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

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National foreword

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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 cadmium content - Flame atomic absorption spectrometric method (FAAS)

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

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

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Foreword

This document (EN 15616:2012) 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of an identical text or by endorsement, at the latest by May 2013, and conflicting national standards shall be withdrawn at the latest by May 2013.

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This document supersedes CEN/TS 15616:2009.

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

CEN/TS 15616:2009, *Copper and copper alloys — Determination of cadmium content — Flame atomic absorption spectrometric method (FAAS)*

In comparison with CEN/TS 15616:2009, the following significant technical changes were made:

a) Conversion into a European Standard;

b) Scope (Clause 1) revised;

c) Principle (Clause 3) completely revised, dissolution process changed;

d) Precision (Clause 9) completely revised and the results of the precision test included.

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1 Scope

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

The method is applicable to products having cadmium mass fractions between 0,000 5 % and 0,1 %.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 nitric acid solution followed, after suitable dilution, by aspiration of the test solution into an air/acetylene flame of an atomic absorption spectrometer. Measurement of the absorption of the 228,8 nm line emitted by a cadmium hollow-cathode lamp.

4 Reagents

During the analysis use only reagents of recognised 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 500 ml of nitric acid (4.2) to 500 ml of water.

4.4 **Cadmium stock solution,** 1,0 g/l Cd

Weigh (1 ± 0,001) g of cadmium (Cd ≥ 99,8 %) and transfer it into a 250 ml beaker. Add 10 ml of nitric 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.

1 ml of this solution contains 1,0 mg of Cd.

4.5 **Cadmium standard solution,** 0,005 g/l Cd

Transfer 2,5 ml of cadmium stock solution (4.4) into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Prepare this solution immediately prior to use.

1 ml of this solution contains 0,005 mg of Cd.

4.6 **Copper base solution,** 50 g/l Cu

Transfer 25,0 g of cadmium-free copper (Cu ≥ 99,95 %) into a 1 000 ml beaker. Add 250 ml of hydrochloric acid (4.1) and, cautiously, 125 ml of nitric acid (4.2). 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.

4.7 **Copper base solution,** 5 g/l Cu

Transfer 50,0 ml of copper base solution (4.6) 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 an air/acetylene burner

5.2 **Cadmium 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 General

Prepare test portion solutions in accordance with 7.1.2 or 7.1.3 depending on the expected cadmium content of the test sample.

7.1.2 Cadmium mass fractions between 0,000 5 % and 0,010 %

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

Transfer the test portion 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 and then bring to boiling point until the nitrous fumes have been expelled. Cool to room temperature, and wash the beaker cover and the sides of the beaker with water.

Transfer the dissolved test portion quantitatively into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix.

NOTE The validation test of this method showed that for cadmium mass fractions until and including 0,01 %, the results are better when the determination is carried out following 7.1.2.

7.1.3 Cadmium mass fractions between 0,01 % and 0,10 %

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

Transfer the test portion 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 and then bring to the boiling point until the nitrous fumes have been expelled. Cool to room temperature, and wash the beaker cover and the sides of the beaker with water.

Transfer the dissolved test portion quantitatively into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix.

Transfer 5,0 ml of this solution into a 100 ml one-mark volumetric flask. 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 cadmium 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, 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 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 (4.6 or 4.7) have been calculated to compensate for chemical interaction effects of copper in test solutions of copper or high-copper alloys. Over-compensation 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 cadmium 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 Cadmium mass fractions between 0,000 5 % and 0,010 %

Into each of a series of five 100 ml one-mark volumetric flasks, introduce the volumes of cadmium standard solution (4.5) and copper base solution (4.6) shown in Table 1. Dilute to the mark with water and mix.

Table 1 — Calibration for cadmium mass fractions between 0,000 5 % and 0,010 %

Cadmium standard solution volume (4.5) ml	Corresponding cadmium mass mg	Corresponding cadmium concentration after final dilution µg/ml	Copper base solution volume (4.6) ml	Corresponding copper mass g	Corresponding cadmium mass fraction of sample %
0[a]	0	0	20	1	0
1	0,005	0,05	20	1	0,000 5
4	0,020	0,20	20	1	0,002 0
10	0,050	0,50	20	1	0,005 0
20	0,100	1,00	20	1	0,010 0

[a] Blank test on reagents for calibration curve.

7.4.1.3 Cadmium mass fractions between 0,01 % and 0,10 %

Into each of a series of five 100 ml one-mark volumetric flasks, introduce the volumes of cadmium standard solution (4.5) and copper base solution (4.7) shown in Table 2. Dilute to the mark with water and mix.

Table 2 — Calibration for cadmium mass fractions between 0,01 % and 0,10 %

Cadmium standard solution volume (4.5) ml	Corresponding cadmium mass mg	Corresponding cadmium concentration after final dilution µg/ml	Copper base solution volume (4.7) ml	Corresponding copper mass g	Corresponding cadmium mass fraction of sample %
0[a]	0	0	10	0,05	0
1	0,005	0,05	10	0,05	0,01
3	0,015	0,15	10	0,05	0,03
6	0,030	0,30	10	0,05	0,06
10	0,050	0,50	10	0,05	0,10

[a] Blank test on reagents for calibration curve.

7.4.2 Adjustment of the atomic absorption spectrometer

Fit the cadmium hollow-cathode lamp (5.2) to the atomic absorption spectrometer (5.1), switch on the current and allow it to stabilise. Adjust the wavelength in the region of 228,8 nm to minimum absorbance. Following manufacturer's instructions, fit the correct burner, light the flame and allow the burner temperature to stabilise. 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 or 7.4.1.3 depending on the expected cadmium 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 or 7.1.3) 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 calculate the concentration directly using the appropriate calibration curve.

