SLOVENSKI STANDARD

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Baker in bakrove zlitine ï Doloļ evanje neļ istoļ v ļ istem bakru ï Metoda ET AAS

Copper and copper alloys - Determination of impurities in pure copper - ET AAS method

Kupfer und Kupferlegierungen - Bestimmung der Verunreinigungen in reinem Kupfer - Elektrothermales Atomabsorptionsspektrometrie-Verfahren (ET-AAS)

Cuivre et alliages de cuivre - Dosage des impuretés dans le cuivre pur - Méthode par spectrométrie d'absorption atomique électrothermique (ET-AAS)

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

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Contents

Page

Foreword 3
1 **Scope** 4
2 **Normative references** 4
3 **Principle** 5
4 **Reagents and materials** 5
5 **Apparatus** 9
6 **Sampling** 9
7 **Procedure** 10
8 **Expression of results** 15
9 **Precision** 16
10 **Test report** 17
Annex A (informative) **Matrix modifiers** 18
Bibliography 19

Foreword

This document (EN 14935:2006) 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of an identical text or by endorsement, at the latest by December 2006, and conflicting national standards shall be withdrawn at the latest by December 2006.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 14935:2006, *Copper and copper alloys — Determination of impurities in pure copper — ET AAS 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.

1 Scope

This European Standard specifies two different electrothermal atomization atomic absorption spectrometric methods (ET AAS) for the determination of silver, arsenic, bismuth, cadmium, cobalt, chromium, iron, manganese, nickel, lead, antimony, selenium, tin, tellurium and zinc in copper (greater than 99,85 %) in the form of unwrought, wrought and cast products.

The standard specifies two methods depending on range of impurity concentrations, see Table 1.

Table 1

Concentration range in µg/g

Element	Method A		Method B	
	from	up to and including	from	up to and including
Ag	1	30	0,02	1,0
As	1	20	0,04	1,0
Bi	1	5	0,09	1,0
Cd	1	5	0,001	1,0
Co	1	10	0,04	1,0
Cr	1	10	0,04	1,0
Fe	1	10	0,01	1,0
Mn	1	10	0,02	1,0
Ni	1	30	0,01	1,0
Pb	1	10	0,01	1,0
Sb	1	10	0,2	1,0
Se	1	10	0,05	1,0
Sn	1	10	0,02	1,0
Te	1	10	0,05	1,0
Zn	1	10	0,01	1,0

Method B (method of additions) is applicable to products containing impurity elements at concentrations below 1,0 µg/g. This method uses special ET AAS equipment fitted with background correction by means of the Zeemann effect.

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 in nitric acid followed, after suitable dilution, by injection into electrothermal atomization equipment of an atomic absorption spectrometer with a suitable background corrector. Measurement of the absorption of the following lines emitted by the relevant hollow-cathode or electrodeless discharge lamps, see Table 2.

Table 2

Element	Wave length nm
Ag	328,1
As	193,7
Bi	223,1
Cd	228,8
Co	240,7
Cr	357,9
Fe	248,3
Mn	279,5
Ni	232,0
Pb	283,3
Sb	217,6
Se	196,0
Sn	224,6
Te	214,3
Zn	213,9

4 Reagents and materials

4.1 General

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

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

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

4.4 Nitric acid solution, 1 + 1

Dilute 500 ml of nitric acid (4.3) in 500 ml of water.

4.5 Nitric acid solution, 1 + 3

Dilute 250 ml of nitric acid (4.3) in 750 ml of water.

4.6 Pure sodium hydroxide, NaOH 1 mol/l.

4.7 Sulfuric acid, H_2SO_4 0,5 mol/l.

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

4.9 Metal stock solutions, containing 1,000 g/l element.

NOTE All these stock solutions have limited life (3 months max.) and should be cold and dark stored.

