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Copper and copper alloys — Determination of magnesium content — Flame atomic absorption spectrometric method (FAAS)

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National foreword

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A list of organizations represented on this committee can be obtained on request to its secretary.

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Cuivre et alliages de cuivre - Détermination du magnésium - Méthode par spectrométrie d'absorption atomique dans la flamme (SAAF)

Kupfer und Kupferlegierungen - Bestimmung des Magnesiumgehaltes - Flammenatomabsorptionsspektrometrisches Verfahren (FAAS)

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Foreword

This document (EN 15025:2010) 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of an identical text or by endorsement, at the latest by January 2011, and conflicting national standards shall be withdrawn at the latest by January 2011.

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This document supersedes CEN/TS 15025:2006.

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 15025:2006, *Copper and copper alloys — Determination of magnesium content — Flame atomic absorption spectrometry method (FAAS)*.

In comparison with the first edition of CEN/TS 15025:2006, the following significant technical changes were made:

- Transformation into a European Standard;
- In 7.4.1.1, text added;
- Clause 9, Precision - completely revised.

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1 Scope

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

The method is applicable to products having magnesium mass fractions between 0,001 % and 0,20 %.

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 hydrochloric-nitric acid mixture followed, after suitable dilution, by aspiration into an air/acetylene flame of an atomic absorption spectrometer. Determination of the magnesium content by measuring the absorption of the 285,2 nm line emitted by a magnesium hollow-cathode lamp.

4 Reagents

During the analysis, 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 Nitric acid, HNO_3 (ρ = 1,40 g/ml).

4.3 Nitric acid solution, 1 + 1.

Add 100 ml of nitric acid (4.2) to 100 ml of water.

4.4 Magnesium stock solution, 0,5 g/l Mg.

Weigh (0,5 ± 0,001) g of magnesium (Mg ≥ 99,9 %) and transfer it into a 250 ml beaker. Add 20 ml of the nitric acid solution (4.3) in small amounts. Cover with a watch glass and heat gently until the magnesium is completely dissolved. Boil the solution until nitrous fumes have been expelled. 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 well.

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

4.5 Magnesium standard solution, 0,01 g/l Mg.

Transfer 5 ml of the magnesium stock solution (4.4) into a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

Prepare this solution immediately prior to use.

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

4.6 Magnesium standard solution, 0,000 5 g/l Mg.

Transfer 5 ml of the magnesium standard solution (4.5) into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

Prepare this solution immediately prior to use.

1 ml of this solution contains 0,000 5 mg of Mg.

4.7 Lanthanum (III) chloride solution, 200 g/l.

Dissolve 100 g of lanthanum chloride heptahydrate ($LaCl_3 \cdot 7H_2O$) in a 1 000 ml beaker with approximately 400 ml of water. Transfer the solution into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

4.8 Copper base solution, 10 g/l Cu.

Weigh (10 ± 0,01) g of electrolytic copper and transfer it into a 1 000 ml beaker. Add 100 ml of hydrochloric acid (4.1) and, in small amounts, 100 ml of the nitric acid solution (4.3). Cover with a watch glass and heat gently until the copper is dissolved, then boil until the nitrous fumes have been expelled. Cool to room temperature and transfer the solution into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

5 Apparatus

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

5.2 Magnesium 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 (4.1) and 10 ml of the nitric acid solution (4.3). 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 nitrous fumes have been expelled. Cool to room temperature. Wash the cover and the sides of the beaker with water. Transfer the solution to a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

Select an aliquot portion from the test portion solution according to the expected magnesium mass fraction as indicated in Table 1.

Table 1 — Aliquot solution

Magnesium (mass fraction) %	**Aliquot of the test portion solution** (7.1.2) ml	**Lanthanum (III) chloride solution volume** (4.7) ml	**Final volume of diluted solution** ml
0,001 to 0,05	10	10	100
0,05 to 0,2	5	10	100

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.

