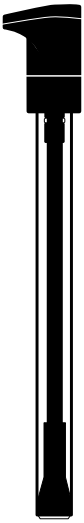
User Guide

Cupric
Ion Selective
Electrode



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The specifications, descriptions, drawings, ordering information and part numbers within this document are subject to change without notice.

This publication supersedes all previous publications on this subject.

Table of Contents

Introduction

This user guide contains information on the preparation, operation and maintenance for the cupric ion selective electrode (ISE). General analytical procedures, electrode characteristics and electrode theory are also included in this user guide. Cupric electrodes measure free cupric 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.

For the latest application and technical resources for Thermo Scientific Orion products, visit www.thermo.com/waterapps.

Cupric ionplus® Sure-Flow® Solid State Combination ISE, Cat. No. 9629BNWP

The cupric combination electrode has the sensing and reference half-cells built into one electrode, which decreases the amount of required solutions and reduces waste. The built-in Sure-Flow reference junction prevents electrode clogging and provides fast and stabile readings. The cupric combination electrode is available with a waterproof BNC connector, Cat. No. 9629BNWP. Electrodes with a waterproof BNC connector can be used on any ISE or mV meter with a BNC connection.

Cupric Solid State Half-Cell ISE, Cat. No. 9429BN and 9429SC

The cupric half-cell electrode must be used with the double junction reference electrode, Cat. No. 900200. The cupric half-cell electrode is available with a BNC connector, Cat. No. 9429BN, and a screw cap connector, Cat. No. 9429SC. Electrodes with a screw cap connector require a separate cable.

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.

   Cupric 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 for details.

2. Thermo Scientific Orion cupric electrode.

   The 9429BN and 9429SC cupric half-cell electrodes require a separate reference electrode, Cat. No. 900200.

3. 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.

4. Volumetric flasks, graduated cylinders and beakers. Plastic labware is required for low level cupric ion analysis.

5. Distilled or deionized water.

6. Cupric electrode filling solution.

   Use Optimum Results™ D filling solution, Cat. No. 900063, for the 9629BNWP cupric combination electrode.

   Use inner chamber filling solution, Cat. No. 900002, and outer chamber filling solution, Cat. No. 900003, for the double junction reference electrode that is used with the 9429BN and 9429SC cupric half-cell electrodes.

7. 0.1 M $Cu(NO_3)_2$ calibration standard, Cat. No. 942906.

8. Cupric 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 standard (635.5 ppm) –**
   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 standard (63.55 ppm) –**
   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 standard (6.355 ppm) –**
   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:

$$\mathbf{C_1 * V_1 = C_2 * V_2}$$

$\mathbf{C_1}$ = concentration of original standard
$\mathbf{V_1}$ = volume of original standard
$\mathbf{C_2}$ = concentration of standard after dilution
$\mathbf{V_2}$ = volume of standard after dilution

For example, to prepare 1000 mL of a 100 ppm cupric standard from a 6355 ppm cupric standard:

$\mathbf{C_1}$ = 6355 ppm

$\mathbf{V_1}$ = unknown

$\mathbf{C_2}$ = 100 ppm

$\mathbf{V_2}$ = 1000 mL

6355 ppm * $\mathbf{V_1}$ = 100 ppm * 1000 mL

$\mathbf{V_1}$ = (100 ppm * 1000 mL) / 6355 ppm = 15.7 mL

Electrode Setup

Electrode Preparation

9429BN and 9429SC Cupric 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.

9629BNWP Cupric Combination Electrode – Remove the protective shipping cap from the sensing element and save the cap for storage. Fill the electrode with Optimum Results D filling solution, Cat. No. 900063.

9629BNWP Cupric Combination Electrode Filling Instructions

1. Lift the flip spout on the filling solution bottle to a vertical position.

2. Insert the spout into the filling hole on the outer body of the electrode and add a small amount of filling solution to the reference chamber. Invert the electrode to moisten the top O-ring and then return the electrode to the upright position.

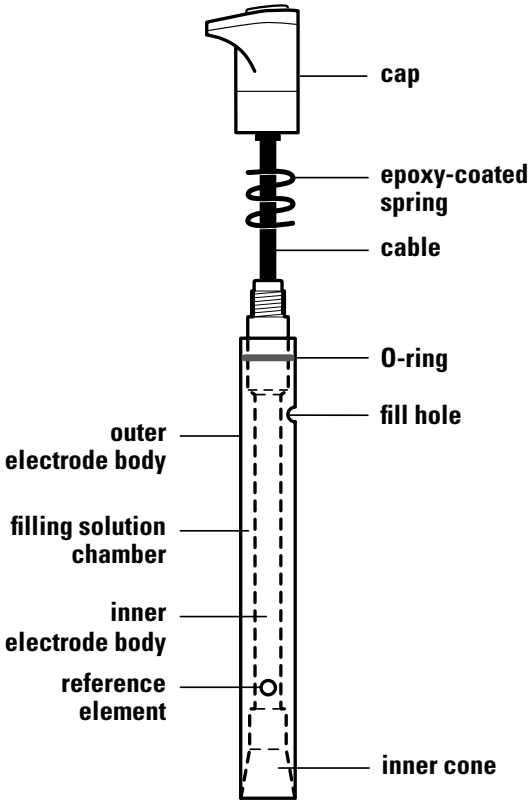
3. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.

4. Release the electrode cap. If the sleeve does not return to its original position, check if the O-ring is moist and repeat steps 2 through 4 until the sleeve returns to the original position.

