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BSI Standards Publication

Copper and copper alloys — Determination of copper content

Part 1: Electrolytic determination of copper in materials with copper content less than 99,85 %

National foreword

This British Standard is the UK implementation of EN 16117-1:2011.

The UK participation in its preparation was entrusted to Technical Committee NFE/34, Copper and copper alloys.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Copper and copper alloys - Determination of copper content - Part 1: Electrolytic determination of copper in materials with copper content less than 99,85 %

Cuivre et alliages de cuivre - Détermination de la teneur en cuivre - Partie 1: Détermination par électrogravimétrie de la teneur en cuivre dans les alliages ayant une teneur en cuivre inférieure à 99,85 %

Kupfer und Kupferlegierungen - Bestimmung des Kupfergehaltes - Teil 1: Elektrolytische Bestimmung von Kupfer in Werkstoffen mit einem Kupfergehalt kleiner als 99,85 %

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Contents

Foreword

This document (EN 16117-1:2011) has been prepared by Technical Committee CEN/TC 133 “Copper and copper alloys”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 2012, and conflicting national standards shall be withdrawn at the latest by April 2012.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

Within its programme of work, Technical Committee CEN/TC 133 requested CEN/TC 133/WG 10 "Methods of analysis" to prepare the following standard:

— EN 16117-1, *Copper and copper alloys — Determination of copper content — Part 1: Electrolytic determination of copper in materials with copper content less than 99,85 %*.

This is one of two parts of the standard for the determination of the copper content of copper and copper alloys. The other part is:

— prEN 16117-2, *Copper and copper alloys — Determination of copper content — Part 2: Electrolytic determination of copper in materials with copper content higher than 99,80 %*.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies an electrolytic method for the determination of the copper content in copper materials with a copper content less than 99,85 % (mass fraction) in the form of unwrought, wrought and cast products.

Silver, if present, is co-deposited and is reported as copper. Approximately one-half of any selenium and tellurium present will co-deposit. Arsenic, antimony, bismuth and tin, if present, also interfere.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 1811-1, *Copper and copper alloys — Selection and preparation of samples for chemical analysis — Part 1: Sampling of cast unwrought products*

ISO 1811-2, *Copper and copper alloys — Selection and preparation of samples for chemical analysis — Part 2: Sampling of wrought products and castings*

3 Principle

Dissolution of a test portion in a fluoroboric and nitric acid mixture. Electrolytic deposition of the copper on a platinum cathode of known weight. Determination of residual copper in the spent electrolyte by atomic absorption spectrometry.

4 Reagents

During the analysis use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Boric acid, H_3BO_3.

4.2 Boric acid solution, 40 g/l H_3BO_3.

Dissolve 40 g of boric acid (4.1) in a 1 000 ml one-mark flask with water, dilute to the mark with water and mix.

4.3 Hydrofluoric acid, HF (ρ = 1,13 g/ml).

4.4 Nitric acid, HNO_3 (ρ = 1,40 g/ml).

4.5 Nitric acid solution, 1 + 1.

Add 500 ml of nitric acid (4.4) to 500 ml of water.

4.6 Ammonia solution, NH_4OH ($\rho \approx$ 0,91 g/ml).

4.7 Hydrochloric acid, HCl, (ρ = 1,19 g/ml).

4.8 Alcohol.

Ethanol: 95 % ± 0,2 %, methanol: min. 99,9 %, other alcohols: higher than 99,9 %.

4.9 Hydrogen Peroxide, H_2O_2 (30 % (mass fraction) solution, ρ = 1,2 g/ml).

5 Apparatus

5.1 Current source.

Preferably, use a 6 V accumulator. If a rectifier is to be used, an additional buffer battery is recommended.

5.2 Electrolysis equipment.

5.2.1 Platinum cathode, Winkler type[1], made preferably from gauze containing approximately 400 meshes per square centimetre, woven from wire of diameter approximately 0,2 mm. The cathode shall be stiffened by doubling the gauze for about 3 mm at the top and the bottom of the cylinder or by reinforcing the gauze at the top and bottom with a platinum band or ring. The diameter of the cylinder shall be 30 mm to 50 mm and the height 40 mm to 60 mm. The stem shall be made from a platinum alloy wire such as platinum-iridium, platinum-rhodium or platinum-ruthenium, having a diameter of approximately 1,3 mm, flattened and welded the entire length of the gauze. The overall height of the cathode shall be approximately 130 mm. The cathode shall be sandblasted.

5.2.2 Spiral anode, made of platinum alloy wire of minimum diameter 1 mm, formed into a spiral of seven turns, having a height of approximately 50 mm and a diameter of 12 mm, the overall height being approximately 130 mm. The spiral section shall be sandblasted.

In the case of an analysis of alloys containing lead, gauze anodes shall be used.

