SLOVENSKI STANDARD

SIST EN 14937-1:2006

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Baker in bakrove zlitine ï Doloļ evanje antimona ï 1. del: Spektrometrijska metoda

Copper and copper alloys - Determination of antimony content - Part 1: Spectrophotometric method

Kupfer und Kupferlegierungen - Bestimmung des Antimongehaltes - Teil 1: Spektrophotometrisches Verfahren

Cuivre et alliages de cuivre - Dosage de l'antimoine - Partie 1 : Méthode spectrophotométrique

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English Version

Copper and copper alloys - Determination of antimony content - Part 1: Spectrophotometric method

Cuivre et alliages de cuivre - Dosage de l'antimoine - Partie 1 : Méthode spectrophotométrique

Kupfer und Kupferlegierungen - Bestimmung des Antimongehaltes - Teil 1: Spektrophotometrisches Verfahren

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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 Central Secretariat has the same status as the official versions.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
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Foreword

This document (EN 14937-1:2006) 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of an identical text or by endorsement, at the latest by December 2006, and conflicting national standards shall be withdrawn at the latest by December 2006.

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 14937-1, *Copper and copper alloys — Determination of antimony content — Part 1: Spectrophotometric method*

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

EN 14937-2, *Copper and copper alloys — Determination of antimony content — Part 2: FAAS method*

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, 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.

1 Scope

This part of this European Standard specifies a Rhodamine B spectrophotometric method for the determination of the antimony content of copper and copper alloys in the form of unwrought, wrought and cast products.

The method is applicable to products having antimony mass fractions in the range between 0,001 % and 0,1 %, or greater by appropriate modification of the mass of the test portion, the volume of the test portion solution to be taken for the extraction and the cell path length.

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*

NOTE Informative references to documents used in the preparation of this standard, and cited at the appropriate places in the text, are listed in the Bibliography.

3 Principle

Extraction of pentavalent antimony into isopropyl ether and spectrophotometric determination of the chloro-antimonate-Rhodamine B complex.

4 Reagents and materials

4.1 General

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

4.2 Isopropyl ether, $(CH_2)_2CHOCH(CH_2)_2$.

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

4.4 Hydrochloric acid solution, 7 + 3

Dilute 700 ml of hydrochloric acid (4.3) in 300 ml of water.

4.5 Hydrochloric acid solution, 1 mol/l

Dilute 83 ml of hydrochloric acid (4.3) in 500 ml of water and make up to 1 000 ml with water.

4.6 Hydrogen peroxide solution, H_2O_2 30 % (mass fraction).

4.7 Cerium(IV) sulfate solution

Dissolve 4 g of cerium(IV) sulfate tetrahydrate [$Ce(SO_4)_2 \cdot 4H_2O$] in 50 ml of 0,5 mol/l sulfuric acid solution and dilute to 100 ml with the same acid.

4.8 Hydroxylammonium chloride solution

Dissolve 1 g of hydroxylammonium chloride [$NH_2OH \cdot HCl$] in water and dilute to 100 ml.

Prepare this solution immediately prior to use.

4.9 Rhodamine B solution

Dissolve 0,01 g of Rhodamine B and dilute to 100 ml with hydrochloric acid solution (4.5).

Filter the solution before use.

4.10 Antimony stock solution, 1,000 g/l Sb

Dissolve 0,274 3 g of potassium antimonyl tartrate hemihydrate [$K(SbO)C_4H_4O_6 \cdot 0{,}5H_2O$] and make up to volume with the hydrochloric acid solution (4.4) in a 100 ml one-mark volumetric flask.

1 ml of this solution contains 1,000 mg of Sb.

4.11 Antimony standard solution, 100 mg/l Sb

Dilute 10 ml of the antimony stock solution (4.10) to the mark with the hydrochloric acid solution (4.4) in a 100 ml one-mark volumetric flask.

1 ml of this solution contains 100 µg of Sb.

5 Apparatus

5.1 Ordinary laboratory apparatus.

5.2 Refrigerator.

5.3 Spectrophotometer.

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 Preparation of the test portion solution

Depending on the expected antimony content of the sample, weigh a test portion in accordance with Table 1 and transfer it into a 250 ml conical flask.

Table 1 — Antimony contents

Expected antimony content w (Sb) %	Mass of test portion m_0 g	Volume of HCl (4.3) V_1 ml	Volume of test portion solution to be taken V_0 ml
0,001 to 0,004	2 ± 0,001	10	5
0,005 to 0,02	1 ± 0,001	15	2
0,03 to 0,1	0,5 ± 0,001	15	1

Dissolve the test portion in 15 ml of the hydrochloric acid solution (4.4) and add 5 ml to 10 ml of the hydrogen peroxide solution (4.6), in small portions. Cool until the violent reaction has ceased. When the test portion is completely dissolved, heat the solution to boiling for several minutes to decompose the excess hydrogen peroxide. Cool to room temperature. Transfer the test portion solution into a 100 ml one-mark volumetric flask. Dilute to the mark with the hydrochloric acid solution (4.4) and mix well.

NOTE In the case of high content of Si, Cr, Zr, contained in the relevant Master Alloys, the dissolution of the test portion might be incomplete.

7.2 Blank test

Carry out a blank test simultaneously with the determination, following the same procedure and using the same quantities of all reagents as used for the determination, but omitting the test portion. Correct the result obtained from the determination in accordance with the result for the blank.

