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COPPER AND COPPER ALLOYS - DETERMINATION OF ZINC CONTENT - PART 2: FLAME ATOMIC ABSORPTION SPECTROMETRY METHOD (FAAS)

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English Version

Copper and copper alloys - Determination of zinc content - Part 2: Flame atomic absorption spectrometry method (FAAS)

Cuivre et alliages de cuivre - Dosage du zinc - Partie 2 : Méthode par spectrométrie d'absorption atomique dans la flamme (SAAF)

Kupfer und Kupferlegierungen - Bestimmung des Zinkgehaltes - Teil 2: Flammenatomabsorptionsspektrometrisches Verfahren (FAAS)

This European Standard was approved by CEN on 18 September 2006.

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Foreword

This document (EN 15024-2:2006) 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of an identical text or by endorsement, at the latest by May 2007, and conflicting national standards shall be withdrawn at the latest by May 2007.

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 15024-2, *Copper and copper alloys — Determination of zinc content — Part 2: Flame atomic absorption spectrometry method (FAAS)*

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

prEN 15024-1, *Copper and copper alloys — Determination of zinc content — Part 1: Titrimetric 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 flame atomic absorption spectrometric method (FAAS) for the determination of the zinc content of copper and copper alloys in the form of unwrought, wrought and cast products.

The method is applicable to products having zinc mass fractions between 0,000 5 % and 6,0 %.

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 a fluoroboric-nitric acid mixture followed, after suitable dilution, by aspiration into an air/ acetylene flame of an atomic absorption spectrometer. Measurement of the absorption of the 213,8 nm line emitted by a zinc hollow-cathode lamp.

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 Fluoroboric-nitric acid mixture

Mix together 300 ml of boric acid, H_3BO_3, 40 g/l solution, 30 ml of hydrofluoric acid, HF, (ρ = 1,13 g/l), 500 ml of nitric acid, HNO_3 (ρ = 1,40 g/ml) and 150 ml of water.

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

4.4 Nitric acid solution, 1 + 1

Dilute 1 000 ml of nitric acid (4.3) in 1 000 ml of water

4.5 Zinc stock solution, 5 g/l Zn

Weigh (2,5 ± 0,001) g of zinc (Zn ≥ 99,99 %) and transfer it into a 250 ml tall-form beaker. Add 50 ml of the nitric acid solution (4.4), cover and heat gently until the zinc is completely dissolved. Boil the solution for several minutes to expel the nitrous fumes. Allow it to cool and transfer the solution quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 5 mg of Zn.

4.6 Zinc standard solution, 0,5 g/l Zn

Transfer 10 ml of the zinc stock solution (4.5) into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 0,5 mg of Zn.

4.7 Zinc standard solution, 0,05 g/l Zn

Transfer 10,0 ml of the zinc stock solution (4.5) into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 0,05 mg of Zn.

4.8 Zinc standard solution, 0,01 g/l Zn

Transfer 5,0 ml of the zinc standard solution (4.6) into a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 0,01 mg of Zn.

4.9 Zinc standard solution, 0,001 g/l Zn

Transfer 5,0 ml of the zinc standard solution (4.7) into a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 0,001 mg of Zn.

4.10 Copper base solution, 20 g/l Cu

Weigh 10,0 g of pure copper containing not more than 0,000 2 % mass fraction zinc into a 1 000 ml polytetrafluoroethylene, polypropylene or low-pressure polyethylene beaker. Add 400 ml of fluoroboric-nitric acid mixture (4.2). Heat gently until the copper is completely dissolved, then boil until the nitrous fumes have been expelled. In the case of polyethylene or polypropylene beakers, use a water bath for heating. Allow to cool and transfer the solution quantitatively into a 500 ml one-mark volumetric flask, dilute to the mark with water and mix well.

50 ml of this solution contains 1 g of Cu and 40 ml of attack solution (4.2).

4.11 Copper base solution, 2 g/l Cu

Transfer, by means of a calibrated pipette, 10,0 ml of the copper base solution (4.10) into a 100 ml PTFE one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 2 mg of Cu.