6 Sampling

Sampling shall be carried out in accordance with ISO 1811-1 or ISO 1811-2, as appropriate.

Test samples shall be in the form of fine drillings, chips or millings with a maximum thickness of 0,5 mm.

7 Procedure

7.1 Test portion

Weigh (2,5 ± 0,001) g of the test sample.

7.2 Determination

7.2.1 Transfer the test portion (7.1) to a 400 ml tall-form beaker. Add 15 ml of the boric acid solution (4.2), 2 ml of the hydrofluoric acid (4.3) and 30 ml of the nitric acid solution (4.5). Cover with a watch glass and allow to stand until the reaction has nearly ceased.

7.2.2 Wash the watch glass and the walls of the beaker and boil the solution, or alternatively heat the solution in a boiling water bath for about one hour, to completely expel the oxides of nitrogen. Cool to ambient temperature and dilute the solution with 50 ml of cold water.

NOTE In cases of copper alloys having a lead content < 0,5 %, addition of 2,5 ml of a 5 g/l lead standard solution may advantageously increase the kinetic of the copper deposition. This standard solution is prepared by dissolution of 2,5 g of pure lead (Pb 99,99 % mass fraction) in 50 ml of nitric acid solution (4.5) and, after boiling in order to expel the oxides of nitrogen, is transferred into a 500 ml one-mark volumetric flask, made up to the mark with water and mixed.

Neutralize with ammonia solution (4.6) until a precipitate appears. Re-acidify with the nitric acid solution (4.5) until the precipitate is dissolved. Add 20 ml of the nitric acid solution (4.5) and dilute the solution with water to 300 ml. Add one drop of hydrochloric acid (4.7).

7.2.3 Weigh the cathode (5.2.1) to the nearest 0,1 mg.

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1) Platinum cathodes formed from plain or perforated sheets may also be used.

7.2.4 Position the electrodes (5.2.1 and 5.2.2) in the solution and cover the beaker with two halves of a watch glass, one of which has two indentations through which the electrode stems may pass. Electrolyse at a current of about 1 A to 3 A while slowly stirring the electrolyte. When the solution becomes colourless, wash the watch glass, the electrode stem and the sides of the beaker. Continue the electrolysis until the deposition of the copper is complete, as indicated by failure to plate on a new surface of the cathode stem, when the level of the solution is raised.

NOTE If manganese is present in the sample and it is oxidized to MnO_4^- during electrolysis, drops of hydrogen peroxide solution (4.9) need to be added until the colour due to the oxidized form of manganese disappears.

7.2.5 Without switching off the current, wash the cathode with a stream of water as it is being removed from the spent solution.

Remove the cathode and dip it in ethanol, methanol or other alcohols (4.8).

Dry at 110 °C for 3 min to 5 min and cool to ambient temperature in a desiccator. Determine the mass of the metallic copper deposited.

Reserve the spent electrolyte.

7.2.6 Determine the residual copper in the spent electrolyte by a convenient spectrometric technique such as atomic absorption spectrometry or Inductively coupled plasma optical emission spectrometry. The flame atomic absorption spectrometry method is described in Annex A.

8 Expression of results

Calculate the copper mass fraction, in percent (%),using Equation (1):

$$w_{\mathrm{Cu}} = \frac{(m_1 - m_2) + m_3}{m_0} \times 100 \qquad (1)$$

where

w_{Cu} is the copper mass fraction in per cent (%);

m_0 is the mass of the test portion (7.1), in grams (g);

m_1 is the mass of the cathode plus the electro-deposited copper, in grams (g);

m_2 is the mass of the cathode (5.2.1), in grams (g);

