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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION R 795

CHEMICAL ANALYSIS OF ALUMINIUM AND ITS ALLOYS

PHOTOMETRIC DETERMINATION OF COPPER

(Oxalyldihydrazide method
applicable to copper content between 0.002 and 0.8 %)

1st EDITION

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BRIEF HISTORY

The ISO Recommendation R 795, *Chemical analysis of aluminium and its alloys – Photometric determination of copper (Oxalyldihydrazide method applicable to copper content between 0.002 and 0.8 %,* was drawn up by Technical Committee ISO/TC 79, *Light metals and their alloys,* the Secretariat of which is held by the Association Française de Normalisation (AFNOR).

Work on this question by the Technical Committee began in 1956 and led, in 1963, to the adoption of a Draft ISO Recommendation.

In June 1966, this Draft ISO Recommendation (No. 968) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Argentina	Korea, Rep. of	Sweden
Austria	India	Switzerland
Belgium	Ireland	Turkey
Brazil	Israel	U.A.R.
Bulgaria	Italy	U.S.A.
Canada	Netherlands	U.S.S.R.
Chile	Norway	Yugoslovia
Czechoslovakia	Poland	
France	South Africa, Rep. of	
Germany	Spain	
Hungary		

One Member Body opposed the approval of the Draft :

United Kingdom

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in July 1968, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 795 July 1968

CHEMICAL ANALYSIS OF ALUMINIUM AND ITS ALLOYS

PHOTOMETRIC DETERMINATION OF COPPER

(Oxalyldihydrazide method applicable to copper content between 0.002 and 0.8 %)

1. SCOPE

1.1 This ISO Recommendation describes a photometric method for the determination of copper in aluminium and its alloys.

1.2 The method is applicable to the determination of copper content between 0.002 and 0.8 %.

1.3 The method does not apply completely to the special case of alloys with silicon contents exceeding 1 %, for which it should be modified as described in the Annex.

2. PRINCIPLE

2.1 Attack with hydrochloric acid.

2.2 Formation between pH 9.1 and pH 9.5, in the presence of acetaldehyde, of the violet-coloured complex, copper-oxalyldihydrazide, the optimum pH range being obtained by adding a controlled amount of ammonia.

2.3 Photometric measurement at a wavelength of about 540 nm.*

3. REAGENTS

3.1 *Hydrochloric acid*, d = 1.19 (approximately 12 N).

3.2 *Hydrofluoric acid*, 40 %, d = approximately 1.15.

3.3 *Nitric acid*, d = 1.23 (approximately 7.4 N).
Take 50 ml of nitric acid, d = 1.40 (approximately 15 N), and make up the volume to 100 ml with water.

3.4 *Sulphuric acid*, d = 1.48 (approximately 17.5 N).
Cautiously pour 50 ml of sulphuric acid, d = 1,84 (approximately 35.6 N), into water and after cooling make up the volume to 100 ml.

3.5 *Hydrogen peroxide*, 36 %, d = 1.12 (approximately 120 volumes).

3.6 *Ammonia solution*, d = 0.90 (approximately 14.4 N).

3.7 *Citric acid solution*, 500 g per litre.
Dissolve 500 g of citric acid ($C_6H_8O_7.H_2O$) in water and make up the volume to 1000 ml.

3.8 *Acetaldehyde solution*, 400 g per litre.
In a 1000 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 1000 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.

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

3.9 *Oxalyldihydrazide solution,* 2.5 g per litre.
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 1000 ml. Filter if necessary.

3.10 *Standard copper solution,* 1 g per litre (1 ml contains 1 mg of copper).

3.10.1 In a tall-form beaker of suitable capacity (e.g. 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 1000 ml volumetric flask, rinse and after cooling make up the volume to 1000 ml with water.

