

**pHoenix Electrode Company
Cupric Ion Electrodes
Instruction Manual**

GENERAL INSTRUCTIONS

Introduction

The pHoenix Electrode Company Cupric Ion Electrodes are used to quickly, simply, accurately, and economically measure cupric ion in aqueous solutions.

Required Equipment

1. A pH/mV meter or an ion meter, either line operated or portable.
2. Semi-logarithmic 4-cycle graph paper for preparing calibration curves when using the meter in the mV mode.
3. A magnetic stirrer.
4. The pHoenix Electrode Company Cupric Ion Combination Glass Electrode, Cat. No. CU21502, or the pHoenix Electrode Company Cupric Ion Combination Epoxy Electrode, Cat. No. CU21508.
5. pHoenix Electrode Company Filling Solution, Cat. No. R001015, for both the CU21502 and CU21508 electrodes.
6. Polishing paper or jeweller's rouge to polish dirty or etched electrode membranes.

Required Solutions

1. Deionized or distilled water for solution and standard preparation.
2. pHoenix Electrode Company Ionic Strength Adjuster (ISA), 5M NaNO₃, Cat. No. CU2IS01. To prepare this solution from your own laboratory stock, add 425 grams reagent-grade sodium nitrate, NaNO₃, to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid. Dilute to the mark with distilled water, cap the flask, and upend it several times to thoroughly mix the solution. To each 100 ml of standard or sample, add 2 ml of ISA. The background ionic strength of the resulting solution will be 0.1M.

3. pHoenix Electrode Company Cupric Nitrate Standard Solution, 0.1M, Cat. No. CU2AS01. This solution may be prepared by adding 24.16 grams of reagent-grade $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid. Fill flask to the mark with distilled water, cap the flask, and upend it several times to mix the solution thoroughly.
4. pHoenix Electrode Company Cupric Nitrate Standard Solution, 1000 ppm Cu^{+2} , Cat. No. CU2AS02. This solution may be prepared by adding 3.80 grams of reagent-grade $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid. Fill the flask to the mark with distilled water, cap the flask, and upend it several times to mix the solution thoroughly.
5. EDTA Titrant (1M) for Cupric Titrations.
To prepare this solution from your own laboratory stock, add 37.2 grams of reagent-grade $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ to a 100 ml volumetric flask about three-fourths full of distilled water. Swirl the flask to dissolve the solid. Add distilled water to the mark, cap the flask, and upend it several times to thoroughly mix the solution.

GENERAL PREPARATION

Electrode Preparation

Remove the rubber cap covering the electrode tip and the rubber insert covering the filling hole of the cupric combination ion electrode. Fill the combination electrode with the filling solution shipped with the electrode to a level just below the fill hole. No preparation is required with a sealed reference electrode. Connect the electrode to the proper terminal(s) as recommended by the meter manufacturer.

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

1. To a 150 ml beaker, add 100 ml of distilled water and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution.

2. Using a pipet, add 1 ml of either the 0.1M or 1000 ppm cupric standard to the beaker. When the reading is stable, record the millivolt reading.
3. Using a pipet, add 10 ml of the standard used above to the beaker. When the reading is stable, record the millivolt reading.
4. Determine the difference between the two readings. A difference of 27 ± 2 mV indicates correct electrode operation, assuming the temperature is between 20° and 25°C. See the **TROUBLESHOOTING GUIDE** and **TROUBLESHOOTING HINTS** sections if the potential change is not within this range.

Slope is defined as the change in potential observed when the concentration changes by a factor of 10.

Electrode Slope Check (with ion meter)
(check electrode each day)

1. Prepare standard cupric solutions whose concentrations vary be tenfold. Use either the 0.1M or 1000 ppm stock solutions and the serial dilution method for this preparation.
2. To a 150 ml beaker, add 100 ml of the lower value standard and 2 ml of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the concentration mode, lower the electrode tip into the solution.
3. After the reading has stabilized, adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions.
4. Rinse the electrode with distilled water and blot dry.
5. To a 150 ml beaker, add 100 ml of the higher value standard and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution.
6. After the reading has stabilized, adjust the meter to the concentration of the standard and fix the value in the memory.

7. Read the electrode slope according to the meter manufacturer's instructions. Correct electrode operation is indicated by a slope of 90-100%. If the slope is not within this range, see the TROUBLESHOOTING GUIDE and TROUBLESHOOTING HINTS sections.

MEASUREMENT

Measuring Hints

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

Constant, but not violent, stirring is necessary for accurate measurements. Magnetic stirrers can generate sufficient heat to change the solution temperature. To counteract this effect, place a piece of insulating material, such as styrofoam sheet, between the stirrer and beaker.

Always rinse the electrode with distilled water and blot dry between measurements. Use a clean, dry tissue to prevent cross-contamination.

For samples with high ionic strength, prepare standards whose composition is similar to the sample. Dilute concentrated samples (>0.1M) before measurement.

Use fresh standards for calibration.

Use 2 ml of ISA for each 100 ml of sample or standard.

Always check to see that the membrane is free from air bubbles after immersion into the standard or sample.

Sample Requirements

All samples must be aqueous and not contain organics which can dissolve the epoxy electrode body and/or the cement bonding the sensing crystal to the electrode body. Infrequent measurements in solutions containing methanol, benzene, or acetonitrile are permitted. Highly polar solvents slowly attack the electrode. Please check with pHOenix Electrode Company Electrode Company before using these electrodes in other organic solvents.

The temperature of the standard and of the sample solution should be the same and below 80 degrees C. About a 4% error in the slope will occur for each 1°C difference in temperature.

Interferences should be absent. If they are present, use the procedure found in the **Interference** and **Electrode Response** sections to remove them.

Adjust sample pH with 1M HNO₃ to below pH 7 to avoid precipitation of cupric hydroxide, Cu(OH)₂.

