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Aluminium alloys — Determination of copper — Electrolytic method

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FOREWORD

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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 now in the process of being transformed into International Standards. As part of this process, International Standard ISO 796 replaces ISO Recommendation R 796-1968 drawn up by Technical Committee ISO/TC 79, *Lights metals and their alloys.*

The Member Bodies of the following countries approved the Recommendation :

Argentina
Austria
Belgium
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Canada
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Czechoslovakia
Egypt, Arab Rep. of
France
Germany
Hungary
Korea, Rep. of
India
Ireland
Israel
Italy
Japan
Netherlands
Norway
Poland
South Africa, Rep. of
Spain
Sweden
Switzerland
Turkey
United Kingdom
U.S.S.R.
Yugoslavia

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

U.S.A.*

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* Subsequently, this Member Body approved the Recommendation.

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Aluminium alloys — Determination of copper — Electrolytic method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies an electrolytic method for the determination of copper in aluminium alloys.

The method is applicable to the determination of copper content greater than or equal to 0,50 %.

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

a) alloys containing tin or antimony (see Annex A);

b) alloys containing bismuth (see Annex B).

2 PRINCIPLE

Attack with a mixture of perchloric acid and nitric acid.

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

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

Electrolysis of the solution after addition of nitric acid.

3 REAGENTS

3.1 Ethanol, ρ approximately 0,816 g/ml, 95 % (*V/V*) solution.

3.2 Sulphamic acid (NH_2SO_3H).

3.3 Hydrobromic acid, ρ approximately 1,49 g/ml, 48 % (*V/V*) solution.

3.4 Hydrochloric acid, ρ 1,1 g/ml, approximately 6 N solution.

Take 500 ml of hydrochloric acid (ρ 1,19 g/ml), approximately 12 N and make up the volume to 1 000 ml with water.

3.5 Hydrofluoric acid, ρ approximately 1,14 g/ml, 40 % (*m/m*) solution.

3.6 Nitric acid, ρ 1,40 g/ml, approximately 15 N solution.

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

Take 500 ml of nitric acid (3.6) and make up the volume to 1 000 ml with water.

3.8 Perchloric acid, ρ 1,67 g/ml, approximately 11,7 N solution.

(Perchloric acid, ρ 1,54 g/ml (approximately 9 N), can also be used. 1 000 ml of perchloric acid (ρ 1,67 g/ml), is equivalent to 1 270 ml of perchloric acid (ρ 1,54 g/ml).)

3.9 Perchloric acid, ρ 1,33 g/ml approximately 5,8 N solution.

Take 500 ml of perchloric acid (3.8) and make up the volume to 1 000 ml with water.

3.10 Sulphuric acid, ρ 1,33 g/ml (approximately 11,7 N).

Carefully add 35 ml of sulphuric acid (ρ 1,84 g/ml) to water and, after cooling, make up the volume to 100 ml.

3.11 Tartaric acid, 300 g/l solution.

Dissolve 300 g of tartaric acid ($C_4H_6O_6$) in a little water and make up the volume to 1 000 ml.

3.12 Ammonia, ρ 0,95 g/ml solution (approximately 7 N).

Take 500 ml of ammonia solution, ρ 0,90 g/ml (approximately 14,4 N), and make up the volume to 1 000 ml with water.

3.13 Bromine water, saturated solution.

3.14 Formic mixture :

Formic acid, ρ 1,20 g/ml (approximately 24 N)	20 ml	made up to 100 ml with water
Ammonia solution, ρ 0,90 g/ml (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 the formic mixture (3.14) to 1 000 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 % (*V/V*) (3.1).

4 APPARATUS

4.1 Ordinary laboratory equipment

4.2 Laboratory electrolyser fitted with a device for stirring the electrolyte (for example 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[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 Test portion

Weigh the test portion with an accuracy of ± 0,001 g, in accordance with the quantities shown in table 1.

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.

Place the test portion in a suitable vessel (porcelain basin or beaker). Just before use, mix the appropriate quantities of the perchloric acid (3.9) and the 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 the 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 min. 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 min.

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

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 (for example a 400 to 1 000 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 the sulphuric acid (3.10), 2 to 5 ml of the hydrofluoric acid (3.5), then the nitric acid (3.7), drop by drop, 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 the perchloric acid (3.9). Dissolve by heating, filter if necessary, and add the solution obtained to the main solution.

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[1] The sampling of aluminium alloys will form the subject of a future International Standard.

6.2.4 *Electrolysis*

Adjust the volume of the solution to about 200 to 300 ml, add 6 to 10 ml of the nitric acid (3.7) and approximately 1 g of the 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 A 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 the ethanol (3.1), dry in an oven (temperature between 100 and 110 °C) until the alcohol has evaporated (about 10 min), 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 the sulphamic acid (3.2) and continue the electrolysis for 15 to 30 min : 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 the ethanol (3.1). Dry the cathode in an oven (100 to 110 °C) until the alcohol evaporates (about 10 min), 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 note to 6.2.4, to check its mass again.

7 EXPRESSION OF RESULTS

Calculate the copper content, as a percentage by mass, by the formula

$$\text{Cu}\ \%\ (m/m) = \frac{m_2 - m_1}{m_0} \times 100$$

where

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

m_1 is the mass, in grams, of the cathode before electrolysis;

m_2 is the mass, in grams, of the cathode and deposited copper.

