International Standard 2771

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Iron ores — Determination of aluminium content — Oxine gravimetric and titrimetric methods

Minerais de fer — Dosage de l'aluminium — Méthodes titrimétrique et gravimétrique à l'oxine

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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.

International Standard ISO 2771 was developed by Technical Committee ISO/TC 102, *Iron ores.*

This second edition was submitted directly to the ISO Council, in accordance with clause 5.10.1 of part 1 of the Directives for the technical work of ISO. It cancels and replaces the first edition (i.e. ISO 2771-1973), which had been approved by the member bodies of the following countries :

Australia	Ireland	Spain
Belgium	Italy	Sweden
Canada	Japan	Thailand
Czechoslovakia	New Zealand	Turkey
Egypt, Arab Rep. of	Poland	United Kingdom
France	Portugal	USA
India	South Africa, Rep. of	USSR

The member body of the following country had expressed disapproval of the document on technical grounds :

Netherlands

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Iron ores — Determination of aluminium content — Oxine gravimetric and titrimetric methods

Second edition

1 Scope and field of application

This International Standard specifies gravimetric and titrimetric methods for the determination of the aluminium content in iron ores using 8-hydroxyquinoline.

These methods are applicable to natural iron ores and iron ore concentrates, and agglomerates including sinter products.

2 References

ISO 2596, *Iron ores — Determination of hygroscopic moisture in analytical samples.*

ISO 3081, *Iron ores — Increment sampling — Manual method.*

ISO 3083, *Iron ores — Preparation of samples.*

3 Principle

Treatment of the sample with hydrochloric, nitric, and perchloric acids and filtration of the solution. Extraction of the filtrate with methyl *iso*butyl ketone to remove the bulk of the iron and retention of the aqueous solution containing most of the aluminium, which forms the principal solution.

Treatment of the insoluble residue with hydrofluoric and sulphuric acids to expel silicon tetrafluoride, then fusion with sodium pyrosulphate. Dissolution of the melt in hydrochloric acid and combination with the main solution. Treatment of this solution with ammonia in slight excess to precipitate aluminium, titanium, and residual iron. After filtration, dissolution of the precipitate in hydrochloric acid and re-precipitation with ammonia. After filtration, dissolution of the precipitate in hydrochloric acid.

Removal of titanium, vanadium and residual iron by precipitation with cupferron from an acid medium, followed by filtration. Evaporation of the filtrate with nitric and perchloric acids to decompose the excess cupferron and dilution of the solution with water and hydrochloric acid. Addition of tartaric acid to the hydrochloric solution, adjustment of the pH to 5,5 and precipitation of the aluminium as the oxinate by the addition of an 8-hydroxyquinoline solution. Collection of the aluminium oxinate by filtration and completion of the final determination of the aluminium by one of the three following procedures :

1) Aluminium content up to 2,5 % (m/m) particularly when less than 0,25 % (m/m) : Titrimetrically by solution of the oxinate precipitate in hydrochloric acid and the addition of a slight excess of a standard solution of potassium bromate. Addition of potassium iodide and titration of the iodine liberated by the reaction with the excess of bromate with a standard volumetric solution of sodium thiosulphate.

NOTE — The titrimetric method is to be preferred for samples containing less than 0,25 % of aluminium.

For samples containing more than 2,5 % of aluminium, it is extremely difficult to remove the excess of reagent by washing, and one of the two gravimetric procedures should be used.

Elimination of the excess reagent may be aided by heating the precipitate to 135 °C before dissolving it in hydrochloric acid.

2) Aluminium content up to 5 % (m/m) : Gravimetrically by drying the oxinate precipitate and weighing.

NOTE — Weighing of the oxinate is quite satisfactory for aluminium contents ranging from 0,25 to 5 %. For greater amounts of aluminium the precipitate becomes so voluminous that the expulsion of the excess reagent by drying at 135 °C may become uncertain.

3) Aluminium content greater than 2,5 % (m/m) and always if aluminium is greater than 5 % (m/m) : Gravimetrically as Al_2O_3, after ignition of the oxinate precipitate.

