BS EN 14938-2:2010

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# Copper and copper alloys — Determination of bismuth content

## Part 2: Flame atomic absorption spectrometric method (FAAS)

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## National foreword

This British Standard is the UK implementation of EN 14938-2:2010. It supersedes DD CEN/TS 14938-2:2006 which is withdrawn.

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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**EN 14938-2**

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English Version

# Copper and copper alloys - Determination of bismuth content - Part 2: Flame atomic absorption spectrometric method (FAAS)

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

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

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## Contents

# Foreword

This document (EN 14938-2:2010) 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of an identical text or by endorsement, at the latest by January 2011, and conflicting national standards shall be withdrawn at the latest by January 2011.

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.

This document supersedes CEN/TS 14938-2:2006.

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 14938-2:2006, *Copper and copper alloys — Determination of bismuth content — Part 2: FAAS method*

In comparison with the first edition of CEN/TS 14938-2:2006, the following significant technical changes were made:

- Revision from a Technical Specification to a European Standard;
- Subclause 7.4.1.1 - text added;
- Clause 9 Precision - completely revised.

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

EN 14938-1, *Copper and copper alloys — Determination of bismuth content — Part 1: Spectrophotometric 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, Croatia, 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 European Standard specifies a flame atomic absorption spectrometric method (FAAS) for the determination of the bismuth content of copper and copper alloys in the form of unwrought, wrought and cast products.

The method is applicable to products having bismuth mass fractions between 0,01 % and 0,25 %.

# 2 Normative references

The following referenced documents are indispensable for the application of this European Standard. 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 mixture of hydrochloric acid/hydrogen peroxide and nitric acid solutions followed, after suitable dilution, by aspiration into an air/acetylene flame of an atomic absorption spectrometer. Measurement of the absorption of the 223,1 nm line emitted by a bismuth hollow-cathode or electrodeless discharge 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 ($\rho$ = 1,19 g/ml)

**4.2 Nitric acid**, $HNO_3$ ($\rho$ = 1,40 g/ml)

**4.3 Hydrogen peroxide**, $H_2O_2$ 30 % (mass fraction) solution

## 4.4 Bismuth stock solution, 1,0 g/l Bi

Weigh (0,25 ± 0,001) g of bismuth (Bi ≥ 99,999 9 %) and transfer it into a 250 ml beaker. Add 50 ml of nitric acid (4.2) and cover with a watch glass. Heat gently until the bismuth is dissolved and then bring to the boiling point until the nitrous fumes have been expelled. Cool to room temperature and transfer the solution quantitatively into a 250 ml one-mark volumetric flask, dilute to the mark with water and mix well.

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

## 4.5 Bismuth standard solution, 0,1 g/l Bi

Transfer 25,0 ml of the bismuth 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 0,1 mg of Bi.

### 4.6 Copper base solution, 20 g/l Cu

Into a 600 ml tall beaker weigh 10,0 g of bismuth-free copper (Bi ≤ 0,005 %). Add 50 ml of distilled water and, in small portions, 50 ml of nitric acid (4.2). Cover and heat gently until the copper is completely dissolved, then continue heating to the boiling point. Cool to room temperature. Wash the beaker cover and the sides of the beaker with water. Transfer the solution quantitatively into a 500 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 Bismuth hollow-cathode or electrodeless discharge 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 distilled water, 0,5 ml of nitric acid (4.2), 0,5 ml of hydrogen peroxide (4.3) and 20 ml of hydrochloric acid (4.1). Cover with a watch glass and heat gently until the test portion is completely dissolved, then continue heating to the boiling point. Cool to room temperature. Wash the beaker cover and the sides of the beaker with water.

Transfer the dissolved test portion 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 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 bismuth 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 and chloride concentrations 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 (4.6) 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 bismuth concentration of the calibration solutions shall be adjusted to suit the sensitivity of the apparatus used, so that the curve of absorbance as a function of concentration is a straight line.

