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

ICS 77.120.30

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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Copper and copper alloys - Determination of lead content - Flame atomic absorption spectrometric method (FAAS)

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

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

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Management Centre: Avenue Marnix 17, B-1000 Brussels

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Foreword

This document (EN 15622:2010) 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of an identical text or by endorsement, at the latest by September 2010, and conflicting national standards shall be withdrawn at the latest by September 2010.

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

EN 15622, *Copper and copper alloys — Determination of lead content — Flame atomic absorption spectrometric method (FAAS).*

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1 Scope

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

The method is applicable to products having lead mass fractions between 0,01 % 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*

3 Principle

Dissolution of a test portion in fluoroboric-nitric acid mixture 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 217,0 nm line emitted by a lead hollow-cathode lamp.

NOTE During the validation exercise of this standard method some laboratories have also carried out the measurements at 283 nm line. These measurements showed a satisfactory trueness. However, the number of results produced was too few and, therefore, insufficient for the estimation of the corresponding precision data.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

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

4.2 Nitric acid solution (1 + 1).

Add 100 ml of nitric acid (4.1) to 100 ml of water.

4.3 Hydrofluoric acid, HF, 40 % solution (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.

4.4 Boric acid, H_3BO_3, 40 g/l solution.

4.5 Fluoroboric-nitric acid mixture.

Add 300 ml of boric acid (4.4), 30 ml of hydrofluoric acid (4.3) and 500 ml of nitric acid (4.1) to 150 ml of water and mix well.

4.6 Lead stock solution, 1,0 g/l Pb.

Weigh (1 ± 0,001) g of lead (Pb ≥ 99,9 %) and transfer it into a 250 ml beaker. Add 20 ml of nitric acid solution (4.2), cover with a watch glass and heat gently until the lead is completely dissolved and then bring to the boiling point until the nitrous fumes have been expelled. Cool to room temperature, transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, add 100 ml of water and 9 ml of nitric acid solution (4.2). Dilute to the mark with water and mix well.

1 ml of this solution contains 0,001 g of Pb.

4.7 Lead standard solution, 0,1 g/l Pb.

Transfer 25,0 ml of the lead stock solution (4.6) into a 250 ml one-mark volumetric flask, add 100 ml of water and 9 ml of nitric acid solution (4.2). Dilute to the mark with water and mix well.

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

4.8 Copper base solution, 20 g/l Cu.

Weigh (10 ± 0,01) g of pure, lead-free copper (Pb < 0,000 2 %) and transfer it into a 600 ml polytetrafluorethylene, polyethylene or low-pressure polypropylene beaker. Add 400 ml of the fluoroboric-nitric acid mixture (4.5) and cover with a watch glass. Heat until the copper is completely dissolved, then boil until the nitrous fumes have been expelled. Allow to cool and transfer the solution into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

50 ml of the solution contain 1,0 g of copper and 40 ml of the fluoroboric-nitric acid mixture.

5 Apparatus

5.1 Beakers, polytetrafluorethylene, polyethylene or polypropylene.

5.2 One-mark volumetric flasks, polytetrafluorethylene, polyethylene or polypropylene.

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

5.4 Lead 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 polytetrafluorethylene, polyethylene or polypropylene beaker (5.1). Add 40 ml of the fluoroboric-nitric acid mixture (4.5). 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 brown fumes have been expelled. If polyethylene or polypropylene beakers are used, heating shall be carried out in water bath. Wash the cover and the sides of the beaker with water and allow to cool. Transfer the dissolved test portion quantitatively into a 100 ml one-mark volumetric flask, dilute the solution to the mark with water and mix well.

7.1.3 Lead mass fractions between 0,01 % and 0,15 %

Proceed as indicated in 7.5.

7.1.4 Lead mass fractions between 0,1 % and 0,75 %

Take a 20 ml aliquot of the test portion solution (7.1.2) and introduce into a 100 ml one-mark volumetric flask. Dilute to the mark with water and mix well. Proceed as indicated in 7.5.

NOTE The validation exercise of this standard method showed that for lead mass fractions between 0,5 % and 0,75 % results are better when the determination is carried out following 7.1.4.

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

Take a 20 ml aliquot of the test portion solution (7.1.2) and introduce into a 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well. Proceed as indicated in 7.5.

