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INTERNATIONAL STANDARD ISO 795

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Aluminium and aluminium alloys — Determination of copper content — Oxalyldihydrazide photometric method

Aluminium et alliages d'aluminium — Dosage du cuivre — Méthode photométrique à l'oxalyldihydrazide

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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 Technial Committees were published as ISO Recommendations; these documents are now in the process of being transformed into International Standards. As part of this process, Technical Committee ISO/TC 79 has reviewed ISO Recommendation R 795 and found it technically suitable for transformation. International Standard ISO 795 therefore replaces ISO Recommendation R 795-1968 to which it is technically identical.

ISO Recommendation R 795 was approved by the Member Bodies of the following countries :

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The Member Body of the following country expressed disapproval of the Recommendation on technical grounds :

United Kingdom

The Member Bodies of the following countries disapproved the transformation of ISO/R 795 into an International Standard :

Switzerland
United Kingdom

Printed in Switzerland

Aluminium and aluminium alloys — Determination of copper content — Oxalyldihydrazide photometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies an oxalyldihydrazide photometric method for the determination of copper content in aluminium and aluminium alloys.

The method is applicable to the determination of copper content between 0,002 and 0,8 % (*m/m*).

The method is not completely applicable in the special case of alloys with silicon contents exceeding 1 % (*m/m*), for which it should be modified as described in the annex.

2 PRINCIPLE

Attack with hydrochloric acid.

Formation between pH 9,1 and pH 9,5, in the presence of acetaldehyde, of the violet-coloured copper-oxalyldihydrazide complex, the optimum pH range being obtained by adding a controlled amount of ammonia.

Photometric measurement at a wavelength of about 540 nm.[1]

3 REAGENTS

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

3.1 Hydrochloric acid, ρ 1,19 g/ml, approximately 12 N.

3.2 Hydrofluoric acid, 40 % (*m/m*), ρ approximately 1,15 g/ml.

3.3 Nitric acid, ρ 1,23 g/ml, approximately 7,4 N.

Take 50 ml of nitric acid, ρ 1,40 g/ml, approximately 15 N, and make up the volume to 100 ml with water.

3.4 Sulphuric acid, ρ 1,48 g/ml, approximately 17,5 N solution.

Cautiously pour 50 ml of sulphuric acid, ρ 1,84 g/ml, approximately 35,6 N, into water and after cooling make up the volume to 100 ml.

3.5 Hydrogen peroxide, 36 % (*m/m*), ρ 1,12 g/ml, approximately 120 volumes.

3.6 Ammonia solution, ρ 0,90 g/ml, approximately 14,4 N.

3.7 Citric acid, 500 g/l solution.

Dissolve 500 g of citric acid ($C_6H_8O_7.H_2O$) in water and make up the volume to 1 000 ml.

3.8 Acetaldehyde, 400 g/l solution.

In a 1 000 ml volumetric flask, place 400 g of acetaldehyde (CH_3CHO), cool to approximately 5 °C, slowly add cooled distilled water (at about 5 °C), and make up the volume to 1 000 ml.

Store at a temperature of about 15 °C.

NOTE — Since heat is produced when water and acetaldehyde are mixed, and since acetaldehyde is very volatile (boiling point 21 °C), it is recommended that the vessel in which the mixing takes place should be cooled by cold water.

3.9 Oxalyldihydrazide, 2,5 g/l solution.

Dissolve 2,5 g of oxalyldihydrazide ($C_2H_6N_4O_2$) in warm water (40 to 50 °C) and, after cooling to 20 °C, make up the volume to 1 000 ml. Filter if necessary.

3.10 Copper, standard solution, corresponding to 1 g of Cu per litre.

3.10.1 In a tall-form beaker of suitable capacity (for example 400 ml), dissolve 1 g of electrolytic copper (not less than 99,95 %) in 10 ml of nitric acid (3.3) to which 20 ml of water have been added. Cover with a watch-glass. When completely dissolved, evaporate on a water bath until crystallization commences. Take up with water, transfer to a 1 000 ml volumetric flask, rinse and after cooling make up the volume to 1 000 ml with water.

1 ml of this solution contains 1 mg of copper.

Alternatively

3.10.2 Dissolve 3,929 6 g of copper(II) sulphate pentahydrate crystals ($CuSO_4.5H_2O$) in water and make up the volume to 1 000 ml.

1 ml of this solution contains 1 mg of copper.

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[1] Aluminium is complexed by citric acid. Alloying elements or impurities present in aluminium and its alloys do not interfere.

