



# SLOVENSKI STANDARD

SIST EN 14936-1:2006

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

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

Cuivre et alliages de cuivre - Dosage de l'aluminium - Partie 1 : Méthode titrimétrique  
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Ta slovenski standard je istoveten z: **EN 14936-1:2006**

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ICS 77.120.30

English Version

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

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

This European Standard was approved by CEN on 15 May 2006.

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

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## Foreword

This document (EN 14936-1:2006) 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of an identical text or by endorsement, at the latest by December 2006, and conflicting national standards shall be withdrawn at the latest by December 2006.

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

EN 14936-1, *Copper and copper alloys — Determination of aluminium content — Part 1: Titrimetric method*

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

EN 14936-2, *Copper and copper alloys — Determination of aluminium content — Part 2: FAAS method*

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, 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.

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## 1 Scope

This part of this European Standard specifies a titrimetric method for the determination of the aluminium content of copper and copper alloys in the form of unwrought, wrought and cast products.

The method is applicable to products having aluminium mass fractions between 0,5 % and 12 %.

## 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

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Determination of aluminium by chelatometric titration at pH about 6, following a sodium fluoride demasking procedure, and using a voltametric indication.

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## 4 Reagents and materials

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### 4.1 General

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

4.2 Hexamethylenetetramine,  $(\text{CH}_2)_6\text{N}_4$ .

4.3 Chloroform,  $\text{CHCl}_3$ .

4.4 Perchloric acid,  $\text{HClO}_4$  ( $\rho = 1,68$  g/ml).

**WARNING — 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 is fumed should not be used for other operations that permit easily oxidizable materials to collect in the ducts and blower.**

4.5 Nitric acid,  $\text{HNO}_3$  ( $\rho = 1,40$  g/ml).

4.6 Nitric acid solution, 1 + 1

Dilute 50 ml of nitric acid (4.5) in 50 ml of water.

4.7 Hydrochloric acid,  $\text{HCl}$  ( $\rho = 1,19$  g/ml).

**4.8 Hydrochloric acid solution, 1 + 1**

Dilute 50 ml of hydrochloric acid (4.7) in 50 ml of water.

**4.9 Disodium salt of ethylenediaminetetra-acetic acid (EDTA),  $C_{10}H_{14}N_2Na_2O_8 \cdot 2 H_2O$ , 0,2 mol/l**

Dissolve 74,448 g Disodium-ethylenediaminetetra-acetic acid dihydrate in water and dilute to 1 000 ml.

**4.10 Hydrogen peroxide,  $H_2O_2$  30 % (mass fraction) solution****4.11 Cupferron solution**

Dissolve 10 g of cupferron in 100 ml water.

**4.12 Manganese solution, 4,55 g/l of  $Mn(NO_3)_2 \cdot 4H_2O$ .****4.13 Copper base solution, 0,05 mol/l solution**

Weigh 3,177 g of copper, ( $Cu \geq 99,9\%$ ) and transfer it into a 250 ml beaker. Add 20 ml of nitric acid (4.5). Heat gently until the copper is 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, dilute to the mark with water and mix well.

**4.14 Sodium fluoride solution, NaF 25 g/l.**

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**5 Apparatus****5.1 Ordinary laboratory apparatus**

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**5.2 Potentiometer in connection with a device for a voltametric indication, i.e. for polarising the electrodes with a constant current of 2  $\mu A$  to 10  $\mu A$ .**

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This attachment can be made in a simple way using, for example, an accumulator or a storage battery of 2 V in series with a 1 M $\Omega$  resistor and the electrodes. The potentiometer shall be in parallel with the electrodes.

**5.3 Double platinum electrode**, made of 1 mm diameter platinum wire, sealed in a glass tube directly or after welding on a copper wire in such a way that each wire electrode is about 4 mm long with a free geometric surface of about 10 mm<sup>2</sup>.

**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 General**

Prepare test portion solutions, ready for titration, in accordance with one of the procedures in 7.1.2 to 7.1.5 depending on the expected aluminium content of the sample and whether it is free from or containing titanium and zirconium.

**7.1.2 Alloys free from titanium and zirconium, having aluminium mass fractions between 0,5 % and 4,0 %**

Weigh ( $0,5 \pm 0,001$ ) g of the sample.

Transfer the test portion into a 250 ml tall-form beaker. Add 5 ml of water and 5 ml of the nitric acid solution (4.6). Heat gently until the test portion is completely dissolved. Evaporate the solution obtained to about 1 ml to 2 ml and dilute with 25 ml of water. Add 1 ml of the manganese solution (4.12), 42 ml of the EDTA solution (4.9) and sufficient hexamethylenetetramine (4.2) to give a pH value 6,0 to 6,2. (The manganese solution may be omitted if the sample contains 0,5 % or more of manganese). Boil for 5 min and cool to room temperature.

**7.1.3 Alloys free from titanium and zirconium, having aluminium mass fractions over 4,0 % up to and including 12,0 %**

Weigh ( $0,2 \pm 0,001$ ) g of the sample.

Transfer the test portion into a 250 ml tall-form beaker. Add 5 ml of water and 3 ml of the nitric acid solution (4.6). Heat gently until the test portion is completely dissolved. Evaporate the solution obtained to about 1 ml to 2 ml and dilute with 25 ml of water. Add 1 ml of the manganese solution (4.12), 22 ml of the EDTA solution (4.9) and sufficient hexamethylenetetramine (4.2) to give a pH value 6,0 to 6,2. (The manganese solution may be omitted if the sample contains 0,5 % or more of manganese.) Boil for 5 min and cool to room temperature.

