
## Lab Report CS/ONH 26

# G6 LEONARDO

- Fast and reliable Oxygen and Hydrogen Determination in Copper

### Introduction

Oxygen is used in smelting processes to remove unwanted elements such as sulfur or iron from copper ore in order to retrieve pure copper. A desire for "oxygen-free copper" (OFC, O ≤10 ppm) makes the determination of oxygen an essential quality control criterion.

Because of its highly conductive character, Cu-ETP (Electrolytic Tough Pitch Copper) is the most widely used type of Cu. It is known to have relatively high oxygen concentrations (up to ~600 ppm) and is as such, together with hydrogen, more prone to be affected by the so called "hydrogen sickness" or "hydrogen disease" of copper.

Hydrogen is the most prominent reason for the formation of voids and "bubbles" in solid metals and can thus create lattice defects altering the mechanical properties of the material.

Hence, determining the amount of oxygen and hydrogen is essential for process and quality control in copper production and refining.

The G6 LEONARDO provides a cost-effective, efficient and reliable means of determining oxygen and hydrogen in this material.

## Measuring Principle

The determination of oxygen and hydrogen in solids is based on fusing the sample in a graphite crucible under a flow of inert gas: inert gas fusion (IGF). The G6 LEONARDO is equipped with a high-power electrode furnace, allowing sample temperatures of up to 3000 °C to decompose even refractories. Under the applied conditions, oxygen in the sample reacts with the carbon of the graphite crucible to quantitatively form carbon monoxide (CO). Hydrogen in the sample is released as $H_2$ during melting.

CO is evaluated by advanced, non-dispersive infrared detectors, while hydrogen is determined using a thermal-conductivity detector. CO and $H_2$ are determined directly, absolutely unchanged, 1:1, and with the ideal detection technique by this Smart Molecule Sequence™. During a standard analytical cycle, the crucible is outgassed to remove contaminants. This is achieved by heating it to a temperature ~200 °C above the analysis temperature in an outgassing step prior analysis, resulting in negligible blank values.

Typical sample masses for the determination of oxygen and hydrogen are 0.3 – 1.0 g which can be analyzed without using additional fluxes. The shielded, rotating sample port of the G6 LEONARDO can transfer samples of different shapes like pieces, chips and granules into the crucible without jamming or usage of additional capsules.

If powdered samples are analyzed, tin or nickel capsules are used, for which a blank must be determined.

Tin can be used as a flux to aid melt homogeneity and release of oxygen and hydrogen of the material.

## FusionControl – Temperature matters

The temperature applied to the sample is monitored by an integrated pyrometer (FusionControl) to prevent overheating and formation of undesirable byproducts. Virtual modes like the "power by temperature" mode ensure stable conditions throughout the whole analysis.

## Sample Preparation

If not present in a suitable form, samples can be produced in pin or piece form by punching or cutting. Particularly in regard to oxygen determination, present surface alteration must be removed by etching, first with concentrated HCl for 3 min., and then with an acid mixture for 1 min: acetic acid (99%), nitric acid (65%) and phosphoric acid (85%), each in equal volumes followed by rinsing with distilled water and acetone, three times each.

If the sample was freshly produced, a rinse in acetone and subsequent drying with warm air is sufficient.

Please refer to ASTM E 2575 for a detailed description of the standard practice for sampling and sample preparation of copper and copper alloys.

