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Steel — Determination of aluminium content — Flame atomic absorption spectrometric method

Aciers — Dosage de l'aluminium — Méthode par spectrométrie d'absorption atomique dans la flamme

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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.

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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 9658 was prepared by Technical Committee ISO/TC 17, *Steel*.

Annex A forms an integral part of this International Standard. Annexes B and C are for information only.

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Steel — Determination of aluminium content — Flame atomic absorption spectrometric method

1 Scope

This International Standard specifies a flame atomic absorption spectrometric method for the determination of acid-soluble and/or total aluminium in non-alloyed steel.

The method is applicable to aluminium contents between 0,005 % (*m*/*m*) and 0,20 % (*m*/*m*).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 377:1989, *Selection and preparation of samples and test pieces of wrought steels — Part 1: Samples and test pieces for mechanical test.*

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

3 Definition

For the purposes of this International Standard, the following definition applies.

acid-soluble aluminium: Aluminium dissolved in the acid mixture as specified in 8.3.1.1.

4 Principle

Dissolution of a test portion in dilute hydrochloric and nitric acids.

Fusion of the acid-insoluble material with a mixture of orthoboric acid and potassium carbonate.

Spraying of the solution into a dinitrogen monoxide-acetylene flame.

Spectrometric measurement of the atomic absorption of the 309,3 nm spectral line emitted by an aluminium hollow cathode lamp.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

5.1 Pure iron, containing less than 0,000 1 % (*m*/*m*) of aluminium, or of low known aluminium content.

5.2 Hydrofluoric acid, ρ about 1,15 g/ml.

5.3 Hydrochloric acid, ρ about 1,19 g/ml, diluted 1 + 1.

5.4 Hydrochloric acid, ρ about 1,19 g/ml, diluted 2 + 100.

5.5 Sulfuric acid, ρ about 1,84 g/ml, diluted 1 + 1.

5.6 Acid mixture.

Mix 3 parts by volume of hydrochloric acid (ρ about 1,19 g/ml), 1 part by volume of nitric acid (ρ about 1,40 g/ml) and 2 parts by volume of water.

Prepare this mixture immediately before use.

5.7 Fusion mixture.

Mix 1 part by mass of orthoboric acid (H_3BO_3) and 1 part by mass of anhydrous potassium carbonate (K_2CO_3) .

5.8 Fusion mixture solution.

Dissolve 20,0 g of the fusion mixture (5.7) in water and dilute to 100 ml.

5,0 ml of this solution contain 1,0 g of the fusion mixture (5.7).

5.9 Aluminium, standard solutions.

5.9.1 Stock solution, corresponding to 2,0 g of Al per litre.

Weigh, to the nearest 0,001 g, 2,000 g of high purity aluminium [≥ 99,9 % (m/m) pure], and dissolve in 40 ml of hydrochloric acid (ρ about 1,19 g/ml) and 10 ml of nitric acid (ρ about 1,40 g/ml). Boil to eliminate oxides of nitrogen. Cool and transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this solution contains 2,0 mg of Al.

5.9.2 Standard solution A, corresponding to 0,20 g of Al per litre.

Transfer 20,0 ml of the stock solution (5.9.1) into a 200 ml one-mark volumetric flask. Dilute to the mark with water and mix. Prepare this standard solution immediately before use.

1 ml of this solution contains 0,20 mg of Al.

5.9.3 Standard solution B, corresponding to 0,020 g of Al per litre.

Transfer 20,0 ml of the standard solution A (5.9.2) into a 200 ml one-mark volumetric flask. Dilute to the mark with water and mix. Prepare this standard solution immediately before use.

1 ml of this standard solution contains 0,020 mg of Al.

6 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 385-1, ISO 648 or ISO 1042 as appropriate.

All glassware shall be cleaned with hot hydrochloric acid (5.3) and then water.

Ordinary laboratory apparatus, and

6.1 Filter media, 0,45 µm cellulose nitrate filter.

6.2 Filter funnel, two-piece acid-resistant filter funnel with a support screen between the funnel body and stem, designed for the vacuum filtration of liquids. The stem of the funnel is fitted with a ground glass cap stopper or a rubber stopper for insertion into an opening of the vacuum vessel.

6.3 Vacuum vessel, flask of capacity 500 ml, or large enough to contain a 100 ml one-mark volumetric flask, with an opening to allow for insertion of the rubber stopper of the filter funnel stem.

6.4 Platinum crucible, of capacity 30 ml.

6.5 Atomic absorption spectrometer.

An aluminium hollow cathode lamp; supplies of dinitrogen monoxide and acetylene sufficiently pure to give a steady clear red-feather flame, free from water and oil, and free from aluminium.

