Oxygen and Hydrogen in Copper and Copper Alloys

LECO Corporation; Saint Joseph, Michigan USA

Instrument: OH836*

*ONH836 also applicable

Introduction

Copper is the most important material in the electrical conductor wire industry due to its high benefit/cost ratio. Copper provides admirable surface quality, mechanical properties, and high conductivity at a cost much less than silver or gold. Aluminum is the only metal that is routinely substituted for copper, but only in applications where weight is a major factor. One of the most important factors when grading copper is the level of residual impurities, primarily the oxygen level. Oxygen levels in electrical conductor wires typically range from 5-10 ppm (OF – oxygen free, OFE – oxygen-free electronic grades) to around 650 ppm (ETP – electrolytic tough pitch grade). Oxygen levels of up to 200 ppm can actually improve conductivity as it acts as a scavenger element that forms metal oxides with metal contaminants.

High oxygen levels have also been associated with an increase in hydrogen embrittlement even though hydrogen itself has a very low permeability through copper. Hydrogen reacts with the oxygen in oxide inclusions and/or oxygen in solution to create voids. Embrittlement is slow at ambient temperature, but the reaction of cuprous oxide and hydrogen is known to produce steam at higher working temperatures which promotes more rapid intergranular failure.

The inert gas fusion infrared detection method is the most widely used and reliable method for broad range and high precision oxygen and hydrogen determination in copper and copper alloys.

LECO Corporation offers several configurations of fusion determination for this analysis. The following application note outlines the process from sample generation to data.

Accessories

782-720S Graphite Crucibles; 502-040 Tin Capsule (for granular samples); 764-242 Tin Pellet; 782-721 Lower Electrode Tip for 782-720S Crucibles without automation; 618-376 Lower Electrode Tip for 782-720S Crucibles with automation

Note: The 618-376 Lower Electrode Tip is only required if the instrument is equipped with automation.

Calibration Samples

LECO 501-147, 501-148, 501-149, 501-990 One-Gram Nickel Plated Copper Pins with O content determined; LECO 501-529, 762-747 One-Gram Steel Pin with H content determined; NIST, BCR or other suitable reference materials.

Note: Most LECO copper calibration materials are plated with nickel for stability and oxidation resistance. Sample preparation is not required, and the samples are suitable for use straight from the bottle. Refer to the certificate of analysis for details.

Sample Preparation

1. Prepare the samples by abrading the surface and rinsing with solvent.

   Note: The sample preparation of copper for oxygen analysis is an important issue because of the oxidation properties of copper. The method of preparation that is required is physical abrading with a flat mill file. The sample can be cut and abraded with a file to remove the surface impurities. Care must be taken not to overheat the sample and change the chemistry of the copper. Subsequently, the prepared sample may be washed in a suitable solvent such as the methanol. The method requires immediate analysis of the prepared sample to minimize the oxidation of the prepared copper.

Solid Sample Analysis Procedure

1. Prepare the instrument as outlined in the operator's instruction manual.
2. Determine the instrument blank.
   a. Login a minimum of three Blank replicates.
   b. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.
   c. Press the Analyze button on the instrument screen again. The loading head slide-block will close, and the lower electrode will open.
   d. Clean the upper and lower electrode either manually or, if applicable, remove and discard the spent crucible and press the Analyze button again to clean with the automatic cleaner.
   e. Firmly place a 782-720S Graphite Crucible on the lower electrode tip.
   f. Add one 764-242 Tin Pellet to the crucible.
   g. Press the Analyze button on the instrument screen. The lower electrode will close, and the analysis sequence will start and end automatically.
   h. Repeat steps 2b through 2g a minimum of three times.
   i. Set the blank following the procedure outlined in the operator's instruction manual.
3. Instrument calibration/drift correction.
   a. Login a minimum of three Standard replicates.
   b. Weigh ~1.0 to 2.0 g of a calibration/drift sample, enter the mass and sample identification into appropriate replicate fields.

   Note: LECO Nickel Plated Copper Pin Reference Materials do not require preparation. See the preparation statement on the Reference Material Certificate.