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 lead 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, salt-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 lead 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 Lead mass fractions between 0,01 % and 0,15 %

Into each of a series of six 100 ml one-mark volumetric flasks, introduce the volumes of lead standard solution (4.7) and of copper base solution (4.8) shown in Table 1. Dilute to the mark with water and mix well.

Table 1 — Calibration for lead mass fractions between 0,01 % and 0,15 %

Lead standard solution volume (4.7) ml	**Corresponding lead mass** mg	**Corresponding lead concentration after final dilution** mg/ml	**Copper base solution volume** (4.8) ml	**Corresponding copper mass** g	**Corresponding lead mass fraction of sample** %
0[a]	0	0	50	1,000	0
1	0,1	0,001	50	1,000	0,01
2	0,2	0,002	50	1,000	0,02
5	0,5	0,005	50	1,000	0,05
10	1,0	0,010	50	1,000	0,10
15	1,5	0,015	50	1,000	0,15

[a] Blank test on reagents for calibration curve.

7.4.1.3 Lead mass fractions between 0,1 % and 0,75 %

Into each of a series of five 100 ml one-mark volumetric flask, introduce the volumes of lead standard solution (4.7) and of copper base solution (4.8) as shown in Table 2. Dilute to the mark with water and mix well.

Table 2 — Calibration for lead mass fractions between 0,1 % and 0,75 %

Lead standard solution volume (4.7) ml	**Corresponding lead mass** mg	**Corresponding lead concentration after final dilution** mg/ml	**Copper base solution volume** (4.8) ml	**Corresponding copper mass** g	**Corresponding lead mass fraction of sample** %
0[a]	0	0	10	0,200	0
2	0,2	0,002	10	0,200	0,10
5	0,5	0,005	10	0,200	0,25
10	1,0	0,010	10	0,200	0,50
15	1,5	0,015	10	0,200	0,75

[a] Blank test on reagents for calibration curve.

7.4.1.4 Lead mass fractions between 0,5 % and 5,0 %

Into each of a series of six 100 ml one-mark volumetric flask, introduce the volumes of lead standard solution (4.7) and of copper base solution (4.8) as shown in Table 3. Dilute to the mark with water and mix well.

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

Lead standard solution volume (4.7) ml	**Corresponding lead mass** mg	**Corresponding lead concentration after final dilution** mg/ml	**Copper base solution volume** (4.8) ml	**Corresponding copper mass** g	**Corresponding lead mass fraction of sample** %
0[a]	0	0	2	0,040	0
2	0,2	0,002	2	0,040	0,50
5	0,5	0,005	2	0,040	1,25
10	1,0	0,010	2	0,040	2,50
15	1,5	0,015	2	0,040	3,75
20	2,0	0,020	2	0,040	5,00

[a] Blank test on reagents for calibration curve.

7.4.2 Adjustment of the atomic absorption spectrometer

Fit the lead 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 217,0 nm to minimum absorbance (see NOTE in Clause 3). 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 or 7.4.1.4 depending on the expected lead 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 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 solutions (7.1.3, 7.1.4, 7.1.5) 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 7.4.1.2, 7.4.1.3 or 7.4.1.4). 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 portion solutions (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 a composition similar to that of the calibration solutions (see 7.4.1), but having lead contents slightly higher and slightly lower (± 10 %) than the estimated lead concentration of the test portion solution.

To prepare these calibration solutions, follow the procedure specified in 7.4.1 using, however, suitable quantities of lead standard solution (4.7).

8 Expression of results

8.1 Use of calibration curve

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

$$w(Pb) = \frac{c_1}{m} \times V_\mathrm{f} \times 100 \quad (1)$$

where

$w(Pb)$ is the lead mass fraction in per cent (%);

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

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

V_f is the total[1] volume of the test portion solution (7.1.3, 7.1.4, 7.1.5), in millilitre (ml).

