermo.com/water](http://www.thermo.com/water).

## Troubleshooting Checklist

- No electrode filling solution added –  
Fill the reference electrode with filling solution up to the fill hole. Refer to the **Electrode Preparation** section for details.
- Incorrect electrode filling solution used –  
Refer to the **Electrode Preparation** section to verify the correct electrode filling solution.
- Electrode junction is dry –  
Push down on the reference electrode cap to allow a few drops of filling solution to drain out of the electrode.
- No reference electrode present –  
The 9458BN thiocyanate half-cell electrode require a separate reference electrode, Cat. No. 900200.
- Electrode is clogged or dirty –  
Refer to the **Electrode Maintenance** section for cleaning instructions.
- Sensing element is dirty or etched –  
Refer to the **Electrode Maintenance** section for cleaning instructions.
- Standards are contaminated or made incorrectly –  
Prepare fresh standards. Refer to the **Measurement Hints** and **Analytical Techniques** sections.
- ISA not used or incorrect ISA used –  
ISA must be added to all standards and samples. Refer to the **Required Equipment** section for information on the ISA.
- Samples and standards at different temperatures –  
Allow solutions to reach the same temperature.
- Air bubble on sensing element –  
Remove air bubble by reimmersing the electrode in solution.
- Electrode not properly connected to meter –  
Unplug and reconnect the electrode to the meter.
- Meter or stir plate not properly grounded –  
Check the meter and stir plate for proper grounding.
- Static electricity present –  
Wipe plastic parts on the meter with a detergent solution.
- Defective meter –  
Check the meter performance. See the meter user guide.

# Ordering Information

<b>Cat. No.</b>	<b>Description</b>
9458BN	Thiocyanate half-cell electrode, BNC connector (requires separate reference electrode)
900200	Double junction reference electrode, pin tip connector
900002	Inner chamber filling solution for the double junction reference electrode, 5 x 60 mL bottles
900003	Outer chamber filling solution for the double junction reference electrode, 5 x 60 mL bottles
940011	ISA for thiocyanate measurements, 475 mL bottle
984201	Polishing strips

# Specifications

## Concentration Range

$5 \times 10^{-5}$  M to 1 M (0.29 ppm to 58,100 ppm)

## pH Range

2 to 10

a pH less than 4 is recommended to avoid OH<sup>-</sup> interference

## Temperature Range

0 to 50 °C continuous use, 50 to 100 °C intermittent use

## Electrode Resistance

Less than 100 K ohms

## Reproducibility

± 2%

## Size

Body Diameter: 12 mm

Body Length: 110 mm

Cap Diameter: 16 mm

Cable Length: 1 meter

\* *Specifications are subject to change without notice*



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