Units of Measurement

Cupric ion concentrations are measured in units of parts per million, moles per liter, equivalents per liter, or any other convenient concentration unit. Table 1 indicates some of these concentration units.

TABLE 1: Concentration Unit Conversion Factors

<u>ppm Cu⁺²</u>	<u>moles/liter</u>
6354.0	1.0X10 ⁻¹
635.0	1.0X10 ⁻²
63.5	1.0X10 ⁻³
6.4	1.0X10 ⁻⁴

MEASUREMENT PROCEDURES

Direct Measurement

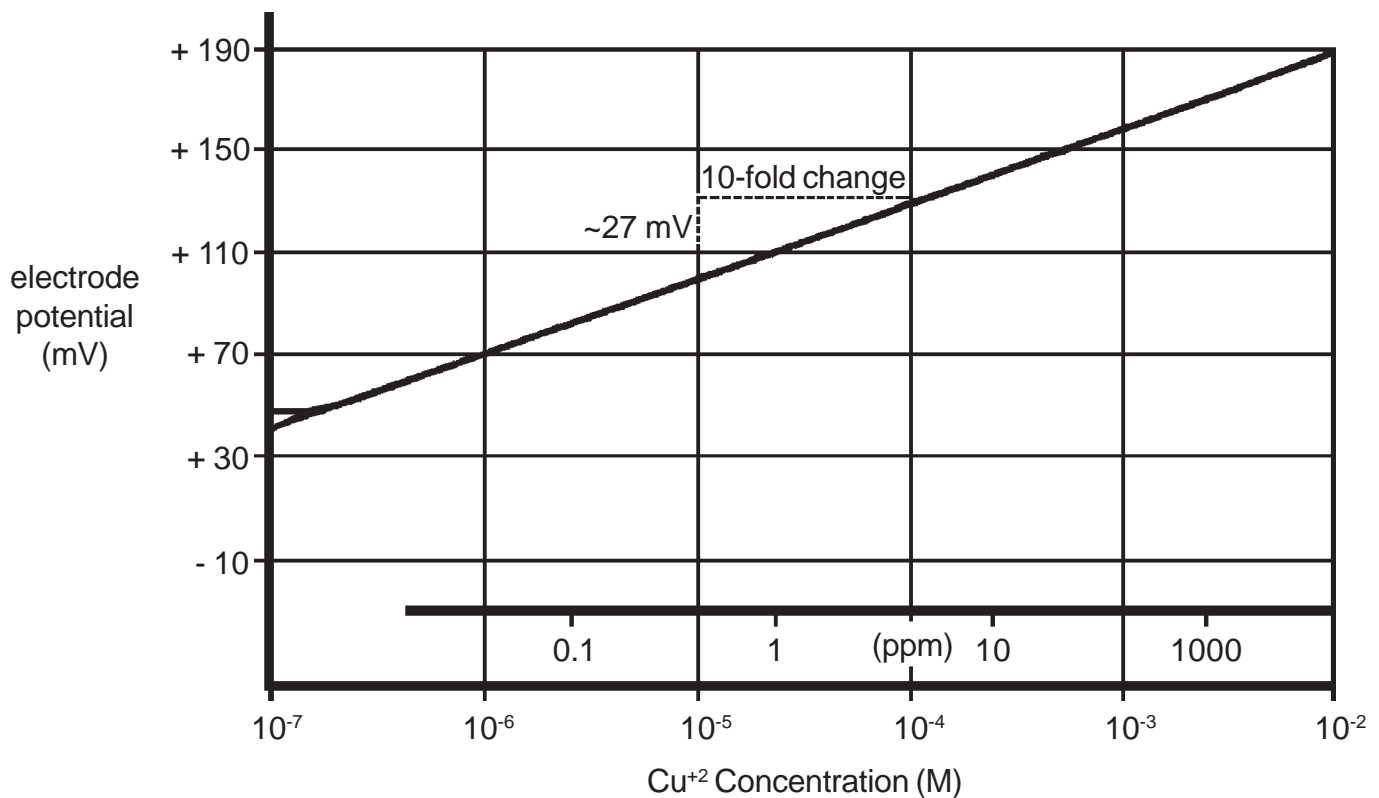
A simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The ionic strength of samples and standards should be made the same by adjustment with ISA. The temperature of both sample solutions and standard solutions should be the same.

Direct Measurement of Cupric Ion (using a standard pH/mV meter)

1. By serial dilution of the 0.1M or 1000 ppm standards, prepare 10⁻², 10⁻³, and 10⁻⁴M or 100 and 10 ppm standards for the cupric ion. To 100 ml of each standard, add 2 ml of ISA. Prepare standards with a composition similar to the samples if the samples have an ionic strength above 0.1M.
2. Place 100 ml of the 10⁻⁴M or 10 ppm standard in a 150 ml beaker, place the beaker on the magnetic stirrer and begin stirring at a constant rate.
3. Lower the electrode tip into the solution. Make sure that the meter is in the mV mode. When the reading has stabilized, record the mV reading.

4. Place 100 ml of the 10^{-3}M or 100 ppm standard in a 150 ml beaker, place the beaker on the magnetic stirrer and begin stirring at a constant rate.
5. After rinsing the electrode with distilled water and blotting dry, immerse the electrode tip in the solution. When the reading has stabilized, record the mV reading.
6. Place 100 ml of the 10^{-2}M or 1000 ppm standard in a 150 ml beaker, place the beaker on the magnetic stirrer and begin stirring at a constant rate.
7. After rinsing the electrode with distilled water and blotting dry, immerse the electrode tip in the solution. When the reading has stabilized, record the mV reading.
8. Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against concentration (log axis). A typical calibration curve can be found in Figure 1.