8.2 Use of bracketing method

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

$$w(Pb) = \frac{c_2}{m} \times V_\mathrm{f} \times 100 \quad (2)$$

---

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

where

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

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

V_f is the total[1)] volume of the test portion solution (7.1.3, 7.1.4 or 7.1.5), in millilitre (ml);

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

where

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

C_2 is the higher lead 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;

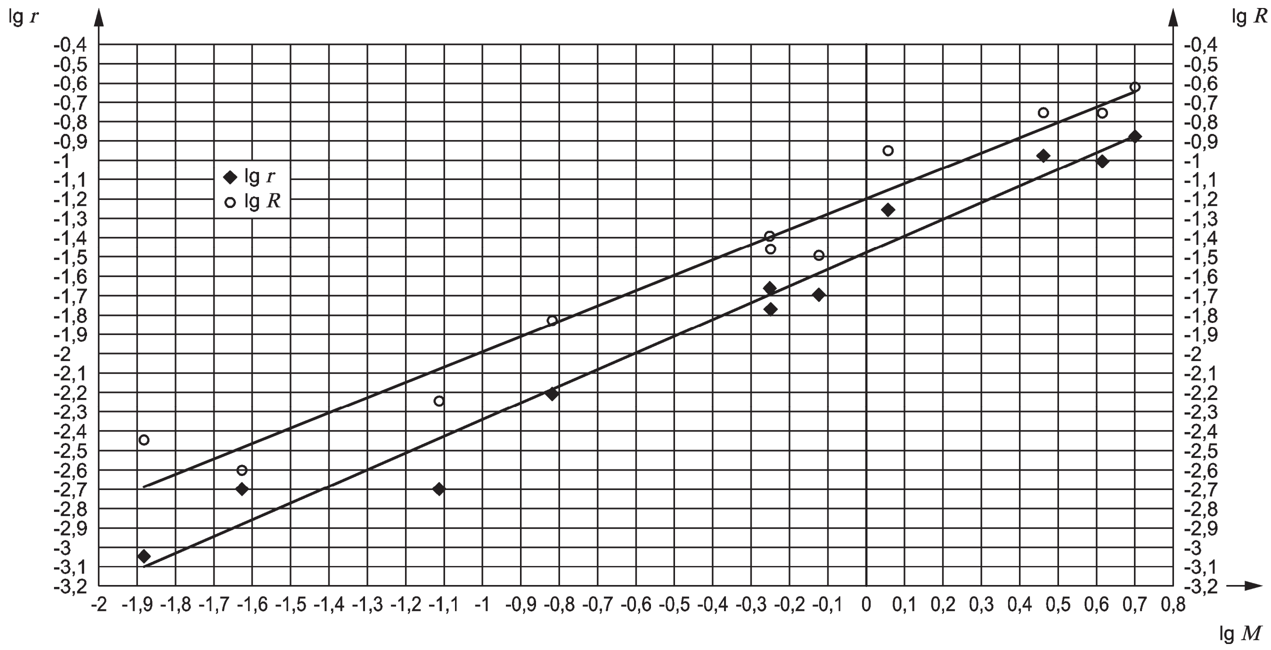
S_2 is the absorbance value of the calibration solution corresponding to concentration C_2.

9 Precision

Seven laboratories co-operated in validating this method and obtained the results summarized in Table 4 and Figure 1 respectively.

Table 4 — Statistical information

Level	Reference value %	Found %	Repeatability r	Reproducibility R
1 (7.4.1.2)	0,013 1	0,013 1	0,000 9	0,003 5
2 (7.4.1.2)	0,023 6	0,023 6	0,002 0	0,002 5
3 (7.4.1.2)	0,079	0,077 1	0,002 0	0,005 7
4 (7.4.1.3)	0,15	0,151 9	0,006 2	0,014 9
5 (7.4.1.3)	0,564	0,563 5	0,017 0	0,034 7
6 (7.4.1.3)	0,74	0,752 3	0,020 2	0,032 1
7 (7.4.1.4)	0,564	0,560 5	0,021 8	0,040 6
8 (7.4.1.4)	1,13	1,140 4	0,055 4	0,112 4
9 (7.4.1.4)	2,90	2,895 1	0,105 7	0,176 5
10 (7.4.1.4)	4,12	4,123 3	0,098 8	0,175 5
11 (7.4.1.4)	5,01	5,021 2	0,132 9	0,240 3



$$\lg r = 0{,}861\,5 \cdot \lg M - 1{,}478\,8$$

$$\lg R = 0{,}789\,9 \cdot \lg M - 1{,}200\,8$$

Figure 1 — lg relationship between lead mass fraction M 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 15622);

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 4749, *Copper alloys — Determination of lead content — Flame atomic absorption spectrometric method*

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

[3] 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*

[4] 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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BSI Group
Headquarters 389
Chiswick High Road,
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Tel +44 (0)20 8996 9001
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