



SLOVENSKI STANDARD
SIST-TS CEN/TS 15656:2010
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Copper and copper alloys - Determination of phosphorus content - Spectrophotometric method

Kupfer und Kupferlegierungen - Bestimmung des Phosphorgehaltes - Spektrophotometrisches Verfahren

iTeh STANDARD PREVIEW

Cuivre et alliages de cuivre - Dosage du phosphore - Méthode spectrophotométrique

Ta slovenski standard je istoveten z: CEN/TS 15656:2009

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ICS:

77.120.30 Baker in bakrove zlitine Copper and copper alloys

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TECHNICAL SPECIFICATION
SPÉCIFICATION TECHNIQUE
TECHNISCHE SPEZIFIKATION

CEN/TS 15656

October 2009

ICS 77.120.30

English Version

**Copper and copper alloys - Determination of phosphorus
content - Spectrophotometric method**

Cuivre et alliages de cuivre - Dosage du phosphore -
Méthode spectrophotométrique

Kupfer und Kupferlegierungen - Bestimmung des
Phosphorgehaltes - Spektrophotometrisches Verfahren

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Foreword

This document (CEN/TS 15656:2009) has been prepared by Technical Committee CEN/TC 133 "Copper and copper alloys", the secretariat of which is held by DIN.

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

— CEN/TS 15656, *Copper and copper alloys — Determination of phosphorus content — Spectrophotometric method.*

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CEN/TS 15656:2009 (E)**1 Scope**

This Technical Specification specifies a molybdovanadate spectrophotometric method for the determination of phosphorus in copper and copper alloys in the form of castings or unwrought or wrought products.

The method is applicable to products having phosphorus mass fractions between 0,001 % and 0,5 %.

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 Technical Specification, and cited at the appropriate places in the text, are listed in the Bibliography.

3 Principle

Dissolution of a test portion in nitric acid. Elimination of interfering elements by fuming with perchloric, hydrofluoric and hydrobromic acids. Decomposition of insoluble phosphates by fusion with sodium carbonate. For concentrations below 0,01 % mass fraction, extraction of phosphorus as phosphomolybdic acid and spectrophotometric determination as molybdenum blue; for concentrations between 0,005 % and 0,05 % mass fraction, extraction and spectrophotometric determination as phosphovanadomolybdic acid.

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 ($\rho = 1,40$ g/ml)

4.2 Nitric acid solution, 1 + 1

Add 500 ml of nitric acid (4.1) to 500 ml of water.

4.3 Hydrofluoric acid, HF 40 % (volume fraction), ($\rho = 1,13$ g/ml)

4.4 Perchloric acid, HClO_4 ($\rho = 1,67$ g/ml)

4.5 Hydrobromic acid, HBr ($\rho = 1,50$ g/ml)

4.6 Isobutanol

4.7 Sodium carbonate, Na_2CO_3

4.8 Methanol

4.9 Methyl isobutyl ketone

4.10 Ammonium molybdate solution, 50 g/l

Dissolve 50 g of ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ in 250 ml of water. Add a solution of 115 ml of the perchloric acid (4.4) and 500 ml of water at room temperature. Dilute to 1 000 ml with water.

NOTE After prolonged storage, a white precipitate may form. While this residue will not affect the analysis, care should be taken to prevent its contamination of the aliquot used in the analysis.

Immediately before use, the aliquot used in the analysis should be purified by shaking with 10 ml of the isobutanol (4.6).

4.11 Ammonium molybdate solution, 150 g/l

Dissolve 150 g of ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ in 1 000 ml of water.

4.12 Hydrochloric acid, HCl ($\rho = 1,19$ g/l)**4.13 Tin(II) chloride stock solution**

Dissolve 10 g of tin(II) chloride dihydrate $(\text{SnCl}_2 \cdot 2\text{H}_2\text{O})$ in 25 ml of hydrochloric acid (4.12). Prepare this solution fresh before use.

4.14 Sulphuric acid, H_2SO_4 ($\rho = 1,84$ g/l)**4.15 Sulphuric acid solution, 10 mol/l**

To 100 ml of water add 56 ml of sulphuric acid (4.14) while cooling.

4.16 Tin(II) chloride, working solution

Dilute 1 ml of the tin(II) chloride stock solution (4.13) with 10 ml of sulphuric acid solution (4.15) and make up to 200 ml with water.

Prepare this solution fresh before use.

4.17 Ammonium vanadate solution, 2,5 g/l

Dissolve 2,5 g of ammonium vanadate (NH_4VO_3) in 1 000 ml of water.

4.18 Citric acid solution, 500 g/l

Dissolve 500 g of citric acid $(\text{C}_6\text{H}_8\text{O}_7)$ in 1 000 ml of water.

