

ISO

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION R 798

CHEMICAL ANALYSIS OF ALUMINIUM AND ITS ALLOYS

iTeh STANDARD PREVIEW

GRAVIMETRIC DETERMINATION OF ZINC IN ALUMINIUM ALLOYS

(Zinc content between 0.50 and 6.5 %)

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1st EDITION

July 1968

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Printed in Switzerland

Also issued in French and Russian. Copies to be obtained through the national standards organizations.

BRIEF HISTORY

The ISO Recommendation R 798, *Chemical analysis of aluminium and its alloys – Gravimetric determination of zinc in aluminium alloys (Zinc content between 0.50 and 6.5 %)*, 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. 971) 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	India	Sweden
Austria	Ireland	Switzerland
Belgium	Israel	Turkey
Brazil	Italy	U.A.R.
Bulgaria	Japan	United Kingdom
Canada	Netherlands	U.S.A.
Chile	Norway	U.S.S.R.
Czechoslovakia	Poland	Yugoslavia
Germany	South Africa,	
Hungary	Rep. of	
Korea, Rep. of	Spain	

One Member Body opposed the approval of the Draft :

France

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.

CHEMICAL ANALYSIS OF ALUMINIUM AND ITS ALLOYS

GRAVIMETRIC DETERMINATION OF ZINC IN ALUMINIUM ALLOYS

(Zinc content between 0.50 and 6.5 %)

1. SCOPE

- 1.1 This ISO Recommendation describes a gravimetric method for the determination of zinc in aluminium alloys.
- 1.2 The method is applicable to the determination of zinc content between 0.50 and 6.5 %.
- 1.3 The method does not apply completely to the special case of alloys with high nickel contents, for which it should be modified as described in the Annex.

2. PRINCIPLE

- 2.1 Attack with oxidizing acid.
- 2.2 Filtration and volatilization of the silica after dehydration in a sulphuric medium. Recovery of any zinc retained in the residue.
- 2.3 Precipitation of Group II metals by treatment with hydrogen sulphide in an acid medium.
- 2.4 Precipitation of zinc with hydrogen sulphide in a formic buffer medium after complexing the aluminium with tartaric acid.
- 2.5 Dissolution of the zinc sulphide with dilute hydrochloric acid. Removal of any traces of heavy metals by means of sodium hydrosulphide.
- 2.6 Oxidation and complexing of the iron with phosphoric acid, followed by precipitation of the zinc as zinc mercuric thiocyanate.
- 2.7 Filtration, washing, drying and weighing of the precipitate.

3. REAGENTS

3.1 *Mixed acids :*

<i>Sulphuric acid</i> , $d = 1.84$ (approximately 35.6 N)	250 ml	} made up to 1000 ml with water
<i>Hydrochloric acid</i> , $d = 1.19$ (approximately 12 N)	200 ml	
<i>Nitric acid</i> , $d = 1.40$ (approximately 15 N)	200 ml	

Carefully add the sulphuric acid to about 300 ml of water, while cooling. Add the hydrochloric acid, then the nitric acid, and make up the volume to 1000 ml with water.

- 3.2 *Sulphuric acid*, $d = 1.26$ (approximately 9 N).
Carefully add 250 ml of sulphuric acid, $d = 1.84$, to water, cool and make up the volume to 1000 ml.
- 3.3 *Sulphuric acid*, $d = 1.01$ (approximately 0.35 N).
Carefully add 10 ml of sulphuric acid, $d = 1.84$, to water, cool and make up the volume to 1000 ml.
- 3.4 *Sulphuric acid*, $d = 1.48$ (approximately 17.5 N).
Carefully add 50 ml of sulphuric acid, $d = 1.84$, to water, cool and make up the volume to 100 ml.
- 3.5 *Hydrofluoric acid*, 40 %, $d =$ approximately 1.15.

