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Baker in bakrove zlitine - Določevanje fosforja - Spektrofotometrična metoda

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

Kupfer und Kupferlegierungen - Bestimmung des Phosphorgehaltes - Spektrophotometrisches Verfahren

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

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77.120.30 Baker in bakrove zlitine Copper and copper alloys

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Supersedes CEN/TS 15656:2009

English Version

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

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

Kupfer und Kupferlegierungen - Bestimmung des Phosphorgehaltes - Spektrophotometrisches Verfahren

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Foreword

This document (CEN/TS 15656:2015) has been prepared by Technical Committee CEN/TC 133 “Copper and copper alloys”, the secretariat of which is held by DIN.

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 15656:2009.

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 15656:2009, *Copper and copper alloys — Determination of phosphorus content — Spectrophotometric method*.

In comparison with CEN/TS 15656:2009 only editorial modifications have been made.

According to the CEN-CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this Technical Specification: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

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 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 nitric acid. Elimination of interfering elements by fuming with perchloric, hydrofluoric and hydrobromic acids. Decomposition of insoluble phosphates by fusion with sodium carbonate. For contents below 0,01 % mass fraction, extraction of phosphorus as phosphomolybdic acid and spectrophotometric determination as molybdenum blue; for contents 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 (ρ = 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 (ρ = 1,13 g/ml)

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

4.5 Hydrobromic acid, HBr (ρ = 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 [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] 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.

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 [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] in 1 000 ml of water.

4.12 Hydrochloric acid, HCl (ρ = 1,19 g/l)

4.13 Tin(II) chloride solution, 400 g/l

Dissolve 10 g of tin(II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$) in 25 ml of hydrochloric acid (4.12). Prepare this solution fresh before use.

4.14 Sulphuric acid, H_2SO_4 (ρ = 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 solution, 2 g/l

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 ($C_6H_8O_7$) 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 into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

1 ml of this stock 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) into a 200 ml one-mark volumetric flask, dilute to the mark with water and mix well.

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

5 Apparatus

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

5.1 PTFE beakers, capacity 100 ml

5.2 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 ± 0,001) g of the test sample.

7.1.2 Test portion solution

7.1.2.1 Dissolve the test portion (7.1.1) in a PTFE beaker (5.1) with 10,0 ml of nitric acid solution (4.2). Heat gently, if necessary. To eliminate silicon, add 0,50 ml of hydrofluoric acid (4.3) and 10,0 ml of 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 hydrobromic acid (4.5). To eliminate interference from arsenic, antimony and tin, heat gently until fuming begins again. If tin content is > 1 % (mass fraction), repeat the fuming step with 10,0 ml of hydrobromic acid (4.5).

7.1.2.3 Dissolve the copper bromide formed during the fuming steps by adding several millilitres of nitric acid solution (4.2) and bring to fuming. Dilute 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 it is 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 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 reference material or a synthetic sample containing a known amount of phosphorus and of composition similar to the material 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 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 spectrophotometer 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 (5.1) introduce in each beaker (1 ± 0,001) g of electrolytic tough pitch copper (P < 0,000 1 %).

Follow exactly the procedure described in 7.1.2. Add the volumes of phosphorus standard solution (4.20) as shown in Table 1, just before heating for fuming with perchloric acid (4.4). Follow the procedure as described in 7.1.2.2, 7.1.2.3 and 7.5.2.1.

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

Phosphorus standard solution volume (4.20)	Corresponding phosphorus mass	Corresponding phosphorus concentration after final dilution	Corresponding phosphorus mass fraction of test sample
ml	mg	mg/ml	%
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.