BRITISH STANDARD

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15690-2:2009

Copper and copper alloys — Determination of iron content

Part 2: Flame atomic absorption spectrometric method (FAAS)

ICS 77.040.30; 77.120.30

BSI
British Standards

National foreword

This British Standard is the UK implementation of EN 15690-2:2009.

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 iron content - Part 2: Flame atomic absorption spectrometric method (FAAS)

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

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

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Foreword

This document (EN 15690-2:2009) 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of an identical text or by endorsement, at the latest by August 2009, and conflicting national standards shall be withdrawn at the latest by August 2009.

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 15690-2, *Copper and copper alloys — Determination of iron content — Part 2: Flame atomic absorption spectrometric method (FAAS)*

This is one of two Parts of the standard for the determination of iron content in copper and copper alloys. The other Part is:

EN 15690-1, *Copper and copper alloys — Determination of iron content — Part 1: Titrimetric method*

Part 1 will be the subject of future work.

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, 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 Part of this European Standard specifies a flame atomic absorption spectrometric method (FAAS) for the determination of the iron content of copper and copper alloys in the form of castings or unwrought or wrought products.

The method is applicable to products having iron mass fractions between 0,005 % and 5,0 %.

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*

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

Dissolution of a test portion in a hydrochloric and nitric acid mixture followed, after suitable dilution and the addition of lanthanum chloride to mask the effect of interfering ions, by aspiration of the test solution into an air/acetylene flame of an atomic absorption spectrometer. Measurement of the absorption of the 248,3 nm or the 372,0 nm line emitted by an iron 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.

Avoid any contamination with iron during the mechanical preparation steps.

4.2 **Hydrochloric acid,** HCl (ρ = 1,19 g/ml)

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

4.4 **Nitric acid,** (1 + 1)

Add 500 ml of nitric acid (4.3) into 500 ml of water.

4.5 **Hydrofluoric acid,** HF (ρ = 1,13 g/ml)

WARNING — Hydrofluoric acid is a hazardous substance. Care shall be taken and it shall be used under an efficient fume hood.

4.6 Lanthanum(III) chloride solution, 100 g/l

Weigh 100 g of lanthanum(III) chloride ($LaCl_3 \cdot 7H_2O$) in a 600 ml beaker, transfer it into a 1 000 ml one-mark volumetric flask and dissolve it with water. Dilute to the mark with water and mix well.

4.7 Iron stock solution, 0,5 g/l Fe

a) Weigh (0,5 ± 0,001) g of high purity iron and transfer it into a 250 ml beaker. Dissolve it in 50 ml of hydrochloric acid (4.2), 25 ml water and 2,5 ml nitric acid (4.3). Cover with a watch glass and, if necessary, heat gently to assist dissolution. When dissolution is complete, allow to cool and transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix well; or

b) Weigh (0,715 ± 0,000 1) g of high purity iron(III) oxide (Fe_2O_3), previously dried and transfer it into a 250 ml beaker. Add 50 ml of hydrochloric acid (4.2). Cover with a watch glass and, if necessary, heat gently to assist dissolution. When dissolution is complete, allow to cool and transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

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

4.8 Iron standard solution, 0,05 g/l Fe

Transfer 20,0 ml of iron stock solution (4.7) into a 200 ml one-mark volumetric flask. Add 5 ml of hydrochloric acid (4.2), dilute to the mark with water and mix well.

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

4.9 Iron standard solution, 0,01 g/l Fe

Transfer 10,0 ml of iron stock solution (4.7) into a 500 ml one-mark volumetric flask. Add 10 ml of hydrochloric acid (4.2), dilute to the mark with water and mix well.

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

4.10 Copper base solution, 20 g/l Cu

Transfer (10 ± 0,01) g of iron-free copper (Cu ≥ 99,95 %) after etching into a 600 ml beaker. Add 100 ml of hydrochloric acid (4.2) and, cautiously, 100 ml of nitric acid solution (4.4). Cover with a watch glass and heat gently until the copper has been completely dissolved, then heat up to the boiling point until the nitrous fumes have been expelled. 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.

1 ml of this solution contains 0,02 g of Cu.