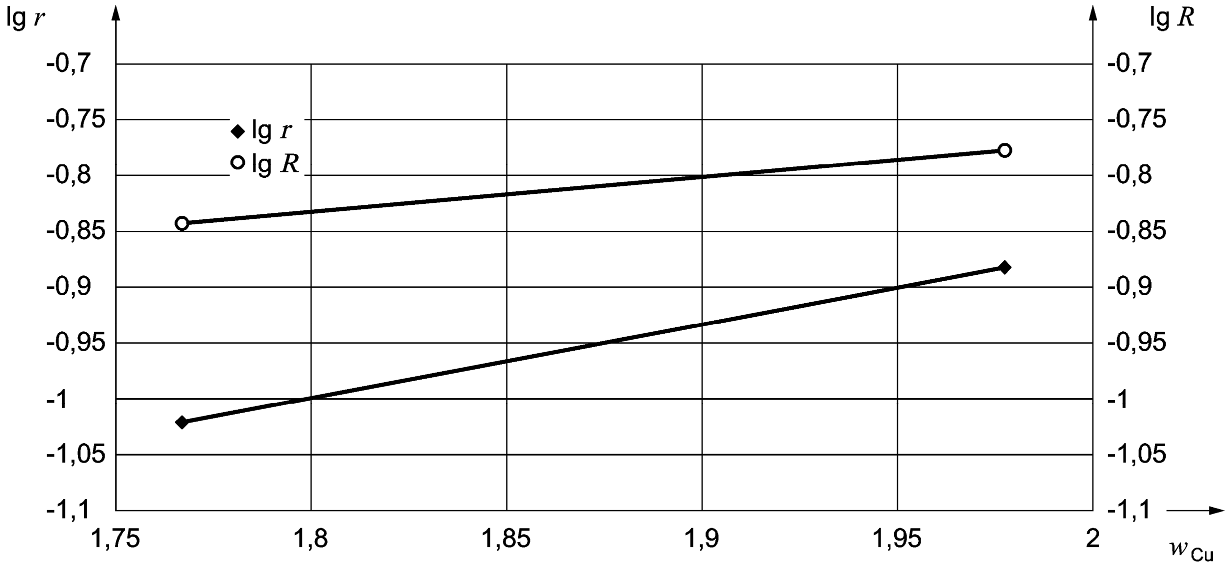
m_3 is the mass of residual copper found in the spent electrolyte (Annex A), in grams (g).

9 Precision

Twelve laboratories co-operated in testing this method and obtained the results summarized in Table 1 and Figure 1 respectively.

Table 1 — Statistical information

Level	Reference value %	Found %	Repeatability r	Reproducibility R
1	58,5	58,494	0,095	0,144
2	95,0	94,977	0,132	0,167



$$\lg R = 0{,}309\,8 \lg w_{Cu} - 1{,}390\,8$$

$$\lg r = 0{,}688\,7 \lg w_{Cu} - 2{,}240\,5$$

Figure 1 — lg relationship between copper concentration w_{Cu} and r and R

10 Test report

The test report shall contain the following information:

a) identification of the test sample;

b) reference to this European Standard (EN 16117-1);

c) method used;

d) results;

e) any unusual characteristics noted during the determination;

f) any operation not included in this European Standard or in the document to which reference is made or regarded as optional;

g) date of the test and/or date of preparation or signature of the test report;

h) signature of the responsible person.

Annex A
(normative)

Spent electrolyte — Determination of residual copper — Flame atomic absorption spectrometric method (FAAS)

A.1 General

This Annex specifies a flame atomic absorption spectrometric method (FAAS) for the determination of the copper content of spent electrolyte after the deposition of copper on the electrode as described in 7.2.4 and 7.2.5.

NOTE Elements and reagents ordinarily present in the spent electrolyte do not interfere.

A.2 Principle

Aspiration of the test solution into an air-acetylene flame of an atomic absorption spectrometer and determination of the copper content by measurement of the absorption of the most convenient lines (324,8 nm or 327,4 nm) emitted by a copper hollow-cathode lamp.

A.3 Reagents

During the analysis use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

A.3.1 Nitric acid, HNO_3 (ρ = 1,40 g/ml).

A.3.2 Nitric acid solution, 1 + 1.

Add 500 ml of nitric acid (A.3.1) to 500 ml of water.

A.3.3 Boric acid, H_3BO_3.

A.3.4 Boric acid solution, 40 g/l H_3BO_3.

Dissolve 10 g boric acid (A.3.3) in a 250 ml one-mark flask in water, dilute to the mark with water and mix.

A.3.5 Hydrofluoric acid, HF (ρ = 1,13 g/ml).

A.3.6 Acid mixture solution.

In a 500 ml one-mark volumetric flask introduce:

- 150 ml of boric acid solution (A.3.4);
- 20 ml of hydrofluoric acid (A.3.5);
- 300 ml of nitric acid solution (A.3.2);

add water up to the mark and mix.

A.3.7 Ammonia solution, NH_4OH ($\rho \approx$ 0,91 g/ml).

A.3.8 Copper stock solution, 1,0 g/l Cu.

Weigh (1 ± 0,001) g of pure copper (Cu ≥ 99,9 %) and transfer it into a 250 ml beaker. Add 10 ml of nitric acid solution (A.3.2) and cover with a watch glass. After dissolution, warm the solution to expel nitrous fumes. Cool to room temperature and transfer into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this solution contains 1,0 mg of Cu.

A.3.9 Copper standard solution, 0,02 g/l Cu.

Transfer 5 ml of the copper stock solution (A.3.8) into a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this solution contains 20 µg Cu.

A.4 Apparatus

A.4.1 Atomic absorption spectrometer, fitted with an air/acetylene burner.

A.4.2 Copper hollow-cathode lamp.