NOTE — Al_2O_3 as the final weighing form offers several advantages : larger quantities of aluminium oxide can be handled and the ignition of the oxinate eliminates the possibility of high results due to retained reagent.

4 Reagents

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

4.1 Hydrochloric acid, ϱ_{20} 1,19 g/ml.

4.2 Hydrochloric acid, diluted 1 + 1.

4.3 Hydrochloric acid, diluted 1 + 2.

4.4 Hydrochloric acid, diluted 1 + 50.

4.5 Hydrochloric acid, diluted 5 + 3.

4.6 Nitric acid, ϱ_{20} 1,42 g/ml.

4.7 Sulphuric acid, ϱ_{20} 1,84 g/ml.

4.8 Sulphuric acid, diluted 1 + 1.

4.9 Perchloric acid, ϱ_{20} 1,54 g/ml, 60 % (*m/m*) solution, or ϱ_{20} 1,67 g/ml, 70 % (*m/m*) solution.

4.10 Hydrofluoric acid, ϱ_{20} 1,13 g/ml, 40 % (*m/m*) solution.

4.11 Tartaric acid, ($C_4H_6O_6$), 20 g/l solution.

4.12 Oxalic acid, crystals.

4.13 Ammonia solution, ϱ_{20} 0,9 g/ml.

4.14 Ammonia solution, diluted 1 + 1.

4.15 Ammonium chloride.

4.16 Ammonium chloride, 20 g/l solution.

4.17 Potassium iodide, crystals.

4.18 Sodium pyrosulphate.

4.19 Methyl *iso*butyl ketone.

4.20 8-hydroxyquinoline (HOC_9H_6N), 25 g/l acetic acid solution.

Dissolve 25 g of 8-hydroxyquinoline (oxine) in 60 ml of glacial acetic acid (ϱ_{20} 1,05 g/ml), add about 200 ml of water while stirring, filter off the undissolved residue, and dilute the filtrate with water to 1 l.

4.21 Cupferron, solution.

Dissolve 6 g of cupferron ($C_6H_9N_3O_2$) in cold water and dilute to 100 ml. Prepare freshly as required.

4.22 Cupferron, wash solution

Dissolve 5 g of cupferron in cold hydrochloric acid (1 + 9) and dilute to 1 l with the same acid.

4.23 Potassium bromate, standard solution, $c(KBrO_3)$ = 0,016 7 mol/l.

Dissolve 2,784 g of potassium bromate (dried at 180 °C) and 10 g of potassium bromide in water in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

4.24 Sodium thiosulphate, standard volumetric solution, $c(Na_2S_2O_3)$ = 0,10 mol/l.

Dissolve 24,819 0 g of sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in 300 ml of water, add 0,1 g of sodium carbonate (Na_2CO_3) and dilute to 1 l. Standardize this solution against the potassium bromate standard solution (4.23).

4.25 Starch solution

Triturate 0,1 g of soluble starch with water, add about 100 ml of hot water, boil the mixture for about 1 min, and allow to cool. Prepared freshly as required. Starch that forms a reddish-brown solution with iodine shall not be used.

4.26 Methyl red solution

Dissolve 0,2 g of methyl red powder in 100 ml of ethyl alcohol, 60 % (*V/V*), and filter any insoluble matter.

4.27 Indigo carmine solution

Dissolve 1 g of indigo carmine powder in 100 ml of water and filter off any insoluble matter.

5 Apparatus

Ordinary laboratory apparatus.

6 Sampling and samples

For analysis, a laboratory sample of minus 100 µm particle size which has been taken in acordance with ISO 3081[1)] and prepared in accordance with ISO 3083[1)] shall be used. In the case of ores with high contents of combined water and/or oxidizable compounds, the particle size shall be minus 160 µm.

7 Procedure

7.1 Number of analyses, determination of hygroscopic moisture, application of certified reference material and blank test

7.1.1 The analysis shall be carried out generally in duplicate, independently (see the note) on one ore sample.

NOTE — The expression "independently" implies the change of the person carrying out the analysis. If the same person must carry out the analysis, the procedure shall be carried out a different time.

