BS EN 15022-4:2011

BSI Standards Publication

Copper and copper alloys — Determination of tin content

Part 4: Medium tin content — Flame atomic absorption spectrometric method (FAAS)

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National foreword

This British Standard is the UK implementation of EN 15022-4:2011. It supersedes DD CEN/TS 15022-4:2006 which is withdrawn.

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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English Version

Copper and copper alloys - Determination of tin content - Part 4: Medium tin content - Flame atomic absorption spectrometric method (FAAS)

Cuivre et alliages de cuivre - Détermination de la teneur en étain - Partie 4: Étain en moyenne teneur - Méthode par spectrométrie d'absorption atomique dans la flamme (SAAF)

Kupfer und Kupferlegierungen - Bestimmung des Zinngehaltes - Teil 4: Mittlerer Zinngehalt - Flammenatomabsorptionsspektrometrisches Verfahren (FAAS)

This European Standard was approved by CEN on 24 September 2011.

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Foreword

This document (EN 15022-4:2011) 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of an identical text or by endorsement, at the latest by May 2012, and conflicting national standards shall be withdrawn at the latest by May 2012.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.

This document supersedes CEN/TS 15022-4:2006.

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

CEN/TS 15022-4:2006, *Copper and copper alloys — Determination of tin content — Part 4: Medium tin content — Flame atomic absorption spectrometry method (FAAS)*.

In comparison with the first edition of CEN/TS 15022-4:2006, the following significant technical changes were made:

a) conversion into a European Standard;

b) Clause 9 completely revised and the results of the precision test included.

This is one of four parts of the standard for the determination of tin content in copper and copper alloys. The other parts are:

— prEN 15022-1, *Copper and copper alloys — Determination of tin content — Part 1: Titrimetric method* (Part 1 will be the subject of a future work);

— CEN/TS 15022-2, *Copper and copper alloys — Determination of tin content — Part 2: Spectrophotometric method*;

— EN 15022-3, *Copper and copper alloys — Determination of tin content — Part 3: Low tin content — Flame atomic absorption spectrometry method (FAAS)*.

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 a flame atomic absorption spectrometric method (FAAS) for the determination of the tin content of copper and copper alloys in the form of unwrought, wrought and cast products.

The method is applicable to products having medium tin mass fractions between 0,2 % and 3,0 %.

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 hydrochloric acid and hydrogen peroxide followed, after suitable dilution, by aspiration into a nitrous oxide/acetylene flame of an atomic absorption spectrometer. Measurement of the absorption of the 286,3 nm line emitted by a tin hollow-cathode lamp.

4 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

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

4.2 Hydrochloric acid solution, 7 + 3.

Add 700 ml of hydrochloric acid (4.1) to 300 ml of water.

4.3 Hydrogen peroxide, H_2O_2 30 % (mass fraction) solution, free from tin base stabilizers.

Hydrogen peroxide may be stabilized by products containing some tin. It is therefore necessary to use exactly the same volume of hydrogen peroxide for the dissolution of the test sample as for the preparation of the corresponding blank test.

4.4 Tin stock solution, 1 g/l Sn.

Weigh (1 ± 0,001) g of tin (Sn ≥ 99 %) and transfer it into a 250 ml beaker. Dissolve it in 100 ml hydrochloric acid (4.1) and several drops of hydrogen peroxide (4.3) and cover with a watch glass. Heat gently until the metal is dissolved. Cool to room temperature and transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this solution contains 1 mg of Sn.

4.5 Copper base solution, 20 g/l Cu.

Weigh 10,0 g of electrolytic copper (Cu ≥ 99,95 %) into a 600 ml beaker. Add 250 ml of the hydrochloric acid solution (4.2) and cover with a watch glass. Cool to room temperature and add successively 5 ml hydrogen peroxide portions (4.3) until dissolution is complete, waiting after each addition until all effervescence ceases. Heat to eliminate the excess of hydrogen peroxide. Cool to room temperature and transfer this solution quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix.

5 Apparatus

5.1 Atomic absorption spectrometer, fitted with a nitrous oxide/acetylene burner.

5.2 Tin hollow-cathode lamp.

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

7.1.1 Test portion

Weigh (1 ± 0,001) g of the test sample.

7.1.2 Test portion solution

Transfer the test portion (7.1.1) into a 250 ml beaker and cover with a watch glass. Add 25 ml of hydrochloric acid solution (4.2), cool and add 5 ml of hydrogen peroxide (4.3). Cool until the violent reaction has ceased and add, if necessary, 2 ml of hydrogen peroxide to continue the dissolution. Repeat this addition several times as necessary to complete the dissolution of the test portion. Heat to eliminate the excess of hydrogen peroxide and cool to room temperature. Transfer the dissolved test portion into a 100 ml one-mark volumetric flask. Add 3,5 ml of hydrochloric acid (4.1). Dilute to the mark with water and mix.