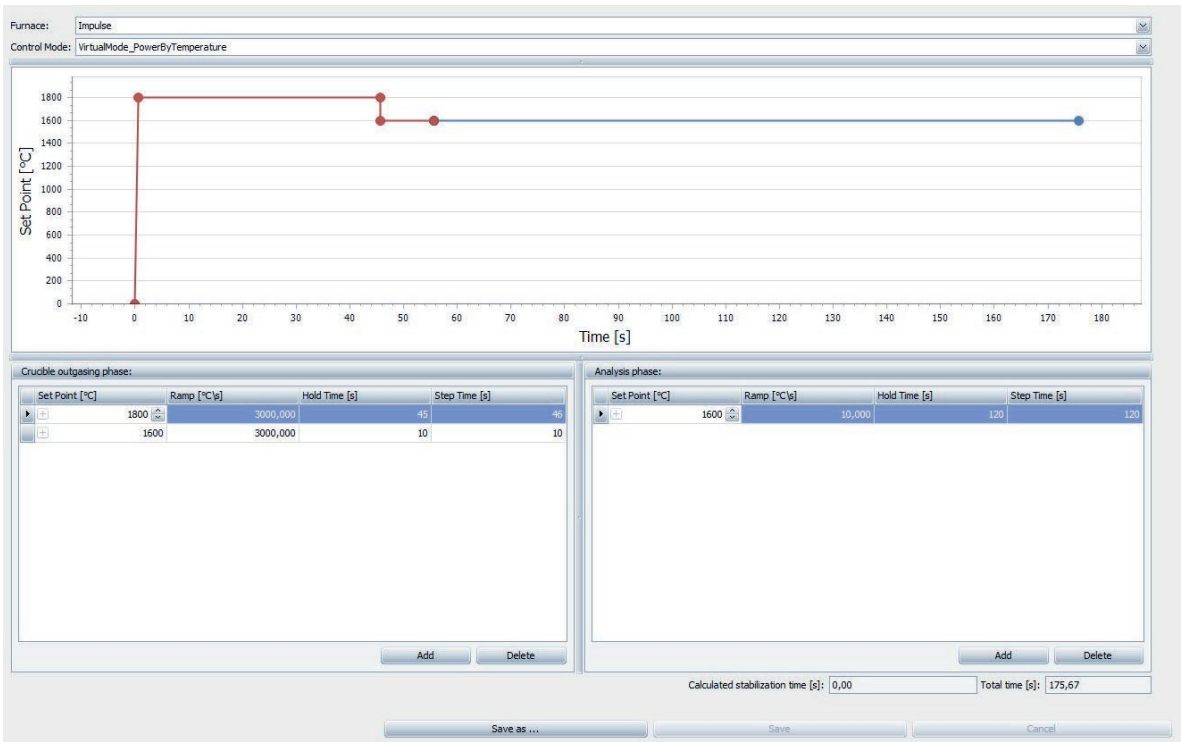


Fig.1: Electrode furnace programming for OH in copper in FUSION.ELEMENTS. Red: outgassing and delay; blue: analysis time.

## Method Parameters

The FUSION.ELEMENTS software introduces virtual control modes for the electrode furnace. This allows direct input of the temperature, although the control mode is power or current.

- Furnace Control: Power (virtual by temperature)
- Outgassing: 1800 °C, 45 s
- Analysis Delay: 1600 °C, 10 s
- Analysis: 1600 °C, isothermal
- Analysis Time: 100-120 s ($N_2$ carrier gas)

The resulting curve of temperature vs. time is graphically visualized in the FUSION.ELEMENTS software.

## Calibration

The calibration of the analyzer is performed by NIST, EZRM or other suitable reference materials. Because of oxygen surface alteration, suitable calibration standards for oxygen are available in pin or ball form and often coated with gold (balls) or tin (pins). There are no certified reference materials (CRM) available for hydrogen in copper. However, for this purpose, steel standards can be used.

## Procedure

### I. Determination of the blank value

From the Calibration Wizard, run a minimum of 3 replicates of the blank value by placing a graphite crucible onto the lower electrode tip and analyze.

To establish a blank for the analysis of powdered samples using capsules: place a capsule (leave capsule open) into the sample port of the analyzer before analyzing. Clean the upper and lower electrode between the replicates.

### II. Measuring reference materials

1. In the calibration wizard, chose the appropriate method. Select CRMs for calibration from the list of standards. If not present, add them with designation, certified concentration and certified error.

2. Weigh ~ 1.0 g of a reference material, transfer its exact mass to the software and place the sample into the sample funnel.

3. Clean upper and lower electrode, place a graphite crucible on the tip of the lower electrode and analyze.

4. Repeat step 2-3, a minimum of three times for each reference material used.

Calibrate the method with the blank values recorded under I. and the results obtained with reference materials II. (for more details refer to the user manual).

### III. Sample measurement

1. In the Measurement Center, weigh an appropriate amount of the prepared sample, transfer its exact mass to the software and place the sample into the sample funnel.

2. Place a graphite crucible on the tip of the lower electrode and analyze.

3. Repeat steps 1-2 for sample analysis. Clean upper and lower electrode at regular intervals and exchange glass wool in the dust trap as needed.

