SLOVENSKI STANDARD
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Baker in bakrove zlitine - Določevanje kroma - 1. del: Titrimetrijske metode

Copper and copper alloys - Determination of chromium content - Part 1: Titrimetric method

Kupfer und Kupferlegierungen - Bestimmung des Chromgehaltes - Teil 1: Titrimetrisches Verfahren

Cuivre et alliages de cuivre - Dosage du chrome - Partie 1: Méthode titrimétrique

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Kupfer und Kupferlegierungen - Bestimmung des Chromgehaltes - Teil 1: Titrimetrisches Verfahren

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Foreword

This document (CEN/TS 14940-1:2009) 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 14940-1, *Copper and copper alloys — Determination of chromium content — Part 1: Titrimetric method*

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

EN 14940-2, *Copper and copper alloys — Determination of chromium content — Part 2: FAAS method*.

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1 Scope

This part of this document specifies a titrimetric method for the determination of the chromium content of copper and copper alloys in the form of castings or unwrought or wrought products.

The method is applicable to products having chromium mass fractions between 0,10 % and 2,0 %.

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*

NOTE Informative references to documents used in the preparation of this standard, and cited at the appropriate places in the text, are listed in the Bibliography.

3 Principle

Dissolution of a test portion followed by oxidation of the greater part of chromium by perchloric acid in the presence of orthophosphoric acid to avoid loss of chromium. Oxidation of residual chromium(III) by potassium permanganate. Reduction of chromium(VI) by iron(II) solution and determination of the equivalence point by measuring the change in potential as a function of the volume of titrant used.

4 Reagents and materials

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

4.1 Hydrochloric acid, HCl (ρ = 1,19 g/ml)

4.2 Hydrochloric acid solution, 1+ 20

Add 5,0 ml of the hydrochloric acid (4.1) to 100 ml of water.

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

4.4 Hydrofluoric acid, HF (ρ = 1,13 g/ml)

CAUTION — Hydrofluoric acid is a hazardous material. Care shall be taken and its use to be made in an efficient fume hood.

4.5 Perchloric acid, $HClO_4$ (ρ = 1,61 g/ml)

CAUTION — Perchloric acid concentrated and hot reacts rapidly, often with violently explosive force with oxidizable materials. Specially designed hoods are specified for handling perchloric acid fumes

and any hood in which perchloric acid may be fumed should not be used for other operations that permit easily oxidizable materials to collect in the ducts and blower.

4.6 Sulphuric acid, H_2SO_4 (ρ = 1,84 g/ml)

4.7 Orthophosphoric acid, H_3PO_4 (ρ = 1,70 g/l)

4.8 Orthophosphoric acid solution, 1 + 2

Add 100 ml of orthophosphoric acid (4.7) to 200 ml of water.

4.9 Potassium permanganate solution, $KMnO_4$, 2,5 g/l

4.10 Potassium dichromate standard solution

Weigh 4,903 3 g of potassium dichromate ($K_2Cr_2O_7$) and transfer to a beaker of suitable capacity and dissolve in reductant-free water. Transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with reductant-free water and mix.

1 ml of this standard solution contains 1,733 mg of chromium.

4.11 Iron(II) ammonium sulphate solution, 46 g/l

4.11.1 Preparation of the solution

Dilute 54 ml of the sulphuric acid (4.6) to 1 litre with water. Dissolve 46 g of iron(II) ammonium sulphate hexahydrate [$(NH_4)_2\ Fe(SO_4)_2 \cdot 6H_2O$] in a small amount of this solution, then dilute to 1 000 ml with the same sulphuric acid solution.

1 ml of this solution is equivalent to approximately 2 mg of chromium.

4.11.2 Potentiometric standardization of the solution

Transfer 30 ml of the potassium dichromate solution (4.10) to a 600 ml beaker containing 15 ml of the sulphuric acid (4.6), 25 ml of the orthophosphoric acid solution (4.8) and about 330 ml of water. Titrate using the procedure specified in 7.4.

The titre of the iron(II) ammonium sulphate solution (4.11), expressed as milligrams of chromium per millilitre of solution, is given by formula 1.

$$c_{Cr} = \frac{V_1}{V_2} \times 1{,}733 \qquad (1)$$

where

V_1 is the volume of the potassium dichromate standard solution (4.10) used, in millilitres (ml);

V_2 is the volume of the iron(II) ammonium sulphate solution (4.11.1) used in the titration, in millilitres (ml).

Daily standardization of the iron(II) ammonium sulphate solution is required.

5 Apparatus

5.1 Beakers, capacities e.g. 600 ml, tall form

5.2 Potentiometric titration apparatus

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 (2 ± 0,001) g of the test sample.

7.1.2 Test portion solution

Transfer the test portion (7.1.1) to a 600 ml tall form beaker (5.1). Add 20 ml of the hydrochloric acid (4.1), 10 ml of the nitric acid (4.3) and 1 ml of the hydrofluoric acid (4.4). When effervescence ceases, add 10 ml of the orthophosphoric acid solution (4.8) and 30 ml of the perchloric acid (4.5). Bring to the boil and evaporate until thick white perchloric acid fumes appear. Maintain until the test portion is totally dissolved. Reduce the heat and boil gently for 5 min, then cool. Add 30 ml of water and boil for 5 min, then cool.

7.1.3 Oxidation of residual chromium(III)

Add 150 ml of water to the test portion solution (7.1.2), bring to the boil and add 5 ml of the potassium permanganate solution (4.9). Boil for 3 min, then add 10 ml of the hydrochloric acid solution (4.2) and boil for 15 min. Allow to cool.

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 method by preparing a solution of a reference material or a synthetic sample containing a known amount of chromium and of a composition similar to the material to be analysed. Carry out the procedure specified in 7.1 and 7.4.

7.4 Determination

Transfer the test portion solution (7.1.3) to a 600 ml tall-form beaker (5.1). Add 20 ml of the sulphuric acid (4.6) and 25 ml of the orthophosphoric acid solution (4.8). Dilute to about 400 ml with water. Allow to cool, if necessary. Place the electrodes of the potentiometric titration apparatus in the solution and, while stirring, titrate with the iron(II) ammonium sulphate solution (4.11) until the potentiometric change occurs. Titrate slowly near the end-point. Using a platinum saturated calomel electrode, the change in potential is of the order of 200 mV and lies between 900 mV and 700 mV.

8 Expression of results

Calculate the chromium mass fraction in per cent (%), as follows:

$$w_{Cr} = \frac{(V - V_{bl}) \times c_{Cr}}{10m} \quad (2)$$

where

V is the volume of the iron(II) ammonium sulphate solution (4.11) used in the determination (7.4), in millilitres (ml);

V_{bl} is the volume of the iron(II) ammonium sulphate solution (4.11) used in the blank test (7.2), in millilitres (ml);

c_{Cr} is the titre of the iron(II) ammonium sulphate solution (4.11), expressed as milligrams of chromium per millilitre (mg/ml) of solution, calculated in 4.11.2;

m is the mass of the test portion (7.1.1), in grams (g).

9 Test report

The test report shall contain the following information:

a) identification of the test sample;

b) reference to this document (CEN/TS 14940-1:2009);

c) test method used;

d) results;

e) any unusual characteristics noted during the determination;

f) any operation not included in this document 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.