Alternatively

3.10.2 Dissolve 3.9296 g of copper sulphate crystals ($CuSO_4 . 5H_2O$) in water and make up the volume to 1000 ml.

3.11 *Standard copper solution,* 0.05 g per litre (1 ml contains 0.05 mg of copper).
Transfer 50.0 ml of standard copper solution (3.10) to a 1000 ml volumetric flask and make up the volume to 1000 ml with water.

3.12 *Standard copper solution,* 0.005 g per litre (1 ml contains 5 µg of copper).
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. Prepare just before use.

3.13 *Standard copper solution,* 0.0025 g per litre (1 ml contains 2.5 µg of copper).
Transfer 50.0 ml of standard copper solution (3.11) to a 1000 ml volumetric flask and make up the volume to 1000 ml with water. Prepare just before use.

4. APPARATUS

4.1 *Ordinary laboratory equipment*

All volumetric apparatus should comply with national standards.

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

5. SAMPLING

5.1 **Laboratory sample**

See the appropriate national standard on sampling.

5.2 **Test sample**

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

6. PROCEDURE

6.1 **Calibration graph**

6.1.1 *Solution in hydrochloric acid.* In a 250 ml beaker, place 30 ml of hydrochloric acid (3.1) and 1 ml of 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 minutes, 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 (e.g. 50 to 100 ml) place 10 ml of hydrochloric acid solution (6.1.1), 10 ml of standard copper solution (3.12) and 2 ml of citric acid solution (3.7); mix and add 10 ml of 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 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 hydrochloric acid (3.1), then respectively 0 (compensating solution), 2.0, 4.0, 6.0, 8.0 and 10.0 ml of standard copper solution (3.13) and in the three remaining flasks respectively 6.0, 8.0 and 10.0 ml of standard copper solution (3.12). Add 2 ml of 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 clause 6.1.2, and 10 ml of acetaldehyde solution (3.8). Cool to approximately 20 °C, and lastly add 10 ml of oxalyldihydrazide solution (3.9).

Make up the volume to 50 ml with water and mix. After 30 minutes, carry out the photometric measurements at the maximum of the absorption graph (wavelength about 540 nm), having set the instrument to zero optical density 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 optical density 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 in clause 6.3.1.

6.3 Determination

6.3.1 *Attack of the test portion.* The size of test portion, degree of dilution of the main solution, and the size of the aliquot, according to the assumed copper content, are shown in the Table below.

TABLE

Assumed 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

Place the test portion in a tall-form beaker of suitable capacity (e.g. 250 ml). Add approximately 20 ml of water and then, in small portions, 30 ml of 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 hydrogen peroxide (3.5) dropwise, then bring to the boil.* Evaporate until a pasty mass is obtained.

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.

* See Annex for modification to the general method in the special case of aluminium alloys containing more than 1 % of silicon.

6.3.2 *Preliminary test for adjusting the pH value.* Take the aliquot as specified in the Table above, place it in a beaker of suitable capacity (e.g. 50 to 100 ml) and add about 10 ml of water. Add 3 ml of 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 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 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 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 clause 6.3.2), then 10 ml of acetaldehyde solution (3.8), then 10 ml of 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 (e.g. 250 ml), place 30 ml of hydrochloric acid (3.1) and 1 ml of 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 described in clause 6.3.2.

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

6.3.5 *Photometric measurement.* After 30 minutes, 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 optical density against the blank test solution.

7. EXPRESSION OF RESULTS

By means of the calibration graph, determine the mass of copper, expressed in milligrammes, corresponding to the value of the photometric measurement of the aliquot from the main solution.

The percentage, by mass, of copper is calculated from the following formula :

$$\text{Cu } \% \text{ (m/m)} = \frac{A \times D}{10\,E}$$

where

A is the mass of copper, expressed in milligrammes, 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, and

E is the mass, expressed in grammes, of the test portion.

8. TEST REPORT

Report the following information :

(*a*) the reference to the method used;

(*b*) the results and the method used to express them;

(*c*) any unusual features noted during the determination;

(*d*) any operation not laid down in this ISO Recommendation or regarded as optional.