5. Add filling solution to the electrode up to the filling hole.

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.*

Figure 1
9629BNWP Cupric Combination Electrode



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 cupric 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 25 to 30 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

Cupric ion 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	63550
10^{-1}	6355
1.57×10^{-2}	1000
10^{-2}	635.5
10^{-3}	63.55
10^{-4}	6.355
1.57×10^{-5}	1

Sample Requirements

The epoxy body of the cupric 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 cupric ion solution will give rise to about a 4% error. The combination cupric electrode, Cat. No. 9629BNWP, when used with Optimum Results D filling solution, produces less than a 2% error in the same solution.

The solution temperature must be less than 80 °C.

Cupric samples must be below pH 6 to avoid precipitation of $Cu(OH)_2$. Acidify samples with 1 M HNO_3 if necessary. See the **pH Effects** section to determine the optimum pH working range for your sample.

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 cupric) 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.

- If the combination electrode is used and the electrode is used in dirty or viscous samples or the electrode response becomes sluggish, empty the electrode completely, hold the junction open and flush the junction with distilled water. Empty any water from the electrode and refill it with fresh filling solution. Press down on the electrode cap to let a few drops of the filling solution flow out of the electrode and then replenish any lost solution.

Electrode Storage

Cupric Half-Cell Electrode Storage, Cat. No. 9429BN and 9429SC

The cupric 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, Cat. No. 900200

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.

Cupric Combination Electrode Storage, Cat. No. 9629BNWP

For storage between measurements and up to one week, store the electrode in a 4 M potassium chloride solution with cupric. The cupric concentration of the storage solution should be close to the least concentrated cupric calibration standard. Do not add ISA to the storage solution. The filling solution inside the electrode should not be allowed to evaporate, as crystallization will result.

For storage longer than one week, drain the electrode, flush the chamber with distilled water and store the electrode dry with the protective shipping cap covering the sensing element.

Electrode Maintenance

Polishing the Cupric Combination Electrode and Cupric 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 cupric standard for ten minutes.

Cupric Combination Electrode and 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.

Disassembling and Reassembling the Cupric Combination Electrode

Note: *Disassembly is usually not required and should not be done unless a thorough cleaning is required.*

1. Tip the electrode so the filling solution moistens the O-ring on the electrode body. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to drain the electrode.

2. Unscrew the cap counterclockwise and then slide the cap and spring up the cable.

3. Hold the outer sleeve with one hand and firmly push down on the threaded portion with your thumb and forefinger to separate the inner body from the sleeve.

4. Grasp the inner cone with a clean, lint-free tissue and withdraw the body from the sleeve using a gentle twisting motion. Do not touch the pellet above the cone, as it will damage to the pellet. Rinse the outside of the electrode body and the entire sleeve with distilled water. Allow it to air dry.

5. Moisten the O-ring on the electrode body with a drop of filling solution. Insert the screw-thread end of the electrode body into the tapered, ground end of the sleeve.

6. Push the body into the sleeve using a gentle twisting motion until the bottom surface of the inner cone is flush with the tapered end of the sleeve.

7. Place the spring onto the electrode body and screw on the cap. Refill the electrode with 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 a similar to the direct calibration technique. This method is recommended when the expected sample concentration is less than 0.6 ppm or 10^{-5} M cupric. 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.

Titrations are quantitative analytical techniques for measuring the concentration of a species by incremental addition of a reagent (titrant) that reacts with the sample species. Sensing electrodes can be used for determination of the titration end point. Ion selective electrodes are useful as end point detectors, because they are unaffected by sample color or turbidity. Titrations are approximately 10 times more precise than direct calibration, but are more time-consuming.

Indicator Titration Method is useful for measuring ionic species where an ion specific electrode does not exist. With this method the electrodes sense a reagent species that has been added to the sample before titration. The cupric electrode may be used in indicator titrations for many different metal ions.

Table 2
Recommended Measuring Techniques

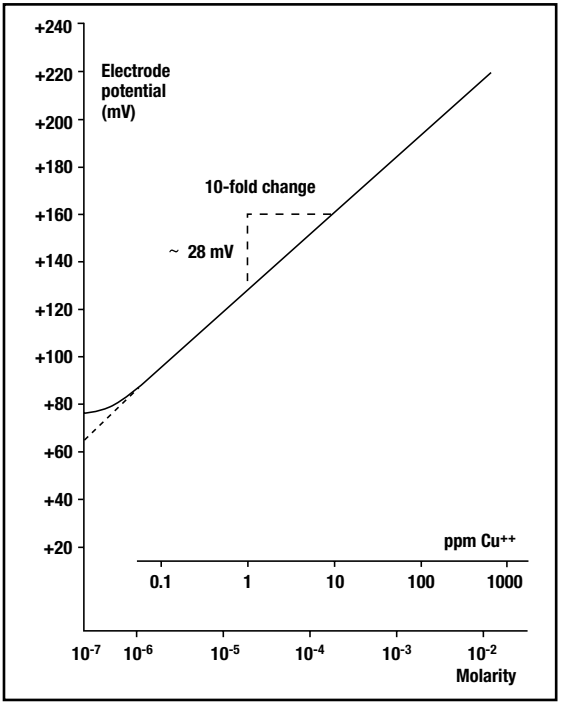
	Direct	Small Volume Direct	Low Level	Known Addition	Titration
$[Cu^{+2}] < 0.6$ ppm			✔		
$[Cu^{+2}] > 0.6$ ppm	✔			✔	✔
$[Cu^{+2}] > 1.0$ ppm		✔			
Increased accuracy					✔
Occasional Sampling				✔	
Small sample volume		✔		✔	
Large number of samples	✔		✔	✔	
Reduce chemical usage		✔			
Field measurement		✔			
Ionic strength greater than 0.1 M	✔			✔	
Other metal analysis					✔ (Indicator Titration)