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 substituting pure copper for the test portion.

7.3 Check test

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

7.4 Establishment of the calibration curve

7.4.1 Preparation of the calibration solutions

7.4.1.1 General

In all cases, copper and chloride concentrations, and acidity in the calibration solutions shall be similar to those of the test portion solutions.

The presence of copper in the calibration solutions compensates for chemical interaction effects of copper in the test portion solution. Normally no similar additions are required to compensate for the effect of alloying elements. If an alloying element is present in the material to be analysed in mass fraction > 10 %, an appropriate mass of this element shall be added to the calibration solutions. The volumes of copper base solution added (4.5) have been calculated to compensate for chemical interaction effects of copper in test solutions of copper or high-copper alloys. Overcompensation may occur if the same volumes are added when the test samples are copper-based alloys where the percentage of copper is lower. In these cases the volumes of copper base solution shall be decreased to match the copper content of the test sample in solution.

The tin concentration of the calibration solutions shall be adjusted to suit the sensitivity of the spectrometer used, so that the curve of absorbance as a function of concentration is a straight line.

7.4.1.2 Tin mass fractions between 0,2 % and 3,0 %

Into each of a series of eight 100 ml one-mark volumetric flasks, introduce the volumes of the tin stock solution (4.4), the copper base solution (4.5) and hydrochloric acid (4.1) shown in Table 1. Dilute to the mark with water and mix.

Table 1 — Calibration for tin mass fractions between 0,2 % and 3,0 %

Tin stock solution volume (4.4) ml	Corresponding tin mass mg	Corresponding tin concentration after final dilution mg/ml	Copper base solution volume (4.5) ml	Corresponding copper mass g	Hydrochloric acid volume (4.1) ml	Corresponding tin mass fraction of sample %
0 [a]	0	0	50	1	3,5	0
2	2	0,02	50	1	3,3	0,20
5	5	0,05	50	1	3,0	0,50
10	10	0,10	50	1	2,5	1,00
15	15	0,15	50	1	2,0	1,50
20	20	0,20	50	1	1,5	2,00
25	25	0,25	50	1	1,0	2,50
30	30	0,30	50	1	0,5	3,00

[a] Blank test on reagents for calibration curve.

7.4.2 Adjustment of the atomic absorption spectrometer

Fit the tin hollow-cathode lamp (5.2) into the atomic absorption spectrometer (5.1), switch on the current and allow it to stabilize. Adjust the wavelength in the region of 286,3 nm to minimum absorbance. Following the

manufacturer's instructions, fit the correct burner, light the flame and allow the burner temperature to stabilize. The flame shall be set up on oxidising conditions. 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.

NOTE The wavelength 286,3 nm was chosen because of its stability, linearity of calibration curve, sensitivity and lack of interference. Similar sensitivity can be obtained by using the 235,5 nm wavelength. Use of other lines is not advised.

7.4.3 Spectrometric measurement of the calibration solutions

Aspirate the series of calibration solutions (7.4.1) 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, see NOTE.

NOTE For certain types of apparatus, instead of water it is preferable to use a solution containing the attack reagents, in the same concentrations as in the test portion solutions.

7.4.4 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.

7.5 Determination

7.5.1 General

The analyses shall be carried out independently, in duplicate.

7.5.2 Preliminary spectrometric measurement

Carry out a preliminary measurement on the test portion solution (7.1.2) following the same procedure specified in 7.4.2 and 7.4.3 at the same time as the spectrometric measurements are carried out on the calibration solutions (7.4.1). Estimate the preliminary analyte amount by using the calibration curve (7.4.4).

7.5.3 Spectrometric measurements

7.5.3.1 Use of the calibration curve

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

7.5.3.2 Use of bracketing method

Carry out a second measurement on the test portion solution (7.1.2) following the procedure specified in 7.4.3, by bracketing between two new calibration solutions with composition similar to that of the calibration solution (7.4.1), but having tin concentrations slightly higher and slightly lower (± 10 %) than the estimated tin concentration of the test portion solution.

To prepare these calibration solutions, follow the procedure specified in 7.4.1 using, however, suitable quantities of tin stock solution (4.4).