4.11 Copper base solution, 2,0 g/l Cu

Transfer quantitatively 25 ml of copper base solution (4.10) into a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains 2,0 mg of Cu.

5 Apparatus

5.1 Atomic absorption spectrometer, fitted with an air/acetylene burner

5.2 Iron 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. Add 10 ml of hydrochloric acid (4.2) and 10 ml of the nitric acid solution (4.4). Cover with a watch glass and heat gently until the test portion is completely dissolved. Allow to cool. If undissolved matter remains, indicating the presence of silicon, filter the solution. Place the filter paper and contained salts in a platinum crucible and ash, taking care that the filter does not flame. Calcine at about 550 °C. Cool and add 5 ml of hydrofluoric acid (4.5) and five drops of nitric acid (4.3). Evaporate to dryness and calcine again for several minutes at about 700 °C to completely volatilize the silicon. Cool, and then dissolve the residue with the least possible volume of nitric acid solution (4.4). Filter, if necessary, and add this filtrate quantitatively to the original filtrate.

7.1.3 Iron mass fractions between 0,005 % and 0,025 %

Transfer the dissolved test portion or the combined filtrates quantitatively into a 100 ml one-mark volumetric flask. Add 10 ml of the lanthanum(III) chloride solution (4.6) and 1 ml of hydrochloric acid (4.2), dilute to the mark with water and mix well.

7.1.4 Iron mass fractions between 0,025 % and 0,5 %

Transfer the dissolved test portion or the combined filtrates quantitatively into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix well. Transfer 20 ml of this solution into a 100 ml one-mark volumetric flask. Add 10 ml of the lanthanum(III) chloride solution (4.6) and 1 ml of hydrochloric acid (4.2), dilute to the mark with water and mix well.

7.1.5 Iron mass fractions between 0,5 % and 5 %

Transfer the dissolved test portion or the combined filtrates quantitatively into a 100 ml one-mark volumetric flask, dilute to the mark with water and mix well. Transfer 5 ml of this solution into a 250 ml one-mark volumetric flask. Add 25 ml of the lanthanum(III) chloride solution (4.6) and 1 ml of hydrochloric acid (4.2), 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 as used for the determination, by pure copper for the test portion (7.1.1). Correct the result obtained from the determination in accordance with the result of 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 iron and of 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, salts concentration and the pH-values of 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 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 (4.10 and 4.11) 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 iron 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 Calibration for iron mass fractions between 0,005 % and 0,025 %

Into each of a series of six 100 ml one-mark volumetric flasks, introduce the volumes of iron standard solution (4.9) and of copper base solution (4.10) as shown in Table 1. Introduce also 10 ml of lanthanum(III) chloride solution (4.6). Dilute to the mark with water and mix well.

Table 1 — Calibration for iron mass fractions between 0,005 % and 0,025 %

Iron standard solution volume (4.9)	**Corresponding iron mass**	**Hydrochloric acid volume** (4.2)	**Corresponding iron concentration after final dilution**	**Copper base solution volume** (4.10)	**Corresponding copper mass**	**Corresponding iron mass fraction of test sample**
ml	mg	ml	mg/ml	ml	g	%
0[a]	0	1	0	50	1	0
5	0,05	0,9	0,000 5	50	1	0,005
10	0,10	0,8	0,001 0	50	1	0,010
15	0,15	0,7	0,001 5	50	1	0,015
20	0,20	0,6	0,002 0	50	1	0,020
25	0,25	0,5	0,002 5	50	1	0,025

[a] Blank test on reagents for calibration curve.

7.4.1.3 Calibration for iron mass fractions between 0,025 % and 0,5 %

Into each of a series of seven 100 ml one-mark volumetric flasks, introduce the volumes of iron standard solution (4.8) and of copper base solution (4.10) as shown in Table 2. Introduce also 10 ml of lanthanum(III) chloride solution (4.6). Dilute to the mark with water and mix well.

