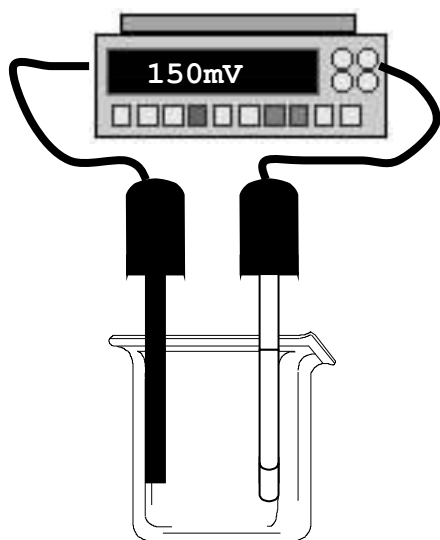
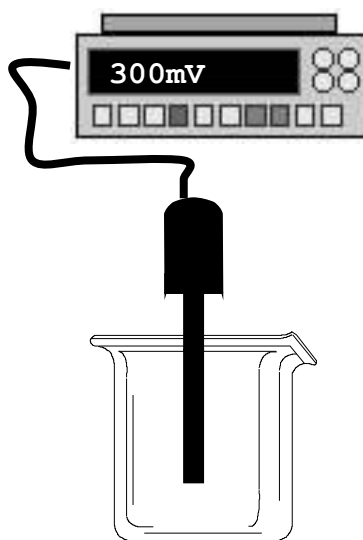


SENTEK

Ion Selective Electrode OPERATING INSTRUCTIONS



Mono/Reference



Combination

SENTEK

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Operating Instructions **Copper Ion Selective Electrode**

This Document includes operating instructions for two types of Ion Selective Electrode. A single sensing Half Cell Copper Electrode which requires a separate Reference Electrode, and a Combination Copper Electrode which has the Reference built into the outer shaft.

For extremely low level work the Half Cell plus Reference Electrode should be used. For general applications the Combination is more convenient.

Depending on the type of ISE chosen you will need to disregard some information for instance if you have the Combination Electrode then disregard any comments about reference electrodes.

A quick guide is included with a more involved section following.

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Quick Guide to Copper ISE

The Copper combination ion selective electrode has a solid state crystalline membrane with an integral driTEK reference. The electrode is designed for the detection and analysis of Copper ions in aqueous solutions and is suitable for use in the field, the laboratory and in on line analysers.

Installation

Connect the ISE to the mV or ion meter.

Remove the black protective cap and keep it in a safe place.

The ISE can be used immediately but pre soaking for 10 minutes in a 100ppm Copper solution is recommended.

The ionic strength of the standards and solutions should be kept constant between all standards and samples. This is achieved by the simple addition of an Ionic strength adjustment buffer (ISAB). Potassium Nitrate is ideal. A typical addition would be 2 ml of 1 molar ISAB to 100 ml of standard and sample.

For low level measurements below around 50ppm in relatively pure samples no ISAB is needed.

No temperature correction is necessary however standards and samples should be measured at the same temperature.

Begin calibration from the lowest concentration standard to avoid cross contamination. Calibration should cover the anticipated range of the samples. Standards should be of similar matrix to the samples being measured. If this is not possible and the results show an offset i.e. are consistently high or low then you should consider using an incremental technique. These techniques are outlined in this manual.

Rinse tip with de-ionised water between measurements.

Avoid strongly acidic or alkaline samples, and organic solvents.

Storage and Maintenance

After use rinse with de-ionised water, replace protective cap and store dry in its box.

If performance becomes sluggish carefully polish the membrane with a fine emery cloth or polishing strip, rinse with de-ionised water and immerse the tip in a 100ppm Copper solution for 10 minutes.

Avoid prolonged exposure to solutions of high concentration.

The Membrane surface should appear shiny and greyish blue in appearance.

Specification

Copper (Cu 2+) is a divalent cation. The electrode is not suitable for measuring monovalent Copper ions.