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 A

SPECIAL CASE OF ALUMINIUM ALLOYS CONTAINING TIN OR ANTIMONY

A.1 PRINCIPLE OF THE SPECIAL METHOD USED

Tin and antimony, which interfere with electrodeposition of copper, are volatilized from the perchloric acid solution as bromides.

A.2 MODIFICATION TO THE GENERAL METHOD

Throughout clause 6, read "table 2" in place of "table 1".

Replace 6.2.1 by the following :

According to the assumed copper, tin or antimony content, take the size of test portion shown in table 2, and use the corresponding quantities of the reagents for the attack.

Place the test portion in a suitable vessel (for example, a porcelain basin of about 600 to 1 000 ml) and add the appropriate quantity of the perchloric acid (3.9). Cover with a watch-glass and cautiously add, in small portions, the hydrobromic acid (3.3) and the bromine water (3.13), mixed just before using. This operation should be carried out in a fume cupboard and the vessel may be heated moderately if required. When the attack is complete, remove the watch-glass and wash it with water, then concentrate the solution by raising the temperature gradually until copious white perchloric acid fumes are emitted. Continue with the evaporation and emission of fumes for 5 min; then cover the dish with a watch-glass and continue heating for about 20 min. Allow to cool and add about 200 to 400 ml of boiling water, depending on the size of test portion used. Stir and boil for about 5 min.

TABLE 2

Assumed copper content	Assumed tin or antimony content	Mass of test portion	Volume of perchloric acid 5.8 N (3.9)	Volume of hydrobromic acid 48 % (3.3)	Volume of bromine water (3.13)
%	%	g	ml	ml	ml
0,50 to 2	⩽ 6	5	250	30	20
	6 to 20	5	250	70	20
over 2 up to 5	⩽ 6	2	110	15	10
	6 to 20	2	110	30	10
greater than 5	⩽ 6	1	70	10	10
	6 to 20	1	70	20	10

ANNEX B

SPECIAL CASE OF ALUMINIUM ALLOYS CONTAINING BISMUTH

B.1 PRINCIPLE

Precipitation of copper and Group II metals by hydrogen sulphide in a formic buffer medium.

Dissolution of the sulphides in nitric acid.

Removal of bismuth as the oxychloride in dilute hydrochloric acid.

Replacement of acid by perchloric acid.

Electrolysis according to the general method.

B.2 MODIFICATIONS TO THE GENERAL METHOD

After 6.2.3 add the following :

6.2.3.1 PRECIPITATION OF GROUP II METALS

Concentrate the solution to approximately 200 ml, then pour it into a conical flask of about 500 ml capacity, carefully wash the beaker with as little water as possible and add the washings to the solution.

Add 25 ml of the tartaric acid solution (3.11) for each gram of test portion and neutralize with the ammonia solution (3.12), using the methyl red solution (3.16) as indicator. Add 25 ml of the formic mixture (3.14) and concentrate the solution to about 200 or 250 ml. Heat to boiling and pass a stream of hydrogen sulphide through the solution, quickly at first and then slowly (approximately 100 to 120 bubbles per minute), until saturated (approximately 15 to 30 min).

Allow to settle at 40 to 50 °C (about 30 to 40 min), filter through a medium texture filter containing a little paper pulp and wash 6 to 8 times with hot formic mixture wash solution (3.15), taking care that the filter never runs dry.

6.2.3.2 DISSOLUTION OF THE SULPHIDES

Place the filter and the precipitate in the vessel used for precipitation of the sulphides, then add approximately 30 to 40 ml of hot nitric acid (3.7) and an equal volume of hot water. Cover the vessel with a watch-glass and heat gently, shaking to disintegrate the filter paper. Concentrate the solution to the appearance of yellow nitrous fumes. Then add 10 ml of the perchloric acid (3.8) and evaporate to the almost complete elimination of white perchloric acid fumes.

6.2.3.3 REMOVAL OF BISMUTH

After cooling, take up with approximately 20 ml of hot water, heat to dissolve the salts, add 2 or 3 drops of the methyl red solution (3.16), and lastly the ammonia solution (3.12), drop by drop, until the indicator turns yellow.

NOTE — When the copper content is high (4 to 5 %), the turning point of the indicator cannot be perceived. In this case, the indicator should not be used and the solution should be neutralized with the ammonia solution (3.12), added drop by drop until the characteristic blue colour of the cuprammonium complex appears. Then carefully acidify with the hydrochloric acid (3.4), added drop by drop, until the cuprammonium complex decomposes and the colour turns light blue. Then add an excess of 2 ml of the hydrochloric acid (3.4) (pH of the solution 0,7) and dilute to 300 ml with boiling water (pH of the solution 1,3 to 1,6).

Add 2 ml of the hydrochloric acid (3.4) (pH of the solution approximately 0,7), dilute to 300 ml with boiling water (pH of the solution 1,3 to 1,6), stir, keep hot (60 to 70 °C) until settling is complete (approximately 4 h) then allow to cool to room temperature. Filter (through a sintered glass crucible of, for example porosity 3 to 15 μm); wash 4 or 5 times using 20 to 25 ml portions of boiling water each time, collecting the filtrate and the washings in a tall-form beaker of suitable capacity (for example approximately 500 ml).

6.2.4 *Electrolysis*

Add to the solution 10 ml of the perchloric acid (3.8) and evaporate to copious white perchloric acid fumes; continue the evaporation for about 10 min. Allow to cool, then add about 200 ml of boiling water and stir until the salts are completely in solution. Add 6 to 10 ml of the nitric acid (3.7) ... [*Continue from this point in 6.2.4 (2nd line) of the general method.*]