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 2
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 0.6 ppm or 10^{-5} M cupric. 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 electrode as described in the **Electrode Preparation** section. If using the 9629BNWP combination cupric electrode, fill the electrode with Cat. No. 900063. If using the 9429BN or 9429SC half-cell cupric electrode with the 900200 reference electrode, fill the reference electrode with inner chamber filling solution, Cat. No. 900002, and outer chamber filling solution, Cat. No. 900003.
2. Connect the electrode 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 electrode with distilled water, blot it dry and place it 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 electrode with distilled water, blot it dry and place it 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 25 and 30 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 electrode with distilled water, blot it dry and place it 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 electrode with distilled water, blot it dry and place it 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 electrode with distilled water, blot it dry and place it 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 electrode with distilled water, blot it dry and place it 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.*

Small Volume Direct Calibration Technique

Take advantage of special design features available with the 9629BNWP ionplus combination cupric electrode to meet your measuring needs. Due to the Sure-Flow reference, this electrode is able to measure sample volumes as small as 5 mL using a modified direct measurement procedure. Because less solution volume is required, the chemical usage of cupric standards and ISA is reduced. This method is also convenient when making field measurements, since the 9629BNWP combination cupric electrode does not require a separate reference electrode. All samples should have a concentration greater than 1 ppm or 1.57×10^{-5} M cupric. A two point calibration is sufficient, although more points can be used. The following procedure recommends using 25 mL of sample. Smaller sample volumes can be used, as long as the final volume of solution is sufficient to cover the bottom of the electrode.

Calibration Hints

- Use the 9629BNWP ionplus combination cupric electrode.
- Standard concentrations should bracket the expected sample concentrations.
- Always keep the ratio of standard or sample to ISA at 50:1.
- 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.
- Calibrate with the same volume of standard as the volume of sample that is available for analysis.

Small Volume Direct Calibration Setup

1. Prepare the 9629BNWP combination cupric electrode as described in the **Electrode Preparation** section and fill the electrode with Optimum Results D filling solution, Cat. No. 900063.

2. Connect the electrode 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.

Small Volume Direct Calibration Procedure Using a Meter with an ISE Mode

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

1. Add 25 mL of the less concentrated standard and 0.5 mL of ISA to a 50 mL beaker and swirl the solution to mix.

2. Rinse the electrode with distilled water, blot it dry and place it 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 25 mL of the more concentrated standard and 0.5 mL of ISA to a second 50 mL beaker and swirl the solution to mix.

4. Rinse the electrode with distilled water, blot it dry and place it 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 25 and 30 mV when the standards are between 20 and 25 °C.

6. Add 25 mL of sample and 0.5 mL of ISA to a clean 50 mL beaker and swirl the solution to mix.

7. Rinse the electrode with distilled water, blot it dry and place it 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.*

Small Volume 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 25 mL of the less concentrated standard and 0.5 mL of ISA to a 50 mL beaker and swirl the solution to mix.

3. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

4. Add 25 mL of the more concentrated standard and 0.5 mL of ISA to a second 50 mL beaker and swirl the solution to mix.

5. Rinse the electrode with distilled water, blot it dry and place it 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 25 mL of sample and 0.5 mL of ISA to a clean 50 mL beaker and swirl the solution to mix.

8. Rinse the electrode with distilled water, blot it dry and place it 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 cupric concentration of less than 0.6 ppm or 10^{-5} M cupric. For solutions low in cupric 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.
- Plastic labware must be used for all low level cupric measurements.
- 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 electrode as described in the **Electrode Preparation** section.

2. Connect the electrode to the meter. Set the meter to the mV mode.

3. Prepare the low level ISA by pipetting 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. Select a standard solution. Use either a 10 ppm cupric standard or a 10^{-4} M cupric standard.

   To prepare the 10 ppm standard, pipet 10 mL of the 1000 ppm standard into a 1 liter volumetric flask. Dilute to the mark with distilled water and mix the solution thoroughly.

   To prepare the 10^{-4} M standard, pipet 1 mL of the 0.1 M standard into a 1 liter volumetric flask. Dilute to the mark with distilled water and mix the solution thoroughly.

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 electrode with distilled water, blot it dry and place it into the beaker. Stir the solution thoroughly.

3. Add increments of the 10 ppm or 10^{-4} M cupric standard mixed with low level ISA to the beaker using the steps outlined in **Table 3**. 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 electrode with distilled water, blot it dry and place the electrode 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 3
Calibration Curve For Low Level Calibrations
Additions of standard to 100 mL distilled water and 1 mL low level ISA solution.

Step	Pipet Size	Volume Added	Concentration (ppm)
1	0.1 mL	0.01 mL	0.001
2	0.1 mL	0.1 mL	0.011
3	1.0 mL	0.9 mL	0.100
4	10 mL	6.0 mL	0.662

Step	Pipet Size	Volume Added	Concentration (M)
1	0.1 mL	0.01 mL	1.0×10^{-8}
2	0.1 mL	0.1 mL	1.11×10^{-7}
3	1.0 mL	0.9 mL	1.0×10^{-6}
4	10 mL	10 mL	9.9×10^{-6}

Known Addition Technique

Known addition is a convenient technique for measuring samples in the linear range of the electrode (greater than 0.6 ppm or 10^{-5} M cupric) 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 electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to the meter.
3. Prepare a standard solution that will cause the cupric concentration of the sample to double when added to the sample solution. Refer to **Table 4** for guidelines.
4. Determine the electrode slope by performing the procedure in the **Checking Electrode Operation (Slope)** section.
5. Rinse the electrode with distilled water.