Inorganic Application Note

Solid Sample Procedure (continued)

c. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.
d. Place the sample into the open port at the top of the loading head.
e. Press the Analyze button on the instrument screen again. The loading head slide-block will close, and the lower electrode will open.
f. Clean the upper and lower electrode either manually or, if applicable, remove and discard the spent crucible and press the Analyze button again to clean with the automatic cleaner.
g. Firmly place a 782-720S Graphite Crucible on the lower electrode tip.
h. Add one 764-242 Tin Pellet to the 782-720S Crucible.
i. Press the Analyze button on the instrument screen. The lower electrode will close, and the analysis sequence will start and end automatically.
j. Repeat steps 3b through 3i a minimum of three times for each calibration/drift sample used.
k. Calibrate/drift following the procedure outlined in the operator's instruction manual.

4. Analyze Samples.
   a. Login the appropriate number of Sample replicates.
   b. Weigh ~1.0 to 2.0 g of freshly prepared sample, enter mass and identification into appropriate replicate fields.
   c. Repeat steps 3c through 3i for sample analysis.

Method Parameters**

General Parameters		
Sample Introduction	Automated Sample Drop	
Analysis Delay	25 s	
Auto Analyze on Mass Entry	No	
Outgas Before Mass Entry	No	
Wait for User to Load Sample	Yes	
Vacuum On Time	18 s	
Element Parameters	**Oxygen**	**Hydrogen**
Integration Delay	5 s	10 s
Starting Baseline	2 s	2 s
Use Comparator	No	No
Integration Time	35 s	60 s
Use Endline	Yes	Yes
Ending Baseline	2 s	2 s
Range Select	Auto	
Range Lower Limit	800	
Range Upper Limit	950	
Furnace Parameters		
Furnace Control Mode	*Current*	
Outgas Furnace Settings		
Cycles	3	
Current Mode	Constant	
Current	850* A	
Time	20 s	
Cool Time	5 s	
Surface Oxide Removal		
Remove Surface Oxide	No	
Analyze Furnace Settings		
Step 1 Current Mode	Constant	
Current	680* A	
Approximate Cycle Time	*3.5 Minutes*	

*May vary, depending on line voltage. Level can be adjusted to facilitate recovery and/or reduce crucible burn-through.
**The method parameters listed in the table above are optimized for the use of helium as a carrier gas. The use of argon as a carrier gas will require lengthened integration times, as well as reduced outgas and analysis current levels. Please contact the LECO Technical Services Laboratory for additional details.

Automation Parameters (if equipped)

General Parameters	
Auto Cleaner State	Enabled
Auto Cleaner Mode	During Analysis
Clean Time	8 s

Typical Results - Solid Samples

Abraded Samples

Sample	Mass (g)	O%	ppm H
CRM	1.0309	0.0580	0.24
CMO Cu600/I	1.3360	0.0582	0.13
0.0581% O	1.1794	0.0582	0.16
	1.0599	0.0581	0.14
	1.6215	0.0580	0.19
	X=	***0.0581***	***0.17***
	s=	***0.0001***	***0.04***
CRM	1.5926	0.0310	0.12
NIST 885	1.5864	0.0312	0.22
0.031% O	1.5706	0.0310	0.18
	1.5775	0.0309	0.16
	1.5680	0.0311	0.12
	X=	***0.0310***	***0.16***
	s=	***0.0001***	***0.04***
CRM	1.0279	0.0075	0.52
BCR 18	1.1495	0.0075	0.44
0.0070% O	1.2313	0.0075	0.55
	1.2081	0.0076	0.51
	1.6368	0.0074	0.57
	X=	***0.0075***	***0.52***
	s=	***0.0001***	***0.05***