Figure 1
Typical Cupric (Copper) Electrode Calibration Curve



A calibration curve is constructed on semi-logarithmic paper when using a pH/mV meter in the millivolt mode. The measured electrode potential in mV (linear axis) is plotted against the standard concentration (log axis). In the linear region of the curve, only three standards are necessary to determine a calibration curve. In the non-linear region, additional points must be measured. The direct measurement procedures given are for the linear portion of the curve. The non-linear portion of the curve requires the use of low level procedures.

9. To a clean, dry 150 ml beaker, add 100 ml of the sample and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.
10. After rinsing the electrode tip in distilled water and blotting dry, lower the electrode tip into the solution. When the reading has stabilized, record the mV reading. Determine the concentration directly from the calibration curve.
11. The calibration should be checked every two hours. Assuming no change in ambient temperature, immerse the electrode tip in the midrange standard. After the reading has stabilized, compare it to the original reading recorded in step 5 above. If the reading differs by more than ± 0.5 mV, or the temperature has changed from ambient, recalibrate the electrode.

Direct Measurement of Cupric Ion (using an ion meter)

1. By serial dilution of the 0.1M or 1000 ppm cupric standard, prepare two cupric standards whose concentration is near the expected sample concentration. Measure out 100 ml of each standard into individual 150 ml beakers and add 2 ml of ISA to each.
2. Place the more dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode.
3. Lower the electrode tip into the solution.
4. Adjust the meter to the concentration of the cupric standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

5. Rinse the electrode with distilled water and blot dry.
6. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate.
7. Lower the electrode tip into the solution
8. Adjust the meter to the concentration of the cupric standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
9. Place 100 ml of the sample and 2 ml of ISA into a 150 ml beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.
10. Immerse the rinsed, dried electrode tip in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.
11. The calibration should be checked every two hours. Assuming no change in ambient temperature, immerse the electrode tip in the more dilute standard. After the reading has stabilized, compare it to the original reading recorded in step 4 above. If the reading differs by more than ± 0.5 units, or the temperature has changed from ambient, recalibrate the electrode.

Low Level Cupric Determination (using a standard pH/mV meter)

This procedure is recommended for solutions with cupric concentrations of less than 10^{-5}M (0.6 ppm). If the solution is high in ionic strength, but low in cupric ion, use the same procedure, but prepare a calibration solution with a composition similar to the sample.

1. Using 20 ml of standard ISA, dilute to 100 ml with distilled water. This low level ISA (1.0M NaNO_3) is added at the rate of 1 ml low level ISA to each 100 ml of solution. The background ionic strength will be $1.0 \times 10^{-2}\text{M}$.
2. Dilute 1 ml of 0.1M standard to 100 ml to prepare a $1.0 \times 10^{-3}\text{M}$ solution. Dilute 1 ml of this solution to prepare a 10^{-5}M standard for measurements in moles per liter. Prepare a 1 ppm standard solution by diluting 1 ml of the 1000 ppm standard to 1 liter of solution for measurements in ppm. Standards should be prepared fresh daily.

3. Add 100 ml of distilled water and 1 ml of low level ISA to a 150 ml beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.
4. Place the electrode tip in the solution. Assure that the meter is in the mV mode.
5. Add increments of the $1.0 \times 10^{-5} \text{M}$ or 1 ppm standard as given in Table 2 below.
6. After the reading has stabilized, record the mV reading.

TABLE 2: Stepwise Calibration for Low Level Cupric Measurements

<u>Step</u>	<u>Pipet</u>	<u>Added Volume (ml)</u>	<u>Concentration</u>	
			<u>ppm</u>	<u>M</u>
1	A	0.1	1.0×10^{-3}	1.0×10^{-8}
2	A	0.1	2.0×10^{-3}	2.0×10^{-8}
3	A	0.2	4.0×10^{-3}	4.0×10^{-8}
4	A	0.2	6.0×10^{-3}	6.0×10^{-8}
5	A	0.4	1.0×10^{-2}	9.9×10^{-8}
6	B	2.0	2.9×10^{-2}	2.9×10^{-7}
7	B	2.0	4.8×10^{-2}	4.8×10^{-7}

Pipet A = 1 ml graduated pipet

Pipet B = 2 ml pipet

Solutions: additions of 1 ppm or $1.0 \times 10^{-5} \text{M}$ standard to 100 ml of solution prepared in Step 3 above.

7. On semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis) as in Figure 1.
8. Rinse the electrode and blot dry.
9. Measure out 100 ml of the sample into a 150 ml beaker. Add 1 ml of low level ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution. After the reading has stabilized, record the mV reading and determine the concentration from the low level calibration curve.

10. Prepare a new low level calibration curve daily. Check the calibration curve every two hours by repeating Steps 3-7 above.

Low Level Cupric Determination (using an ion meter)

1. Using 20 ml of standard ISA, dilute to 100 ml with distilled water. This low level ISA (1.0M NaNO_3) is added at the rate of 1 ml low level ISA to each 100 ml of solution. The background ionic strength will be $1.0 \times 10^{-2} \text{M}$.
2. Follow the steps given in **Direct Measurement of Cupric Ion (using an ion meter)** to the end of Step 7.
3. Add 100 ml of distilled water and 1 ml of low level ISA to a 150 ml beaker. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.
4. Lower the electrode tip into the solution. When the reading has stabilized, fix the blank value in the meter according to the meter manufacturer's instructions.
5. Continue with Steps 8-10 in **Direct Measurement of Cupric Ion (using an ion meter)**, remembering to use the low level ISA described in Step 1 above.

Titration

A very accurate determination of total cupric ion concentration. This method makes use of the electrode as an endpoint detector when EDTA is used as a titrant.

Titration of Cupric Ion

The method outlined in this section makes use of the cupric ion electrode as a highly sensitive endpoint detector for cupric-containing samples. The titrant used is EDTA.

