International Standard 4743

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Copper alloys — Determination of nickel content — Titrimetric method

Alliages de cuivre — Dosage du nickel — Méthode titrimétrique

First edition — 1984-10-15

UDC 669.3 : 546.74 : 543.24 **Ref. No. ISO 4743-1984 (E)**

Descriptors : copper, copper alloys, chemical analysis, determination of content, nickel, volumetric analysis.

Price based on 3 pages

Foreword

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International Standard ISO 4743 was prepared by Technical Committee ISO/TC 26, *Copper and copper alloys.*

Printed in Switzerland

INTERNATIONAL STANDARD **ISO 4743-1984 (E)**

Copper alloys — Determination of nickel content — Titrimetric method

1 Scope and field of application

This International Standard specifies a titrimetric method for the determination of the nickel content of copper alloys.

The method is applicable to contents of nickel as an alloying element in all types of copper alloys listed in International Standards.

2 Principle

Separation of nickel from an ammoniacal solution of a test portion by precipitation as the diacetyldioxime complex, followed by extraction of the complex into chloroform. After evaporation of the solvent and wet digestion of the complex, determination of the nickel content by indirect complexiometric titration using voltammetric end-point indication.

3 Reagents

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

3.1 **Ammonia,** solution, ϱ 0,91 g/ml.

3.2 **Ammonia,** solution, diluted 1 + 10.

Dilute 100 ml of the ammonia solution (3.1) to 1 100 ml with water.

3.3 **Nitric acid,** solution, diluted 1 + 1.

Dilute 100 ml of the nitric acid, ϱ 1,40 g/ml with 100 ml of water.

3.4 **Perchloric acid,** ϱ 1,70 g/ml.

3.5 **Hydroxylammonium chloride (Hydroxylamine hydrochloride).**

3.6 **Chloroform.**

3.7 **Hexamethylene tetramine.**

3.8 **Tartaric acid,** 500 g/l solution.

Dissolve 500 g of tartaric acid ($C_4H_6O_6$) in water and dilute to 1 000 ml.

3.9 **Sodium tartrate,** 100 g/l solution.

Dissolve 100 g of *di*sodium tartrate dihydrate ($Na_2C_4H_4O_6 \cdot 2H_2O$) in water and dilute to 1 000 ml.

3.10 **Diacetyldioxime,** 10 g/l methanolic solution.

Dissolve 10 g of diacetyl-dioxime ($C_4H_8N_2O_2$) in methanol and dilute to 1 000 ml with methanol.

3.11 **Hydrochloric acid,** solution, diluted 1 + 1.

Dilute 100 ml of hydrochloric acid, ϱ 1,19 g/ml, to 200 ml with water.

3.12 ***Di*sodiumethylenediaminetetraacetate** dihydrate (Na_2EDTA), standard volumetric solution, $c(Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O) \simeq 0{,}01$ mol/l.

3.12.1 Preparation of the solution

Dissolve 3,722 g of Na_2EDTA in water and dilute to the mark in a 1 000 ml one-mark volumetric flask.

3.12.2 Standardization of the solution

Pipette 20,00 ml of the copper solution (3.14) into a 250 ml beaker. Add 25,00 ml of the Na_2EDTA solution (3.12.1) and adjust the pH to 6,2 to 6,4 with the hexamethylene tetramine (3.7). Add 2,5 ml of the MnEDTA solution (3.13) and titrate the excess EDTA with the copper solution (3.14) as specified in 5.6.

The factor of the EDTA solution, F, is given by the formula

$$\frac{20{,}00 + V_0}{25{,}00}$$

where V_0 is the volume, in millilitres, of copper solution used for the determination.

3.13 Manganese(II)EDTA, solution corresponding to 0,2 g of Mn per litre. Dissolve 0,615 5 g manganese (II) sulphate monohydrate ($MnSO_4.H_2O$), 1,064 2 g of ethylenediamine tetraacetic acid, and 10 g of the hexamethylene tetramine (3.7) in 200 ml of water and dilute to the mark in a 1 000 ml one-mark volumetric flask.

1 ml of this solution contains 0,2 mg of Mn(II).