Refer to the table below for the full specification

Parameter	Specification
Overall length	155 mm
Body Diameter	12 mm
Cap Diameter	16mm
Connector	BNC
Cable length	1000 mm
Resistance at 25 Deg C	< 2.5 Meg Ohm
Concentration Range	0.006 to 64,000 ppm
Slope	23 to 29 mV per decade
Potential Drift	2 mV per day
Operating pH range	2 to 7
Temperature range	5 to 50 Deg C
Endpoint time	Typically 30 to 60 seconds
ISAB	2 Molar KNO3
Interferences: Ions with coefficients above 0.001.	Mercury Silver Sulphide

For Further information or technical assistance please contact your nearest distributor.

Operating Instructions for Copper I.S.E.
Specifications

Range: The Copper Electrode responds to uncomplexed copper ion activity over the range 1×10^{-1} to $1 \times 10^{-5}M$
Linear detection limit is about $5 \times 10^{-5}M$

Interference's:

Interferent	LEVEL
Ag+ Hg ²⁺ S ²⁻	Must be absent
Fe ²⁺ Cd ²⁺ Cl- Br-	

pH Range: The Copper Electrode can be used in the pH range 1-7 but the response decreases about 7 due to hydroxide formation.

Response Time: The Copper Electrode will reach equilibrium in 20 or 30 seconds after a step change in cupric ion concentration.

Temperature Range: 0-80°C

Stability: The long term drift in E_o 2-4mV/day

Section 1

Recommended Equipment

Meter: If using a mV meter without direct reading facility ensure it resolves to 0.1mV

Reference Electrode:
Double Junction with 0.1M KNO₃ in the outer chamber

Magnetic Stirrer

Anglepoise Stand

Required Solutions:

Reference electrode filling solutions.

Inner chamber KCl 3M
Outer Chamber KNO₃ 0.1M

Standard solutions

0.1M Cu (NO₃)₂
1000ppm Cu (NO₃)₂

Ionic Strength Adjustment Buffer (ISAB)

KNO₃ 5M

NB: Only highest quality de-ionised water should be used when preparing solutions and standards.

Section 2

Activity Coefficients

The activity coefficient of copper ion depends upon the ionic strength of the solution.

The following table can be used to calculate the approximate activity coefficients at various ionic strengths.

Ionic Strength	0.001	0.005	0.01	0.05	0.1	0.2
Activity Coeff.	0.975	0.946	0.926	0.853	0.808	0.755

The ionic strength of the solution to be tested can be calculated from the formula:

$$\text{Ionic Strength} = \frac{1}{2} \sum C_i Z_i^2$$

Where C_i is the concentration of species i , Z_i is its charge and all species, cations and anions must be taken into account.

Once the ionic strength is calculated and the activity coefficient found from table above, then the activity of the ion of interest is found from:

$$\text{Activity } (a_i) = \text{Concentration } (c_i) \times \text{Activity Coeff. } (f)$$

If the total ionic strength of all solutions is kept constant by the addition of a solution of high ionic strength that does not react or interfere with standards or samples, then the electrode can be calibrated in concentration units without considering the effects of activity. (see p.5.)

Section 3

Setting Up

The Sensing Electrode

1. Inspect the electrode for damage, particularly to the highly polished membrane which forms the sensing end of the electrode.
2. Place in the special electrode holder and lower into a solution of 0.1M Cu (NO₃)₂.
3. Soak for two hours until the electrode potential remains stable when measured against a double junction reference electrode (Overnight soaking is recommended).
4. The Electrode is now ready for use.

The Reference Electrode

The reference electrode should be prepared as indicated in the reference electrode instruction manual.

Points to remember.

1. Remove protective teat from the end of reference electrode.
2. The fill hole should be left uncovered during use.

The Standard Solutions

10⁻¹M and 1000ppm Cu (NO₃)₂ Solutions are available from the supplier.