The atomic absorption spectrometer used will be satisfactory if after optimization according to 8.3.4 the limit of detection and characteristic concentration are in reasonable agreement with the values given by the manufacturer and if it meets the precision criteria given in 6.5.1 to 6.5.3.

It is also desirable that the instrument should conform to the additional performance requirement given in 6.5.4 .

6.5.1 Minimum precision (see clause A.1).

Calculate the standard deviation of 10 measurements of the absorbance of the most concentrated calibration solution. The standard deviation shall not exceed 1,5 % of the mean absorbance.

Calculate the standard deviation of 10 measurements of the absorbance of the least concentrated calibration solution (excluding the zero member). The standard deviation shall not exceed 0,5 % of the mean absorbance of the most concentrated calibration solution.

6.5.2 Limit of detection (see clause A.2).

This is defined as twice the standard deviation of 10 measurements of the absorbance of a solution containing the appropriate element at a concentration level selected to give an absorbance just above that of the zero member.

The limit of detection of aluminium in a matrix similar to the final test portion solution shall be better than 0,1 µg of Al per millilitre.

6.5.3 Graph linearity (see clause A.3).

The slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) shall not be less than 0,7 times the value of the slope for the bottom 20 % of the concentration range determined in the same way.

For instruments with automatic calibration using two or more standards, it shall be established prior to the analysis, by obtaining absorbance readings, that the above requirements for graph linearity are fulfilled.

6.5.4 Characteristic concentration
(see clause A.4).

The characteristic concentration for aluminium in a matrix similar to the final test portion solution shall be better than 1,0 µg of Al per millilitre.

6.6 Ancillary equipment.

A strip chart recorder and/or digital readout device is recommended to evaluate the criteria of 6.5 and for all subsequent measurements.

Scale expansion can be used until the noise observed is greater than the readout error and is always recommended for absorbances below 0,1. If scale expansion has to be used and the instrument does not have the means to read the value of the scale expansion factor, the value can be calculated by measuring a suitable solution with and without scale expansion and simply dividing the signal obtained.

7 Sampling

Carry out sampling in accordance with ISO 377 or appropriate national standards for steel.

8 Procedure

8.1 Test portion

Weigh, to the nearest 0,001 g, approximately 2,0 g of the test sample.

8.2 Blank test

Parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all the reagents without the addition of pure iron.

Background correction may be required.

8.3 Determination

8.3.1 Preparation of the test solution

8.3.1.1 Decomposition of the test portion

Place the test portion (8.1) in a 250 ml beaker. Add, in small portions, 40 ml of acid mixture (5.6) and cover the beaker with a watch-glass. Heat until solvent action ceases. Boil to eliminate oxides of nitrogen and cool.

8.3.1.2 Filtration of the test solution

Place a filter (6.1) on the suppport screen of a filter funnel (6.2). Moisten the filter with water and join the body and stem of the funnel. Insert the stopper of the filter funnel stem into a vacuum vessel (6.3). Apply vacuum gently to the vacuum vessel and filter the solution.

Wash the funnel sides and residue with warm hydrochloric acid (5.4) and warm water alternately until they are visually free from iron.

Stop the vacuum gently.

When the filtrate is collected in a 500 ml vacuum vessel:

- if the volume of the filtrate and the washings is less than about 70 ml, transfer the solution quantitatively to a 100 ml one-mark volumetric flask, and proceed to 8.3.1.3 or 8.3.1.4;
- if the volume of the filtrate and the washing is greater than about 70 ml, transfer the solution quantitatively to a 200 ml beaker, reduce the volume of the solution to about 70 ml by evaporation, cool and then transfer it quantitatively to a 100 ml one-mark volumetric flask, and proceed to 8.3.1.3 or 8.3.1.4.

When the filtrate is collected in a 100 ml one-mark volumetric flask placed in the vacuum vessel:

- if the volume of the filtrate and the washings is less than about 70 ml, proceed to 8.3.1.3 or 8.3.1.4;
- if the volume of the filtrate and the washings is greater than about 70 ml, transfer the solution to a 200 ml beaker, reduce the volume of the solution to about 70 ml by evaporation, cool and transfer it quantitatively again to the original 100 ml one-mark volumetric flask, and proceed to 8.3.1.3 or 8.3.1.4.

8.3.1.3 Preparation of the test solution for the determination of acid-soluble aluminium

If acid-soluble aluminium only is required, add 5,0 ml of fusion mixture solution (5.8) to the 100 ml one-mark volumetric flask, cool, and allow any carbon dioxide produced to escape, then dilute to the mark with water and mix. Discard the insoluble residue and cellulose nitrate filter. Retain this solution for the determination of acid-soluble aluminium.

