INTERNATIONAL STANDARD

ISO 1169

Second edition
2006-07-01

Zinc alloys — Determination of aluminium content — Titrimetric method

Alliages de zinc — Dosage de l'aluminium — Méthode titrimétrique

Reference number
ISO 1169:2006(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 1169 was prepared by Technical Committee ISO/TC 18, *Zinc and zinc alloys*, Subcommittee SC 1, *Methods of sampling and analysis of zinc and zinc alloys*.

This second edition cancels and replaces the first edition (ISO 1169:1975), which has been technically revised. It is based on European Standard EN 12441-1:2001, *Zinc and zinc alloys — Chemical analysis — Part 1: Determination of aluminium in zinc alloys — Titrimetric method*.

Zinc alloys — Determination of aluminium content — Titrimetric method

1 Scope

This International Standard specifies a titrimetric method for the determination of aluminium in zinc alloys. It is applicable to the products specified in ISO 301.

It is suitable for the determination of aluminium contents (mass fractions) between 3 % and 30 %.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 301, *Zinc alloy ingots intended for casting*

ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 5725-3, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method*

ISO 20081, *Zinc and zinc alloys — Method of sampling — Specifications*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 20081 apply.

4 Principle

An excess of EDTA is added to the hydrochloric solution of a test portion. This is followed by quantitative complexing of the excess with a standard zinc solution. The aluminium-EDTA complex is decomposed with sodium fluoride and the liberated EDTA is titrated against a standard zinc solution.

5 Reagents

5.1 General

During the test, use only reagents of known analytical grade and distilled or demineralised water.

5.2 Hydrochloric acid, $\rho = 1{,}19$ g/ml.

5.3 Nitric acid, $\rho = 1{,}4$ g/ml.

5.4 Hydrochloric acid (1+1).

Mix 1 volume of hydrochloric acid (5.2) with 1 volume of water.

5.5 Hydrogen peroxide, 30 % (mass fraction).

5.6 Hydroxylammonium chloride, 200 g/l solution.

5.7 Ethylenediamine tetra-acetic acid disodium salt (EDTA), 65 g/l solution.

5.8 Ammonia solution, $\rho = 0{,}91$ g/ml.

5.9 Sodium fluoride, saturated solution.

Dissolve 60 g of sodium fluoride in 1 litre of boiling water. Cool to room temperature and filter.

5.10 Sodium acetate, buffer solution.

Dissolve 135 g of sodium acetate ($CH_3COONa \cdot 3H_2O$) in approximately 300 ml of water. Add 13 ml of glacial acetic acid (5.16). Check that the pH is within the range 5 to 5,5. Make up the volume to 500 ml with water.

5.11 Standard zinc solution, 0,05 M.

Dissolve 3,269 g of high purity zinc in 40 ml of hydrochloric acid (1+1) (5.4) in a 250 ml beaker fitted with a watch-glass. Dilute with 100 ml of water. Add 2 drops of methyl red solution (5.12). Neutralize with ammonia solution (5.8). Add hydrochloric acid (1+1) (5.4) drop by drop until the colour changes to red. Transfer quantitatively to a 1 litre volumetric flask. Add 5 ml of hydrochloric acid (1+1) (5.4), dilute to the mark with water and mix.

5.12 Methyl red, ethanolic solution.

Dissolve 0,02 g of methyl red in 100 ml of ethanol.

5.13 Xylenol orange, 10 g/l solution.

5.14 Aqua regia.

Mix 3 volumes of hydrochloric acid (5.2) with 1 volume of nitric acid (5.3).

5.15 Xylene cyanol, 1 g/l solution.

NOTE The use of this reagent is optional.

5.16 Glacial acetic acid, $\rho = 1{,}05$ g/ml.

6 Apparatus

All glassware used for the preparation of the solutions and for the implementation of the method shall be cleaned with boiling aqua regia (5.14) prior to use.

7 Sampling

The test sample shall be selected and prepared in accordance with the procedure given in ISO 20081.

8 Procedure

8.1 Test portion

Weigh 5 g of the test sample to the nearest 0,001 g.

8.2 Determination

8.2.1 Put the test portion (8.1) in a 500 ml beaker fitted with a watch-glass and dissolve by carefully adding 50 ml of hydrochloric acid (1+1) (5.4). Oxidize and complete the dissolution by adding a few drops of hydrogen peroxide (5.5).

8.2.2 Add 5 ml of hydroxylammonium chloride solution (5.6) to decompose the excess of hydrogen peroxide. Heat the solution carefully.

Dilute to 100 ml with water and cool to room temperature. Transfer quantitatively:

a) for Al contents (mass fractions) $\leqslant$ 15 %: to a 250 ml volumetric flask;

b) for Al contents (mass fractions) $>$ 15 %: to a 1 000 ml volumetric flask.

Dilute to the mark with water and mix.

