INTERNATIONAL STANDARD 1553

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Unalloyed copper containing not less than 99,90 % of copper — Determination of copper content — Electrolytic method

Cuivres non alliés à teneur en cuivre supérieure ou égale à 99,90 % — Dosage du cuivre — Méthode électrolytique

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

Prior to 1972, the results of the work of the technical committees were published as ISO Recommendations; these documents are in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 26, *Copper and copper alloys,* has reviewed ISO Recommendation R 1553-1971 and found it technically suitable for transformation. International Standard ISO 1553 therefore replaces ISO Recommendation R 1553-1971, to which it is technically identical.

ISO Recommendation R 1553 had been approved by the member bodies of the following countries :

Australia
Belgium
Canada
Cuba
Czechoslovakia
Egypt, Arab Rep. of
Finland
France
Germany
Hungary
India
Iran
Israel
Italy
Japan
Netherlands
New Zealand
Norway
Peru
Poland
South Africa, Rep. of
Spain
Sweden
Switzerland
Thailand
Turkey
United Kingdom
U.S.A.
Yugoslavia

No member body had expressed disapproval of the Recommendation.

The member bodies of the following countries disapproved the transformation of the Recommendation into an International Standard :

Hungary
Italy

Printed in Switzerland

Unalloyed copper containing not less than 99,90 % of copper – Determination of copper content – Electrolytic method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies an electrolytic method for the determination of the copper content of unalloyed copper containing not less than 99,90 % of copper. Silver, if present, is deposited with the copper and is reported as copper.

The method is applicable to coppers free from elements which leave insoluble residues in the solution for electrolysis, and having a low content of impurities which can be deposited electrolytically together with the copper.

A spectrophotometric method for the determination of residual copper in the electrolyte after deposition of copper on the cathode is given in annex B.

2 REFERENCE

ISO/R 1811, *Chemical analysis of copper and copper alloys – Sampling of copper refinery shapes.*

3 PRINCIPLE

Electrolytic determination of the copper content of a sulphuric/nitric acid solution of a test portion.

4 REAGENTS

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

4.1 Sulphuric/nitric acid, solution.

Add slowly, while stirring, 300 ml of sulphuric acid, ρ approximately 1,83 g/ml, to 750 ml of water. Cool, and add 210 ml of nitric acid, ρ approximately 1,38 g/ml.

5 APPARATUS

Ordinary laboratory apparatus and

5.1 Current source.

For preference, use a 6 V accumulator. If a rectifier is to be used, an additional buffer battery is recommended.

5.2 Electrolysis equipment, the electrodes of which meet the following requirements :

5.2.1 Platinum cathode, Winkler type[1], made preferably from gauze containing approximately 400 meshes per square centimetre (50 meshes per linear inch), woven from wire of diameter approximately 0,20 mm. The cathode shall be stiffened by doubling the gauze for about 3 mm at the top and the bottom of the cylinder or by reinforcing the gauze at the top and bottom with a platinum band or ring. The diameter of the cylinder shall be 30 to 50 mm and the height 40 to 60 mm. The stem shall be made from a platinum alloy wire, such as platinum-iridium, platinum-rhodium, or platinum-ruthenium, having a diameter of approximately 1,30 mm, flattened and welded along the entire length of the gauze. The overall height of the cathode shall be approximately 130 mm. The cathode shall be sandblasted.

5.2.2 Spiral anode, made of platinum alloy wire of minimum diameter 1 mm, formed into a spiral of seven turns, having a height of approximately 50 mm and a diameter of 12 mm, the overall height being approximately 130 mm. The spiral section of the anode shall be sandblasted.

5.3 Electric oven, capable of being controlled at 110 °C.

6 SAMPLING

Sampling shall be carried out according to the procedure given in ISO/R 1811.

7 PROCEDURE

7.1 Test portion

Weigh, to the nearest 0,001 g, 5 g of the test sample (see annex A).

7.2 Determination

7.2.1 Transfer the test portion (7.1) to a 400 ml tall-form lipless beaker provided with a close-fitting watch glass. Add

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[1] Platinum cathodes formed from plain or perforated sheets may also be used.

45 ml of the sulphuric/nitric acid solution (4.1) and allow to stand for a few minutes until the reaction has nearly ceased. Heat at a temperature of 80 to 90 °C to complete dissolution and maintain the solution at this temperature for 2 to 3 h to expel the oxides of nitrogen quantitatively. Wash the watch glass and walls of the beaker, and dilute the solution to 300 ml.

7.2.2 Insert the electrodes (5.2.1 and 5.2.2) in the solution and cover the beaker with two halves of a watch glass, one of which has two indentations through which the electrode stems may pass. Electrolyse, without stirring, at a current density of about 0,6 A per square decimetre of cathode surface. When the solution becomes colourless, reduce the current density to about 0,3 A/dm^2 and wash the watch glasses, electrode stems, and walls of the beaker. Continue the electrolysis until the deposition of the copper is complete, as indicated by failure to plate on an unplated surface of the electrode stem when the level of the solution is raised.

7.2.3 Without switching off the current, quickly replace the beaker by another of the same size containing approximately 350 ml of distilled water. Continue the electrolysis for 15 min. Remove the cathode and dip it in ethanol or methanol. Dry in the oven (5.3), maintained at 110 °C, for 3 to 5 min and cool. Determine the mass of the deposit of metallic copper as indicated in annex A.

