INTERNATIONAL
STANDARD

ISO
10213

First edition
1991-12-15

Aluminium ores — Determination of total iron content — Titanium trichloride reduction method

Minerais alumineux — Dosage du fer — Méthode de réduction au trichlorure de titane

Reference number
ISO 10213:1991(E)

Foreword

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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.

International Standard ISO 10213 was prepared by Technical Committee ISO/TC 129, *Aluminium ores*, Sub-Committee SC 2, *Methods of analysis*.

Annex A forms an integral part of this International Standard. Annex B is for information only.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland
Printed in Switzerland

Aluminium ores — Determination of total iron content — Titanium trichloride reduction method

1 Scope

This International Standard specifies a titrimetric method, free from mercury pollution, for the determination of the total iron content in aluminium ores, using potassium dichromate as titrant after reduction of the trivalent iron by tin(II) chloride and titanium(III) chloride. The excess reductant is then oxidized by perchloric acid.

The method is applicable to ores containing between 2 % (*m*/*m*) and 50 % (*m*/*m*) of iron oxide (Fe_2O_3).

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

ISO 6140:1991, *Aluminium ores — Preparation of samples.*

ISO 8558:1985, *Aluminium ores — Preparation of pre-dried test samples.*

ISO 8685:—[1], *Aluminium ores — Sampling procedures.*

3 Principle

Decomposition of the test portion by sintering with sodium peroxide followed by a brief fusion. Dissolution of the melt in water and hydrochloric acid. Reduction of the major portion of the iron(III) by tin(II) chloride and reduction of the remainder of the iron by titanium(III) chloride. Oxidation of the excess reductant with dilute perchloric acid. Titration of the reduced iron with potassium dichromate solution using sodium diphenylaminesulfonate indicator.

4 Reagents

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

4.1 Sodium peroxide, dry powder.

WARNING — Sodium peroxide should be protected against humidity when stored and should not be used once it has begun to agglomerate.

4.2 Hydrochloric acid, ρ_{20} between 1,16 g/ml and 1,19 g/ml.

4.3 Hydrochloric acid, ρ_{20} between 1,16 g/ml and 1,19 g/ml, diluted 1 + 10.

4.4 Perchloric acid, 72 % (*m*/*m*) (ρ_{20} = 1,67 g/ml), diluted 1 + 1.

4.5 Sulfuric acid-phosphoric acid mixture.

Pour 150 ml of phoshoric acid (ρ_{20} = 1,70 g/ml) into about 400 ml of water while stirring, add 150 ml of sulfuric acid (ρ_{20} = 1,84 g/ml), cool in a water bath and dilute with water to 1 litre.

4.6 Potassium permanganate, 25 g/l solution.

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[1] To be published.

4.7 Tin(II) chloride, 100 g/l solution.

Dissolve 100 g of crystalline tin(II) chloride dihydrate ($SnCl_2.2H_2O$) in 200 ml of hydrochloric acid (4.2) by heating the solution on a water bath. Cool the solution and dilute with water to 1 litre.

This solution should be stored in a brown glass bottle with a small quantity of granular tin metal.

4.8 Titanium(III) chloride, 15 g/l solution.

Dilute 1 volume of titanium(III) chloride solution (about 15 % $TiCl_3$) with 9 volumes of hydrochloric acid diluted 1 + 1. Alternatively, dissolve 1 g of titanium sponge in about 30 ml of hydrochloric acid (4.2) in a covered beaker, by heating on a water bath. Cool the solution and dilute with water to 250 ml.

Prepare fresh solutions as needed.

4.9 Iron, 0,1 mol/l standard solution.

Transfer 5,585 g of pure iron to a 500 ml Erlenmeyer flask and place a small filter funnel in the neck. Add 75 ml of hydrochloric acid diluted 1 + 1 in small increments and heat until dissolved. Cool and oxidize with 5 ml of a 3 % (*m*/*m*) hydrogen peroxide solution added in small portions. Heat to boiling and boil to decompose the excess hydrogen peroxide and to remove chlorine. Transfer to a 1 000 ml volumetric flask (5.3) and dilute to the mark with water.

1,00 ml of this standard solution is equivalent to 1,00 ml of the standard volumetric potassium dichromate solution (4.10).

4.10 Potassium dichromate, standard volumetric solution, $c(K_2Cr_2O_7) = 1/60$ mol/l.

Pulverize about 6 g of potassium dichromate in an agate mortar, dry at 140 °C to 150 °C for 2 h, and cool to room temperature in a desiccator. Dissolve 4,903 5 g of this dried powder in water, cool to 20 °C and transfer to a 1 000 ml volumetric flask (5.3). Dilute to the mark with water and mix.