Table 2 — Calibration for iron mass fractions between 0,025 % and 0,5 %

Iron standard solution volume (4.8)	**Corresponding iron mass**	**Hydrochloric acid volume** (4.2)	**Corresponding iron concentration after final dilution**	**Copper base solution volume** (4.10)	**Corresponding copper mass**	**Corresponding iron mass fraction of test sample**
ml	mg	ml	mg/ml	ml	g	%
0[a]	0	1	0	10	0,2	0
1	0,05	0,94	0,000 5	10	0,2	0,025
2	0,10	0,88	0,001 0	10	0,2	0,050
4	0,20	0,76	0,002 0	10	0,2	0,100
8	0,40	0,64	0,004 0	10	0,2	0,200
14	0,70	0,52	0,007 0	10	0,2	0,350
20	1,00	0,4	0,010	10	0,2	0,500

[a] Blank test on reagents for calibration curve.

7.4.1.4 Calibration for iron mass fractions between 0,5 % and 5,0 %

Into each of a series of seven 100 ml one-mark volumetric flasks, introduce the volumes of iron standard solution (4.8) and of copper base solution (4.11) as shown in Table 3. Introduce also 10 ml of lanthanum(III) chloride solution (4.6). Dilute to the mark with water and mix well.

Table 3 — Calibration for iron mass fractions between 0,5 % and 5,0 %

Iron standard solution volume (4.8)	**Corresponding iron mass**	**Hydrochloric acid volume** (4.2)	**Corresponding iron concentration after final dilution**	**Copper base solution volume** (4.11)	**Corresponding copper mass**	**Corresponding iron mass fraction of test sample**
ml	mg	ml	mg/ml	ml	g	%
0[a]	0	1	0	10	0,02	0
2	0,1	0,97	0,001	10	0,02	0,5
4	0,2	0,94	0,002	10	0,02	1,0
8	0,4	0,88	0,004	10	0,02	2,0
12	0,6	0,76	0,006	10	0,02	3,0
16	0,8	0,58	0,008	10	0,02	4,0
20	1,0	0,4	0,010	10	0,02	5,0

[a] Blank test on reagents for calibration curve.

7.4.2 Adjustment of the atomic absorption spectrometer

Fit the iron hollow-cathode lamp (5.4) into the atomic absorption spectrometer (5.3), switch on the current and allow to stabilize. Adjust the wavelength to minimum absorbance in the region of 248,3 nm or 372,0 nm for iron content up to 0,5 % (Tables 1 and 2) and iron content over 0,5 % (Table 3) respectively. 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

Aspirate the relevant series of calibration solutions (7.4.1.2, 7.4.1.3, 7.4.1.4 depending on the expected iron 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 spectrometer, 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 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 or 7.1.5) 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 (see 7.4.1.2, 7.4.1.3, 7.4.1.4) and using the appropriate wavelength, either 248,3 nm or 372,0 nm. 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 (7.1.3, 7.1.4 or 7.1.5) following the procedure specified in 7.4.3, by bracketing between two new calibration solutions with composition similar to that of the calibration solution (see 7.4.1), but having iron contents slightly higher and slightly lower (± 10 %) than the estimated iron concentration of the test portion solution.

To prepare these calibration solutions, follow the procedure specified in 7.4.1 using, however, suitable quantities of iron standard solutions (4.8, 4.9).

8 Expression of results

8.1 Use of calibration curve

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

$$w_{\mathrm{Fe}} = \frac{A_1}{B} \times V_{\mathrm{f}} \times D_{\mathrm{r}} \times 100 \qquad (1)$$

where

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

B is the test 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 or 7.1.5) in millilitre (ml);

D_{r} is the dilution ratio.

For 7.1.4, $D_{\mathrm{r}} = 5$;

for 7.1.5, $D_{\mathrm{r}} = 50$.

8.2 Use of bracketing method

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

$$w_{\mathrm{Fe}} = \frac{A_2}{B} \times V_{\mathrm{f}} \times D_{\mathrm{r}} \times 100 \qquad (2)$$

where

A_2 is the iron concentration, calculated using Equation (3), 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 or 7.1.5) in millilitre (ml);

D_{r} is the dilution ratio.

For 7.1.4, $D_{\mathrm{r}} = 5$;

for 7.1.5, $D_{\mathrm{r}} = 50$.