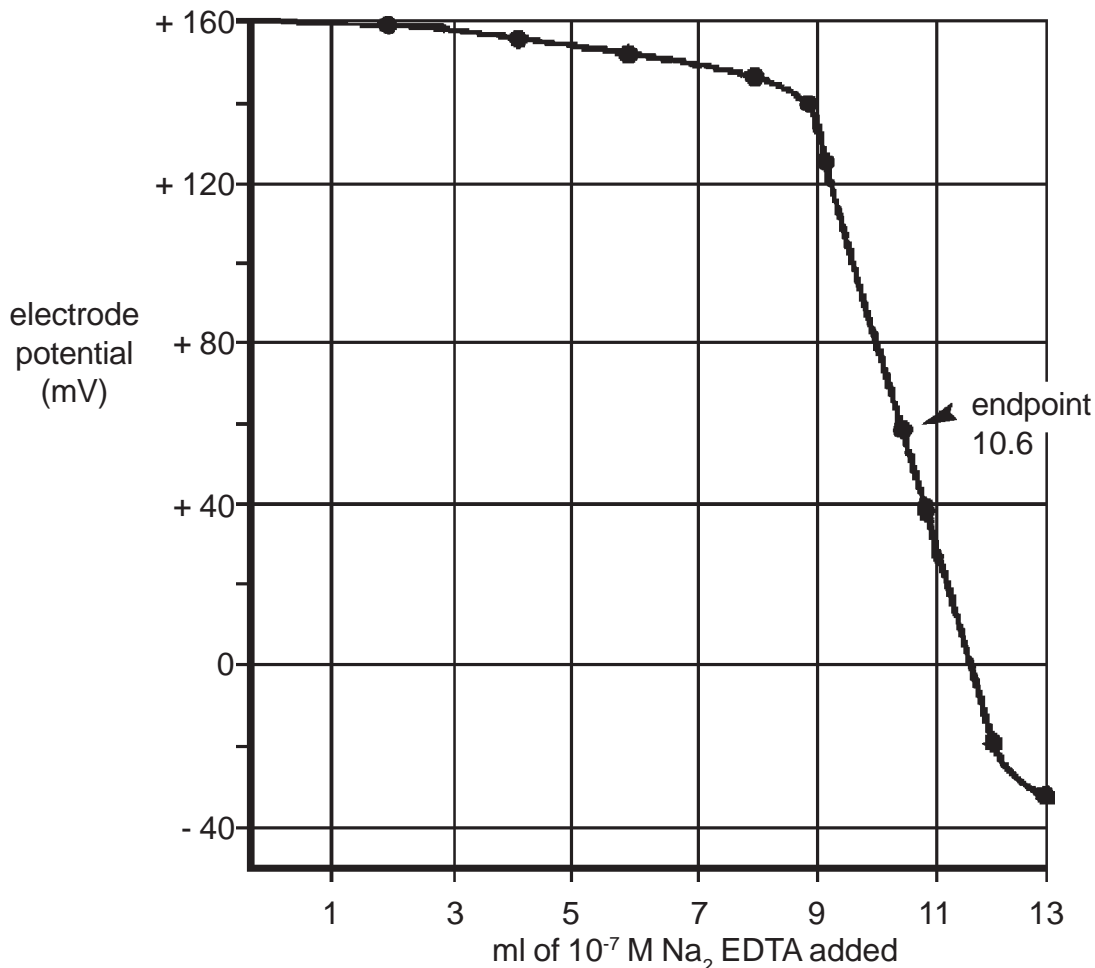
EDTA complexes cupric as well as other cations. The sample pH can be adjusted to a low pH by adding HNO_3 to eliminate unwanted ion complexes. Masking agents may be added in some cases.

1. Prepare the stock EDTA titrant as given in the section **Required Solutions**. Dilute the EDTA to 10 to 20 times as concentrated as the suspected sample concentration. The sample should contain at least $1.0 \times 10^{-3} \text{M}$ cupric ion for a good detection of the end point.

2. Fill a 50 ml buret with the EDTA solution. Pipet 100 ml of the sample into a 150 ml beaker, place the beaker on the magnetic stirrer and begin stirring at a constant rate. Adjust the sample to a low pH by adding HNO_3 .
3. Position the buret tip in the beaker, slightly above the liquid level in the beaker and slightly off center. Position the electrode tip in the solution about halfway between the center of the beaker and the beaker wall.
4. Begin adding the EDTA in 0.5 ml to 1.0 ml increments, followed by smaller increments down to about 0.1 ml to 0.2 ml increments as the potential change increases. Record the mV potential after each addition. Continue the additions several milliliters past the endpoint until little change is noted in the mV reading even when adding 0.5-1.0 ml increments.
5. Plot the milliliters of EDTA added against the mV potential on standard coordinate graph paper. See Figure 2. The point of greatest potential change is the endpoint.

Figure 2

Typical Titration of 100 ml of 10^{-3} M CuCl_2 with 10^{-3} M Na_2EDTA



6. The cupric ion concentration from the unknown is calculated as follows:

$$M_{\text{Cu}}^{+2} = \frac{V_t M_t}{V_{\text{Cu}}^{+2}}$$

where:

M_{Cu}^{+2} = concentration of cupric ion
in the sample (moles/liter)
 V_t = volume of EDTA added at endpoint
 M_t = EDTA concentration (moles/liter)
 V_{Cu}^{+2} = volume of unknown sample (100 ml)

ELECTRODE CHARACTERISTICS

Reproducibility

Electrode measurements reproducible to $\pm 2\%$ can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuations, drift, and noise limit reproducibility. Reproducibility is independent of concentration within the electrode's operating range.

Interferences

A surface layer of silver metal may be formed by strongly reducing solutions. A layer of silver salt may be deposited on the membrane if high levels of ions forming very insoluble salts are present in the sample. Proper performance can be restored by polishing. See the section entitled **Electrode Response** for proper polishing procedure.