Analyzed as Received

Sample	Mass (g)	O%	ppm H
LECO	1.0015	0.0349	0.78
501-148	0.9989	0.0349	0.73
0.0346% O	1.0022	0.0348	0.70
	1.0019	0.0345	0.50
	1.0018	0.0347	0.88
	X=	***0.0348***	***0.72***
	s=	***0.0002***	***0.14***
LECO	1.0021	0.0240	0.70
501-147	1.0015	0.0240	0.67
0.0239% O	1.0051	0.0239	0.76
	1.0062	0.0241	0.80
	1.0025	0.0240	0.78
	X=	***0.0240***	***0.74***
	s=	***0.0001***	***0.05***
LECO	1.001	0.00029	0.36
501-953	1.0005	0.00029	0.30
0.00027% O	0.9986	0.00026	0.28
	1.0031	0.00029	0.34
	1.0023	0.00033	0.41
	X=	**0.00029**	**0.34**
	s=	**0.00002**	**0.05**

Calibrated with CMO Cu600/I for Oxygen results using a single standard calibration forced through origin.
Calibrated Hydrogen with a steel standard using a single standard calibration forced through origin.

Chip Sample Analysis Procedure

1. Prepare the instrument as outlined in the operator's instruction manual.
2. Determine the instrument blank.
   a. Login a minimum of three Blank replicates.
   b. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.
   c. Place an empty 502-040 Tin Capsule into the open port at the top of the loading head.
   d. Press the Analyze button on the instrument screen again, the loading head slide-block will close and the lower electrode will open.
   e. Clean the upper and lower electrode either manually or, if applicable, remove and discard the spent crucible and press the Analyze button again to clean with the automatic cleaner.
   f. Firmly place the 782-720S Graphite Crucible on the lower electrode tip.
   g. Add one 764-242 Tin Pellet to the crucible.
   h. Press the Analyze button on the instrument screen, the lower electrode will close and the analysis sequence will start and end automatically.
   i. Repeat steps 2b through 2h a minimum of three times.
   j. Set the blank following the procedure outlined in the operator's instruction manual.
3. Instrument calibration/drift correction.
   a. Login a minimum of three Standard replicates.
   b. Weigh ~1.0 g of a calibration/drift sample, enter the mass and sample identification into appropriate replicate fields. Place the sample into an open 502-040 Tin Capsule.

   Note: LECO Nickel Plated Copper Pin Reference Materials do not require preparation. See the preparation statement on the Reference Material Certificate.
   c. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.
   d. Place the tin capsule containing the sample into the open port at the top of the loading head.
   e. Press the Analyze button on the instrument screen again, the loading head slide-block will close and the lower electrode will open.
   f. Clean the upper and lower electrode either manually or, if applicable, remove and discard the spent crucible and press the Analyze button again to clean with the automatic cleaner.
   g. Firmly place the 782-720S Graphite Crucible on the lower electrode tip.
   h. Add one 764-242 Tin Pellet to the crucible.
   i. Press the Analyze button on the instrument screen, the lower electrode will close and the analysis sequence will start and end automatically.

j. Repeat steps 3b through 3i a minimum of three times for each calibration/drift sample used.
k. Calibrate/drift following the procedure outlined in the operator's instruction manual.

4. Analyze Samples.
   a. Login the appropriate number of Sample replicates.
   b. Weigh ~1.0 g of sample into a 502-040 Tin Capsule; enter mass and identification into appropriate replicate fields.
   c. Repeat steps 3c through 3i for sample analysis.

Typical Results - Chip Samples

Sample	*Mass(g)*	*O%*	*ppm H*
Copper Sticks	0.9971	0.0416	5.8
	1.0325	0.0415	5.4
	1.0188	0.0417	5.9
	0.9935	0.0410	5.7
	1.0113	0.0415	5.7
	X=	***0.0415***	***5.7***
	s=	***0.0003***	***0.2***
Copper Chips	1.0118	0.0247	0.55
	0.9974	0.0248	0.47
	1.0084	0.0249	0.55
	0.9962	0.0246	0.48
	1.0092	0.0245	0.47
	X=	***0.0247***	***0.50***
	s=	***0.0002***	***0.04***

Calibrated with CMO Cu600/I for Oxygen results using a single standard calibration forced through origin.
Calibrated Hydrogen with a steel standard using a single standard calibration forced through origin.

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