A.5 Procedure

A.5.1 Test solution

If necessary, evaporate the spent electrolyte (see 7.2.5) to below 250 ml and cool. Transfer to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

A.5.2 Preparation of the calibration

A.5.2.1 Preparation of the calibration solutions

Into each of a series of six 100 ml one-mark volumetric flasks, introduce 0 ml, 5 ml, 10 ml, 15 ml, 20 ml and 25 ml respectively of the copper standard solution (A.3.9), equivalent to 0 mg, 0,25 mg, 0,50 mg, 0,75 mg, 1,00 mg and 1,25 mg of copper per 250 ml. Add 20 ml of acid mixture solution (A.3.6) to each flask, neutralize with ammonia solution (A.3.7), using, for example, an indicator paper, then add 8 ml of nitric acid solution (A.3.2), cool, dilute to the mark with water and mix. The zero term of the calibration solutions corresponds to the blank test of the reagents for the calibration curve.

A.5.2.2 Adjustment of the atomic absorption spectrometer

Fit the copper hollow-cathode lamp (A.4.2) into the spectrometer (A.4.1), switch on the current and allow it to stabilize. Adjust the wavelength in the region of the most convenient lines (324,8 nm or 327,5 nm) to minimum absorbance. Following the manufacturer's instructions, fit the correct burner, light the flame and allow the burner temperature to stabilize. Taking careful note of the manufacturer's instructions regarding the minimum flow rate of acetylene, aspirate the calibration solution of highest concentration of analyte and adjust the burner configuration and gas flows to obtain maximum absorbance.

A.5.2.3 Spectrometric measurement of the calibration solutions

Aspirate the series of calibration solutions (A.5.2.1) in succession into the flame and measure the absorbance for each. Take care to keep the aspiration rate constant throughout the preparation of the calibration curve. Spray water through the burner after each measurement.

A.5.2.4 Calibration curve

Establish the calibration curve using measured absorbances and corresponding analyte amounts. Use appropriate spectrometer software or an off-line computer for regression calculations or prepare a graphical representation.

A.5.2.5 Plotting the calibration curve

Plot a curve having the masses, in grams of copper contained in 250 ml of the calibration solutions, as abscissas and the corresponding values of the measured absorbance, deduced by the value of the absorbance measured in the blank test of the reagents for calibration, as ordinates.

A.5.3 Determination

A.5.3.1 Preliminary spectrometric measurements

Carry out a preliminary measurement on the test solution (A.5.1) following the procedure specified in A.5.2.3 at the same time as the spectrometric measurements are carried out on the calibration solutions (A.5.2.1). Estimate the preliminary analyte amount by using the calibration curve according to A.5.2.4 and A.5.2.5.

A.5.3.2 Spectrometric measurements

A.5.3.2.1 Use of the calibration curve

Repeat the measurements and determine the concentration directly using the calibration curve.

A.5.3.2.2 Use of bracketing method

Carry out a second measurement on the test solution (A.5.1) following the procedure specified in A.5.2.3 by bracketing between two new calibration solutions with composition similar to that of the calibration solutions (A.5.2.1) but having copper concentrations slightly higher and slightly lower (± 10 %) than the estimated copper concentration of the test solution (A.5.1).

To prepare these standard calibration solutions, follow the procedure specified in A.5.2.1 using, however, suitable quantities of copper standard solution (A.3.9).

A.6 Expression of results

A.6.1 Use of the calibration curve

Calculate the copper mass (m_3) in grams (g) using Equation (A.1):

$$m_3 = A_1 \times V_\mathrm{f} / 1000 \quad \text{(A.1)}$$

where

A_1 is the copper concentration from the calibration curve, in milligram per millilitre (mg/ml);

V_f is the volume of the final test solution (A.5.1) in millilitre (ml).

A.6.2 Use of bracketing method

Calculate the copper mass (m_3) in grams (g) using Equation (A.2):

$$m_3 = A_2 \times V_\mathrm{f} / 1000 \quad \text{(A.2)}$$

where

A_2 is the copper concentration calculated using Equation (A.3), in milligram per millilitre (mg/ml);

V_f is the volume of the final test solution (A.5.1), in millilitre (ml).

$$A_2 = C_1 + (C_2 - C_1) \times \frac{S_0 - S_1}{S_2 - S_1} \qquad \text{(A.3)}$$

where

C_1 is the lower copper concentration of the calibration solution used (A.5.3.2.2), in milligram per millilitre (mg/ml);

C_2 is the higher copper concentration of the calibration solution used (A.5.3.2.2), in milligram per millilitre (mg/ml);

S_0 is the absorbance value of the test solution (A.5.1);

S_1 is the absorbance value of the calibration solution corresponding to the concentration C_1;

S_2 is the absorbance value of the calibration solution corresponding to the concentration C_2.

Bibliography

[1] ISO 1554, *Wrought and cast copper alloys — Determination of copper content — Electrolytic method*

[2] ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

[3] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[4] ISO 5725-3, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method*

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