The cupric ion electrodes do not respond to anions or most cations. The electrode membrane is poisoned by solutions containing mercury and silver. These ions must be absent from the solution.

If the level of ferric ion is greater than one-tenth the level of cupric ion in the sample, the measurement will be affected. Sodium fluoride added to the sample will eliminate ferric ion.

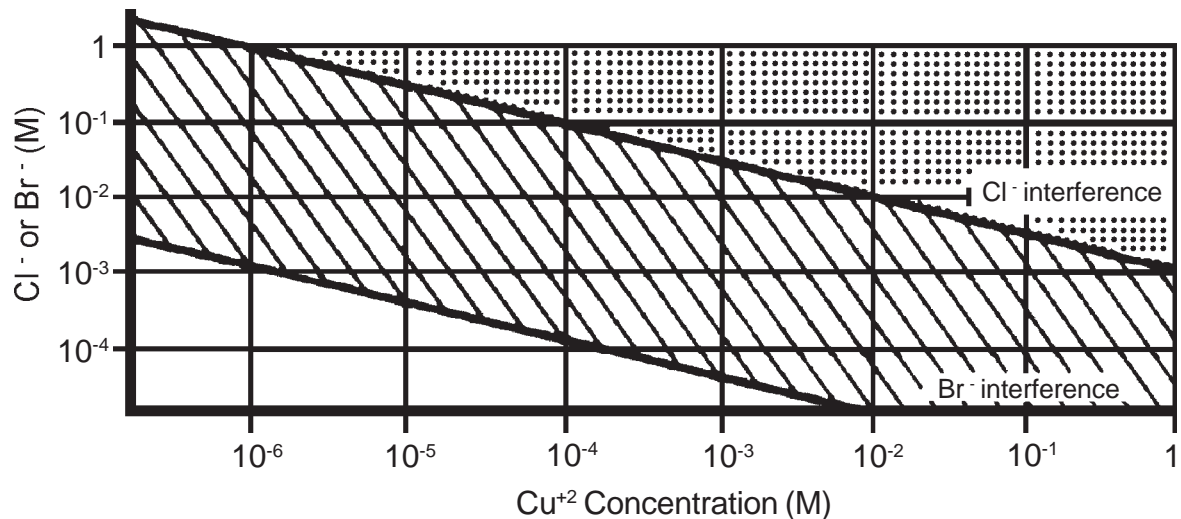
Occasionally, chloride and bromide ions interfere with the electrode's operation. The level of chloride or bromide ion relative to the level of cupric ion in the sample is the determining factor for interference. Interference will occur if the concentrations are outside the following limits (mole/liter).

$$(\text{Cu}^{+2})(\text{Cl}^{-1})^2 > 1.6 \times 10^{-6}$$

$$(\text{Cu}^{+2})(\text{Br}^{-1})^2 > 1.3 \times 10^{-12}$$

Figure 3 indicates the regions in which cupric ion and chloride or bromide ion levels are high enough to cause electrode interference.

Figure 3
Interference from Chloride and Bromide Ion



Precipitation and Complexation

Sulfide, phosphate, hydroxide, and other ions precipitate insoluble cupric salts. The level of cupric ion, the level of the precipitated ion, and the pH of the sample determine formation of a precipitate.

A wide variety of species, including acetate, ammonia, amino acids, citrate, cyanide, and EDTA, form complexes with cupric ion. The total cupric concentration, the concentration of the complexing species, the solution pH, and the ionic strength all determine the extent of complexation. Complexation reduces the free cupric ion concentration and, since the electrode responds only to free cupric ions, a false reading results.

Temperature Influences

Samples and standards should be within $\pm 1^\circ\text{C}$ of each other, since the electrode potentials are influenced by changes in temperature. A 1°C difference in temperature results in a 4% error at $1.0 \times 10^{-3}\text{M}$ cupric ion concentration. Because of the solubility equilibria on which the electrode depends, the absolute potential of the reference electrode changes slowly with temperature. The slope of the electrode, as indicated by

the factor "S" in the Nernst equation, also varies with temperature. Table 3 gives values for the "S" factor in the Nernst equation for the cupric ion.

TABLE 3: Temperature vs. Values for the Electrode Slope.

<u>Temp. (°C)</u>	<u>S</u>
0	27.10
10	28.10
20	29.08
25	29.58
30	30.07
40	31.07
50	32.06

If changes in temperature occur, the electrode should be re-calibrated.