7.5.3.2 Use of bracketing method

Carry out a second measurement on the test portion solution (7.1.2 or 7.1.3) 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 (7.4.1), but having cadmium contents slightly higher and slightly lower (± 10 %) than the estimated cadmium concentration of the test portion solution.

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

8 Expression of results

8.1 Use of calibration curve

Calculate the cadmium mass fraction, in percent (%), using Formula (1):

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

where

w_{Cd} is the cadmium mass fraction in per cent (%)

c_1 is the cadmium concentration from the calibration curve, in microgram per millilitre (µg/ml) to be converted in milligram per millilitre (mg/ml);

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

V_f is the total[1)] volume of the test portion solution (7.1.2 or 7.1.3), in millilitre (ml).

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1) Is the final volume corrected by a dilution ratio (if the case).

8.2 Use of bracketing method

Calculate the cadmium mass fraction, in percent (%), using Formula (2):

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

where

c_2 is the cadmium concentration, calculated using Formula (3), in microgram per millilitre (µg/ml) to be converted in milligram per millilitre (mg/ml);

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

V_f is the total[1)] volume of the test portion solution (7.1.2 or 7.1.3), 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 cadmium concentration of the calibration solution used, in microgram per millilitre (µg/ml) to be converted in milligram per millilitre (mg/ml);

C_2 is the higher cadmium concentration of the calibration solution used, in microgram per millilitre (µg/ml) to be converted 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 the concentration C_1;

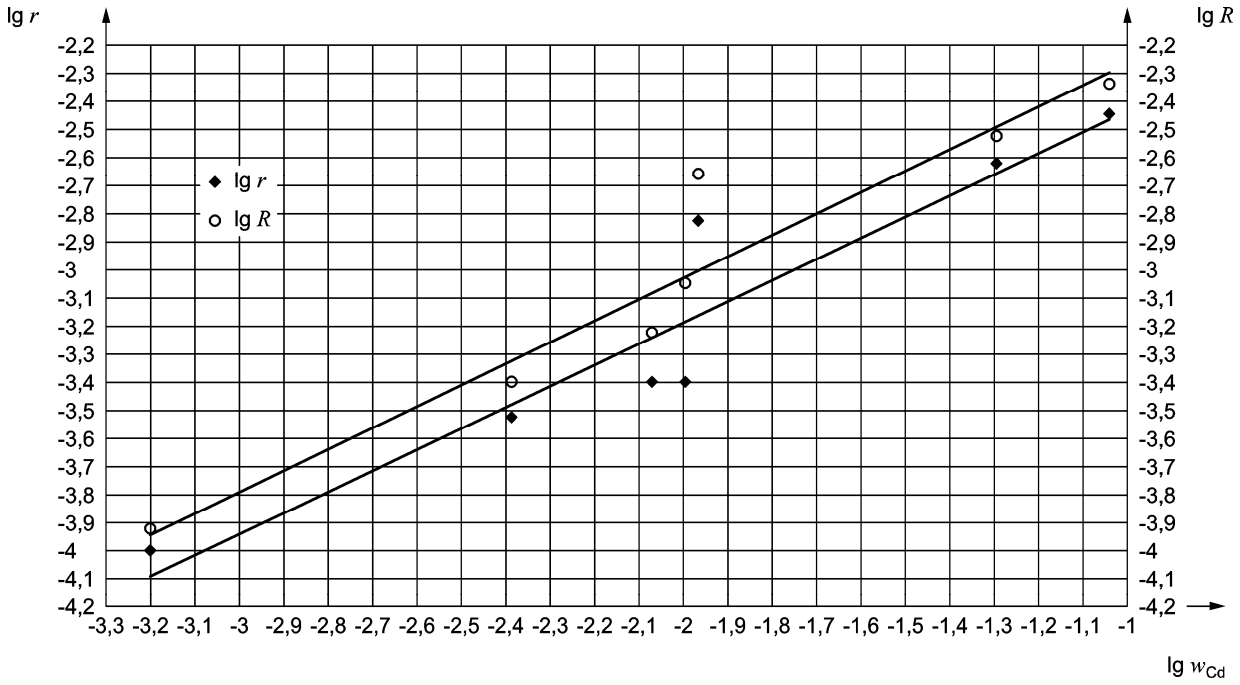
S_2 is the absorbance value of the calibration solution corresponding to the concentration C_2.

9 Precision

Seven laboratories co-operated in validating this method and obtained the results summarised in Table 3 and Figure 1 respectively.

Table 3 — Statistical information

Level		Reference value %	Found %	Repeatability r	Reproducibility R
1	(7.4.1.2)	0,000 57	0,000 63	0,000 10	0,000 12
2	(7.4.1.2)	0,003	0,004 1	0,000 3	0,000 4
3	(7.4.1.2)	0,008 6	0,008 5	0,000 4	0,000 6
4	(7.4.1.2)	0,010 1	0,010 1	0,000 4	0,000 9
5	(7.4.1.3)	0,010 1	0,010 8	0,001 5	0,002 2
6	(7.4.1.3)	0,050	0,050 7	0,002 4	0,003 0
7	(7.4.1.3)	0,090	0,091 0	0,003 6	0,004 6



$$\lg r = 0{,}753\ 7 \lg w_{Cd} - 1{,}680$$

$$\lg R = 0{,}762\ 8 \lg w_{Cd} - 1{,}503$$

Figure 1 — lg relationship between cadmium mass fraction w_{Cd}, 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 15616);

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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