SLOVENSKI STANDARD
SIST EN 16117-1:2011

01-december-2011

Baker in bakrove zlitine - Določevanje bakra - 1. del: Elektrolitsko določevanje bakra v materialih z deležem bakra, manjšim od 99,85 %

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

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

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

Ta slovenski standard je istoveten z: EN 16117-1:2011

ICS:

77.120.30	Baker in bakrove zlitine	Copper and copper alloys

SIST EN 16117-1:2011 en,fr,de

EUROPEAN STANDARD
NORME EUROPÉENNE
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EN 16117-1

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ICS 77.120.30

English Version

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 %

This European Standard was approved by CEN on 27 August 2011.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of 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 United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. EN 16117-1:2011: E

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);

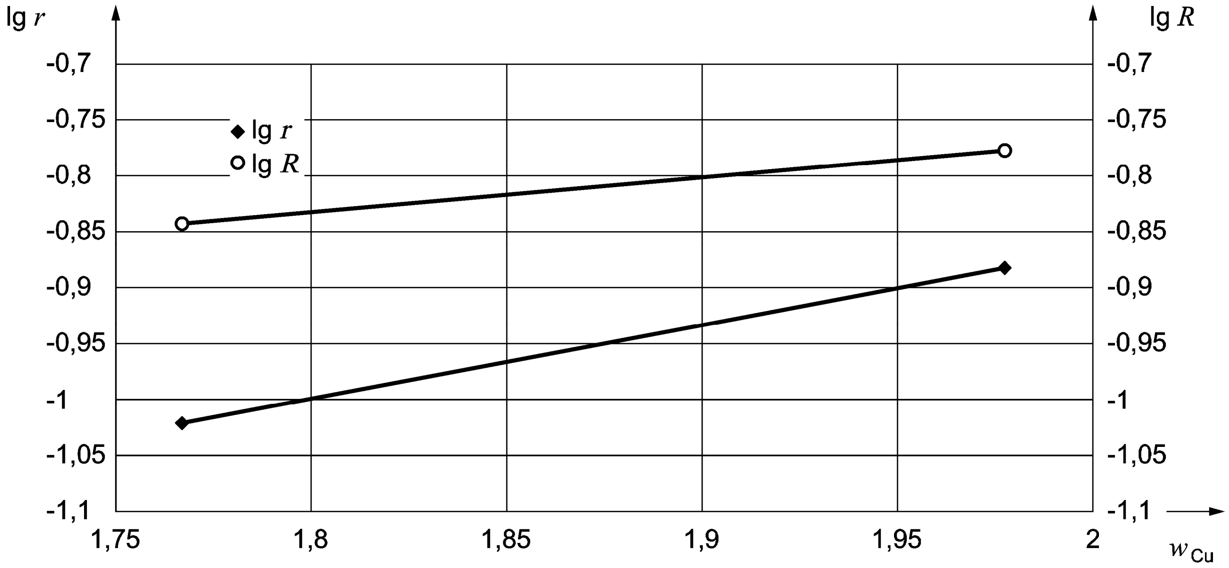
m_3 is the mass of residual copper found in the spent electrolyte (Annex A), in grams (g).

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



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

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

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.