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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION

R 796

CHEMICAL ANALYSIS OF ALUMINIUM AND ITS ALLOYS

ELECTROLYTIC DETERMINATION OF COPPER IN ALUMINIUM ALLOYS

(Copper content greater than or equal to 0.50 %)

1st EDITION
July 1968

For each individual country the only valid standard is the national standard of that country.

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BRIEF HISTORY

The ISO Recommendation R 796, *Chemical analysis of aluminium and its alloys – Electrolytic determination of copper in aluminium alloys (Copper content greater than or equal to 0.50 %)*, 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. 969) 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
Austria
Belgium
Brazil
Bulgaria
Canada
Chile
Czechoslovakia
France
Germany
Hungary
Korea, Rep. of
India
Ireland
Israel
Italy
Japan
Netherlands
Norway
Poland
South Africa, Rep. of
Spain
Sweden
Switzerland
Turkey
U.A.R.
United Kingdom
U.S.S.R.
Yugoslavia

One Member Body opposed the approval of the Draft :

U.S.A.

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 796 July 1968

CHEMICAL ANALYSIS OF ALUMINIUM AND ITS ALLOYS

ELECTROLYTIC DETERMINATION OF COPPER IN ALUMINIUM ALLOYS

(Copper content greater than or equal to 0.50 %)

1. SCOPE

1.1 This ISO Recommendation describes an electrolytic method for the determination of copper in aluminium alloys.

1.2 The method is applicable to the determination of copper content greater than or equal to 0.50 %.

1.3 The method does not apply completely to the following special cases for which it should be modified as described in Annex A and Annex B :

- (*a*) alloys containing tin or antimony (see Annex A);
- (*b*) alloys containing bismuth (see Annex B).

2. PRINCIPLE

2.1 Attack with a mixture of perchloric acid and nitric acid.

2.2 Dehydration of the silica in a perchloric medium and filtration of the insoluble residue.

2.3 Volatilization of the siliceous residue and recovery of copper from the residue.

2.4 Electrolysis of the solution after addition of nitric acid.

3. REAGENTS

3.1 *Ethanol,* 95 %, d = approximately 0.816.

3.2 *Sulphamic acid* (NH_2SO_3H).

3.3 *Hydrobromic acid,* 48 %, d = approximately 1.49.

3.4 *Hydrochloric acid,* $d = 1.1$ (approximately 6 N).
Take 500 ml of hydrochloric acid, $d = 1.19$ (approximately 12 N), and make up the volume to 1000 ml with water.

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

3.6 *Nitric acid,* $d = 1.40$ (approximately 15 N).

3.7 *Nitric acid,* $d = 1.23$ (approximately 7.4 N).
Take 500 ml of nitric acid, $d = 1.40$, and make up the volume to 1000 ml with water.

3.8 *Perchloric acid,* $d = 1.67$ (approximately 11.7 N).
(Perchloric acid, $d = 1.54$ (approximately 9 N), can also be used. 1000 ml of perchloric acid, $d = 1.67$, is equivalent to 1270 ml of perchloric acid, $d = 1.54$).

3.9 *Perchloric acid,* $d = 1.33$ (approximately 5.8 N).
Take 500 ml of perchloric acid, $d = 1.67$, and make up the volume to 1000 ml with water.

3.10 *Sulphuric acid,* $d = 1.33$ (approximately 11.7 N).
Carefully add 35 ml of sulphuric acid, $d = 1.84$, to water and, after cooling, make up the volume to 100 ml.

3.11 *Tartaric acid solution,* 300 g per litre.
Dissolve 300 g of tartaric acid ($C_4H_6O_6$) in a little water and make up the volume to 1000 ml.

3.12 *Ammonia solution, d* = 0.95 (approximately 7 N).
Take 500 ml of ammonia solution, d = 0.90 (approximately 14.4 N), and make up the volume to 1000 ml with water.

3.13 *Bromine water,* saturated solution.

3.14 *Formic mixture :*

Formic acid, d = 1.20 (approximately 24 N)	20 ml	made up to 100 ml with water
Ammonia solution, d = 0.90 (approximately 14.4 N)	3 ml	

Dilute 20 ml of formic acid (HCOOH) with about 50 ml of water, add 3 ml of ammonia solution and make up the volume to 100 ml with water.

3.15 *Formic mixture wash solution.*
Dilute 25 ml of formic mixture (3.14) to 1000 ml with water, heat to 50 to 60 °C and saturate with hydrogen sulphide. Prepare just before use.

3.16 *Methyl red solution.*
Dissolve 0.10 g of methyl red in 100 ml of ethanol, 95 % (3.1).

4. APPARATUS

4.1 *Ordinary laboratory equipment*
All volumetric apparatus should comply with national standards.

4.2 *Laboratory electrolyser* fitted with a device for stirring the electrolyte (e.g. a rotating anode or a magnetic stirrer).