NOTE The amount of $HNO_3$ in the sample solutions is different from that in the calibration solutions. This does not effect the measurement.

**7.4.1.2** Bismuth mass fractions between 0,01 % and 0,05 %

Into each of a series of five 100 ml one-mark volumetric flasks, introduce 20,0 ml of hydrochloric acid (4.1) and the volumes of the bismuth standard solution (4.5) and of the copper base solution (4.6) shown in Table 1. Dilute to the mark with water and mix well.

**Table 1 — Calibration for bismuth mass fractions between 0,01 % and 0,05 %**

| **Bismuth standard solution volume** (4.5) ml | **Corresponding bismuth mass** mg | **Corresponding bismuth concentration after final dilution** mg/ml | **Copper base solution volume** (4.6) ml | **Corresponding copper mass** g | **Corresponding bismuth mass fraction of sample** % |
|---|---|---|---|---|---|
| 0[a] | 0 | 0 | 50 | 1,000 | 0 |
| 1 | 0,10 | 0,001 0 | 50 | 1,000 | 0,010 |
| 2 | 0,20 | 0,002 0 | 50 | 1,000 | 0,020 |
| 3 | 0,30 | 0,003 0 | 50 | 1,000 | 0,030 |
| 5 | 0,50 | 0,005 0 | 50 | 1,000 | 0,050 |

[a] Blank test on reagents for calibration curve.

**7.4.1.3** Bismuth mass fractions between 0,050 % and 0,25 %

Into each of a series of five 100 ml one-mark volumetric flasks, introduce 20,0 ml of hydrochloric acid (4.1) and the volumes of the bismuth stock solution (4.4) and of the copper base solution (4.6) shown in Table 2. Dilute to the mark with water and mix well.

**Table 2 — Calibration for bismuth mass fractions between 0,05 % and 0,25 %**

| **Bismuth stock solution volume** (4.4) ml | **Corresponding bismuth mass** mg | **Corresponding bismuth concentration after final dilution** mg/ml | **Copper base solution volume** (4.6) ml | **Corresponding copper mass** g | **Corresponding bismuth mass fraction of sample** % |
|---|---|---|---|---|---|
| 0[a] | 0 | 0 | 50 | 1,00 | 0 |
| 0,5 | 0,50 | 0,005 | 50 | 1,00 | 0,050 |
| 1,0 | 1,00 | 0,010 | 50 | 1,00 | 0,10 |
| 1,5 | 1,50 | 0,015 | 50 | 1,00 | 0,15 |
| 2,5 | 2,50 | 0,025 | 50 | 1,00 | 0,25 |

[a] Blank test on reagents for calibration curve.

### 7.4.2 Adjustment of the atomic absorption spectrometer

Fit the bismuth hollow-cathode or electrodeless discharge 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 223,1 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 (see 7.4.1.2 or 7.4.1.3 depending on the expected bismuth 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 portion solution (7.1.2) following the procedure specified in 7.4.3, by bracketing between two new calibration solutions with composition similar to that of the calibration solution (7.4.1), but having bismuth concentrations slightly higher and slightly lower (± 10 %) than the estimated bismuth concentration of the test portion solution.

To prepare these standard calibration solutions, follow the procedure specified in 7.4.1 using, however, suitable quantities of bismuth stock or standard solutions (4.4 and 4.5).

## 8 Expression of results

### 8.1 Use of calibration curve

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

$$w_{\mathrm{Bi}} = \frac{c_1}{m} \times V_{\mathrm{f}} \times 100 \tag{1}$$

where

$w_{\mathrm{Bi}}$ is the bismuth mass fraction in percent (%);

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

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

$V_{\mathrm{f}}$ is the volume of the final test portion solution (7.1.2), in millilitres (ml).