4.9.1 Silver

a) Weigh (1 ± 0,001) g of silver (Ag ≥ 99,90 %) and transfer it into a 250 ml beaker. Add 40 ml of nitric acid solution (4.4). Heat gently until the silver has been completely 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.

b) Weigh 1,5748 g of pure silver nitrate ($AgNO_3$) and dissolve it in 100 ml of water previously acidified with 20 ml of nitric acid solution (4.4). Transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

4.9.2 Arsenic

a) Weigh 0,660 g of pure arsenic trioxide (As_2O_3) and transfer it into a 250 ml PTFE beaker. Add 50 ml of sodium hydroxide (4.6) and, after complete dissolution, add 150 ml of sulfuric acid (4.7). Transfer the solution quantitatively into a 500 ml one-mark volumetric flask, dilute to the mark with water and mix well.

b) Weigh 4,1650 g of pure sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) and dissolve it in 200 ml of water. Transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well.

4.9.3 Bismuth

Weigh (1 ± 0,001) g of bismuth (Bi ≥ 99,90 %) and transfer it into a 250 ml beaker. Add 40 ml of nitric acid solution (4.4). Heat gently until the bismuth has been completely 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.

4.9.4 Cadmium

Weigh (1 ± 0,001) g of cadmium (Cd ≥ 99,90 %) and transfer it into a 250 ml beaker. Add 40 ml of nitric acid solution (4.4). Heat gently until the cadmium has been completely 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.

4.9.5 Cobalt

Weigh (1 ± 0,001) g of cobalt (Co ≥ 99,90 %) and transfer it into a 250 ml beaker. Add 40 ml of nitric acid solution (4.4). Heat gently until the cobalt has been completely 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.

4.9.6 Chromium

Weigh (1 ± 0,001) g of chromium (Cr ≥ 99,90 %) and transfer it into a 250 ml beaker. Add 40 ml of nitric acid solution (4.4). Heat gently until the chromium has been completely 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.

4.9.7 Iron

Weigh (1 ± 0,001) g of iron (Fe ≥ 99,90 %) and transfer it into a 250 ml beaker. Add 40 ml of nitric acid solution (4.4). Heat gently until the iron has been completely 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.

4.9.8 Manganese

Weigh (1 ± 0,001) g of manganese (Mn ≥ 99,90 %) and transfer it into a 250 ml beaker. Add 40 ml of nitric acid solution (4.4). Heat gently until the manganese has been completely 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.

4.9.9 Nickel

Weigh (1 ± 0,001) g of nickel (Ni ≥ 99,90 %) and transfer it into a 250 ml beaker. Add 40 ml of nitric acid solution (4.4). Heat gently until the nickel has been completely 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.

4.9.10 Lead

Weigh (1 ± 0,001) g of lead (Pb ≥ 99,90 %) and transfer it into a 250 ml beaker. Add 40 ml of nitric acid solution (4.4). Heat gently until the lead has been completely 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.

4.9.11 Antimony

Weigh (1 ± 0,001) g of antimony (Sb ≥ 99,90 %) and transfer it into a 250 ml beaker. Add 25 ml of hydrochloric acid (4.2) and 50 ml of nitric acid solution (4.4). Heat gently until the antimony has been completely dissolved. Cool to room temperature. Transfer the solution quantitatively into a 1 000 ml of one-mark volumetric flask. Add 100 ml of hydrocloric acid (4.2). Dilute to the mark with water and mix well.

4.9.12 Selenium

Weigh (1 ± 0,001) g of selenium (Se ≥ 99,90 %) and transfer it into a 250 ml beaker. Add 40 ml of nitric acid solution (4.4). Heat gently until the selenium has been completely 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.

4.9.13 Tin

Weigh (1 ± 0,001) g of tin (Sn ≥ 99,90 %) and transfer it into a 250 ml PTFE beaker. Add 40 ml of nitric acid solution (4.4) and 2 ml of hydrofluoric acid (4.8). After dissolution, transfer it quantitatively into a 1 000 ml plastics one-mark volumetric flask containing 500 ml of water. Dilute to the mark with water and mix well.

4.9.14 Tellurium

Weigh (1 ± 0,001) g of tellurium (Te ≥ 99,90 %) and transfer it into a 250 ml beaker. Add 40 ml of nitric acid solution (4.4). Heat gently until the tellurium has been completely 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.

4.9.15 Zinc

Weigh (1 ± 0,001) g of zinc (Zn ≥ 99,90 %) and transfer it into a 250 ml beaker. Add 40 ml of nitric acid solution (4.4). Heat gently until the zinc has been completely 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.