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 magnesium and of a composition similar to the material to be analysed. Carry out the procedure specified in 7.5.

7.4 Preparation of the calibration curve

7.4.1 Preparation of the calibration solutions

7.4.1.1 General

In all cases, copper, chloride and nitrate 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 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 (4.8) 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 magnesium 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 Magnesium mass fractions between 0,001 % and 0,20 %

Into each of a series of 100 ml one-mark volumetric flasks, introduce the volumes of magnesium standard solution (4.5 or 4.6) and of copper base solution (4.8) shown in Tables 2 or 3, depending on the expected magnesium content, followed by 10 ml of lanthanum (III) chloride solution (4.7). Dilute to the mark with water and mix well.

The range of calibration solutions is appropriate for most current models of equipment of average performance. The range and operating conditions shall be selected for optimum measurements by the particular equipment available.

Table 2 — Calibration for magnesium mass fractions between 0,001 % and 0,05 %

Magnesium standard solution volume		**Corresponding magnesium mass**	**Corresponding magnesium concentration after final dilution**	**Copper base solution volume**	**Corresponding copper mass**	**Corresponding magnesium mass fraction of sample**
(4.6)	(4.5)			(4.8)		
ml	ml	mg	mg/ml	ml	g	%
0[a]	—	0	0	10	0,1	0
2	—	0,001	0,000 01	10	0,1	0,001
4	—	0,002	0,000 02	10	0,1	0,002
10	—	0,005	0,000 05	10	0,1	0,005
20	—	0,01	0,000 1	10	0,1	0,010
—	2	0,02	0,000 2	10	0,1	0,020
—	3	0,03	0,000 3	10	0,1	0,030
—	4	0,04	0,000 4	10	0,1	0,040
—	5	0,05	0,000 5	10	0,1	0,050

[a] Blank test on reagents for calibration curve.

Table 3 — Calibration for magnesium mass fractions between 0,05 % and 0,20 %

Magnesium standard solution volume (4.5)	**Corresponding magnesium mass**	**Corresponding magnesium concentration after final dilution**	**Copper base solution volume** (4.8)	**Corresponding copper mass**	**Corresponding magnesium mass fraction of sample**
ml	mg	mg/ml	ml	g	%
0[a]	0	0	5	0,050	0
2,5	0,025	0,000 25	5	0,050	0,05
5,0	0,050	0,000 50	5	0,050	0,10
7,5	0,075	0,000 75	5	0,050	0,15
10,0	0,1	0,001	5	0,050	0,20

[a] Blank test on reagents for calibration curve.

7.4.2 Adjustment of the atomic absorption spectrometer

Fit the magnesium 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 285,2 nm to minimum 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 (Tables 2 or 3 depending on the expected magnesium content) 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 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). 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 appropriate calibration curve.

7.5.3.2 Use of bracketing method

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

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

8 Expression of results

8.1 Use of calibration curve

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

$$w_{\mathrm{Mg}} = \frac{c_1}{m} \times V_{\mathrm{f}} \times 100 \qquad (1)$$

where

w_{Mg} is the magnesium mass fraction in percent (%);

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

m is the sample mass of the test portion, in milligrams (mg) (see Table 2 or 3, fifth column);

V_{f} is the volume of the test portion solution, in millilitres (ml) (see Table 1, fourth column).

8.2 Use of bracketing method

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

$$w_{\mathrm{Mg}} = \frac{c_2}{m} \times V_{\mathrm{f}} \times 100 \qquad (2)$$

where

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

m is the sample mass of the test portion, in milligrams (mg) (see Table 2 or 3, fifth column);

V_{f} is the volume of the test portion solution, in millilitres (ml) (see Table 1, fourth column);

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

where

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

C_2 is the higher magnesium 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