### 8.2 Use of bracketing method

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

$$w_{\mathrm{Bi}} = \frac{c_2}{m} \times V_{\mathrm{f}} \times 100 \tag{2}$$

where

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

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

$V_{\mathrm{f}}$ is the volume of the final test portion solution (7.1.2), in millilitres (ml);

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

where

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

$C_2$ is the higher bismuth 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 $C_2$.

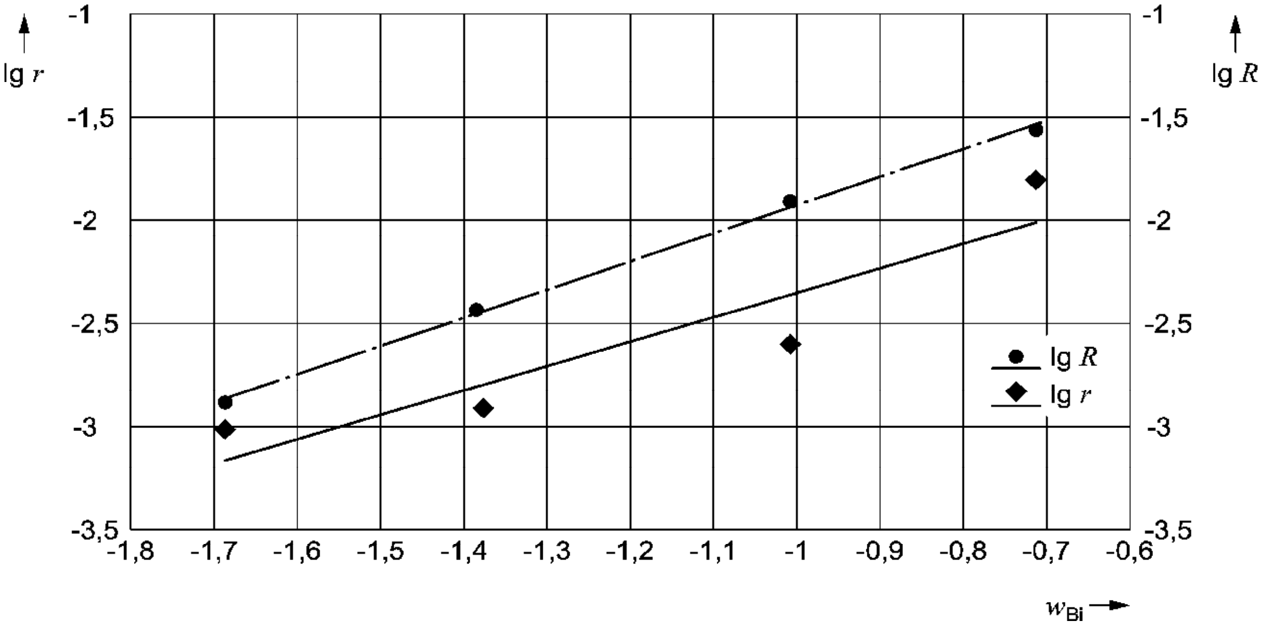
## 9 Precision

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

The data for $r$ and $R$ conform to the method given in ISO 5725.

**Table 3 — Statistical information**

| Level | Reference value<br>% | Found<br>% | Repeatability<br>$r$ | Reproducibility<br>$R$ |
|---|---|---|---|---|
| 1 | 0,020 | 0,020 5 | 0,001 0 | 0,001 3 |
| 2 | 0,04 | 0,042 0 | 0,001 2 | 0,003 7 |
| 3 | 0,10 | 0,098 2 | 0,002 5 | 0,012 5 |
| 4 | 0,162 | 0,194 1 | 0,015 7 | 0,027 4 |



**Key**

lg $r$ = 1,180 1 lg $w_{Bi}$ – 1,170 6

lg $R$ = 1,361 lg $w_{Bi}$ – 0,566 9

**Figure 1 — lg relationship between bismuth concentration $w_{Bi}$ 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 14938-2);

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

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

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*

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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