3.11 Copper, standard solution, corresponding to 0,05 g of Cu per litre.

Transfer 50,0 ml of standard copper solution (3.10) to a 1 000 ml volumetric flask and make up the volume to 1 000 ml with water.

1 ml of this solution contains 0,05 mg of copper.

3.12 Copper, standard solution, corresponding to 0,005 g of Cu per litre.

Transfer 50,0 ml of standard copper solution (3.11) to a 500 ml volumetric flask and make up the volume to 500 ml with water.

1 ml of this solution contains 5 µg of copper.

Prepare just before use.

3.13 Copper, standard solution, corresponding to 0,002 5 g of Cu per litre.

Transfer 50,0 ml of standard copper solution (3.11) to a 1 000 ml volumetric flask and make up the volume to 1 000 ml with water.

1 ml of this solution contains 2,5 µg of copper.

Prepare just before use.

4 APPARATUS

Ordinary laboratory apparatus and

4.1 Electrophotometer or **spectrophotometer** (wavelength about 540 nm).

5 SAMPLING

5.1 Laboratory sample[1]

5.2 Test sample

Chips not more than 1 mm thick shall be obtained from the laboratory sample by drilling or milling.

6 PROCEDURE

6.1 Calibration graph

6.1.1 *Dissolution in hydrochloric acid*

In a 250 ml beaker, place 30 ml of the hydrochloric acid (3.1) and 1 ml of the hydrogen peroxide (3.5), then evaporate the liquid almost completely. Add 50 ml of water, bring to the boil and keep boiling for about 5 min, cool and transfer to a 200 ml volumetric flask. Make up the volume to 200 ml with water.

6.1.2 *Preliminary test for adjusting the pH value*

In a beaker of suitable capacity (for example 50 or 100 ml), place 10 ml of the hydrochloric acid solution (6.1.1), 10 ml of the standard copper solution (3.12) and 2 ml of the citric acid solution (3.7); mix and add 10 ml of the acetaldehyde solution (3.8).

By means of a graduated pipette or burette, add sufficient ammonia solution (3.6), while stirring, to bring the pH of the solution to about 9,3 (within the range 9,1 to 9,5).

Note the number of millilitres of the ammonia solution used for adjusting the pH value (the amount will be about 7 to 9 ml). Discard this test solution.

6.1.3 *Plotting of the calibration graph*

In each of a series of nine 50 ml volumetric flasks, place 10 ml of the hydrochloric acid solution (6.1.1), then respectively 0 (compensation solution) – 2,0 – 4,0 – 6,0 – 8,0 and 10 ml of the standard copper solution (3.13) and in the three remaining flasks respectively 6,0 – 8,0 and 10,0 ml of the standard copper solution (3.12). Add 2 ml of the citric acid solution (3.7) to each flask and mix, then add the amount of ammonia solution (3.6) established in the preliminary test for adjusting the pH value as indicated in 6.1.2, and 10 ml of the acetaldehyde solution (3.8). Cool to approximately 20 °C, and lastly add 10 ml of the oxalyldihydrazide solution (3.9).

Make up the volume to 50 ml with water and mix. After 30 min, carry out the photometric measurements at the maximum of the absorption graph (wavelength about 540 nm), having set the instrument to zero absorbance against the compensating solution.

Draw a graph plotting, for example, the amount of copper contained in 50 ml as abscissae against the corresponding values of absorbance as ordinates.

6.2 Test portion

Weigh the test portion with an accuracy of ± 0,001 g, in accordance with the quantities shown in the table.

6.3 Determination

6.3.1 *Attack of the test portion*

The mass of test portion, degree of dilution of the main solution, and the volume of the aliquot, according to the expected copper content, are shown in the table.

Place the test portion in a tall-form beaker of suitable capacity (for example 250 ml). Add approximately 20 ml of water and then, in small portions, 30 ml of the hydrochloric acid (3.1). Cover with a watch-glass and, if necessary, heat gently in order to speed up the attack. Add 1 ml of the hydrogen peroxide (3.5) drop by drop, then bring to the boil.[2] Evaporate until a pasty mass is obtained.

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[1] Sampling of aluminium and aluminium alloys will be the subject of a future International Standard.

[2] See annex for modification to the general method in the special case of aluminium alloys containing more than 1 % (*m*/*m*) of silicon.

TABLE

Expected copper content	Mass of test portion	Volume of main solution	Volume of aliquot to be taken	Mass of copper present in aliquot
%	g	ml	ml	µg
0,002 to 0,02	2	100	10,0	4 to 40
over 0,02 to 0,08	1	200	10,0	10 to 40
over 0,08 to 0,2	1	500	10,0	16 to 40
over 0,2 to 0,4	1	500	5,0	20 to 40
over 0,4 to 0,8	0,5	500	5,0	20 to 40

Take up with about 50 ml of hot water and heat in order to dissolve the salts completely. Allow to cool, filter if necessary through a medium texture filter paper and collect the filtrate in the appropriate volumetric flask (see column headed "Volume of main solution" in the table). Rinse the beaker and the filter with warm water and add the washings to the main solution.