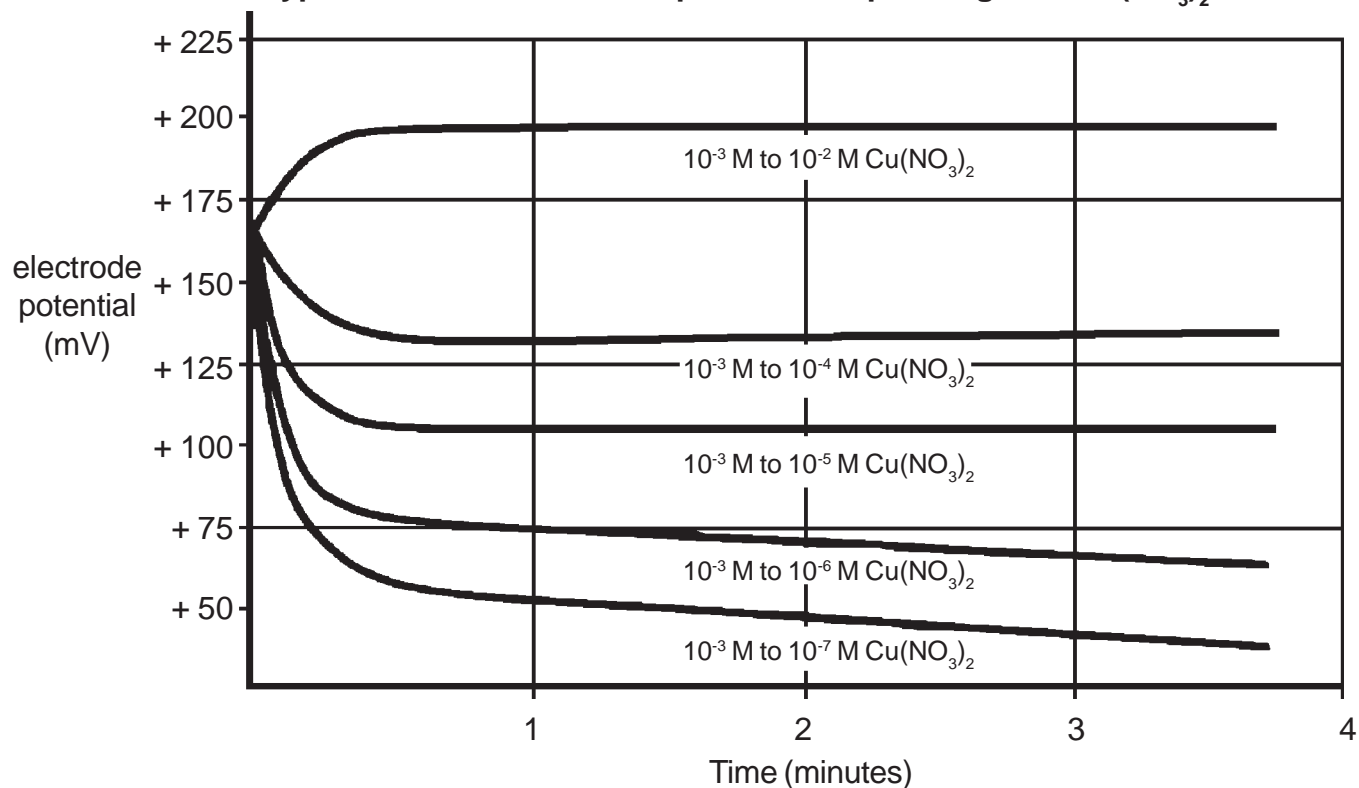
The temperature range for the pHOenix Electrode Company Cupric Ion Electrode is 0°-80°C, provided that temperature equilibrium has occurred. If the temperature varies substantially from room temperature, equilibrium times up to one hour are recommended.

Electrode Response

Plotting the mV potential against the cupric ion concentration on semi-logarithmic graph paper results in a straight line with a slope of about 27 mV per decade. Refer to Figure 1.

The time needed to reach 99% of the stable electrode potential reading, the electrode response time, varies from several seconds in highly concentrated solutions to several minutes near concentrations of $1.0 \times 10^{-5} \text{M}$ cupric ion. Below 10^{-5}M , considerably longer response time can be expected. See Figure 4.

Figure 4
Typical Electrode Time Response to Step Changes in $\text{Cu}(\text{NO}_3)_2$



A drifting potential reading or a decrease in electrode slope may mean that the electrode membrane needs polishing.

To polish the membrane:

1. If using polishing paper, cut off a 1-2" piece and place it face up on the lab bench.
2. Put a few drops of distilled or deionized water in the center of the paper.
3. Holding the paper (cotton) steady with one hand, bring the membrane of the electrode down perpendicular to the paper and, with a slight swirling motion, gently polish the tip of the electrode against the surface of the polishing paper (cotton) for a few seconds.
4. Rinse the electrode surface with distilled or deionized water and soak the electrode tip in standard solution for about five minutes before use.
5. If using jeweller's rouge, place a cotton ball on the table top and flatten it using the bottom of a beaker.

6. Put 1-2 drops of distilled or deionized water in the center of the cotton pad.
7. Add a small amount of jeweller's rouge to the damp cotton.
8. Continue with Steps 3 and 4 above.

Limits of Detection

The upper limit of detection in pure cupric nitrate solutions is 0.1M. In the presence of other ions, the upper limit of detection is above 1.0×10^{-2} M copper, but two factors influence this upper limit. Both the possibility of a liquid junction potential developing at the reference electrode and the salt extraction effect influence this upper limit. Some salts may extract into the electrode membrane at high salt concentrations, causing deviation from the theoretical response. Either dilute samples between 0.1M and 1.0×10^{-2} M or calibrate the electrode at 4 or 5 intermediate points.