4.11 Sodium diphenylaminesulfonate, indicator solution.

Dissolve 0,2 g of the reagent ($C_6H_5NHC_6H_4SO_3Na$) in water and dilute to 100 ml.

Store the solution in a brown glass bottle.

5 Apparatus

Use ordinary laboratory apparatus and the following.

5.1 Crucible, zirconium metal or vitreous carbon, of capacity 25 ml to 30 ml.

5.2 Burette, class A.

5.3 One-mark volumetric flasks, of capacity 1 000 ml.

5.4 Muffle furnace, suitable for operation in the range 500 °C to 800 °C.

6 Sampling and samples

6.1 Sampling

Laboratory samples shall be taken and crushed to pass a 150 µm test sieve in accordance with the procedures specified in ISO 6140 and ISO 8685.

6.2 Preparation of the test sample

Prepare the test sample by drying it in an oven in accordance with the procedure described in ISO 8558. (This is the pre-dried test sample.)

7 Procedure

7.1 Number of determinations

Carry out the analysis at least in duplicate, independently, on one test sample (6.2).

NOTE 1 The expression "independently" means that the second and any subsequent result is not affected by the previous result(s). For this particular analytical method, this condition implies that the repetition of the procedure shall be carried out either by the same operator at a different time, or by a different operator, with appropriate recalibration in both cases.

7.2 Test portion

Taking several increments, weigh, to the nearest 0,2 mg, approximately 0,4 g of the test sample (6.2).

NOTE 2 When pre-dried test samples are used, the test portion should be taken on the day of pre-drying and weighed immediately to avoid reabsorption of moisture.

7.3 Blank test

Carry out a blank test using the same quantities of each reagent and the same procedure as in the actual determination, but omit the test portion.

When the analysis is carried out on several samples at the same time, the blank test value may be represented by one test, provided that the procedure is the same and the reagents used are from the same bottles.

7.4 Check test

In each run, one analysis of a certified reference material of the same type of ore shall be carried out in parallel with the analysis of the ore sample(s) and under the same conditions.

When the analysis is carried out on several samples of the same type of ore at the same time, the analytical value of one certified reference material may be used.

NOTES

3 The certified reference material should be of the same type as the sample to be analysed. Such certified reference materials cannot, however, be considered as being of the same type if the properties of the sample to be analysed differ from those of the certified reference material to such an extent that the analytical procedure must be changed substantially.

4 The certified reference material is used only to validate the performance of the analytical procedure and not to standardize the potassium dichromate solution.

7.5 Determination

7.5.1 Decomposition of the test portion

Transfer the test portion (7.2) into a crucible (5.1), add 5 g ± 0,1 g of the sodium peroxide (4.1) and mix using a nickel spatula. Place the crucible and contents in the muffle furnace (5.4), maintained at 480 °C to 500 °C for 45 min. Remove the crucible and contents from the furnace and heat over a burner to melt the sinter (about 30 s). Continue heating the melt, while swirling, for a total time of 2 min.

Allow the crucible to cool to room temperature (a metal block can be used to expedite this process), and place the crucible on its side in a 400 ml beaker. Carefully add 50 ml of water and cover the beaker immediately with a watch glass.

When the reaction ceases, add 30 ml of the hydrochloric acid (4.2) and heat until effervescence from the decomposition of the peroxide ceases. Remove the crucible and rinse well with water, adding the rinsings to the solution. Maintain the volume of solution in the beaker below 100 ml.

7.5.2 Oxidation of excess titanium(III) chloride solution with perchloric acid

To the solution obtained in 7.5.1, add 3 to 5 drops of the potassium permanganate solution (4.6) and heat the solution to just below the boiling point. Maintain at this temperature for 5 min to oxidize any arsenic or organic matter. Wash the cover and inside wall of the beaker with a small amount of hot hydrochloric acid (4.3). Immediately add the tin(II) chloride solution (4.7) drop by drop while swirling, until only a light yellow colour remains.

NOTE 5 It is essential that some iron(III) remains unreduced. If all the iron is inadvertently reduced, a small amount should be reoxidized with a drop of the potassium permanganate solution (4.6).

Reduce the remaining iron(III) by adding the titanium(III) chloride solution (4.8) drop by drop, until the yellow colour has disappeared, then add an additional 3 to 5 drops. Wash the inside wall of the beaker with a small amount of water and heat until boiling starts. Remove from the source of heat and add, all at once, 5 ml of the perchloric acid (4.4). Mix well by swirling for about 5 s. Dilute immediately with cold water (below 10 °C) to 200 ml. Cool rapidly to below 15 °C and follow the procedure specified in 7.5.3.