Table 4
Guideline For Known Addition

Volume of Addition	Concentration of Standard
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 electrode with distilled water and place it 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 electrode with distilled water, blot it dry and place the electrode 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 ΔE.

6. Use **Table 6** to find the Q value that corresponds to the change in potential, ΔE. To determine the original sample concentration, multiply Q by the concentration of the added standard:

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

   $C_{standard}$ = standard concentration
   C_{sample} = sample concentration
   Q = value from **Table 6**

   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.

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

   Q = value from **Table 6**
   $\Delta E = E_2 - E_1$
   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 5**. The numbers shown are examples, but the formulas and their locations should be copied exactly.

Table 5
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	28.2
9		
10		Derived Values
11	Delta E	+C7 - C6
12	Solution volume ratio	+C3/C2
13	Antilog term	+10^ (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 6
Q Values for a 10% volume change,
slopes (in column heading) are in units of mV/decade

ΔE	Q Concentration Ratio			
	28.6	**29.1**	**29.6**	**30.1**
2.5	0.2917	0.2957	0.2996	0.3035
3.0	0.2512	0.2550	0.2586	0.2623
3.5	0.2196	0.2230	0.2264	0.2298
4.0	0.1941	0.1973	0.2005	0.2036
4.5	0.1732	0.1762	0.1791	0.1821
5.0	0.1557	0.1585	0.1613	0.1640
5.1	0.1525	0.1553	0.1580	0.1608
5.2	0.1495	0.1522	0.1549	0.1576
5.3	0.1465	0.1492	0.1519	0.1546
5.4	0.1437	0.1463	0.1490	0.1516
5.5	0.1409	0.1435	0.1461	0.1487
5.6	0.1382	0.1408	0.1434	0.1459
5.7	0.1356	0.1382	0.1407	0.1432
5.8	0.1331	0.1356	0.1381	0.1406
5.9	0.1306	0.1331	0.1356	0.1381
6.0	0.1282	0.1307	0.1331	0.1356
6.1	0.1259	0.1283	0.1308	0.1332
6.2	0.1236	0.1260	0.1284	0.1308
6.3	0.1214	0.1238	0.1262	0.1285
6.4	0.1193	0.1217	0.1240	0.1263
6.5	0.1172	0.1195	0.1219	0.1242
6.6	0.1152	0.1175	0.1198	0.1221
6.7	0.1132	0.1155	0.1178	0.1200
6.8	0.1113	0.1136	0.1158	0.1180
6.9	0.1094	0.1117	0.1139	0.1161
7.0	0.1076	0.1098	0.1120	0.1142
7.1	0.1058	0.1080	0.1102	0.1123
7.2	0.1041	0.1063	0.1084	0.1105
7.3	0.1024	0.1045	0.1067	0.1088
7.4	0.1008	0.1029	0.1050	0.1071
7.5	0.0992	0.1012	0.1033	0.1054
7.6	0.0976	0.0997	0.1017	0.1037
7.8	0.0946	0.0966	0.0986	0.1006
8.0	0.0917	0.0936	0.0956	0.0976
8.2	0.0889	0.0908	0.0928	0.0947
8.4	0.0863	0.0882	0.0900	0.0919
8.6	0.0837	0.0856	0.0874	0.0893
8.8	0.0813	0.0831	0.0849	0.0868
9.0	0.0790	0.0808	0.0825	0.0843
9.2	0.0767	0.0785	0.0803	0.0820
9.4	0.0746	0.0763	0.0780	0.0798
9.6	0.0725	0.0742	0.0759	0.0776
9.8	0.0706	0.0722	0.0739	0.0755
10.0	0.0687	0.0703	0.0719	0.0735
10.2	0.0668	0.0684	0.0700	0.0716
10.4	0.0651	0.0666	0.0682	0.0698
10.6	0.0634	0.0649	0.0665	0.0680
10.8	0.0617	0.0633	0.0648	0.0663
11.0	0.0602	0.0617	0.0631	0.0646
11.2	0.0586	0.0601	0.0616	0.0630
11.4	0.0572	0.0586	0.0600	0.0615