- 3.6 *Nitric acid*, $d = 1.23$ (approximately 7.4 N).
Take 50 ml of nitric acid, $d = 1.40$, and make up the volume to 100 ml with water.
- 3.7 *Hydrogen sulphide wash solution*.
Saturate cold sulphuric acid (3.3) with hydrogen sulphide.
Prepare just before use.
- 3.8 *Tartaric acid solution*, 300 g per litre.
Dissolve 300 g of tartaric acid ($C_4H_6O_6$) in water and make up the volume to 1000 ml.
- 3.9 *Ammonia solution*, $d = 0.95$ (approximately 7 N).
Take 50 ml of ammonia solution, $d = 0.90$, and make up the volume to 100 ml with water.
- 3.10 *Formic mixture* :
- | | | | |
|---|--------|---|----------------------------------|
| <i>Formic acid</i> , $d = 1.20$ (approximately 24 N) | 200 ml | } | made up to 1000 ml
with water |
| <i>Ammonium sulphate</i> | 250 g | | |
| <i>Ammonia solution</i> , $d = 0.90$ (approximately 14.4 N) | 30 ml | | |
- Dissolve 250 g of ammonium sulphate [$(NH_4)_2SO_4$] in about 600 ml of water, add 200 ml of formic acid (HCOOH), then 30 ml of ammonia solution, and make up the volume to 1000 ml with water.
- 3.11 *Gelatine solution*, 0.20 g per litre.
Dissolve 0.020 g of pure gelatine (with ash content of less than 0.1 %) in about 80 ml of warm water while heating gently. Cool and make up the volume to 100 ml.
Renew weekly.
- 3.12 *Formic wash solution*.
Dilute 25 ml of formic mixture (3.10) to 1000 ml with water and saturate the cold solution with hydrogen sulphide.
- 3.13 *Hydrochloric acid*, $d = 1.05$ (approximately 3 N).
Take 25 ml of hydrochloric acid, $d = 1.19$, and make up the volume to 100 ml with water.
- 3.14 *Nitric acid*, $d = 1.40$ (approximately 15 N).
- 3.15 *Sodium hydroxide solution*.
Dissolve 0.25 g of sodium hydroxide (NaOH) in 100 ml of water and saturate with hydrogen sulphide at room temperature.
- 3.16 *Hydrogen peroxide*, 6 % (approximately 20 volumes).
Add 5 ml of hydrogen peroxide, 36 %, $d = 1.12$, to 25 ml of water.
- 3.17 *Phosphoric acid*, $d = 1.35$ (approximately 22.5 N).
Take 50 ml of phosphoric acid, $d = 1.71$ (approximately 45 N), and make up the volume to 100 ml with water.
- 3.18 *Mercuric thiocyanate reagent*.
Dissolve 27 g of mercuric chloride ($HgCl_2$) in about 800 ml of water, while heating gently. After cooling, add 39 g of potassium thiocyanate (KSCN) [or, alternatively, 33 g of sodium thiocyanate (NaSCN)] and make up the volume to 1000 ml with water.
- NOTE. – If neither potassium thiocyanate nor sodium thiocyanate is available, proceed as follows :
Dissolve 31 g of ammonium thiocyanate (NH_4SCN) and 20 g of sodium hydroxide in 200 ml of water in a 500 ml conical flask. Boil to the disappearance of ammoniacal vapours, make up the volume to 200 ml with water and neutralize (against litmus paper) with dilute sulphuric acid. Dissolve 27 g of mercuric chloride ($HgCl_2$) in 300 ml of lukewarm water. Mix the two solutions and make up the volume to 1000 ml with water.
- 3.19 *Mercuric thiocyanate wash solution*.
Take 10 ml of mercuric thiocyanate reagent (3.18) and make up the volume to 500 ml with water.
- 3.20 *Lead acetate paper*.
- 3.21 *Methyl red solution*.
Dissolve 0.10 g of methyl red in 100 ml of ethanol, 95 %.

4. APPARATUS

Ordinary laboratory equipment

All volumetric apparatus should comply with national standards.

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

Mass of test portion : 2 ± 0.001 g.

6.2 Blank test

Carry out a blank test in parallel with the determination, following the same procedure and using the same quantities of all reagents.

6.3 Determination

6.3.1 Attack of the test portion and preparation of the main solution. Place the test portion in a beaker of suitable capacity (400 ml), provided with a watch-glass, and carefully add 70 ml of mixed acids (3.1) in small portions, while cooling. When the reaction subsides, heat moderately to complete the reaction. Place a glass triangle between the watch-glass and the beaker, then increase the heating and evaporate to copious white fumes which should be maintained for about 15 to 20 minutes.