4.10 Diluted metal stock solutions

4.10.1 Metal stock solutions 0,05 g/l element

Group A: Bismuth and Cadmium

Transfer individually 5,00 ml of the metal stock solution (4.9.3 and 4.9.4) into two 100 ml one-mark volumetric flasks. Dilute to the mark with water and mix well.

1 ml of each of these solutions contains 0,05 mg of the corresponding element.

Discard these solutions after the normal analysis time (8 h max.).

4.10.2 Metal stock solutions 0,1 g/l element

Group B: Arsenic, Cobalt, Chromium, Iron, Manganese, Lead, Antimony, Selenium, Tin, Tellurium and Zinc.

Transfer individually 10,00 ml of the metal stock solution (4.9.2, 4.9.5 to 4.9.8 and 4.9.10 to 4.9.15) into twelve 100 ml one-mark volumetric flasks. For tin provide 100 ml plastics one-mark volumetric flasks. Dilute to the mark with water and mix well.

1 ml of each of these solutions contains 0,10 mg of the corresponding element.

Discard these solutions after the normal analysis time (8 h max.).

4.10.3 Metal stock solutions 0,2 g/l element

Group C: Silver and Nickel.

Transfer individually 20,00 ml of the metal stock solution (4.9.1 and 4.9.9) into two 100 ml one-mark volumetric flasks. Dilute to the mark with water and mix well.

1 ml of each of these solutions contains 0,20 mg of the corresponding element.

Discard these solutions after the normal analysis time (8 h max.).

4.11 Multi-element standard solution

This solution may contain a maximum of four elements.

Select up to four elements of interest and transfer 2,50 ml of the metal stock solutions (see 4.10) into the same 100 ml one-mark volumetric flask. If tin is present, use a plastics 100 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

1 ml of this solution contains:

— Group A: 0,001 25 mg of the corresponding elements;
— Group B: 0,002 5 mg of the corresponding elements;
— Group C: 0,005 mg of the corresponding elements.

Discard these solutions after the normal analysis time (8 h max.).

4.12 Metal stock solutions 0,02 g/l element

4.12.1 General

Transfer individually 5,00 ml of each of the metal stock solutions (4.9.1 to 4.9.15) into 250 ml one-mark volumetric flasks. For tin, use plastics 250 ml one-mark volumetric flasks. Dilute to the mark with water and mix well.

1 ml of each of these solutions contains 0,02 mg of the corresponding element.

Discard these solutions after the normal analysis time (8 h max.).

4.12.2 Multi-element standard solution 100 µg/l element

This solution may contain a maximum of four elements.

Select up to four elements of interest and transfer 10,00 ml of the metal stock solutions (see 4.12.1) into the same 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well. Transfer 25,00 ml of this solution into a 100 ml one-mark volumetric flask, dilute to the mark with water and mix well. If tin is present use plastics 500 ml and 100 ml one-mark volumetric flasks.

1 ml of this solution, contains 100 ng of the corresponding elements.

Discard these solutions after the normal analysis time (8 h max.).

4.12.3 Multi-element standard solution 10 µg/l element

This solution may contain a maximum of four elements.

Select up to four elements of interest and transfer 10,00 ml of the metal stock solutions (see 4.12.1) into the same 500 ml one-mark volumetric flask. Dilute to the mark with water and mix well. Transfer 25,00 ml of this solution into a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix well. If tin is present use plastics 500 ml and 1 000 ml one-mark volumetric flasks.

1 ml of this solution contains 10 ng of the corresponding elements.

Discard these solutions after the normal analysis time (8 h max.).

4.13 High purity copper, Cu ≥ 99,999 %.

5 Apparatus

5.1 Ordinary laboratory equipment, thoroughly cleaned by washing many times with nitric acid solution (4.5) followed by rinsing with water (4.1).

5.2 Atomic absorption spectrometer, fitted with graphite tube furnace equipped with a suitable background corrector unit and automatic dispenser.

5.3 Hollow-cathode lamps or electrodeless discharge lamps.

5.4 Volumetric flasks made of plastics (e.g. PP, PE or PFA), 50 ml, 100 ml, 250 ml, 500 ml and 1 000 ml, thoroughly cleaned by washing many times with nitric acid solution (4.5) followed by rinsing with water (4.1).

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.