ΔE	Q Concentration Ratio			
	28.6	**29.1**	**29.6**	**30.1**
11.6	0.0557	0.0572	0.0586	0.0600
11.8	0.0544	0.0558	0.0572	0.0585
12.0	0.0530	0.0544	0.0558	0.0572
12.2	0.0518	0.0531	0.0545	0.0558
12.4	0.0505	0.0518	0.0532	0.0545
12.6	0.0493	0.0506	0.0519	0.0532
12.8	0.0481	0.0494	0.0507	0.0520
13.0	0.0470	0.0483	0.0495	0.0508
13.2	0.0459	0.0472	0.0484	0.0497
13.4	0.0449	0.0461	0.0473	0.0485
13.6	0.0438	0.0450	0.0462	0.0474
13.8	0.0428	0.0440	0.0452	0.0464
14.0	0.0419	0.0430	0.0442	0.0454
14.2	0.0409	0.0421	0.0432	0.0444
14.4	0.0400	0.0411	0.0423	0.0434
14.6	0.0391	0.0402	0.0413	0.0425
14.8	0.0382	0.0393	0.0404	0.0416
15.0	0.0374	0.0385	0.0396	0.0407
15.5	0.0354	0.0365	0.0375	0.0386
16.0	0.0335	0.0345	0.0356	0.0366
16.5	0.0318	0.0328	0.0337	0.0347
17.0	0.0302	0.0311	0.0320	0.0330
17.5	0.0286	0.0295	0.0305	0.0314
18.0	0.0272	0.0281	0.0290	0.0298
18.5	0.0258	0.0267	0.0275	0.0284
19.0	0.0246	0.0254	0.0262	0.0270
19.5	0.0234	0.0242	0.0250	0.0258
20.0	0.0223	0.0230	0.0238	0.0246
20.5	0.0212	0.0219	0.0227	0.0234
21.0	0.0202	0.0209	0.0216	0.0224
21.5	0.0192	0.0199	0.0206	0.0213
22.0	0.0183	0.0190	0.0197	0.0204
22.5	0.0175	0.0181	0.0188	0.0195
23.0	0.0167	0.0173	0.0179	0.0186
23.5	0.0159	0.0165	0.0171	0.0178
24.0	0.0152	0.0158	0.0164	0.0170
24.5	0.0145	0.0151	0.0157	0.0162
25.0	0.0139	0.0144	0.0150	0.0155
25.5	0.0132	0.0138	0.0143	0.0149
26.0	0.0126	0.0132	0.0137	0.0142
26.5	0.0121	0.0126	0.0131	0.0136
27.0	0.0116	0.0120	0.0125	0.0131
27.5	0.0110	0.0115	0.0120	0.0125
28.0	0.0106	0.0110	0.0115	0.0120
28.5	0.0101	0.0106	0.0110	0.0115
29.0	0.0097	0.0101	0.0105	0.0110
29.5	0.0093	0.0097	0.0101	0.0105
30.5	0.0085	0.0089	0.0093	0.0097
31.5	0.0078	0.0081	0.0085	0.0089
32.0	0.0074	0.0078	0.0082	0.0085
32.5	0.0071	0.0075	0.0078	0.0082

ΔE	Q Concentration Ratio			
	28.6	29.1	29.6	30.1
33.0	0.0068	0.0072	0.0075	0.0079
33.5	0.0065	0.0069	0.0072	0.0076
34.0	0.0063	0.0066	0.0069	0.0072
34.5	0.0060	0.0063	0.0066	0.0070
35.0	0.0058	0.0061	0.0064	0.0067
35.5	0.0055	0.0058	0.0061	0.0064
36.0	0.0053	0.0056	0.0059	0.0062
36.5	0.0051	0.0053	0.0056	0.0059
37.0	0.0049	0.0051	0.0054	0.0057
37.5	0.0047	0.0049	0.0052	0.0055
38.0	0.0045	0.0047	0.0050	0.0052
38.5	0.0043	0.0045	0.0048	0.0050
39.0	0.0041	0.0043	0.0046	0.0048
39.5	0.0039	0.0042	0.0044	0.0046
40.0	0.0038	0.0040	0.0042	0.0045
40.5	0.0036	0.0038	0.0041	0.0043
41.0	0.0035	0.0037	0.0039	0.0041
41.5	0.0033	0.0035	0.0037	0.0040
42.0	0.0032	0.0034	0.0036	0.0038
42.5	0.0031	0.0033	0.0035	0.0037
43.0	0.0029	0.0031	0.0033	0.0035
43.5	0.0028	0.0030	0.0032	0.0034
44.0	0.0027	0.0029	0.0031	0.0032
44.5	0.0026	0.0028	0.0029	0.0031
45.0	0.0025	0.0027	0.0028	0.0030
45.5	0.0024	0.0026	0.0027	0.0029
46.0	0.0023	0.0024	0.0026	0.0028
46.5	0.0022	0.0024	0.0025	0.0027
47.0	0.0021	0.0023	0.0024	0.0026
47.5	0.0020	0.0022	0.0023	0.0025
48.0	0.0019	0.0021	0.0022	0.0024
48.5	0.0019	0.0020	0.0021	0.0023
49.0	0.0018	0.0019	0.0021	0.0022
49.5	0.0017	0.0018	0.0020	0.0021
50.0	0.0017	0.0018	0.0019	0.0020
50.5	0.0016	0.0017	0.0018	0.0019
51.0	0.0015	0.0016	0.0018	0.0019
51.5	0.0015	0.0016	0.0017	0.0018
52.0	0.0014	0.0015	0.0016	0.0017
52.5	0.0013	0.0015	0.0016	0.0017
53.0	0.0013	0.0014	0.0015	0.0016
53.5	0.0012	0.0013	0.0014	0.0015
54.0	0.0012	0.0013	0.0014	0.0015
54.5	0.0011	0.0012	0.0013	0.0014
55.0	0.0011	0.0012	0.0013	0.0014
55.5	0.0011	0.0011	0.0012	0.0013
56.0	0.0010	0.0011	0.0012	0.0013
56.5	0.0010	0.0011	0.0011	0.0012
57.0	0.0009	0.0010	0.0011	0.0012
57.5	0.0009	0.0010	0.0011	0.0011
58.0	0.0009	0.0009	0.0010	0.0011
58.5	0.0008	0.0009	0.0010	0.0010
59.0	0.0008	0.0009	0.0009	0.0010
59.5	0.0008	0.0008	0.0009	0.0010
60.0	0.0007	0.0008	0.0009	0.0009

Cupric Titration Technique

The cupric electrode makes a highly sensitive endpoint detector for titration with EDTA of copper samples. Titrations are more time consuming than direct electrode measurement, but results are more accurate and reproducible. With careful technique, titrations accurate to ± 0.1% of the total cupric ion concentration of the sample can be performed.