To prepare calibration standards (M)

1. Pipette 50ml of 10⁻¹M into a 50ml volumetric flask and make up to the mark with de-ionised water. = 10⁻²M
2. Pipette 10ml of 10⁻²M standard prepared in 1. Into 100ml volumetric flask and make up to the mark with de-ionised water. = 10⁻³M
3. Pipette 1ml of 10⁻²M standard prepared in 1. Into 100ml volumetric flask and make up to the mark with de-ionised water. = 10⁻⁴M

For standards of 1000;100;10 and 1ppm follow procedure 1 to 3 above but use 1000ppm standard as stock solution.

This process of preparation of a series of standards is known as "Serial Dilution".

The Ionic Strength Adjustment Buffer (ISAB)

This is a solution of high ionic strength added to dilute samples and standards before measurement, the purpose of which is to:

1. Ensure that the background ionic strength of all solutions is kept constant.
2. Minimise the difference in ionic strength between samples and standards.
3. Adjust the pH to the correct value for measurement.

The ISAB for the copper electrode can be supplied by the supplier, or it can be prepared by dissolving 126.4g of KNO₃ in a 250ml volumetric flask and making up to the line with de-ionised water.

A Note About Interference's.

An interference is defined as any species (apart from the ion being measured) which affects the measured potential of the sensing electrode/reference electrode pair.

Interference's can be:

1. Species that give a similar response to the ion being measured.
2. Species that interact with the membrane.
3. Species that interact with the ion being measured so decreasing its activity.

The level at which interference occurs for different ions is given on p.1.

Section 4

Calibration and Making a Measurement.

General Hints for Accurate Results.

a) Temperature

ALWAYS ensure that standards and samples are kept at the same temperature and that the temperature remains constant.

b) Stirring

It is preferable to stir standards and samples. Stir such that no vortex is visible. If using a magnetic stirrer it is a good policy to place a piece of insulating material between the plate and the beaker to eliminate any temperature effects arising from the stirrer itself. Some samples are impossible to stir consistently. If this is the case it may be better not to stir but remember to treat any standards in the same way.

Calibration and Measurement Using a pH/mV Meter.

Set the mode or function switch on meter to mV.

1. Prepare standards and electrodes as described in Section 3. Pipette 100ml of 10⁻¹M standard into a beaker and add (accurately) 2.0ml of Ionic Strength Adjustment Buffer (ISAB). Repeat for each of 10⁻², 10⁻³, and 10⁻⁴M standards.
2. Connect the Copper and reference electrode to the meter and place in the special electrode holder in a vertical position.
3. Place electrodes in the 10⁻¹M standard. Wait for a stable reading and record mV value.
4. Raise the electrodes from the solution, rinse with de-ionised water, blot with a tissue and place in the 10⁻²M standard. Wait for a stable reading and record the mV value.
5. Repeat this process sequentially for 10⁻³M and 10⁻⁴M copper solutions and plot the calibration curve of mV reading against the corresponding standard solution concentration using semi-log graph paper. (linear scale = mV; Log scale = concentration)
6. Pipette 100ml of sample into a beaker and add (accurately) 2.0ml of ISAB. Rinse the electrodes with deionised water, blot with a tissue and place in the sample. Wait for a stable reading, record mV value the graph.

Calibration Using a Direct Readout Concentration Meter.

Set the mode or function switch on meter to "Concentration".

1. Prepare standards and electrodes as described in Section 3. Select two standards such that their concentrations bracket the expected sample concentration and are a decade apart. For each standard pipette 100ml into a clean beaker and add (accurately) 2.0ml of Ionic Strength Adjustment Buffer (ISAB)
2. Connect the copper and reference electrode to meter and place in the special electrode holder in a vertical position.
3. Lower electrodes into standard of highest concentration. Wait for a stable reading and enter correct value in the concentration units in which you wish to work.
4. Remove electrodes, rinse with de-ionised water, blot with a tissue and place in second standard. Wait for a stable reading and enter the correct value in concentration units.
5. Pipette 100ml of sample into a beaker and add (accurately) 2.0ml of ISAB. Rinse the electrodes with de-ionised water, blot with a tissue and place in the sample. Wait for a stable reading and read the concentration of the sample directly from the display in concentration units.

Checking the Electrode Slope

This can be done using either of the meter types above.

Set the mode switch on the meter to "mV".