5 Apparatus

5.1 Ordinary laboratory apparatus

5.2 Burette, graduated in 0,05 ml or calibrated pipette.

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

5.4 Zinc 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 PTFE, polypropylene or low-pressure polyethylene beaker. Add 40 ml of the attack reagent (4.2). Cover with a watch glass and heat gently until the test portion is completely dissolved, then heat at a temperature of approximately 90 °C until the nitrous fumes have been expelled. Wash the beaker cover and the sides of the beaker with water and cool.

7.1.3 Zinc mass fractions between 0,000 5 % and 0,01 %

Transfer the test portion solution (7.1.2) quantitatively into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

7.1.4 Zinc mass fractions between 0,005 % and 0,06 %

Transfer the test portion solution (7.1.2) quantitatively into a 200 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

7.1.5 Zinc mass fractions between 0,05 % and 0,60 %

Transfer the test portion solution (7.1.2) quantitatively into a 200 ml one-mark volumetric flask. Dilute to the mark with water and mix well. Transfer 10,0 ml of this solution, by means of a 25 ml burette or a calibrated pipette, into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

7.1.6 Zinc mass fractions between 0,5 % and 6 %

Transfer the test portion solution (7.1.2) quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well. Transfer 2,50 ml of this solution, by means of a 25 ml burette or a calibrated pipette, into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

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 and of pure copper as used for the determination, but omitting the test portion.

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 zinc 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, nitrate, fluoride and borate 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 effects of alloying elements.

If any alloying element is present in the material to be analysed in a mass fraction > 10 %, an appropriate mass of this element shall be added to the calibration solutions.

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

7.4.1.2 Zinc mass fractions between 0,000 5 % and 0,001 %

Into each of a series of three 100 ml one-mark volumetric flasks, introduce the volumes of zinc standard solutions (4.9) and copper base solutions (4.10) as shown in Table 1. Dilute to the mark with water and mix well.

Table 1 — Calibration for zinc mass fractions between 0,000 5 % and 0,001 %

Zinc standard solution volume (4.9) ml	Corresponding zinc mass mg	Corresponding zinc concentration after final dilution mg/ml	Copper base solution volume (4.10) ml	Corresponding copper mass mg	Corresponding Zinc mass fraction of sample %
0[a]	0	0	50	1 000	0
5	0,005	0,000 05	50	1 000	0,000 5
10	0,010	0,000 1	50	1 000	0,001

[a] Blank test on reagents for calibration curve.

7.4.1.3 Zinc mass fractions between 0,001 % and 0,01 %

Into each of a series of four 100 ml one-mark volumetric flasks, introduce the volumes of zinc standard solutions (4.8) and copper base solutions (4.10) as shown in Table 2. Dilute to the mark with water and mix well.

Table 2 — Calibration for zinc mass fractions between 0,001 % and 0,01%

Zinc standard solution volume (4.8) ml	Corresponding zinc mass mg	Corresponding zinc concentration after final dilution mg/ml	Copper base solution volume (4.10) ml	Corresponding copper mass mg	Corresponding Zinc mass fraction of sample %
0[a]	0	0	50	1 000	0
1	0,01	0,000 1	50	1 000	0,001
5	0,05	0,000 5	50	1 000	0,005
10	0,10	0,001	50	1 000	0,01

[a] Blank test on reagents for calibration curve.

7.4.1.4 Zinc mass fractions between 0,005 % and 0,06 %

Into each of a series of six 200 ml one-mark volumetric flasks, introduce the volumes of zinc standard solutions (4.7) and copper base solutions (4.10) as shown in Table 3. Dilute to the mark with water and mix well.

Table 3 — Calibration for zinc mass fractions between 0,005 % and 0,006 %

Zinc standard solution volume (4.7) ml	Corresponding zinc mass mg	Corresponding zinc concentration after final dilution mg/ml	Copper base solution volume (4.10) ml	Corresponding copper mass mg	Corresponding Zinc mass fraction of sample %
0[a]	0	0	50	1 000	0
1	0,05	0,000 25	50	1 000	0,005
2	0,1	0,000 5	50	1 000	0,01
4	0,2	0,001	50	1 000	0,02
8	0,4	0,002	50	1 000	0,04
12	0,6	0,003	50	1 000	0,06

[a] Blank test on reagents for calibration curve.