EDTA complexes other cations besides cupric ion. Interferences from alkaline earths and other ions, whose EDTA complexes are stable only at high pH, can be eliminated by performing the titration for cupric ion at a low pH. In many cases, other interferences can be eliminated by a suitable choice of sample pH and the addition of masking agents to the sample solution. A comprehensive list of methods is given in the Handbook of Analytical Chemistry, L. Meites, (ed.) McGraw Hill Book Co., New York, (1st edit.), pp. 3-76, 3-225.

Cupric Titration Setup

1. Prepare the electrode as described in the **Electrode Preparation** section. If using the 9629BNWP combination cupric electrode, fill the electrode with Cat. No. 900063. If using the 9429BN or 9429SC half-cell cupric electrode with the 900200 reference electrode, fill the reference electrode with inner chamber filling solution, Cat. No. 900002, and outer chamber filling solution, Cat. No. 900003.

2. Connect the electrode to the meter.

3. Prepare a 1 M EDTA stock solution by adding 38.0 grams of reagent-grade Na_4EDTA to a 100 mL volumetric flask. Dissolve the solids with about 75 mL of distilled water and then dilute to the mark with distilled water.

4. Prepare an EDTA titrant solution 10 to 20 times as concentrated as the sample by dilution of the 1 M EDTA stock solution. For a good endpoint break, the sample concentration should be at least 10^{-3} M in total copper.

Cupric Titration Procedure

1. Place 100 mL of sample into a 150 mL beaker. Place the electrode in the sample and stir the solution thoroughly.

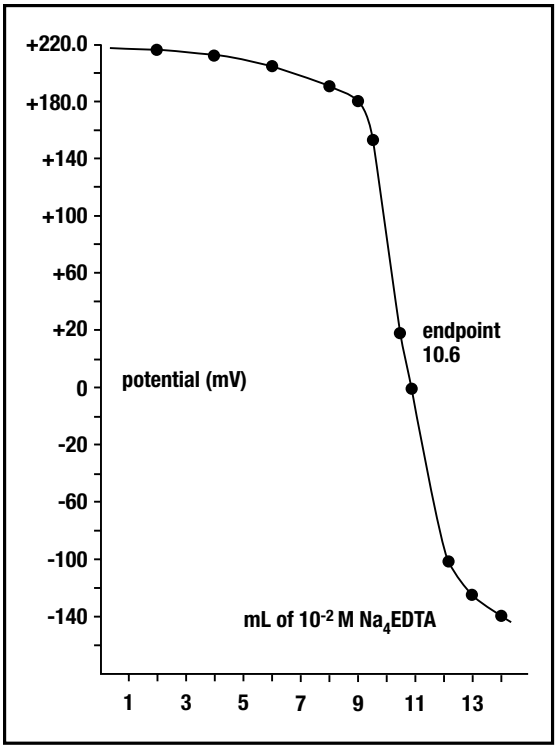
2. Using a 10 mL burette, add increments of titrant and plot the electrode potential against mL of titrant added. The endpoint is the point of greatest slope (inflection point). See **Figure 3**.

3. Calculate the sample concentration before dilution:

   $$C_{sample} = C_t (V_t / V_{sample})$$

   C_{sample} = sample concentration
   C_t = titrant concentration
   V_{sample} = sample volume
   V_t = titrant volume added at endpoint.

Figure 3
Typical Titration of 10^{-3} M $CuCl_2$ with 10^{-2} M Na_4EDTA



Indicator Titrations

The cupric electrode can be used to detect the endpoint in titrations of other metal ions. A small amount of copper complex is added to the sample, and a complexometric titration is done. The endpoint volume of titrant is used to calculate the sample concentration. The minimum level of sample ion that can be determined by indicator titration is above 10^{-4} M. **Table 7** lists several species that can be titrated, with appropriate reagents and titrants.

1. Prepare the 10^{-2} M reagent by titrating the 0.1 M cupric standard exactly to the endpoint with a 0.1 M solution of the titrant to be used (see **Table 7**). Dilute the solution obtained five-fold, using a volumetric flask, to make the reagent.

2. Prepare a titrant solution about 10 times as concentrated as the sample. Place the titrant in a 10 mL burette.

3. Place the electrode in 50 to 100 mL of the sample. Record the sample volume. Add 1 mL of reagent to the sample. Adjust the sample to pH 9. Stir the solution thoroughly during the titration.

4. Add increments of the titrant and record electrode potential. Plot electrode potential as a function of titrant volume on linear graph paper (see **Figure 4**).

5. Calculate the sample concentration:

   $$\mathbf{C_{sample} = C_t\,(V_t\,/\,V_{sample})}$$

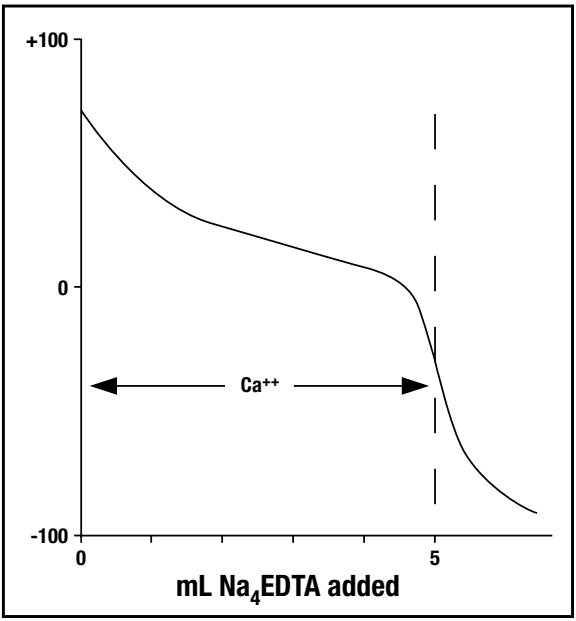
   C_{sample} = sample concentration
   C_t = titrant concentration
   V_{sample} = sample volume
   V_t = titrant volume added at endpoint.