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

where

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

C_2 is the higher iron 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

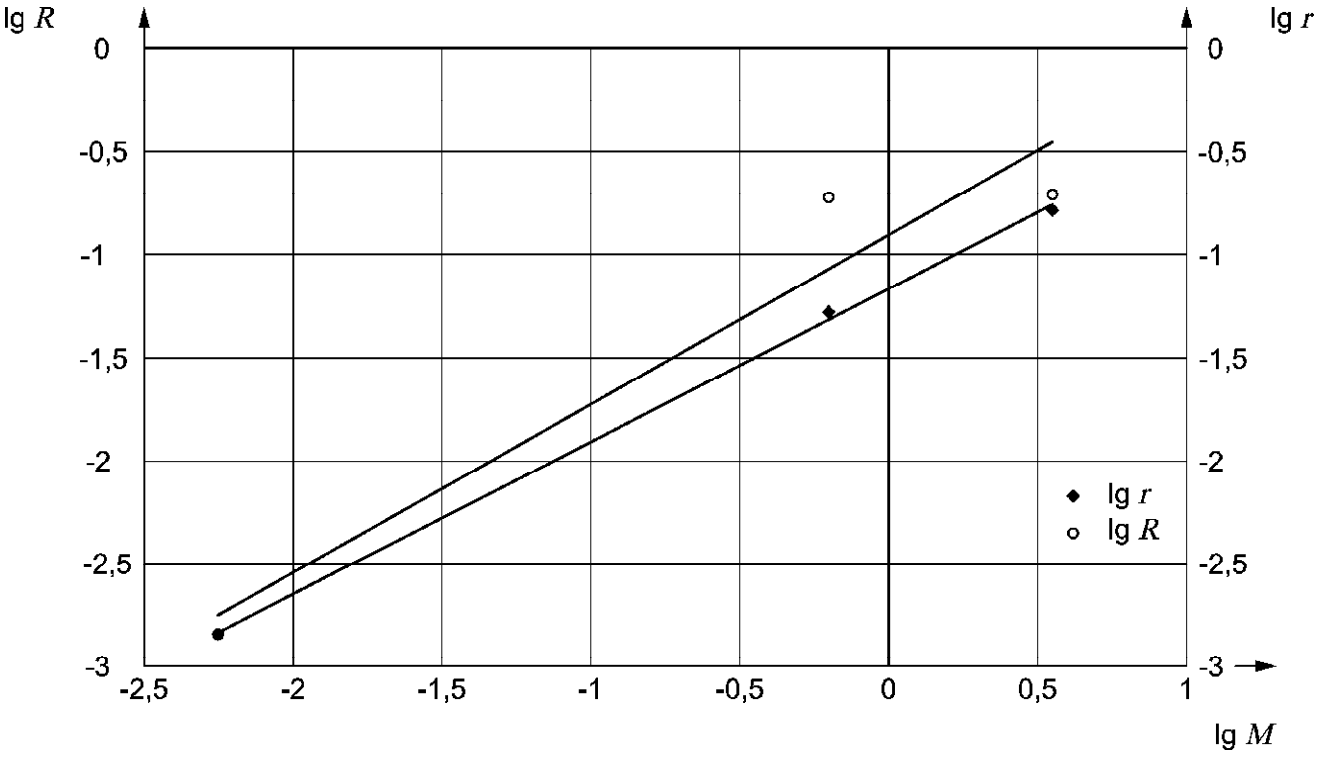
Three laboratories tested this method and obtained the results summarized in Table 4 and Figure 1 respectively.

These data comply with ISO 5725 method.

Table 4 — Statistical information

Level	Found %	Repeatability r	Reproducibility R	Reference value %
1	0,005 6	0,001 43	0,001 43	[a]
2	0,629 3	0,052 6	0,189 3	[a]
3	3,555	0,164	0,196	[a]

[a] Sample concentration unknown.



lg r = 0,741 4 lg M – 1,166 0

lg R = 0,820 1 lg M – 0,905 3

Figure 1 — lg relationship between iron mass fraction (lg M), repeatability r and reproducibility 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 15690-2);

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

In the preparation of this European Standard, use was made of a number of documents for reference purposes. The relevant publications are listed hereafter.

[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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