8.3.1.4 Preparation of the test solution for the determination of total aluminium

Transfer the filter containing the insoluble residue into a platinum crucible (6.4). Char the residue at low temperature and ignite slowly to 1 000 °C. Cool the crucible. Add several drops of water, several drops of sulfuric acid (5.5) and 5 ml of hydrofluoric acid (5.2). Evaporate to dryness and again ignite slowly to 1 000 °C. Cool the crucible and add 1,0 g of the fusion mixture (5.7). Fuse the contents of the crucible in a muffle furnace at 1 000 °C for 15 min. Cool the crucible and add 1 ml or 2 ml of hydrochloric acid (5.3) and 8 ml of water to the solidified melt.

Heat gently to dissolve the fusion products. Allow the crucible to cool and transfer the solution quantitatively to the filtrate in the 100 ml one-mark volumetric flask. Dilute to the mark with water and mix. Retain this solution for the determination of total aluminium.

8.3.2 Preparation of the calibration solutions

8.3.2.1 Aluminium contents $< 0,010$ % (*m*/*m*)

Introduce into a series of five 250 ml beakers (2,00 ± 0,01) g of the pure iron (5.1). Add 40 ml of acid mixture (5.6), in small portions, to each beaker and cover them with watch-glasses. Heat until the iron is in solution, then boil to eliminate oxides of nitrogen. Cool and transfer the solutions into five 100 ml one-mark volumetric flasks. Using a burette add the volumes of aluminium standard solution B (5.9.3) as indicated in table 1.

Add 5,0 ml of fusion mixture solution (5.8) to each flask. Cool and allow any carbon dioxide produced to escape, then dilute to the mark with water and mix.

Table 1

Volume of aluminium standard solution B (5.9.3) ml	Corresponding concentration of aluminium in final test solution µg/ml	Corresponding content of aluminium in test sample % (*m*/*m*)
0 1)	0	0,000 0
2,5	0,5	0,002 5
5,0	1,0	0,005 0
7,5	1,5	0,007 5
10,0	2,0	0,010 0

1) Zero member.

8.3.2.2 Aluminium content between 0,010 % (*m*/*m*) and 0,20 % (*m*/*m*)

Proceed as specified in 8.3.2.1, using table 2 instead of table 1.

Table 2

Volume of aluminium standard solution A (5.9.2) ml	Corresponding concentration of aluminium in final test solution µg/ml	Corresponding content of aluminium in test sample % (*m*/*m*)
0 1)	0	0,000
5,0	10,0	0,050
10,0	20,0	0,100
15,0	30,0	0,150
20,0	40,0	0,200

1) Zero member.

8.3.3 Adjustment of atomic absorption spectrometer

See table 3.

8.3.4 Optimizing the atomic absorption spectrometer settings

Follow the manufacturer's instructions for preparing the instrument for use.

When the current to the lamp, the wavelength and the flow of gas have been adjusted and the burner lit, spray water until the indication has stabilized.

Table 3

Element	Characteristic
Type of lamp	Aluminium hollow cathode.
Wavelength	309,3 nm
Flame	Dinitrogen monoxide-acetylene non-luminous oxidizing flame. The height of the red-feather flame shall be 10 mm to 20 mm adjusted for maximum aluminium response.
Lamp current	Follow manufacturer's recommendations.
Bandwidth	Follow manufacturer's recommendations. If no recommendation is stated, a bandwidth between 0,2 nm and 0,7 nm is suggested.
Background correction	If the zero member gives an absorbance comparable with the precision of the lowest calibration solution, background correction may be required.

WARNING — The manufacturer's recommendations should be closely followed and particular attention is drawn to the following safety points:

a) **the explosive nature of acetylene, and regulations concerning its use;**

b) **the need to shield the eyes of the operator from ultraviolet radiation by means of tinted glass;**

c) **the need to keep the burner head clear of deposits because a badly clogged burner may cause a flashback;**

d) the need to ensure that the liquid trap is filled with water;

e) always spray distilled water between the test solutions, blank solution and/or calibration solutions.

Set the absorbance value to zero using water.

Choose a damping setting or integration time to give a signal steady enough to fulfil the precision criteria of 6.5.1 to 6.5.3.

Adjust the flame to be non-luminous and oxidizing with an approximate 10 mm to 20 mm of red feather. Spraying alternately the calibration solution of highest concentration and the zero member (see table 1), adjust the gas flow and burner position (horizontally, vertically and rotationally) until the difference in absorbance between the calibration solution is at a maximum. Check that the spectrometer is set accurately on the required wavelength.

Evaluate the criteria of 6.5.1 to 6.5.3 and the additional performance requirement of 6.5.4, to ensure that the instrument is suitable for the determination.