7.5.3 Titration

To the cold solution obtained in 7.5.2, add 30 ml of the sulfuric acid-phosphoric acid mixture (4.5) and titrate with the potassium dichromate standard volumetric solution (4.10) contained in the burette (5.2) using 5 drops of the sodium diphenylaminesulfonate solution (4.11) as indicator.

The end point is reached when the green colour of the solution changes to a blue-green and a final drop of the titrant imparts a violet colour.

7.5.4 Blank test

Determine the blank test value (7.3) using the same amounts of all reagents and following all the steps of the procedure. Immediately before reduction (7.5.2) with the tin(II) chloride solution (4.7), add 1,0 ml of the iron standard solution (4.9) and titrate the solution as described in 7.5.3. Record the volume of this titration as V_0. The blank test value of this titration, V_2, is calculated as:

$$V_2 = V_0 - 1{,}00$$

NOTE 6 In the absence of iron, the sodium diphenylaminesulfonate indicator does not react with the dichromate solution. The addition of the iron(III) solution is therefore necessary to promote indicator response in the blank solution and thus allow a suitable correction for the blank in terms of its equivalent in millilitres of the potassium dichromate standard volumetric solution.

8 Expression of results

8.1 Calculation of total iron content

The total iron content, expressed as a percentage by mass of iron oxide (Fe_2O_3) is given by the formula

$$\frac{V_1 - V_2}{m} \times 0{,}007\,985 \times 100$$

where

V_1 is the volume, in millilitres, of the potassium dichromate solution (4.10) used for the titration of the analytical sample;

V_2 is the volume, in millilitres, of the potassium dichromate solution used for the titration in the blank test, corrected for the iron standard solution added in 7.5.4;

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

0,007 985 is a sub-multiple of the relative molecular mass of iron(III) oxide.

8.2 General treatment of results

8.2.1 Precision

A planned trial of this method was carried out by eight laboratories at five levels of iron, each laboratory making four determinations at each level.

The results obtained were treated statistically in accordance with ISO 5725 and the resultant data are presented in table 1.

The data obtained showed a logarithmic relationship between iron content, repeatability (r) and reproducibility (R) of the test results as summarized in table 1.

The graphical presentation of the precision data is given in annex B.

8.2.2 Acceptance of test results (see annex A)

The analytical value for the test sample shall be accepted when the analytical value obtained for the corresponding certified reference material agrees with the certified value within the limit of the value shown for R in table 1 and when the difference between the two values for the test sample does not exceed r, as calculated from the appropriate value of r given in table 1.

When the difference exceeds the value of r, one or more additional tests shall be carried out in accordance with annex A, simultaneously with a corresponding blank test and an analysis of a certified reference material.

When the analytical value obtained for the certified reference material is outside the limits of the value shown for R in table 1, an additional analysis shall be carried out simultaneously on one test sample and one certified reference material, with one blank test. The analytical value obtained for the certified reference material shall be examined for the acceptance of the value for the test sample, as above. If the value obtained for the certified reference material is again outside the limits, the procedure shall be repeated with a different reference material of the same type of ore until two acceptable values for the test sample are obtained.

8.2.3 Calculation of final result

The final result is the arithmetic mean of the acceptable analytical values for the test sample or as otherwise determined by the operations specified in annex A, calculated to the fourth decimal place and rounded off to the second decimal place as follows:

a) when the figure in the third decimal place is less than 5, it is discarded and the figure in the second decimal place is kept unchanged;

b) when the figure in the third decimal place is 5 and there is a figure other than 0 in the fourth decimal place, or when the figure in the third decimal place is greater than 5, the figure in the second decimal place is increased by one;

c) when the figure in the third decimal place is 5 and the figure 0 is in the fourth decimal place, the 5 is discarded and the figure in the second decimal place is kept unchanged if it is 0, 2, 4, 6 or 8 and increased by one if it is 1, 3, 5, 7 or 9.

Table 1 — Precision data for iron determination

Values in mass percentage

Sample	Ore type	Mean Fe_2O_3 content	Repeatability r	Reproducibility R
MT/12/15	—	1,778	0,119 6	0,571 8
MT/12/3	Gibbsite, boehmite, hematite	5,637	0,171 8	0,459 6
MT/12/4	Gibbsite, boehmite, hematite	12,893	0,337 3	0,666 8
MT/12/13	Boehmite, hematite, chamosite	26,64	0,361 7	0,725 6
MT/12/2	Gibbsite, hematite, goethite	43,44	0,363 1	0,650 9

9 Test report

The test report shall include the following information:

a) details necessary for the identification of the sample;

b) reference to this International Standard (including a reference to the method used);