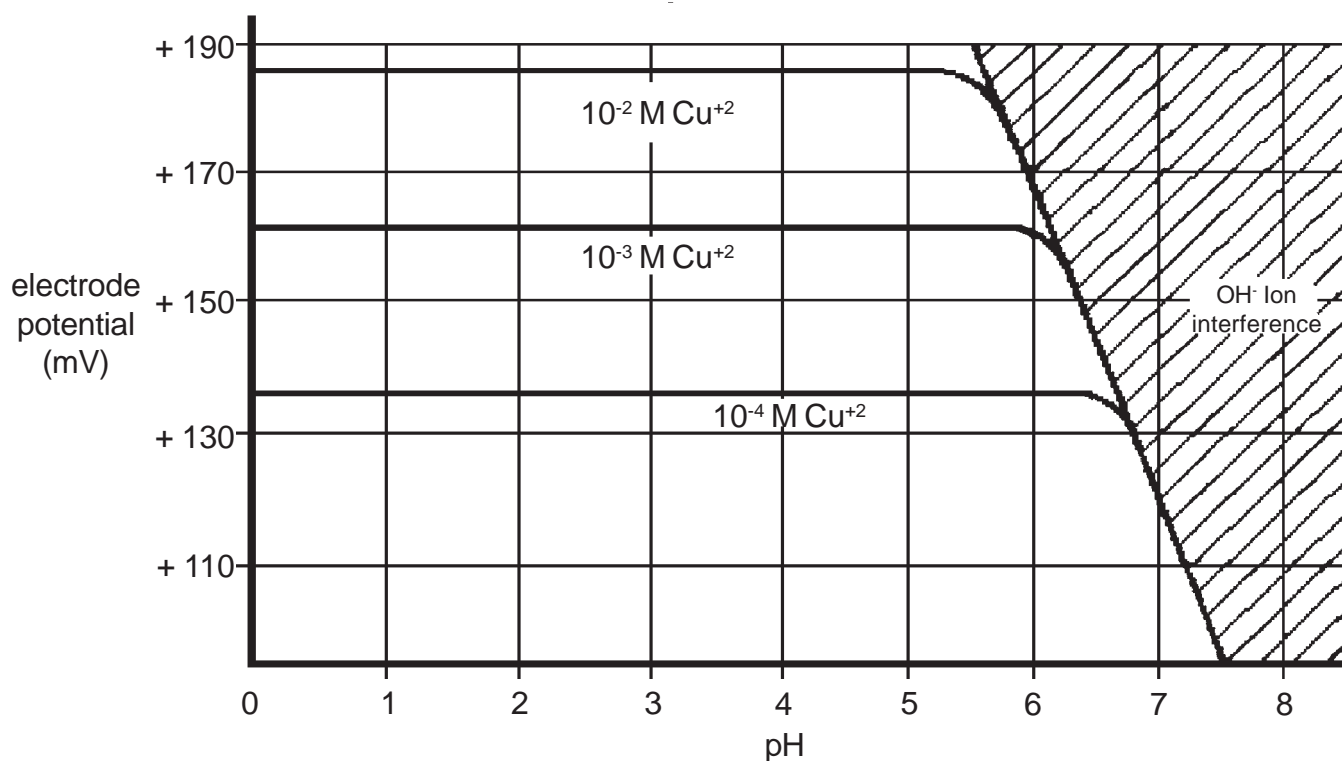
The lower limit of detection is influenced by the slight water solubility of the electrode pellet. Refer to Figure 1 for a comparison of the theoretical response to the actual response at low levels of cupric ion. Neutral solutions containing free cupric ions can be measured down to 1.0×10^{-8} M (0.0006 ppm). Extreme care must be taken with measurements below 1.0×10^{-5} M (0.6 ppm) to avoid contamination of samples.

pH Effects

Figure 5 shows how the electrode responds to cupric ion in solution at various pH levels.

At a high pH, free cupric ion precipitates with hydroxide ion, thereby reducing the cupric ion concentration. The maximum pH at which cupric concentration can be measured without interference from hydroxide is given by a solid line to the left of the lined area on Figure 5. Within this lined area, cupric ion combines with hydroxide to form $\text{Cu}(\text{OH})_2$. Since only free cupric concentration can be measured with the cupric ion electrodes, a false reading results.

Figure 5
Precipitation of Cupric Ion By Hydroxide Ion



Electrode Life

The pHOenix Electrode Company Cupric Ion Electrodes will last six months in normal laboratory use. On-line measurements might shorten operational lifetime to several months. In time, the response time will increase and the calibration slope will decrease to the point calibration is difficult and electrode replacement is required.

Electrode Storage

The pHOenix Electrode Company Cupric Ion Electrodes may be stored for short periods of time in $1.0 \times 10^{-2} \text{ M}$ cupric solution. For longer storage (longer than two weeks), rinse and dry the sensing pellet and cover the membrane tip with any protective cap shipped with the electrode. The reference portion of the combination electrode should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

ELECTRODE THEORY

Electrode Operation

The Phoenix Electrode Company Cupric Ion Electrode is composed of sulfides of copper and other metals bonded into an epoxy or glass body. When an electrode potential develops across the membrane, the membrane is in contact with a solution containing cupric ions. The electrode potential is measured against a constant reference potential, using a standard pH/mV meter. The level of cupric ions, corresponding to the measured potential, is described by the Nernst equation:

$$E = E_o + S \log X$$

where:

E = measured electrode potential
E_o = reference potential (a constant)
S = electrode slope (~27mV)
X = level of cupric ions in solution

The activity, X, represents the effective concentration of free cupric ions in solution. Both bound, C_b, and free, C_f, cupric ions are included in the total cupric ion concentration, C_t. The cupric ion electrode will only respond to free cupric ions, the concentration of which is:

$$C_f = C_t - C_b$$

The activity is related to the free cupric ion by the activity coefficient, \tilde{a} , by:

$$X = \tilde{a} C_f$$

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

$$I = \frac{1}{2} \sum C_x Z_x^2$$

where:

C_x = concentration of ion X
Z_x = charge of ion X
Σ = sum of all the types of ions in the

solution

In the case of high and constant ionic strength relative to the sensed ion concentration, the activity coefficient, \tilde{a} , is constant and the activity, X, is directly proportional to the concentration.

To adjust the background ionic strength to a high and constant value, ionic strength adjuster is added to samples and standards. The recommended ISA solution for the cupric electrodes is sodium nitrate, NaNO_3 . Solutions other than this may be used as ionic strength adjusters as long as ions that they contain do not interfere with the electrode's response to cupric ions.

The reference electrode must also be considered. When two solutions of different composition are brought into contact with one another, liquid junction potentials arise. Millivolt potentials occur from the interdiffusion of ions in the two solutions. Electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions, since ions diffuse at different rates. When making measurements, it is important to remember that this potential be the same when the reference is in the standardizing solution as well as in the sample solution or the change in liquid junction potential will appear as an error in the measured electrode potential.

The composition of the liquid junction filling solution in the reference electrode is most important. The speed with which the positive and negative ions in the filling solution diffuse into the sample should be as nearly equal as possible, that is, the filling solution should be equitransferent. No junction potential can result if the rate at which positive and negative charge carried into the sample is equal.