7.2.4 Verify the absence of copper in the electrolyte by a colorimetric test; if the determined content of copper is less than or equal to the prescribed figure, determine the residual copper in the electrolyte in accordance with the method given in annex B.

8 EXPRESSION OF RESULTS

8.1 Method of calculation

The copper content is given, as a percentage by mass, by the formula

$$\frac{m_1}{m_0} \times 100$$

where

m_0 is the mass, in grams, of the test portion (7.1);

m_1 is the mass, in grams, of copper deposited.

8.2 Repeatability

The determination shall be carried out twice, and the results obtained shall agree within 0,015 % (m/m) of copper.

9 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard or in the document to which reference is made, or regarded as optional.

ANNEX A

DETERMINATION OF MASS OF TEST PORTION AND COPPER DEPOSIT

A.1 USING A TWO-PAN BALANCE

Using a marked 5 g weight, weigh 5,005 0 to 5,007 0 g of the test sample, this mass constituting the test portion. Weigh the cathode, placing the marked 5 g weight used in weighing the test portion on the same balance-pan as the cathode, and noting the other weights used. Deduct 5 g from the observed mass to obtain the mass of the cathode.

Weigh the cathode with the copper deposit, using the same weights as were used in weighing the cathode before the electrolysis, except that the marked 5 g weight used on the pan with the cathode shall be omitted.

A.2 USING A SINGLE-PAN BALANCE

First weigh the cathode alone and then, without removing the cathode from the balance, weigh accurately about 5 g of the test sample, this mass constituting the test portion. In subsequent weighing of the cathode with the copper deposit, use the same weights.

The mass of the test portion is the difference between the masses of the cathode plus the test portion and the cathode alone.

The mass of the copper deposit is the difference between the masses of the cathode with the deposit and the cathode alone.

ANNEX B

DETERMINATION OF RESIDUAL COPPER IN THE ELECTROLYTE – SPECTROPHOTOMETRIC METHOD

B.1 SCOPE AND FIELD OF APPLICATION

This annex specifies a spectrophotometric method for the determination of copper content.

The method is applicable to the determination of residual copper in the electrolyte after the deposition of copper on the cathode.

B.2 PRINCIPLE

Formation of the copper-oxalyl dihydrazide complex at pH 8,8 in the presence of acetaldehyde. Spectrophotometric measurement at a wavelength of approximately 540 nm.

B.3 REAGENTS

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

B.3.1 Ammonia solution, ρ approximately 0,91 g/ml.

B.3.2 Sulphuric/nitric acid solution.

For the preparation, see 4.1.

B.3.3 Citric acid, 200 g/l solution.

B.3.4 Acetaldehyde, 40 % (*m/m*) solution in water or methanol.

B.3.5 Oxalyl dihydrazide, 2,50 g/l solution.

Dissolve 2,50 g of oxalyl dihydrazide ($[H_2NNH(CO)_2]_2$) in 1 l of water, heating gently.

B.3.6 Copper, 0,01 g/l standard solution.

In a 250 ml beaker, dissolve 1 g of electrolytic copper in 10 ml of nitric acid, ρ approximately 1,38 g/ml, diluted with an equal volume of water. Evaporate almost to dryness to remove the excess acid. Add 50 ml of water to dissolve the residue. Transfer to a 1 000 ml one-mark volumetric flask, rinse the beaker and dilute to the mark with water. Transfer 10 ml of this solution to a 1 000 ml one-mark volumetric flask and dilute to the mark with water.

1 ml of this standard solution contains 0,010 mg of Cu.

B.4 APPARATUS

Ordinary laboratory apparatus and

B.4.1 Spectrophotometer, suitable for measurements at a wavelength of approximately 540 nm.

B.5 PROCEDURE

B.5.1 Determination

After weighing the deposit of cathodic copper, concentrate the electrolyte to approximately 200 ml, cool and transfer to a 250 ml one-mark volumetric flask. Dilute to the mark with water.

Transfer 10 ml of this solution to a 50 ml one-mark volumetric flask.

Add in the following order, shaking after each addition,

- 2 ml of the citric acid solution (B.3.3);
- 11 ml of the ammonia solution (B.3.1);
- 10 ml of the acetaldehyde solution (B.3.4);
- 10 ml of the oxalyl dihydrazide solution (B.3.5).

Cool, dilute to the mark with water and allow to stand for 30 min.

Make the spectrophotometric measurement of this solution at a wavelength of approximately 540 nm after having adjusted the spectrophotometer (B.4.1) to zero absorbance against the zero term of the calibration graph.1)

B.5.2 Plotting the calibration graph

Transfer 45 ml of the sulphuric/nitric acid solution (B.3.2) to a 250 ml one-mark volumetric flask. Dilute to the mark with water.

Place 10 ml of this solution into each of a series of six 50 ml one-mark volumetric flasks.

Add the following amounts of the standard copper solution (B.3.6) : 0 – 1 – 2 – 3 – 4 and 5 ml, corresponding respectively to 0 – 0,01 – 0,02 – 0,03 – 0,04 and 0,05 mg of copper.

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1) The zero term of the calibration graph corresponds to the blank test of the reagents.

Continue as indicated in paragraphs 3 and 4 of B.5.1 and make the spectrophotometric measurements of the standard matching solutions at a wavelength of approximately 540 nm after having adjusted the spectrophotometer (B.4.1) to zero absorbance against the zero term of the graph.

Plot the calibration graph.

B.6 EXPRESSION OF RESULTS

From the calibration graph, deduce the mass of residual copper in the electrolyte.

B.7 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard or regarded as optional.