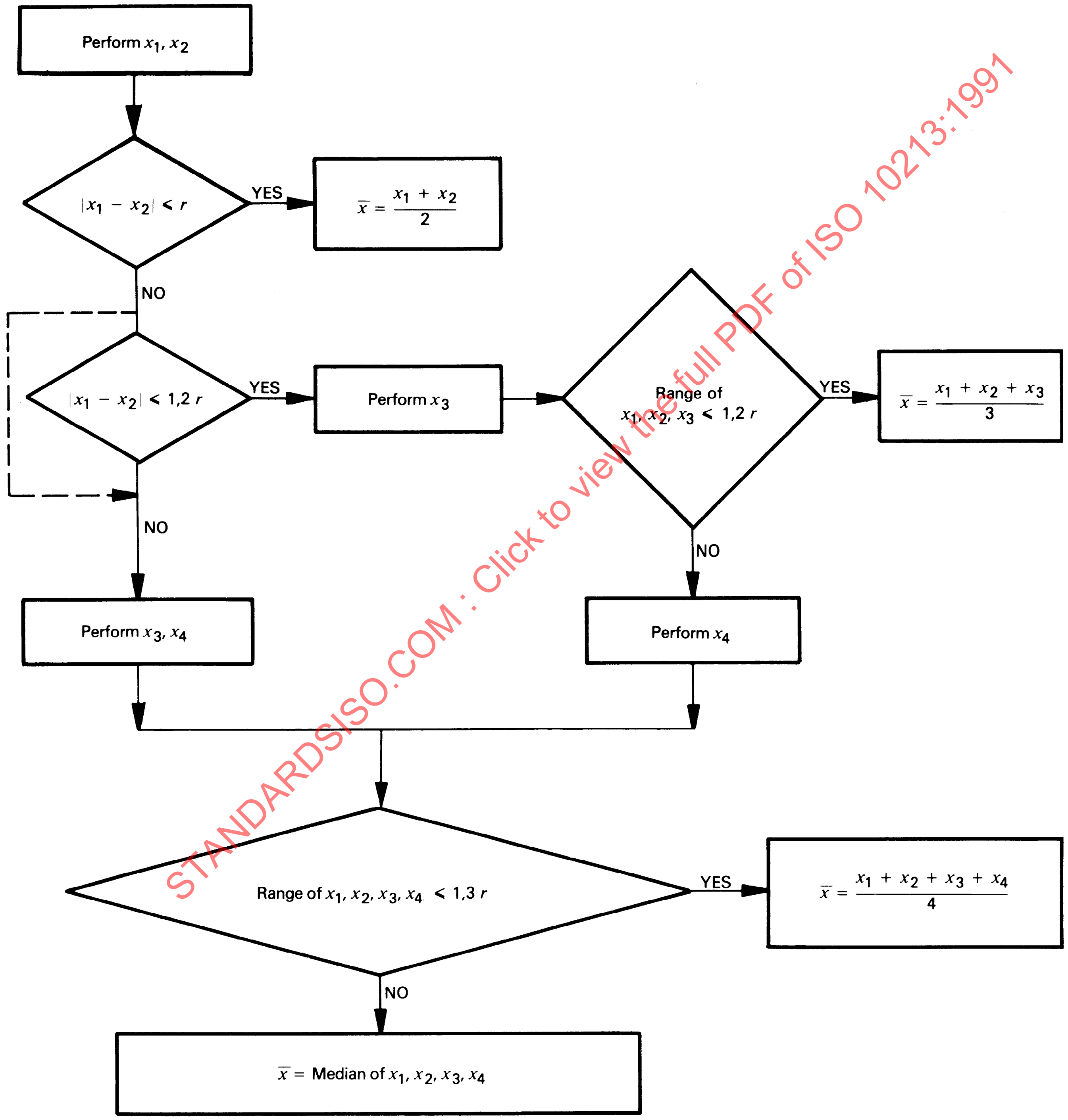
c) the result of the analysis;

d) reference number of the result;

e) any characteristics noticed during the determination and any operations not specified in this International Standard which may have had an influence on the results, either for the test sample or the certified reference material(s).

Annex A
(normative)

Flowsheet of the procedure for the acceptance of test results



r : as defined in 8.2.1.

Annex B

(informative)

Graphical representation of precision data

Coefficients (i)

$r = A + B(\ln x)$

where

r = repeatability

A = 0,064 4

B = 0,086 6

x = % (m/m) of Fe_2O_3

Regression coefficient = 0,948 3

(ii)

$R = A + B(\ln x)$

where

R = reproducibility

A = 0,490 3

B = 0,052 3

x = % (m/m) of Fe_2O_3

Regression coefficient = 0,647 1