1. Select two standard solutions whose concentration are one decade part. For each standard pipette 100ml into a clean beaker and add (accurately) 2.0ml of Ionic Strength Adjustment Buffer (ISAB).
2. Place the copper and reference electrode in the first standard. Wait for a stable reading and record mV value.
3. Remove electrodes, rinse with de-ionised water, blot with a tissue and place in the second standard. Wait for a stable reading and record mV value.
4. The difference between the two recorded mV values should be 27 ± 2 mV. (If slope is too low see section 5)

Section 5

Problem	Possible Cause (s)	Solution
Wildly erratic readings	<p>Air bubble trapped on outside surface of membrane.</p> <p>Poor connections inside electrode plug.</p> <p>Meter or stirrer not grounded properly.</p> <p>Excessively violent stirring.</p> <p>Reference electrode junction blocked</p> <p>Defective meter</p>	<p>Check outside of membrane and tap electrode to release bubble.</p> <p>Open plug and check wiring.</p> <p>Ground meter or stirrer</p> <p>Reduce stirrer speed</p> <p>Clean junction (see section 6)</p> <p>Check meter with shorting plug.</p>
Steady continuous drift in one direction	<p>Membrane leaking</p> <p>Excessive leakage from reference electrode junction.</p> <p>Temperature drift</p>	<p>Replace electrode</p> <p>Replace reference electrode.</p> <p>Thermostat all solutions or allow to come to room temp. before measurement.</p>
Electrode slope less than 25mV/Decade	<p>Presence of an interfering ion in a constant concentration, swamping the selected ions.</p> <p>Electrode aged</p>	<p>Check performance with fresh standards and ISAB</p> <p>Replace Electrode</p>
Over range reading	<p>Air bubble trapped on inside of membrane.</p> <p>Reference electrode not filled</p> <p>Poor connections inside electrode plugs</p>	<p>Shake electrode (with membrane facing downwards) to release air bubble</p> <p>Fill reference electrode with correct solution</p> <p>Open plugs and check wiring</p>

	Defective meter	Check meter with shorting plug.
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Section 6

Storage and Maintenance

The Copper Electrode

Storage: Short Term: Rinse with distilled water, dry and clamp in air.
 Long Term: Rinse with distilled water, dry and return to the electrode box.

Maintenance: The factors which reduce membrane life, are damage to the membrane surface and hydrolysis of adhesives used to mount the membrane in position.

Do not store in solution.

Inspect the membrane surface for scratches on a regular basis. We can re-polish a damaged membrane (if scratches are not too deep). An occasional polish with a tissue or soft cloth will help keep the membrane shiny.

Check the slope of the electrode on a regular basis. If the slope is less than 25 mV/Decade, it is probably necessary to replace the electrode but first check other possible causes of low slope given in Section 5.

The Reference Electrode

(Always refer to the reference electrode instruction manual)

Storage: Short Term: Overnight the reference can be left soaking in a solution of 0.1M KNO₃.

 Long Term: For periods of storage of longer than two days flush out the external chamber and refill with 3M KCl. Replace the electrode storage teat containing 3M KCl and return electrode to the reference box. (Don't forget to refill with correct filling solution before use).

Maintenance: To ensure good results the internal filling solution should be replaced at least every six months. (More often if necessary). The external chamber should be flushed and refilled about every two weeks.

Always ensure that the level of internal filling solution covers the internal element. Top up the electrode via the side filling hole when needed.

If the external filling solution becomes contaminated by influx of extraneous solutions through the liquid junction: Remove external filling solution using a hypodermic syringe; rinse the outer chamber with de-ionised water followed by 0.1M KNO₃ and then refill with 0.1M KNO₃.

If the inner element becomes contaminated the electrode should be discarded.

The major cause of reference electrode failure is junction blockage, the following steps can be taken to unclog a reference junction.

1. Replace filling solution and soak overnight in filling solution.
2. Force filling solution through the junction by applying pressure to the filling hole, or vacuum to the junction.
3. Soak junction for 10 minutes in dilute filling solution heated to 50 °C Maximum.