8.2.3 Transfer a 25 ml aliquot to a 500 ml conical flask.

8.2.4 Add successively:

a) approximately 100 ml of water;

b) EDTA solution:

   1) for Al contents (mass fractions) $\leqslant$ 15 %: 55 ml of EDTA solution (5.7);

   2) for Al contents (mass fractions) $>$ 15 %: 25 ml of EDTA solution (5.7);

c) 5 drops of methyl red solution (5.12).

NOTE Bromothymol blue may be used as the indicator for neutralization instead of methyl red.

8.2.5 Neutralize exactly with ammonia solution (5.8) until the colour changes to yellow. Add 25 ml of buffer solution (5.10).

8.2.6 Boil for 2 min to 3 min. Cool to room temperature.

8.2.7 Add 2 to 3 drops of xylenol orange solution (5.13).

NOTE For some operators, the end-point can be made even more readily detectable by the addition of not more than 1 ml of xylene cyanol solution (5.15).

8.2.8 Titrate the excess of EDTA with standard zinc solution (5.11) until the colour changes to purple.

8.2.9 Add 25 ml of sodium fluoride solution (5.9). Boil for 2 min to 3 min. Cool to room temperature.

8.3 Volumetric measurement

Titrate the liberated EDTA with the standard zinc solution (5.11) until the colour changes to purple.

9 Calculation and expression of results

9.1 Method of calculation

The aluminium content, w_{Al}, shall be given, as a percentage by mass,

a) for Al contents (mass fractions) $\leqslant$ 15 %: by the formula $V \times$ 0,269 8;

b) for Al contents (mass fractions) $>$ 15 %: by the formula $V \times$ 1,079 2;

where V is the volume, in millilitres, of standard zinc solution used to titrate the liberated EDTA (see 8.3).

If a number of determinations are carried out, then the mean of all the results shall be calculated.

The results shall be expressed as specified in ISO 301.

NOTE The simplified calculation given in a) and b) is based on the following full formula:

$$w_{Al} = \frac{V \text{ titrant (ml)} \times 1{,}349 \text{ (mg/ml)} \times V \text{ final(ml)} \times 1 \text{ (g)} \times 100}{\text{Mass (g)} \times V \text{ aliquot (ml)} \times 1\,000 \text{ (mg)}}$$

9.2 Precision

A planned trial of this method was carried out by 13 laboratories, using 7 samples with 5 levels of aluminium contents, each laboratory making three determinations of aluminium content in each sample (see Notes 1 and 2).

NOTE 1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725-1; i.e. one operator, same apparatus, dentical operating conditions and a minimum period of time.

NOTE 2 The third determination was carried out at a different time (on a different day), by the same operator as in Note 1 using the same apparatus.

The details of the samples used and the mean results obtained are given in Tables A.1 and A.2.

The results obtained were treated statistically in accordance with ISO 5725-2 and ISO 5725-3.

The data obtained showed a logarithmic relationship between the aluminium content and the repeatability limit (r) and reproducibility limits (R_w and R) of the test results (see Note 3), as summarized in Table 1. The graphical representation of the data is shown in Figure B.1.

NOTE 3 From the two values obtained on day 1, the repeatability limit (r) and the reproducibility limit (R) were calculated using the procedure specified in ISO 5725-3. From the first value obtained on day 1 and the value obtained on day 2, the within-laboratory reproducibility limit (R_w) day was calculated using the procedure specified in ISO 5725-3.

Table 1 — Repeatability and reproducibility limits

Aluminium content	Repeatability limit	Reproducibility limits	
% (mass fraction)	r	R_w	R
2	0,028	0,025	0,050
5	0,050	0,050	0,102
10	0,078	0,085	0,175
20	0,120	0,143	0,300
30	0,155	0,195	0,410

10 Test report

The test report shall include the following information:

a) identification of the sample;

b) test method used (i.e. a reference to this International Standard);

c) aluminium content, expressed as percentage by mass, giving, where possible, the results for the individual and mean values;

d) any unusual occurrence during the determination;

e) any steps in the procedure beyond those specified in this International Standard, and any circumstances that may have affected the results;

f) date of test report;

g) name of laboratory or testing organization;

h) signature of the laboratory manager or other responsible person.

Annex A
(informative)

Additional information on international interlaboratory test

Table A1 was derived from the results of an international interlaboratory test carried out in 1998 on 7 test samples in 6 countries involving 13 laboratories.

The results of the trials are shown in Table A.1.

The composition of the test samples used is shown in Table A.2.