**7.1.4 Alloys containing titanium and zirconium, having aluminium mass fractions between 0,5 % and 4,0 %**

Weigh ( $0,5 \pm 0,001$ ) g of the sample.

Transfer the test portion into a 250 ml tall-form beaker and dissolve with 30 ml of the hydrochloric acid solution (4.8) by adding a total amount of 10 ml of the hydrogen peroxide (4.10) in several small portions. Cool the solution during this operation. Destroy the excess peroxide by boiling for about 5 min. After cooling to room temperature, transfer the solution into a separating funnel of approximately 150 ml, using as little water as necessary for rinsing. The total volume of the solution shall amount to approximately 50 ml.

Depending on the amount of iron, titanium and zirconium present, add 2 ml to 5 ml of the cupferron solution (4.11) and 20 ml of the chloroform (4.3) and shake vigorously for about 1 min. After separation of the phases, draw off the organic phase and repeat the extraction of the aqueous phase using 1 ml of the cupferron solution and 10 ml of the chloroform. Repeat this extraction once more if the organic phase shows a yellowish colour at this step. Discard the chloroform phases. Transfer the aqueous solution, now free of iron, titanium and zirconium, into a 250 ml tall-form beaker and evaporate to about 5 ml. Add 5 ml of the perchloric acid (4.4) and 5 ml of the nitric acid (4.5) and destroy any organic matter which may be present by wet combustion. Fume the perchloric acid to about 1 ml, dilute with about 25 ml of water and filter off any insoluble matter.

**7.1.5 Alloys containing titanium and zirconium, having aluminium mass fractions over 4,0 % up to and including 12,0 %**

Weigh ( $0,2 \pm 0,001$ ) g of the sample.

Transfer the test portion into a 250 ml tall-form beaker and dissolve with 25 ml of the hydrochloric acid solution (4.8) by adding a total amount of 5 ml of the hydrogen peroxide (4.10) in several small portions. Cool the solution during this operation. Destroy the excess peroxide by boiling for about 5 min. After cooling to room temperature, transfer the solution into a separating funnel of approximately 150 ml, using as little water as necessary for rinsing. The total volume of the solution shall amount to approximately 50 ml.

Depending on the amount of iron, titanium and zirconium present, add 2 ml to 5 ml of the cupferron solution (4.11) and 20 ml of the chloroform (4.3) and shake vigorously for about 1 min. After separation of the phases, draw off the organic phase and repeat the extraction of the aqueous phase using 1 ml of the cupferron solution and 10 ml of the chloroform. Repeat this extraction once more if the organic phase shows a yellowish colour at this step.

Discard the chloroform phases. Transfer the aqueous solution, now free of iron, titanium and zirconium, to a 250 ml tall-form beaker and evaporate into about 5 ml. Add 5 ml of the perchloric acid (4.4) and 5 ml of the nitric acid (4.5) and destroy any organic matter which may be present, by wet combustion. Fume the perchloric acid to about 1 ml, dilute with about 25 ml of water and filter off any insoluble matter.



## 7.2 Blank test

Carry out a blank test simultaneously with the determination, following the same procedure and using the same quantities of all the 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 standard material or a synthetic sample containing a known amount of aluminium and of composition similar to the material to be analysed. Carry out the procedure specified in 7.4.

## 7.4 Determination

Titrate the excess EDTA present in the test portion solution (see 7.1.2 to 7.1.5) with the copper base solution (4.13) employing voltametric indication using the polarised double platinum electrode (5.3). The copper solution shall be added drop by drop, rapidly at first, and near the end-point in 1 drop steps. The end-point is indicated by a sharp potential break of more than 100 mV per drop (note the volume used,  $V_1$ ). To the solution titrated in this way add 20 ml of sodium fluoride solution (4.14). Check the pH value and if necessary correct it by adding a few drops of nitric acid solution (4.6). Boil for 2 min. Cool again to room temperature and, using the same burette without refilling, titrate the liberated EDTA (primarily bonded to aluminium) with the copper solution in the same manner as described above (total volume used,  $V_2$ ).

NOTE 1 During the titrations the anode becomes coated with manganese oxide ( $\text{MnO}_2$ ). This precipitate should be dissolved after each titration by immersing the electrode for at least 15 min in a solution of hydrochloric acid containing a few drops of hydrogen peroxide.

NOTE 2 The titration curves should be evaluated in the same way as for potentiometrically indicated titrations. Care should be taken that the small amount of titrating solution added in excess during the first titration (back-titration of the EDTA in excess) is added to the volume used in the second (titration of the primarily aluminium-bonded EDTA liberated by the sodium fluoride).

NOTE 3 If the aluminium content of the alloy is less than 1%, a microburette for the second titration should be used.

NOTE 4 In the case of analysis of tin-rich alloys, the tin oxide ( $\text{SnO}_2$ ) precipitated during dissolution should be filtered off. This precipitate is free of aluminium and can be rejected.

## 8 Expression of results

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

— for procedures according to 7.1.2 and 7.1.4:

$$\text{Aluminium mass fraction} = 0,270 (V_2 - V_1)$$

— for procedures according to 7.1.3 and 7.1.5:

$$\text{Aluminium mass fraction} = 0,674 5 (V_2 - V_1)$$

where

$V_1$  is the volume of copper solution required for the titration before the demasking with sodium fluoride, in millilitre (ml);

$V_2$  is the total volume of copper solution required for the titration both before and after the demasking with sodium fluoride, in millilitre (ml).

## 9 Precision

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

These data conform to the method given in ISO 5725 including the Cochran's Test and Grubb's Test.