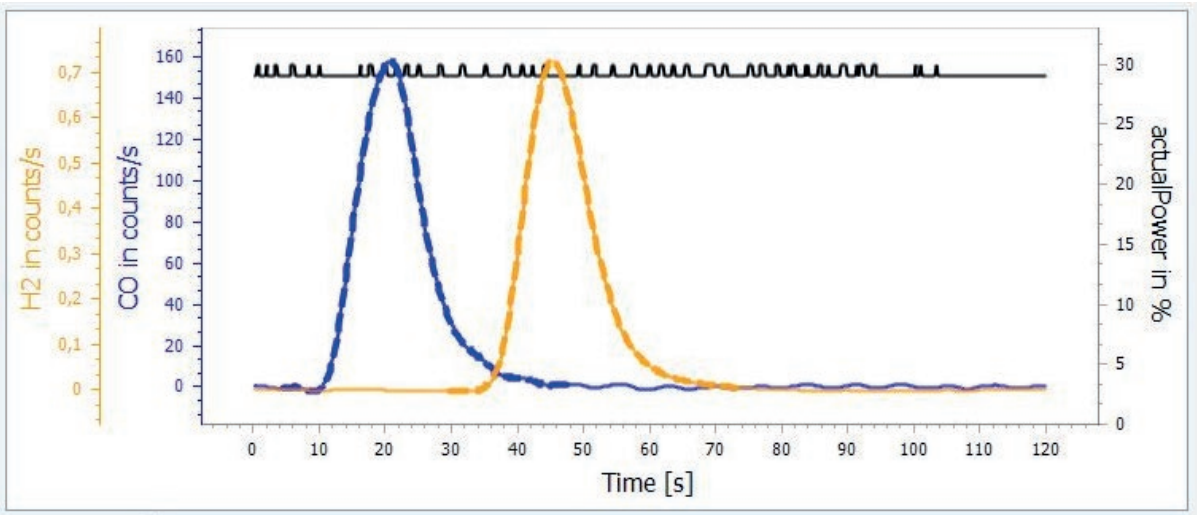


Fig.2: Peak example OFC

## Typical Results

The reproducibility of the G6 LEONARDO and the method outlined is demonstrated by a series of repetitive measurements of standards and production samples.

## Summary

The G6 LEONARDO provides the required precision in a compact and easy to maintain form. Its SampleCare™ mechanism and the powerful but easy to use software allow robust and economic operation. This makes the G6 LEONARDO an ideal choice for the quality control of any metal production industry.

**AR 149**
certified values: O: 0.0312 (± 0.0005) %
H: not certified

| Mass / g | Oxygen / % | Hydrogen / ppm |
|---|---|---|
| 0.3379 | 0.0314 | 0.7 |
| 0.2842 | 0.0313 | 0.4 |
| 0.3299 | 0.0309 | 0.4 |
| 0.3455 | 0.0315 | 0.7 |
| 0.3776 | 0.0310 | 0.4 |
| Mean | 0.0312 | 0.5 |
| STD | 0.0003 | 0.2 |

**AR 147**
certified values: O: 7 (±1) ppm
H: not certified

| Mass / g | Oxygen / ppm | Hydrogen / ppm |
|---|---|---|
| 0.5361 | 6.7 | 0.9 |
| 0.4750 | 6.5 | 0.9 |
| 0.4521 | 7.0 | 1.0 |
| 0.5586 | 6.4 | 0.9 |
| 0.5092 | 6.9 | 1.1 |
| Mean[1)] | 6.7 | 1.0 |
| STD[1)] | 0.3 | 0.1 |

[1)] Mean = arithmetic average; STD = absolute standard deviation (1σ)

**Cu-Rod** (untreated production sample)

| Mass / g | Oxygen / % | Hydrogen / ppm |
|---|---|---|
| 0.5112 | 0.0250 | 3.9 |
| 1.0013 | 0.0256 | 3.3 |
| 0.8679 | 0.0251 | 4.0 |
| 0.9841 | 0.0254 | 3.6 |
| 0.6237 | 0.0246 | 3.2 |
| Mean[1)] | 0.0251 | 3.6 |
| STD[1)] | 0.0004 | 0.4 |



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