8.3.5 Spectrometric measurements

Set the scale expansion so that the calibration solution of highest concentration gives nearly full scale deflection. Spray the calibration solutions in ascending order repetitively until each gives the specified precision, thus showing that the instrument has achieved stability. Select two calibration solutions, one having an absorbance just lower than the test portion solution and one just higher. Spray these first in ascending order, then in descending order, with the test solution as the middle solution, in each case measuring the absorption in relation to water.

Spray the complete range of calibration solutions, including the zero member. Then spray again in ascending and descending order. The means of the last ascending and descending series of calibration solutions are used for the calibration graph.

It is recognized that these procedures cannot be followed with automatic instruments which accept two calibration solutions only. In this case it is suggested that the two "sandwiching" solutions should not be used for the primary calibration but should be analysed alternately with the test solution.

Spray calibration solutions at frequent intervals during the measurement of a batch of determinations. Clean the burner if the results show loss of precision caused by clogging.

Obtain the mean absorbance of the test solution and the mean absorbance of the blank solution.

8.4 Plotting the calibration graph

It is necessary to prepare a new calibration graph for each series of determinations, and for the range of aluminium contents expected.

If pure metals and reagents have been used, the blank test and zero member should give very small absorbance readings with a negligibly small difference. In this case, prepare a calibration graph by plotting the mean absorbance values of the calibration solutions against micrograms of aluminium per millilitre. Refer the mean test solution absorbance and the absorbances of the two adjacent calibration solutions to the graph.

If, however, the zero member has a significant absorbance, a more complicated procedure is required. In this case, the concentration of aluminium ρ_z in the zero member can be calculated using the formula

$$\rho_z = \rho_{c1} \times \frac{A_z}{A_{c1} - A_z}$$

where

ρ_{c1} is the concentration of aluminium, expressed in micrograms per millilitre, added to the first calibration solution;

A_z is the absorbance of the zero member;

A_{c1} is the absorbance of the first calibration solution.

The derived value ρ_z is then added to each of the nominal calibration concentrations in order to obtain a mean calibration graph passing through the origin. Refer the absorbances of the blank solution, the test solution and the two adjacent calibration solutions to this graph. Subtract the concentration of the blank solution from the other concentrations.

Prepare a calibration graph by plotting the absorbance values of the calibration solutions against aluminium content, expressed in micrograms per millilitre. Refer the absorbances of the two adjacent calibration solutions to the graph. If these two calibration readings do not deviate from the graph by more than the permitted precision criteria then the test solution readings are also acceptable.

9 Expression of results

9.1 Method of calculation

Convert the absorbance of the test solution and the blank solution to micrograms of aluminium per millilitre by reference to the calibration graph (8.4).

The aluminium content w_{Al} , expressed as a percentage by mass, is given by the equation

$$w_{Al} = \frac{(\rho_{Al,1} - \rho_{Al,0}) \times 100}{10^6} \times \frac{100}{m}$$

$$= \frac{\rho_{Al,1} - \rho_{Al,0}}{100m}$$

where

$\rho_{Al,0}$ is the concentration, expressed in micrograms per millilitre, of aluminium in the blank test (8.2);

$\rho_{Al,1}$ is the concentration, expressed in micrograms per millilitre, of aluminium in the test solution (8.3.1);

m is the mass, in grams, of the test portion (8.1).

9.2 Precision

A planned trial of this method was carried out by 28 laboratories for acid-soluble and total aluminium. All laboratories made three determinations for acid soluble and total aluminium of each of the test samples (see notes 1 and 2).

The test samples used are listed in annex B.

The results obtained were treated statistically in accordance with ISO 5725.

The data obtained showed a logarithmic relationship between aluminium content and repeatability (r) and reproducibility (R and R_w) of the test results (see note 3), as summarized in table 4. The graphical representation of the data is shown in figure C.1 and figure C.2 of annex C.

Table 4

Aluminium content % (*m*/*m*)	Acid-soluble aluminium			Total aluminium		
	r	R	R_w	r	R	R_w
0,005	0,000 73	0,002 24	0,000 71	0,001 11	0,002 12	0,000 77
0,010	0,001 03	0,003 14	0,001 14	0,001 42	0,002 82	0,001 17
0,020	0,001 47	0,004 41	0,001 84	0,001 82	0,003 74	0,001 76
0,050	0,002 34	0,006 92	0,003 46	0,002 53	0,005 45	0,003 05
0,10	0,003 32	0,009 72	0,005 58	0,003 25	0,007 23	0,004 61
0,20	0,004 72	0,013 6	0,008 94	0,004 16	0,009 61	0,006 97

NOTES

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

2 The third determination was carried out at a different time (on a different day) by the same operator as in note 1 above using the same apparatus with a new calibration.

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

10 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis;

b) the method used by reference to this International Standard;

c) the results, and the form in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this International Standard, or any optional operation which may have influenced the results.