After cooling to room temperature, make up to volume with water and mix.

6.3.2 *Preliminary test for adjusting the pH value*

Take the aliquot as specified in the table, place it in a beaker of suitable capacity (for example 50 or 100 ml) and add about 10 ml of water. Add 3 ml of the citric acid solution (3.7) for a 2 g test portion, or 2 ml for a 1 g or 0,5 g test portion. Mix and then add 10 ml of the acetaldehyde solution (3.8).

By means of a graduated pipette or burette, add sufficient ammonia solution (3.6), while stirring, to bring the pH of the solution to approximately 9,3 (within the range 9,1 to 9,5).

Note the number of millilitres of the ammonia solution that were used for the adjustment of the pH value (the amount will be about 7 to 9 ml). Discard this test solution.

6.3.3 *Colour reaction*

In a 50 ml volumetric flask, place an aliquot of the main solution of the same size as the one used in the preliminary test for adjusting the pH value. Add 3 ml of the citric acid solution (3.7) for a 2 g test portion, or 2 ml for a 1 g or 0,5 g test portion, and mix.

Add the quantity of ammonia solution (3.6) established in the preliminary test (see 6.3.2), then 10 ml of the acetaldehyde solution (3.8), then 10 ml of the oxalyldihydrazide solution (3.9); cool to about 20 °C. Make up the volume to 50 ml with water and mix.

6.3.4 *Blank test*

In a tall-form beaker of suitable capacity (for example 250 ml), place 30 ml of the hydrochloric acid (3.1) and 1 ml of the hydrogen peroxide (3.5). Cover with a watch-glass and evaporate almost completely. Take up with water, transfer the solution to a volumetric flask of the same capacity as the flask used for the main solution of the test portion, and make up to volume at room temperature.

Take an aliquot of the same size as the one used in the colour reaction and adjust the pH value by the procedure specified in 6.3.2.

Then take a second aliquot of the blank test solution and follow the procedure specified in 6.3.3.

6.3.5 *Photometric measurement*

After 30 min, carry out the photometric measurement of the coloured solution at the maximum of the absorption graph (wavelength about 540 nm), having set the instrument to zero absorbance against the blank test solution.

7 EXPRESSION OF RESULTS

By means of the calibration graph (6.1.3), determine the mass of copper, in milligrams, corresponding to the value of the photometric measurement of the aliquot from the main solution.

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

$$\frac{m_1 \times D}{10\, m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass of copper, in milligrams, contained in the aliquot from the main solution;

D is the ratio of the volume of the main solution of the test portion to the volume of the aliquot taken.

8 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.

ANNEX

SPECIAL CASE OF ALUMINIUM ALLOYS CONTAINING MORE THAN 1 % (*m*/*m*) OF SILICON

A.1 PRINCIPLE OF THE SPECIAL METHOD USED

Graphitic silicon which remains as an insoluble residue after the attack of the test portion retains appreciable traces of copper. It is therefore necessary to filter and wash the graphitic silicon, to evaporate it with hydrochloric acid, and to recover the copper from the residue.

A.2 MODIFICATION TO THE GENERAL METHOD

In 6.3.1, after "... bring to the boil.[2]*", continue as follows :*

Dilute to approximately 70 to 80 ml with water, cool and filter through a double medium texture filter paper, washing the beaker and filter with boiling water. Collect the filtrate and washings in a tall-form beaker of suitable capacity (main solution). Place the filter paper and residue in a platinum crucible, dry at 110 to 120 °C in a hot-air oven, then ignite carefully, until combustion of the filter paper is complete, at a temperature not exceeding 600 °C, taking care that the filter paper does not burst into flames (to avoid loss of copper). After cooling, place in the crucible approximately 5 ml of the hydrofluoric acid (3.2), 1 ml of the sulphuric acid (3.4) and lastly, drop by drop, nitric acid (3.3) until the solution becomes perfectly clear. Evaporate until the white sulphuric acid fumes are completely driven off, allow to cool, then take up with a few millilitres of hot water and one or two drops of the hydrochloric acid (3.1). Heat gently, filter if necessary, and add the solution obtained to the main solution. Evaporate this until a pasty mass is obtained.

Take up with about 50 ml ... *From this point, 6.3.1 remains unchanged.*