1) A further International Standard now in preparation (ISO 3082) will specify mechanical methods of increment sampling and will also specify methods of sample preparation.

7.1.2 Simultaneously with the analysis, two test portions shall be taken to determine the hygroscopic moisture in accordance with ISO 2596.

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

NOTE — The certified reference material should be of the same type as the sample analysed. The certified reference material cannot 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.

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

When 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.

7.2 Test portion

Weigh, to the nearest 0,000 2 g, approximately 1 g of the test sample.

7.3 Determination

7.3.1 Decomposition of test portion

7.3.1.1 Place the test portion (7.2) in a 300 ml beaker, add 30 ml of hydrochloric acid (4.1), cover with a watch glass, and heat gently without boiling the solution, until decomposition of the test portion is complete.

NOTE — To achieve a rapid decomposition of the sample, place the beaker for over 1 h in a low temperature zone and heat for about 10 min to just below boiling.

7.3.1.2 Add 5 ml of the nitric acid (4.6) and 20 ml of perchloric acid (4.9), cover and heat the solution to dense white fumes of perchloric acid. Allow the acid to reflux on the walls of the beaker for about 10 min.

NOTE — In the case of higher contents of fluorine [about 0,1 % (m/m) F], the solution has to fume strongly.

7.3.1.3 Allow the solution to cool, add 10 ml of hydrochloric acid (4.1) and heat gently to dissolve the soluble salts. Add about 30 ml of warm water and boil for about 2 min. Collect the precipitate on a close-texture filter paper. Wash the precipitate first with the warm hydrochloric acid solution (4.4) and then with warm water, until the washings are no longer acid. Place the precipitate and filter paper in a platinum crucible, dry and ignite at a low temperature, then finally at about 950 °C. Cool and continue as directed in 7.3.3.

7.3.2 Extraction of the bulk of the iron

Evaporate the filtrate and washings in a 300 ml beaker to white fumes of perchloric acid and allow the solution to cool to room temperature.

Add 30 ml of the hydrochloric acid solution (4.5) and transfer the solution to a 200 ml separating funnel. Wash the beaker with the same hydrochloric acid solution and add the washings to the separating funnel.

Add an amount of methyl *iso*butyl ketone (4.19) equal to the volume of the sample solution, shake thoroughly for about 1 min, and allow to stand until the layers separate. Draw off the lower aqueous layer into the original 300 ml beaker. Wash the organic layer by adding 5 ml of the hydrochloric acid solution (4.5) and shake for about 1 min. Allow to stand until layers separate. Draw off the aqueous layer and add to the 300 ml beaker. Discard the solution remaining in the separating funnel.

Evaporate, by boiling, most of the dissolved organic solvent. Add 5 ml of nitric acid (4.6) and 10 ml of perchloric acid (4.9) and heat the solution to dense white fumes of perchloric acid. Allow to cool, add about 50 ml of warm water, heat gently to dissolve the salts and reserve as the main solution.

7.3.3 Treatment of residue

Moisten the residue from 7.3.1 with the sulphuric acid solution (4.8). Add about 5 ml of hydrofluoric acid (4.10), heat gently to expel silica, and fume off the sulphuric acid. Allow the crucible to cool, add 3 g of sodium pyrosulphate (4.18) and heat, gently at first, then finally at about 650 °C, to fuse the residue. Cool, then add 10 ml of the hydrochloric acid solution (4.3) to the crucible. Heat until the salts have dissolved and add the solution to the main solution.

7.3.4 First and second precipitation with ammonia solution

Dissolve 3 g of ammonium chloride (4.15) in the main solution, then neutralize most of the acid with the ammonia solution (4.14). Heat to near boiling, add 5 drops of the methyl red indicator solution (4.26) and continue adding the ammonia solution (4.14) until the colour of the solution turns yellow. This will precipitate iron, aluminium and titanium. Continue heating until initial boiling and remove from the source of heat.