NOTE — To establish whether the solution contains Mn and EDTA in stoichiometric combination, add several milligrams of the hydroxylamine hydrochloride (3.5) and a drop of Eriochrome Black T indicator solution. The resulting colour should be a dirty pink or blue which should turn to a pure red on the addition of 1 drop of the copper solution (3.14) or to pure blue on the addition of 1 drop of the Na_2EDTA solution (3.12).

3.14 Copper, 0,01 mol/l solution.

Dissolve 0,635 4 g of copper (> 99,9 % purity) in as little nitric acid (3.3) as necessary. Dilute to the mark in a 1 000 ml one-mark volumetric flask.

3.15 Complexing solution

Dissolve 200 g of ammonium acetate in 500 ml of water and adjust to pH 9 with the ammonia solution (3.1). Add 400 g of sodium thiosulphate and dilute to 1 000 ml.

4 Apparatus

Ordinary laboratory apparatus and

4.1 Potentiometer, equipped with a device to permit voltammetric end-point indication.

NOTE — This device, which polarizes the electrodes with a constant current between 1 and 5 µA, can be made simply by using an accumulator or storage battery of, for example 2 V in series with a 1 MΩ resistor and the electrodes. The potentiometer is connected in parallel with the electrodes.

4.2 Double platinum electrode, made of 1 mm diameter platinum wire, sealed in a glass tube either directly or after welding on copper wire in such a way that each wire electrode is about 4 mm in length with a free geometric surface of about 10 mm^2.

4.3 Suction-assisted membrane filtering apparatus, with ground glass joint, to fit 250 ml separating funnel.

4.4 Membrane filters, 1 µm porosity, to fit the filtering apparatus (4.3).

5 Procedure

5.1 Test portion, dissolution, and dilution

Weigh, to the nearest 0,001 g, 1,000 g of finely divided sample into a 250 ml tall-form beaker. Add 5 ml of the tartaric acid solution (3.8) and 20 ml of the nitric acid solution (3.3). When dissolution is complete, dilute with about 30 ml of water and boil for approximately 5 min to expel nitrous oxides.

Cool to room temperature. As indicated in the table, transfer the test solution to a 100 ml one-mark volumetric flask if the nickel content of the sample is expected to be less than 10 % *(m/m)*, or to a 500 ml one-mark volumetric flask if the nickel content is expected to be 10 % *(m/m)* or greater.

Dilute to the mark with water and mix.

According to the expected nickel content, pipette an aliquot portion of the diluted test solution into a 250 ml beaker, as indicated in the table. Dilute, if necessary, to 50 ml with water.

Expected nickel content	Dilution	Aliquot	Mass of sample in solution	Volume of Na_2 EDTA solution (3.12) to be added
% *(m/m)*	ml	ml	g	ml
2	100	50	0,5	25
5	100	20	0,2	25
10	500	50	0,1	25
20	500	50	0,1	50
40	500	25	0,05	50
60	500	20	0,04	50

5.2 Complex formation

Add, in sequence, the following, mixing after each addition:

- 10 ml of the sodium tartrate solution (3.9);
- ammonia solution (3.1) until all of the nickel and copper present are redissolved;
- hydroxylamine hydrochloride (3.5) until the solution is decolorized (0,1 to 0,2 g, depending on the amount of copper present);
- 20 ml of the complexing solution (3.15) (30 ml if an aliquot corresponding to more than 0,2 g of the sample was taken);
- 15 ml of the diacetyldioxime solution (3.10).

5.3 Filtration and first extraction

Filter the precipitate through a 1 µm membrane filter directly into a 250 ml separating funnel using a Witt's filter apparatus (4.3). Wash the beaker three times with 5 ml of the ammonia solution (3.2) and twice with 5 ml of water. Shake the filtrate with 25 ml of the chloroform (3.6), reserving the organic phase. Repeat the extraction with 20 ml of the chloroform. Combine the organic extracts.

5.4 Treatment of precipitate

Dissolve the filter in 10 ml of the nitric acid solution (3.3), and repeat the precipitation of nickel and the extraction of the filtrate as specified in 5.2 and 5.3.