Allow to cool sufficiently, then take up with 20 ml of sulphuric acid (3.2) and 100 to 150 ml of hot water. Heat gently until the salts are completely dissolved, wash the watch-glass, the triangle and the walls of the beaker with hot sulphuric acid (3.3) and filter through a medium texture filter paper containing a little paper pulp. Collect the filtrate and the washings in a conical flask and carefully wash the beaker, the residue collected on the filter, and the filter paper itself, with hot sulphuric acid (3.3).

Place the filter paper and the residue in a platinum crucible and calcine at 500 to 600 °C. After cooling, add to the crucible 1 ml of sulphuric acid (3.4) then 3 to 5 ml of hydrofluoric acid (3.5) and, carefully, dilute nitric acid (3.6) until the solution becomes clear (approximately 1 ml).

Evaporate carefully to copious white fumes, allow to cool, take up with a few millilitres of hot water and add the solution to the main solution, washing the crucible with hot water.

6.3.2 Precipitation of Group II metals. Make up the volume of the solution to about 300 ml, warm to a temperature between 60 and 70 °C and pass a rapid stream of hydrogen sulphide until the solution is saturated (about 20 minutes). Heat for a few minutes at just below the boiling point (if there is only a small sulphide precipitate, add a little medium texture paper pulp before heating) then allow to settle. Filter through a medium texture filter, collecting the filtrate and the washings in a 500 ml beaker and taking care that the precipitate is always kept moist by the solution. Wash the conical flask and the precipitate six or seven times with hot hydrogen sulphide wash solution (3.7). (Discard the precipitate).

6.3.3 *Precipitation of zinc sulphide.* Place a few glass balls (diameter about 5 to 6 mm) in the solution and boil vigorously until the hydrogen sulphide is completely removed, testing by means of lead acetate paper (3.20).

Transfer the solution to a 200 ml volumetric flask, taking care to wash the beaker thoroughly; cool, make up the volume to 200 ml and mix.

Transfer the aliquot of the solution shown in the Table below to a 500 ml conical flask.

TABLE

Assumed zinc content	Volume of main solution	Volume of aliquot to be taken	Mass of test portion corresponding to aliquot	Volume of tartaric acid solution (3.8)
%	ml	ml	g	ml
0.50 to 1	200	200.0	2	50
over 1 to 3	200	100.0	1	25
over 3 to 5	200	50.0	0.50	25
over 5 to 6.5	200	25.0	0.25	25

Make up the volume of the aliquot to about 250 ml, then add the quantity of tartaric acid solution (3.8) shown in the Table, and a few drops of methyl red solution (3.21). Neutralize with ammonia solution (3.9), then add 25 ml of formic mixture (3.10), heat to a temperature between 70 and 80 °C and pass a stream of hydrogen sulphide* quickly at first, then more slowly until saturation is reached (about 30 minutes). Add 2 ml of gelatine solution (3.11) and allow to stand, maintaining the temperature between 40 and 50 °C until the precipitate settles. [It is better to carry out the sulphide precipitation under pressure of hydrogen sulphide. After heating, close the conical flask with a two-holed stopper fitted with two glass tubes. Pass a stream of hydrogen sulphide quickly at first, then more slowly until saturation is reached (about 30 minutes). Add 2 ml of gelatine solution (3.11), close the outlet tube and maintain the pressure of hydrogen sulphide via the inlet tube, maintaining the temperature between 40 and 50 °C, until the precipitate settles].

Then filter through a medium texture filter paper containing a little paper pulp and carefully wash the conical flask, the glass tubes, the precipitate and the filter with hot formic mixture wash solution (3.12). (Discard the filtrate).

6.3.4 *Dissolution of the zinc sulphide.* Dissolve the precipitate on the filter by means of hot hydrochloric acid (3.13), taking care that any traces still adhering to the hydrogen sulphide inlet tube are also dissolved. Collect the filtrate and the washings in the first conical flask, then wash the filter thoroughly, using small portions of hot hydrochloric acid (3.13) and hot water alternately.** Add to the solution 15 ml of sulphuric acid (3.4) and 2 ml of nitric acid (3.14), then heat to copious white fumes and allow to cool.