8 Expression of results

8.1 Use of calibration curve

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

$$w_{Sn} = \frac{c_1}{m} \times V_f \times 100 \quad (1)$$

where

w_{Sn} is the tin mass fraction in per cent (%);

c_1 is the tin concentration from the calibration curve, in milligram per millilitre (mg/ml);

m is the sample mass of the test portion, in milligram (mg);

V_f is the volume of the test portion solution (7.1.2), in millilitre (ml).

8.2 Use of bracketing method

Calculate the tin mass fraction, in percent (%), using Equation (2):

$$w_{Sn} = \frac{c_2}{m} \times V_f \times 100 \quad (2)$$

where

c_2 is the tin concentration, calculated using Equation (3), in milligram per millilitre (mg/ml);

m is the sample mass of the test portion, in milligram (mg);

V_f is the volume of the test portion solution (7.1.2), in millilitre (ml).

$$c_2 = C_1 + (C_2 - C_1) \times \frac{S_0 - S_1}{S_2 - S_1} \quad (3)$$

where

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

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

S_0 is the absorbance value of the test portion solution;

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

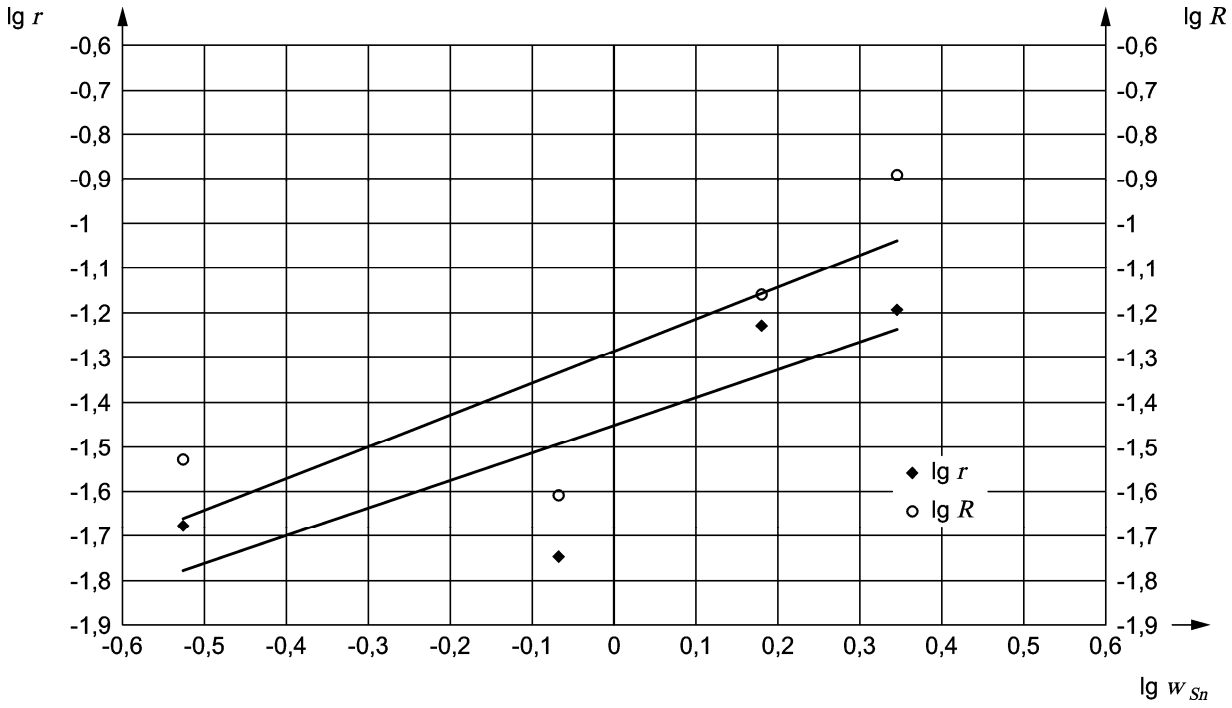
S_2 is the absorbance value of the calibration solution corresponding to concentration C_2.

9 Precision

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

Table 2 — Statistical information

Level	Reference value %	Found %	Repeatability r	Reproducibility R
1	0,284	0,297 8	0,021 0	0,029 6
2	0,857	0,855 5	0,017 9	0,024 6
3	1,505	1,513 9	0,059 1	0,069 3
4	2,25	2,215 2	0,064 1	0,128 6



$\lg r = 0{,}620\ 9 \lg w_{Sn} - 1{,}451\ 4$

$\lg R = 0{,}714\ 2 \lg w_{Sn} - 1{,}285\ 1$

Figure 1 — lg relationship between tin concentration w_{Sn}, 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 (i.e. EN 15022-4);

c) test 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.

Bibliography

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

[2] 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*

[3] 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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