Table 7
Reagents and Titrants for Indicator Titrations

Species	Reagent (10^{-2} M)	Titrant
Barium	CuCDTA	CDTA
Calcium	CuEGTA	EGTA
Cobalt (2+)	CuEDTA	EDTA
Magnesium	CuEDTA	EDTA
Manganese (2+)	CuEDTA	EDTA
Nickel	CuTEPA	TEPA
Strontium	CuEDTA	EDTA
Vanadium	CuEDTA	EDTA
Zinc	CuTEPA	TEPA

Chelometric Indicator Titrations with the Solid-State Cupric Ion Selective Electrode, Ross, J.W., and Frant, M.S.; Anal. Chem., 1969, 41(13), 1900.

Figure 4
Titration of 100 mL of 10^{-3} M Ca^{+2} (CuEDTA indicator added to sample)



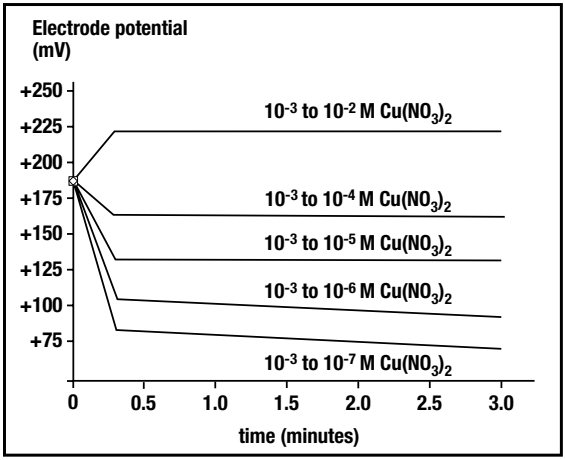
Electrode Characteristics

Electrode Response

The electrode potential plotted against concentration on semi-logarithmic paper results in a straight line with a slope of about 25 to 30 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 5
Typical Electrode Response to Step Changes in $Cu(NO_3)_2$ 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 ± 4 % can be obtained.

Limits of Detection

In neutral solutions, cupric ion concentrations can be measured down to 10^{-8} M or 6 x 10^{-4} ppm. Extreme care must be taken in making determinations below 10^{-5} M or 0.6 ppm to avoid sample contamination or adsorption of cupric ion on container walls.

Temperature Effects

Since electrode potentials are affected by changes in temperature, samples and standard solutions should be within ± 1 °C (± 2 °F) of each other. At the 10^{-3} M level, a 1 °C difference in temperature results in errors greater than 4 %. 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 8**. If the temperature changes, the meter and electrode should be recalibrated.

The electrode can be used at temperatures from 0 to 80 °C, provided that temperature equilibrium has occurred. For use at temperatures substantially different from room temperature, calibration standards should be at the same temperature as samples. The electrode must be used only intermittently at solution temperatures above 80 °C.

Table 8
Theoretical Slope vs. Temperature Values

Temperature (°C)	Slope (mV)
0	27.1
10	28.1
20	29.1
25	29.6
30	30.1
40	31.1
50	32.1

If sample temperatures vary, use of the 9629BNWP combination cupric electrode is recommended. The Optimum Results D filling solution that is included with the electrode will minimize junction potentials and provide optimum temperature and time response.

Interferences

Mercury and silver ions poison the cupric electrode sensing element and must by absent from the sample solution. Exposure to either of these species at levels greater than 10^{-7} M will require polishing of the electrode sensing surface. Ferric ions affect the sensing element only if the ferric ion level is greater than one tenth of cupric ion level (ferric ion can be eliminated from the sample by adding sodium fluoride and adjusting the sample to pH 4 to 6).

If the electrode is exposed to high levels of interfering ions, it may become unstable and sluggish in response. When this happens, restore normal electrode performance by polishing it. Refer to the **Electrode Maintenance** section.

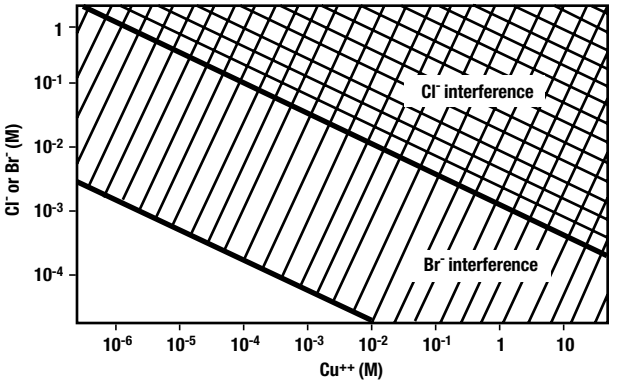
In some cases chloride and bromide ions interfere with the electrode operation. Interference is dependent on the level of chloride or bromide ions relative to the level of cupric ions in the sample and occurs only if the concentrations (in moles per liter) are outside the limits:

$(Cu^{+2})(Cl^{-})_2 > 1.6 \times 10^{-6}$

$(Cu^{+2})(Br)_2 > 1.3 \times 10^{-12}$

Figure 6 shows the regions above the lines in which the cupric ion and chloride or bromide ion levels are high enough to cause electrode malfunction.