6.3.5 *Purification of the zinc solution.* (To be carried out if the zinc sulphide is not white). Take up with 50 ml of water, bring to the boil and add 25 ml of the sodium hydrosulphide solution (3.15).

* and ** See the Annex for the modification to the general method in the special case of aluminium alloys with high nickel content.

Leave to settle for about 30 minutes, filter off any precipitate and wash it with hot hydrogen sulphide wash solution (3.7) (discard the precipitate), collecting the filtrate and washings in the 400 ml beaker. Boil the solution vigorously until the hydrogen sulphide is completely removed, testing by means of lead acetate paper (3.20).

6.3.6 *Precipitation of mercuric zinc thiocyanate.* Take up in a little hot water and dilute to about 120 ml, allow to cool, oxidize with a few drops of hydrogen peroxide (3.16), add 5 ml of phosphoric acid (3.17) and, stirring vigorously (for this purpose mechanical stirring is recommended), add 40 ml of mercuric thiocyanate reagent (3.18). Continue stirring until precipitation begins, remove the stirrer, washing it well with mercuric thiocyanate wash solution (3.19), then allow to stand for 12 hours.

6.3.7 *Filtration, washing and weighing of the mercuric zinc thiocyanate.* Filter the precipitate *under slight suction* through a weighed sintered glass crucible, porosity between 3 and 15 μm , then wash with mercuric thiocyanate wash solution (3.19) in small portions, without using more than 150 ml altogether. When the washing is finished, *increase* the suction for a few minutes. Dry to constant mass at 110 °C and weigh.

7. EXPRESSION OF RESULTS

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

$$\text{Zn } \% \text{ (m/m)} = \frac{(A - B) \times 0.1312 \times R}{E} \times 100$$

where

- A* is the mass, expressed in grammes, of mercuric zinc thiocyanate $[\text{ZnHg}(\text{SCN})_4]$ corresponding to the aliquot taken;
- B* is the mass, expressed in grammes, of mercuric zinc thiocyanate $[\text{ZnHg}(\text{SCN})_4]$ corresponding to the same aliquot of the solution in the blank test;
- R* is the ratio of the volume of the main solution to the volume of the aliquot taken;
- E* is the mass, expressed in grammes, of the test portion;
- 0.1312 is the conversion factor of mercuric zinc thiocyanate $[\text{ZnHg}(\text{SCN})_4]$ to zinc.

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.

ANNEX

Special case of aluminium alloys with high nickel content

INTRODUCTION

The presence of a fairly large quantity of ammonium sulphate in the formic mixture should ensure that all the nickel is kept in solution. However, part of the nickel might precipitate as the sulphide with the zinc sulphide (colouring the precipitate more or less grey). In addition, during the treatment of sulphides with dilute hydrochloric acid intended to dissolve the zinc sulphide selectively, part of the nickel sulphide might go into solution and then contaminate the precipitate of mercuric zinc thiocyanate.

A.1 PRINCIPLE OF THE SPECIAL METHOD USED

The hydrochloric solution obtained by dissolving the sulphides, precipitated with hydrogen sulphide in a formic buffer medium, is given a second treatment with hydrogen sulphide to ensure that the zinc sulphide is precipitated selectively. The precipitation in the formic buffer medium is carried out with a further addition of ammonium sulphate.

A.2 MODIFICATION TO THE GENERAL METHOD (standards.iteh.ai)

*In clause 6.3.4, after the double asterisk (**) continue as follows :*

Dilute the solution to about 200 ml, then add 5 ml of tartaric acid solution (3.8) and a few drops of methyl red solution (3.21).

Neutralize with ammonia solution (3.9), then add 25 ml of formic mixture (3.10) and 2 g of ammonium sulphate crystals $[(\text{NH}_4)_2\text{SO}_4]$, reheat to 70 to 80 °C, then pass a stream of hydrogen sulphide ... [Continue from the asterisk (*) at this point in clause 6.3.3, without change].