Strongly acidic (pH = 0 - 2) and strongly basic (pH = 12 - 14) solutions are particularly troublesome to measure. The high mobility of hydrogen and hydroxide ions in samples make it impossible to mask their effect on the junction potential with any concentration of an equitransferent salt. One must either calibrate the electrode(s) in the same pH range as the sample or use a known increment method for ion measurement.

TROUBLESHOOTING GUIDE

The goal of troubleshooting is the isolation of a problem through checking each of the system components in turn: the meter, the glassware, the electrode, the reagents, the sample, and the technique.

Meter

The meter may be checked by following the checkout procedure in the instrument instruction manual.

Glassware

Clean glassware is essential for good measurement. Be sure to wash the glassware well with a mild detergent and rinse very well with distilled or deionized water. Clean glassware will drain without leaving water droplets behind.

Electrode

The electrodes may be checked by using the procedure found in the sections entitled **Electrode Slope Check**.

1. Be sure to use distilled or deionized water when following the procedures given in **Electrode Slope Check**.
2. If the electrode fails to respond as expected, see the sections **Measuring Hints** and **Electrode Response**. Repeat the slope check.
3. If the electrode still fail to respond as expected, substitute another cupric ion electrode that is known to be in good working order for the questionable electrode. If the problem persists and you are using an electrode pair, try the same routine with a working reference electrode.
4. If the problem persists, the reagent may be of poor quality, interferences in the sample may be present or the technique may be faulty. See **Reagents**, **Sample**, and **Technique** sections below.
5. If another electrode is not available for test purposes, or if the electrode in use is suspect, review the instruction manual and be sure to:
 - Clean and rinse the electrode thoroughly.
 - Prepare the electrode properly.
 - Use the proper filling solution.
 - Adjust the pH and the ionic strength of the solution by the use of the proper ISA.
 - Measure correctly and accurately.
 - Review **TROUBLESHOOTING HINTS**.

Reagents

Whenever problems arise with the measuring procedure that has been used successfully in the past, be sure to check the reagent solutions. If in doubt about the credibility of any of the

reagents, prepare them again. Errors may result from contamination of the ISA, incorrect dilution, poor quality distilled/deionized water, or a simple mathematical miscalculation.

Sample

Look for possible interferences, complexing agents, or substances which could affect the response or physically damage the sensing electrode (or the reference electrode) if the electrode(s) work perfectly in the standard, but not in the sample.

Try to determine the composition of the samples prior to testing to eliminate a problem before it starts. See **Measuring Hints**, **Sample Requirements**, and **Interferences**.

Technique

Be sure that the electrode's limit of detection has not been exceeded.

Be sure that the analysis method is clearly understood and that Good Laboratory Practice has been followed.

Refer to the instruction manual again. Reread **GENERAL PREPARATION** and **ELECTRODE CHARACTERISTICS**.

If trouble still persists, call pHOenix Electrode Company at 1-800-522-7920 and ask for the Technical Services Department.

TROUBLESHOOTING HINTS

Symptom	Possible Causes	Next Step
Out of Range Reading	defective meter	check meter with shorting strap see meter instruction manual
	defective electrode	check electrode operation
	electrode not plugged in properly	unplug electrode and reseat
	reference electrode not filled	be sure reference electrode is filled
	air bubble on membrane	remove air bubble by re-dipping electrode
	electrode not in solution	put electrode in solution
Noisy or Unstable Readings (readings continuously or rapidly changing)	defective meter	check meter with shorting strap
	air bubble on membrane	remove air bubble by re-dipping electrode
	ISA not used	use recommended ISA
	meter or stirrer not grounded	ground meter or stirrer
	defective electrode	replace electrode
	electrode exposed to interferences	soak electrode in cupric standard
Drift (reading slowly changing in one direction)	samples and standards at different temperatures	allow solutions to come to room temperature before measurement
	electrode exposed to complexing agents	check section entitled Precipitation and Complexation
	incorrect reference filling solution	use recommended filling solution
Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	ISA not used	use recommended ISA

TROUBLESHOOTING HINTS

Symptom	Possible Causes	Next Step
Low Slope or No Slope	defective electrode	check electrode operation
	air bubble on membrane	remove bubble by re-dipping probe
	electrode exposed to complexing agents	check section entitled Precipitation and Complexation
	standard used as ISA	use ISA
“Incorrect Answer” (but calibration curve is good)	incorrect scaling of semi-log paper	plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration
	incorrect sign	be sure to note sign of millivolt number correctly
	incorrect standards	prepare fresh standards
	wrong units used	apply correct conversion factor: $1.0 \times 10^{-3} \text{ M} = 63.5 \text{ ppm Cu}^{+2}$
	complexing agents in sample	check section entitled Precipitation and Complexation ; use titration

SPECIFICATIONS

Concentration Range: 1×10^{-1} to 10^{-8}M Cu^{+2}
(6354 to 6.4×10^{-4} ppm)

pH Range: 2 to 12

Temperature Range: 0° - 80°C

Resistance: $< 1 \text{ Mohm}$

Reproducibility: $\pm 2\%$

Samples: aqueous solutions only:
no organic solvents

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

Storage: store in cupric solution

ORDERING INFORMATION

P/N	DESCRIPTION
CU21502	Cupric Ion Electrode, combination, glass body
CU21508	Cupric Ion Electrode, combination, epoxy body
CU2AS01	Cupric Nitrate Standard, $0.1 \text{M Cu}(\text{NO}_3)_2$
CU2AS02	Cupric Nitrate Standard, 1000 ppm $\text{Cu}(\text{NO}_3)_2$
CU2IS01	Ionic Strength Adjuster (ISA), 5M NaNO_3
R001015	Electrode Filling Solution, 1M KNO_3 , for both the CU21502 and CU21508 electrodes

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