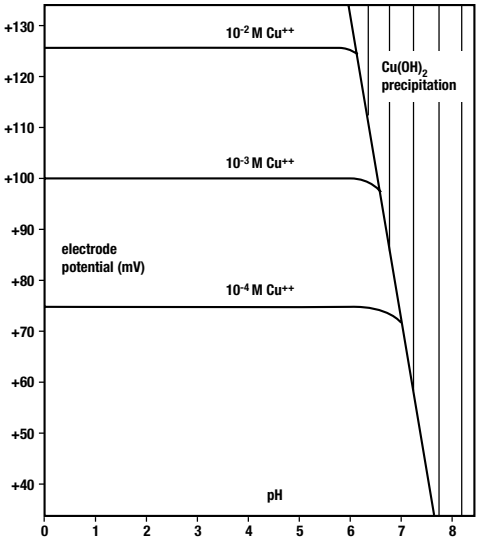
Figure 6
Interference from Chloride and Bromide Ions



pH Effects

The formation of insoluble $Cu(OH)_2$ limits the pH range over which cupric ion measurements can be made. **Figure 7** shows the effects of OH^- in solutions of various cupric ion concentrations. The shaded region indicates the pH range in which the hydroxide ion concentration is high enough to cause precipitation of $Cu(OH)^2$, reducing the level of free cupric ion in the sample. As the figure indicates, the greater the cupric ion concentration, the lower the pH in which cupric hydroxide precipitates. Adjusting sample and standard pH below 6 avoids hydroxide precipitation.

Figure 7
Precipitation of Cupric Ion by Hydroxide Ion



Complexation

Cupric forms complexes with a wide variety of species including acetate, ammonia and organic amines, citrate, amino acids and EDTA. The extent of complexation depends on the concentration of the cupric ion, concentration of the complexing agent and the solution pH. Since the electrode only responds to free cupric ions, complexation reduces the measured concentration. In a large excess (50 to 100 times) of a complexing agent, the total cupric concentration can be measured by known addition.

Soluble cupric salts are precipitated by sulfide, phosphate, hydroxide and other ions. The formation of a precipitate depends on the level of cupric ion, the level of the precipitating ion in the sample solution and the solution pH.

Theory of Operation

The cupric electrode consists of a sensing element bonded into an epoxy body. When the sensing element is in contact with a solution containing cupric ions, an electrode potential develops across the sensing element. This potential, which depends on the level of free cupric 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 cupric ion in solution is described by the Nernst equation.

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

E = measured electrode potential
E_o = reference potential (a constant)
A = cupric ion activity level in solution
S = electrode slope (about 28 mV per decade)
S = (2.3 R T) / nF
R and F are constants, T = temperature in degrees K
and n = ionic charge

The level of cupric ions, A, is the activity or "effective concentration" of free cupric ions in solution. The cupric ion activity is related to free cupric ion concentration, C_f, by the activity coefficient, y.

$$\mathbf{A = y * C_f}$$

The cupric electrode measures cupric ion activity in the same way a pH electrode measures hydrogen ion activity. This can be useful in the study of biological effects and in understanding copper speciation. To measure the cupric ion activity, copper standards are assigned activity values and no ISE or pH adjustments are made to the samples. Estimated cupric ion activities for the cupric nitrate standard are given below. For other cupric solutions, the presence of other species will affect the ion activity.

Table 9
Concentration and activity values of cupric nitrate standardizing solutions at 25 °C

Concentration (M)	Activity (M)
10^{-1}	3.2×10^{-2}
5×10^{-2}	9.6×10^{-3}
10^{-2}	5.5×10^{-3}
5×10^{-3}	1.4×10^{-3}
10^{-3}	7.9×10^{-4}
10^{-4}	9.2×10^{-5}
10^{-5}	10^{-5}

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.

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

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 cupric standards and samples so that the background ionic strength is high and constant relative to variable concentrations of cupric. For cupric, the recommended ISA is 5 M $NaNO_3$. Other solutions can be used as long as they do not contain ions that would interfere with the electrode response to cupric.

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. Optimum Results filling solutions are specifically designed to meet all reference electrode conditions.

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 electrode with fresh filling solution.

4. Repeat the procedure in the **Checking Electrode Operation (Slope)** section.

5. It the electrode fails this procedure again and the half-cell cupric electrode is being used, determine whether the cupric 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, pH Effects** 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.

For the latest application and technical resources for Thermo Scientific Orion products, visit www.thermo.com/waterapps.

Warranty

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

Troubleshooting Checklist

- No electrode filling solution added –
  Fill the 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 electrode cap to allow a few drops of filling solution to drain out of the electrode.

- No reference electrode present –
  The 9429BN and 9429SC cupric half-cell electrodes 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

Cat. No.	Description
9629BNWP	Cupric ionplus Sure-Flow combination electrode, waterproof BNC connector
900063	Optimum Results D electrode filling solution, 5 x 60 mL bottles
9429BN	Cupric half-cell electrode, BNC connector (requires separate reference electrode)
9429SC	Cupric half-cell electrode, screw cap 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
942906	0.1 M cupric standard, 475 mL bottle
940011	ISA for cupric measurements, 475 mL bottle
984201	Polishing strips

Specifications

Concentration Range

10^{-8} M to 0.1 M (6.4 x 10^{-4} ppm to 6354 ppm)

pH Range

2 to 12

Temperature Range

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

Electrode Resistance

Less than 1 megohms

Reproducibility

± 4%

Minimum Sample Size (9629BNWP)

5 mL in a 50 mL beaker

Size– 9629BNWP

Body Diameter: 13 mm

Body Length: 110 mm

Cap Diameter: 16 mm

Cable Length: 1 meter

Size– 9429BN and 9429SC

Body Diameter: 12 mm

Body Length: 110 mm

Cap Diameter: 16 mm

Cable Length: 1 meter (9429BN only)

** Specifications are subject to change without notice*

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