7.4.1.5 Zinc mass fractions between 0,05 % and 0,60 %

Into each of a series of six 200 ml one-mark volumetric flasks, introduce the volumes of zinc standard solutions (4.6) and copper base solutions (4.10) as shown in Table 4. Dilute to the mark with water and mix well. Transfer 10,0 ml of these solutions into each of six 100 ml one-mark volumetric flasks. Dilute to the mark with water and mix well.

Table 4 — Calibration for zinc mass fractions between 0,05 % and 0,60%

Zinc standard solution volume (4.6) ml	Corresponding zinc mass mg	Corresponding zinc concentration after final dilution mg/ml	Copper base solution volume (4.10) ml	Corresponding copper mass mg	Corresponding Zinc mass fraction of sample %
0[a]	0	0	50	1 000	0
1	0,5	0,000 25	50	1 000	0,05
2	1,0	0,000 50	50	1 000	0,10
4	2,0	0,001	50	1 000	0,20
8	4,0	0,002	50	1 000	0,40
12	6,0	0,003	50	1 000	0,60

[a] Blank test on reagents for calibration curve.

7.4.1.6 Zinc mass fractions between 0,5 % and 6 %

Into each of a series of six 500 ml one-mark volumetric flasks, introduce the volumes of zinc stock solutions (4.5) and copper base solutions (4.10) as shown in Table 5. Dilute to the mark with water and mix well. Transfer 2,5 ml of these solutions into each of six 100 ml one-mark volumetric flasks. Dilute to the mark with water and mix well.

Table 5 — Calibration for zinc mass fractions between 0,5% and 6%

Zinc standard stock volume (4.5) ml	Corresponding zinc mass mg	Corresponding zinc concentration after final dilution mg/ml	Copper base solution volume (4.10) ml	Corresponding copper mass mg	Corresponding Zinc mass fraction of sample %
0[a]	0	0	50	1 000	0
1	5,0	0,000 25	50	1 000	0,5
2	10,0	0,000 50	50	1 000	1
4	20,0	0,001	50	1 000	2
8	40,0	0,002	50	1 000	4
12	60,0	0,003	50	1 000	6

[a] Blank test on reagents for calibration curve.

7.4.2 Adjustment of the atomic absorption spectrometer

Fit the zinc hollow-cathode lamp (5.4) into the atomic absorption spectrometer (5.3), switch on the current and allow it to stabilize. Adjust the wavelength in the region of 213,8 nm to minimize 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.

7.4.3 Spectrometric measurement of the calibration solutions

Aspirate the relevant series of calibration solutions (7.4.1.2, 7.4.1.3, 7.4.1.4, 7.4.1.5 or 7.4.1.6) depending on the expected zinc content) in succession into the flame and measure the absorbance for each solution. 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 it is preferable to use a solution containing the attack reagents in the same concentrations as in the test portion solutions, instead of water.

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 (7.1.3, 7.1.4, 7.1.5 or 7.1.6) following the same procedures specified in 7.4.2 and 7.4.3 at the same time as the spectrometric measurements are carried out on the calibration solutions (see 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 derive 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 (7.1.3, 7.1.4, 7.1.5 or 7.1.6) following the procedures specified in 7.4.3, by bracketing between two new calibration solutions with a composition similar to that of the calibration solutions (see 7.4.1), but having zinc contents slightly higher and slightly lower (± 10 %) than the estimated zinc concentration of the test portion solution.

To prepare these calibration solutions, follow the procedure specified in 7.4.1 using, however, suitable quantities of zinc standard solutions (4.5, 4.6, 4.7, 4.8 or 4.9).

8 Expression of results

8.1 Use of the calibration curve

Calculate the zinc mass fraction, in percent (%), as follows:

$$\text{Zinc mass fraction} = \frac{A_1}{B} \times V_\text{f} \times D_\text{r} \times 100 \tag{1}$$

where

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

B is the sample mass represented in the test portion, in milligram (mg);

V_f is the volume of the test portion solution (7.1.3, 7.1.4, 7.1.5 or 7.1.6), in millilitre (ml);

D_r is the dilution ratio (intermediate).

NOTE For 7.1.5, D_r = 20;
For 7.1.6, D_r = 200.