7.3 Check test

Make a preliminary check of the apparatus by preparing a solution of a standard material or a synthetic sample containing a known amount of antimony and of composition similar to the material to be analysed. Carry out the procedure specified in 7.1 and 7.5.

7.4 Preparation of the calibration

Into each of a series of at least four 250 ml conical flasks transfer 1 g of pure antimony-free copper (Cu ≥ 99,95 %) and 0 ml to 6 ml of antimony standard solution (4.11). Dissolve the copper in accordance with 7.1. Using 15 ml of hydrochloric acid (4.3) and 1 ml of the calibration solutions, proceed to 7.5. The solutions for spectrophotometric measurements thus prepared will contain 0 µg to 6 µg of Sb.

7.5 Determination

In accordance with Table 1, transfer into a separating funnel V_1 ml of hydrochloric acid (4.3) previously cooled to 5 °C or below in the refrigerator (5.2) and V_0 ml of the test portion solution.

Carry out the following operations without interruption. Add 6 drops of the cerium (IV) sulfate solution (4.7) and mix well. After 2 min add 3 drops of the hydroxylammonium chloride solution (4.8) and mix again. Add 10 ml of the isopropyl ether (4.2) at a maximum temperature of 20 °C. Shake for 30 s. Add 75 ml of water previously cooled to 5 °C or below and shake for 15 s. Allow to stand for 5 min.

Discard the aqueous layer and wash the organic layer twice with 3 ml of the hydrochloric acid solution (4.5). Add 20 ml of the Rhodamine B solution (4.9), shake for 30 s and allow to stand for 2 min. Drain the aqueous layer together with a small amount of the organic layer. Collect the remaining organic layer in a small, dry, stoppered flask. Swirl the flask to collect water droplets on the bottom. Transfer the organic phase into a 1 cm cell and immediately measure the absorbance against water at about 550 nm.

8 Expression of results

Calculate the antimony mass fraction, in per cent (%), as follows:

$$\text{Antimony mass fraction} = \frac{m_1}{V_0 \times m_0 \times 100} \quad (1)$$

where

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

m_1 is the mass of antimony determined in the volume V_0, in microgram (µg);

V_0 is the volume of the test portion solution taken, in millilitre (ml).

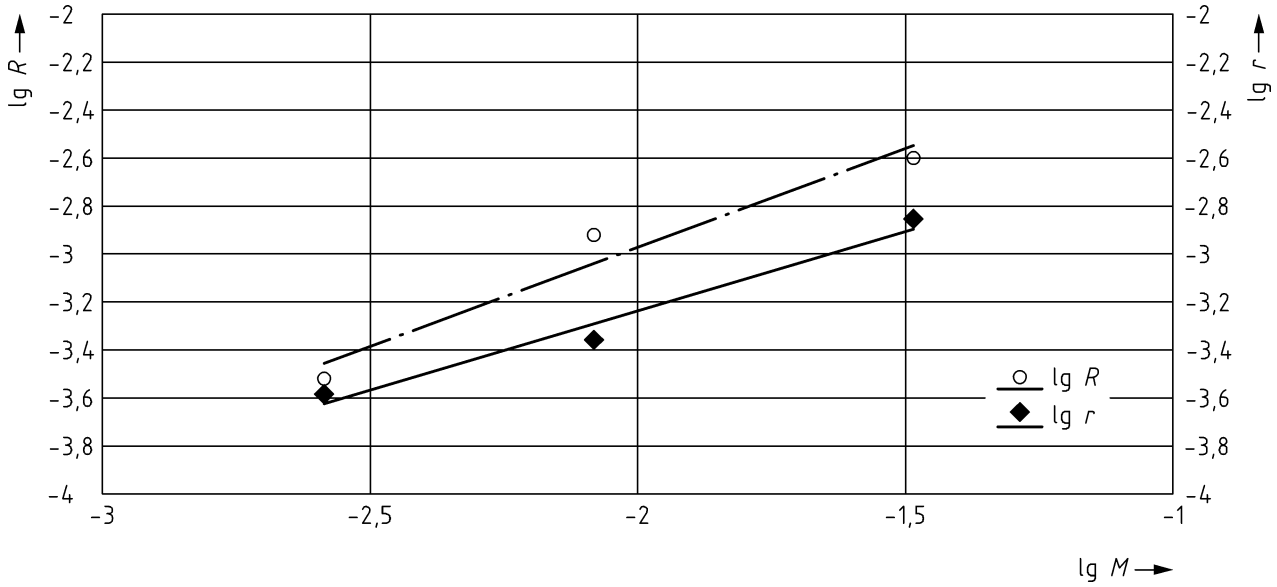
9 Precision

Eight laboratories co-operated in validating this method and obtained the results summarized in Table 2 and Figure 1 respectively.

These data conform to the method given in ISO 5725 including the Cochran's Test and Grubbs' Test.

Table 2 — Statistical information

Levels	Reference value %	Found %	Repeatability r	Reproducibility R
1	0,033	0,033	0,001 4	0,002 5
2	0,008 4	0,008 3	0,000 44	0,001 2
3	0,002 6	0,002 6	0,000 26	0,000 3



$$\lg R = 0{,}825 \lg M - 1{,}3248$$

$$\lg r = 0{,}668 \lg M - 1{,}8962$$

Figure 1 — lg relationship between Antimony concentration (lg M) and r and R