4.3 *Cylindrical platinum-iridium wire gauze cathode* (Winkler electrode).

4.4 *Platinum-iridium anode* (spiral, or gauze, etc.).

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 Test portion

Weigh the test portion with an accuracy of ± 0.001 g, in accordance with the quantities shown in Table 1, below.

6.2 Determination

6.2.1 *Attack of the test portion.* Depending on the assumed copper content, take the size of test portion shown in Table 1 and use the corresponding quantities of the reagents.

TABLE 1

Assumed copper content	Mass of test portion	Volume of perchloric acid 5.8 N (3.9)	Volume of nitric acid 15 N (3.6)
%	g	ml	ml
0.50 to 2	5	180	5
over 2 up to 5	2	75	5
greater than 5	1	40	5

Place the test portion in a suitable vessel (porcelain basin or beaker). Just before use, mix the appropriate quantities of perchloric acid (3.9) and nitric acid (3.6) and add a small portion of this nitroperchloric mixture to the test portion. Cover the vessel with a watch-glass, heat moderately in order to start the reaction and then stop heating immediately. Cautiously add the remainder of the nitroperchloric mixture in small portions, cooling as required.

If the test portion is difficult to attack, add a few drops of hydrochloric acid (3.4). When the attack is complete, evaporate to copious white fumes of perchloric acid, avoiding spattering, and continue evaporating and fuming for 15 to 20 minutes. Allow to cool and add approximately 200 to 400 ml of boiling water, depending on the size of the test portion. Stir and boil for about 5 minutes.

6.2.2 *Filtration and washing.* Allow the residue to settle while hot (40 to 60 °C), then filter through a medium texture filter containing a little paper-pulp. Carefully wash the vessel, the residue and the filter with boiling water, collecting the filtrate and the washings in a suitable vessel (e.g. a 400 to 1000 ml beaker).

NOTE. – Washing should be thorough because any perchloric acid retained by the silica might lead to spattering during incineration of the filter paper.

6.2.3 *Recovery of copper from the residue.* Place the filter and the residue in a platinum vessel; dry at 110 to 120 °C in a hot-air oven, then incinerate carefully at 500 to 600 °C until combustion of the filter is complete, taking care that the filter paper does not burst into flames (to avoid loss of copper). Allow to cool, add 1 ml of sulphuric acid (3.10), 2 to 5 ml of hydrofluoric acid (3.5), then nitric acid (3.7), dropwise, until the solution becomes perfectly clear. Evaporate to dryness without calcining and take up the residue with a little hot water and about 1 ml of perchloric acid (3.9). Dissolve by heating, filter if necessary, and add the solution obtained to the main solution.

6.2.4 *Electrolysis.* Adjust the volume of the solution to about 200 to 300 ml, add 6 to 10 ml of nitric acid (3.7) and approximately 1 g of sulphamic acid (3.2) and put the electrodes in position. Cover the beaker and connect the electrodes to the electrolysis apparatus. Electrolyse the solution at room temperature (or at 40 to 50 °C), with a current density of 0.5 to 1 ampère per square decimetre of cathode surface, while stirring the electrolyte.

NOTE. – Before electrolysis, calcine the gauze cathode at 800 to 900 °C then allow to cool. Dip the cathode in ethanol (3.1), dry in an oven (temperature between 100 and 110 °C) until the alcohol has evaporated (about 10 minutes), place it in a desiccator and weigh after cooling.

In order to test whether the deposition of copper on the cathode is complete, raise the level of the electrolyte by about 1 cm by adding water. Add approximately 1 g of sulphamic acid (3.2) and continue the electrolysis for 15 to 30 minutes : no further copper will be deposited on the newly immersed portion of the cathode if deposition is complete; if deposition occurs, continue electrolysis for a few minutes, after adding more water, until there is no further deposition. Having achieved this result, without interruption of the current remove the beaker containing the electrolyte and quickly replace it with a beaker containing sufficient water to cover the electrodes completely.

A few seconds later, remove the beaker, switch off the current, disconnect the electrodes from the electrolyser and wash the cathode by quickly immersing it in ethanol (3.1). Dry the cathode in an oven (100 to 110 °C) until the alcohol evaporates (about 10 minutes), leave it to cool in a desiccator and weigh it. When electrolysis is finished, the combined wash water and electrolyte should not give a significant reaction with a sensitive reagent for copper.

NOTE. – It is advisable, in order to make a further check of the mass of the cathode, to dissolve the deposited copper in nitric acid, to wash the cathode carefully and, after calcination at 800 to 900 °C according to the procedure described in the preceding Note, to check its weight again.

7. EXPRESSION OF RESULTS

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

$$\text{Cu}\ \%\ (\text{m/m}) = \frac{M - m}{E} \times 100$$

where

M is the mass, expressed in grammes, of the cathode and deposited copper;

m is the mass, expressed in grammes, of the cathode before electrolysis;

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.