Table A.1 — Detailed results obtained in the interlaboratory test

Sample	Aluminium content % (mass fraction)		Precision data		
			Repeatability	Reproducibility	
	Reference value	Found value	r	R_w	R
ZL 2	4,00	3,999	0,039 6	0,044 9	0,079 0
ZL 3	4,00	3,990	0,036 2	0,030 6	0,082 4
ZL 5	3,97	3,948	0,060 3	0,063 2	0,104 8
ZL 6	5,75	5,743	0,051 9	0,043 9	0,102 8
ZL 8	8,37	8,353	0,061 3	0,060 1	0,125 0
ZL 12	11,00	10,985	0,090 0	0,129 0	0,247 5
ZL 27	26,83	26,909	0,146 5	0,168 9	0,360 0

Table A.2 — Test samples used in the interlaboratory test

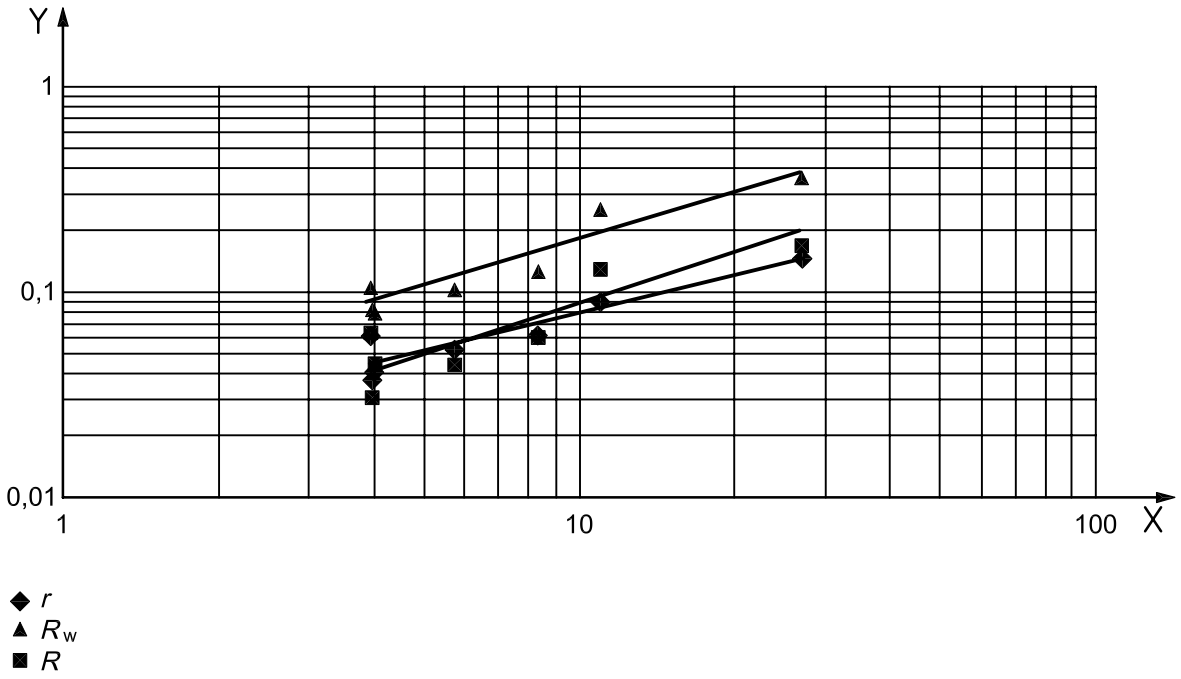
Contents in % (mass fraction)

Sample	Al	Cu	Mg	Fe	Pb	Sn	Cd	Ni	Si
ZL 2	4,00	2,9	0,037	0,006	0,002	< 0,001	< 0,001	< 0,001	< 0,02
ZL 3	4,00	< 0,01	0,035	0,002	0,002	< 0,001	< 0,001	< 0,001	< 0,02
ZL 5	3,97	0,8	0,036	0,003	0,002	< 0,001	< 0,001	< 0,001	< 0,02
ZL 6	5,75	1,3	< 0,001	0,006	0,002	< 0,001	< 0,001	—	< 0,02
ZL 8	8,37	1,1	0,021	0,003	0,003	< 0,001	< 0,001	< 0,001	< 0,02
ZL 12	11,00	0,8	0,023	0,01	0,002	< 0,001	< 0,001	—	< 0,02
ZL 27	26,83	2,3	0,012	0,04	0,002	< 0,001	< 0,001	—	< 0,02

Annex B
(informative)

Graphical representation of precision data

Figure B.1 indicates the logarithmic relationships between aluminium content and the repeatability limit (r) and reproducibility limits (R_w and R).



$$\lg r = 0{,}633\ 6 \times \lg w_{Al} - 1{,}744\ 4$$

$$\lg R_w = 0{,}757\ 4 \times \lg w_{Al} - 1{,}829\ 9$$

$$\lg R = 0{,}774\ 6 \times \lg w_{Al} - 1{,}531\ 0$$

where w_{Al} is the average aluminium content, expressed as a percentage by mass, obtained from the three determinations in each laboratory.

Key

X aluminium content (mass fraction) in percent (%)

Y precision in percent (%)

Figure B.1 — Logarithmic relationship between aluminium content and the repeatability limit (r) and the reproducibility limits (R_w and R)

ICS 77.120.60

Price based on 7 pages