8.2 Use of bracketing method

Calculate the zinc mass fraction, in percent (%), as follows:

$$\text{Zinc mass fraction} = \frac{A_2}{B} \times V_\text{f} \times D_\text{r} \times 100 \tag{2}$$

where

A_2 is the zinc concentration, calculated using Formula (3), in milligrams per millilitre (mg/ ml);

B is the sample mass represented in the test portion, in milligrams (mg);

V_f is the volume of the test portion solution (7.1.3, 7.1.4, 7.1.5 or 7.1.6), in millilitres (ml);

D_r is the dilution ratio.

NOTE For 7.1.5, D_r = 20;
For 7.1.6, D_r = 200.

$$\mathrm{A}_2 = \mathrm{C}_1 + (\mathrm{C}_2 - \mathrm{C}_1) \times \frac{\mathrm{S}_0 - \mathrm{S}_1}{\mathrm{S}_2 - \mathrm{S}_1} \tag{3}$$

where

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

C_2 is the higher zinc concentration of the calibration solution used, in milligrams 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;

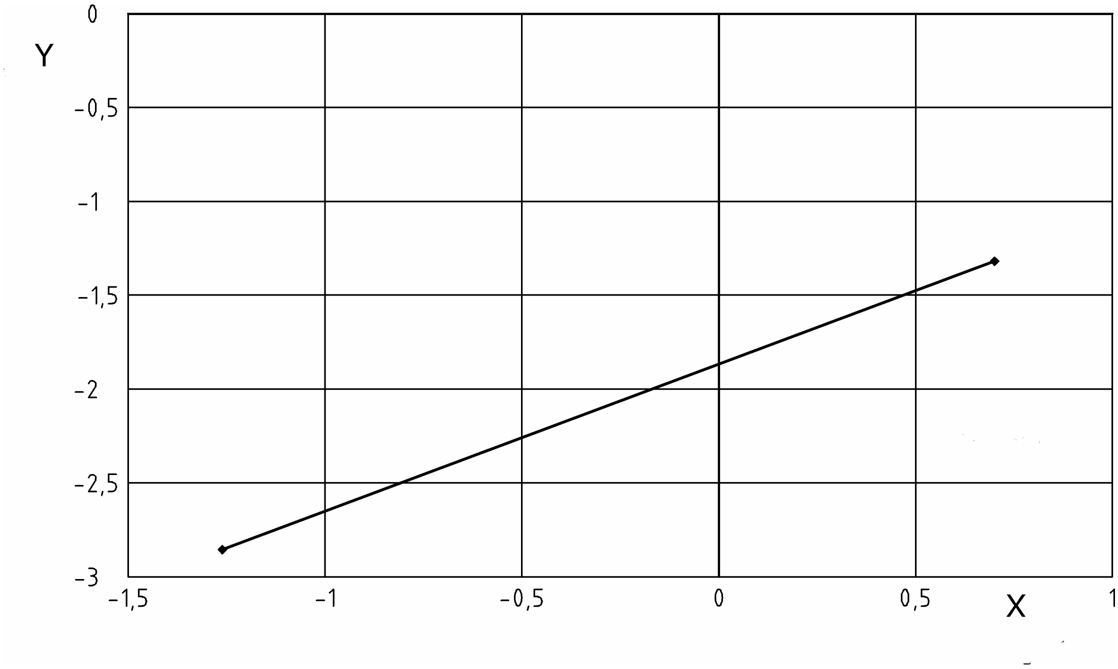
S_2 is the absorbance value of the calibration solution corresponding to concentration C_2.

9 Precision

One laboratory tested this method and obtained the results summarized in Table 6 and Figure 1, respectively.

Table 6 — Statistical information

Levels	Reference value %	Found %	Repeatability *r*	Reproducibility *R*
1	5,02	5,03	0,048	—
2	0,055	0,055	0,001 1	—



lg r = 0,783 7 lg M – 1,866 6

Key

X lg *M*
Y lg *r*

—◆— lg *r*

Figure 1 — lg relationship between zinc concentration *M* and *r*

10 Test report

The test report shall contain the following information:

a) identification of the test sample;

b) test method used;

c) results;

d) any unusual characteristics noted during the determination;

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

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

g) 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*

[4] ISO 4740, *Copper and copper alloys — Determination of Zinc content — Flame atomic absorption spectrometric method*