4.19 Phosphorus stock solution, 100 mg/l

Dissolve 0,439 3 g of potassium dihydrogen orthophosphate (KH_2PO_4) , freshly dried at 105 °C, with water and dilute to the mark of a 1 000 ml one-mark volumetric flask.

1 ml of this standard solution contains 0,1 mg of phosphorus.

4.20 Phosphorus standard solution, 10 mg/l

Transfer 20 ml of the phosphorus stock solution (4.19) to a 200 ml one-mark volumetric flask, dilute with water and mix.

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

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CEN/TS 15656:2009 (E)**5 Apparatus**

All vessels shall be free of contamination by phosphorus. Cleaning with hot hydrochloric acid (4.12), is recommended.

5.1 Ordinary laboratory apparatus**5.2 PTFE beakers**, capacity 100 ml**5.3 Spectrophotometer**, fitted with cells of optical path lengths 1 cm and 4 cm**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 $(1 \pm 0,001)$ g of the test sample.

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7.1.2 Test portion solution

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7.1.2.1 Dissolve the test portion (7.1.1) in a PTFE beaker (5.2) with 10,0 ml of the nitric acid solution (4.2). Heat gently, if necessary. To eliminate silicon, add 0,50 ml of the hydrofluoric acid (4.3) and 10,0 ml of the perchloric acid (4.4) and heat until fuming begins.

7.1.2.2 Dilute the solution with 10 ml of water and add 10,0 ml of the hydrobromic acid (4.5). To eliminate interference from arsenic, antimony and tin, heat gently until fuming begins again. If tin contents of > 1 % mass fraction are present, repeat the fuming step with 10,0 ml of the hydrobromic acid (4.5).

7.1.2.3 Dissolve the copper bromide formed during the fuming steps by adding several millilitres of the nitric acid solution (4.2) and bring to fuming. Dilute this solution with 30 ml of water. Heat to boiling for 10 min, then cool to room temperature. Filter the solution through a fine pored filter. Wash the filter with hot water until free of acid, then dry and ignite the filter in a small platinum crucible covered with a platinum cover. The temperature has to be increased slowly. Mix the residue with about 0,3 g of sodium carbonate and fuse.

NOTE If the test sample contains zirconium, titanium, niobium and/or tantalum, phosphorus can be found totally or partially as insoluble phosphates. The procedure for dissolving these residues is described below.

After cooling, dissolve the melt with a small amount of water. Filter off any insoluble residue and wash with hot water, adding the washings to the filtrate. Neutralize the combined filtrate and washings with the perchloric acid (4.4). Add the neutralized solution of the original copper-containing filtrate. The total volume should not exceed 50 ml; if necessary, the volume should be reduced by evaporating.

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 and of pure copper as used for the determination, but omitting the test portion. Correct the result obtained from the determination in accordance with the result for the blank.

7.3 Check test

Make a preliminary check of the apparatus by preparing a solution of standard material or a synthetic sample containing a known amount of phosphorus and of composition similar to the test sample to be analysed. Carry out the procedure specified in 7.1 and 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 acidity in the calibration solutions shall be similar to those of the test portion solutions.

The phosphorus 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.

7.4.1.2 Phosphorus mass fraction between 0,001 % and 0,005 %

Into each of a series of five PTFE beakers (5.2) introduce in each beaker ($1 \pm 0,001$) g of electrolytic tough pitch copper ($P < 0,000 1$ %).

Follow exactly the procedure described in 7.1.2, adding the volumes of phosphorus standard solution (4.20) as shown in Table 1, just before heating for fuming. Follow the procedure as described in 7.1.2.2, 7.1.2.3 and 7.5.2.1.

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Table 1 — Calibration for phosphorus mass fractions between 0,001 % and 0,005 %

Phosphorus standard solution volume (4.20) ml	Corresponding phosphorus mass mg	Corresponding phosphorus concentration after final dilution mg/ml	Corresponding phosphorus mass fraction of test sample %
0 ^a	0	0	0
1	0,01	0,000 2	0,001
2	0,02	0,000 4	0,002
4	0,04	0,000 8	0,004
5	0,05	0,001 0	0,005

^a Blank test on reagents for calibration curve.

7.4.1.3 Calibration for phosphorus mass fraction between 0,005 % and 0,01 %

Into each of a series of seven PTFE beakers (5.2) introduce in each beaker ($1 \pm 0,001$) g of electrolytic tough pitch copper ($P < 0,000 1$ %).

Follow exactly the procedure described in 7.1.2, adding the volumes of phosphorus standard solution (4.20) as shown in Table 2, just before heating for fuming. Follow the procedure as described in 7.1.2.2, 7.1.2.3 and 7.5.2.2.