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

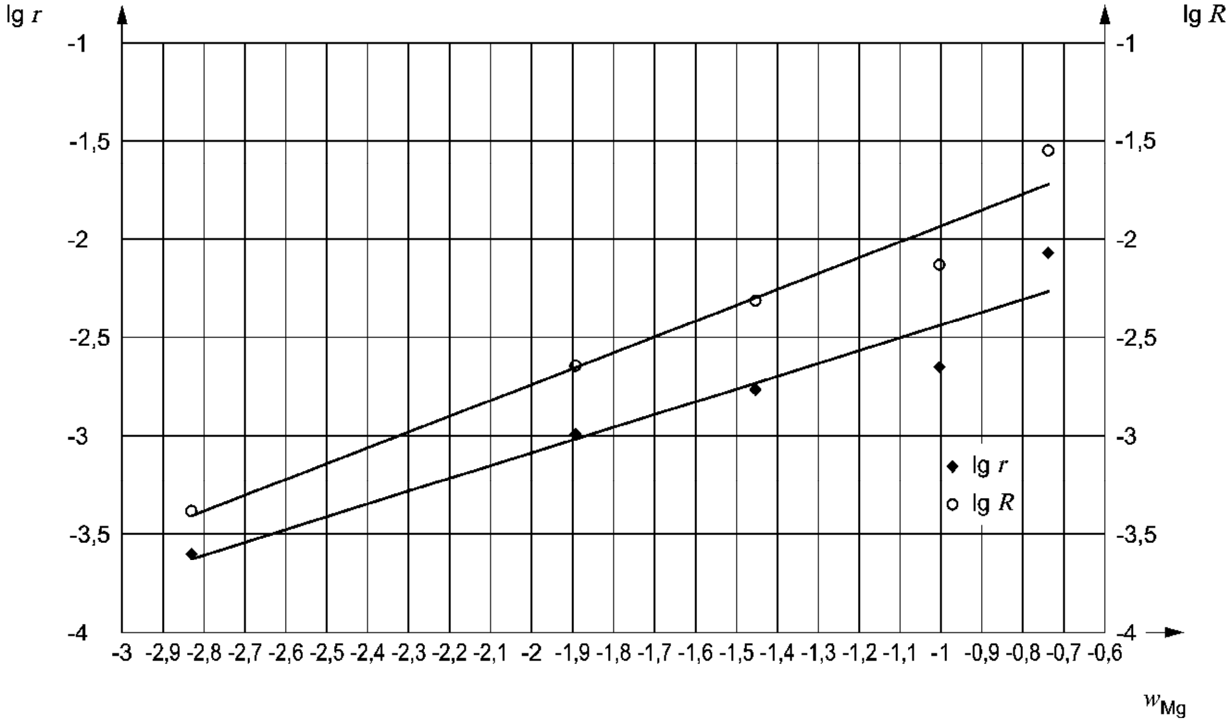
NOTE The laboratories that performed the tests of this method used different dilution conditions. Some of them operate as indicated in 7.1.2 and 7.4.1, the others, for sensitivity reasons took lower test portions (5 ml instead of 10 ml for magnesium mass fractions between 0,001 % and 0,05 % and 2 ml instead of 5 ml for magnesium mass fractions between 0,05 % and 0,20 %).

For the statistical evaluation, the sets of results were taken all together, independently of the dilution conditions under which they were obtained (see 7.4.1.1).

Moreover, some laboratories operated under both dilution conditions and it was shown that the results obtained were statistically equivalent.

Table 4 — Statistical information

Level	Reference value %	Found %	Repeatability r	Reproducibility R
1	0,001 4	0,001 48	0,000 25	0,000 41
2	0,012 4	0,012 8	0,001 0	0,002 3
3	0,034 7	0,035 2	0,001 7	0,004 9
4	0,10	0,099 3	0,002 2	0,007 4
5	0,175	0,182 5	0,008 5	0,028 4



Key

lg r = 0,651 4 lg w_{Mg} – 1,785 1

lg R = 0,806 4 lg w_{Mg} – 1,126 5

Figure 1 — lg relationship between magnesium concentration w_{Mg} 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 15025);

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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