Allow the precipitate to settle for approximately 1 min (see the note), then collect it on a rapid filter paper. Wash the precipitate several times with the ammonium chloride solution (4.16) which has been rendered sightly alkaline with a few drops of ammonia solution. Discard the filtrate.

NOTE — To prevent the oxidation of manganese and its subsequent co-precipitation, the time between the precipitation and filtration should be kept to a minimum.

Wash the precipitate back into the original beaker with hot water, add 10 ml of the hydrochloric acid (4.1), and heat the mixture to dissolve the precipitate.

Dilute to 100 ml with water. Dissolve 3 g of ammonium chloride in the main solution, then neutralize most of the acid with the ammonia solution (4.14). Heat to near boiling, add 5 drops of the methyl red indicator solution and continue adding ammonia solution (4.14) until the colour of the solution turns yellow. Continue heating until initial boiling and remove from the source of heat.

Allow the precipitate to settle for approximately 1 min (see the note), then collect it on the original filter paper. Wash the precipitate several times with the ammonium chloride solution (4.16) which has been rendered slightly alkaline with a few drops of ammonia solution. Discard the filtrate.

Wash the precipitate back into the original beaker with hot water, add 10 ml of hydrochloric acid (4.1), and heat the mixture to dissolve the precipitate.

Filter the warm hydrochloric acid solution through the original filter paper, wash the paper twice with the hot hydrochloric acid solution (4.3), several times with the warm hydrochloric acid solution (4.4), and finally thoroughly with warm water.

7.3.5 Aliquotting

Collect the filtrate and washings in a 300 ml beaker. If the final determination of the aluminium will be based on weighing the aluminium oxinate [aluminium content up to 5 % (m/m)] or titrating the oxinate [aluminium content up to 2,5 % (m/m)], proceed as instructed in table 1.

Table 1 — Aliquotting

Aluminium content % (m/m) Al	Aliquotting
less than 0,5	Use total solution.
0,5 up to 1,5	Transfer to a 250 ml flask and take a 100 ml aliquot.
1,5 up to 2,5	Transfer to a 250 ml flask and take a 50 ml aliquot.
2,5 up to 5	Transfer to a 250 ml flask and take a 25 ml aliquot.

If the final determination of the aluminium will be based on the ignition of the oxinate to Al_2O_3 [aluminium content greater than 2,5 % (m/m)], proceed without aliquotation.

7.3.6 Cupferron separation

Dilute or evaporate the solution after aliquotation to approximately 100 ml. Add 10 ml of hydrochloric acid (4.1) and cool the solution to 5 °C. Add an excess of the cupferron solution (4.21) cooled to 5 °C, and some macerated filter pulp. Allow to stand for 5 min or until the precipitate coagulates, whichever is shorter. Filter through a rapid filter paper and wash ten times with the cold cupferron wash solution (4.22).

Collect the filtrate and washings in a 600 ml beaker. Discard the precipitate. To the filtrate add 40 ml of nitric acid (4.6) and 20 ml of perchloric acid (4.9) and evaporate to fumes of perchloric acid. Fume until the organic matter has been completely destroyed and the solution is clear.

Dilute the cold solution with 200 ml of water, then add 5 ml of hydrochloric acid (4.1). Warm and filter through a fine-texture filter paper, collecting the filtrate in a 600 ml beaker. Wash the paper five times with the hot hydrochloric acid solution (4.4), then five times with hot water. Discard the paper and precipitate.

7.3.7 Precipitation with 8-hydroxyquinoline

Add 5 ml of the tartaric acid solution (4.11), a few drops of the methyl red indicator solution (4.26) and the ammonia solution (4.14), until the colour of the indicator just changes. Add sufficient of the 8-hydroxyquinoline solution (4.20) to precipitate the aluminium and provide a slight excess.

NOTE — Fifteen millilitres of the 8-hydroxyquinoline solution (4.20) are suficient for the precipitation of aluminium in amounts specified in table 1 (7.3.5).

Al_2O_3 as the final weighing form anticipates the precipitation of aluminium of greater than 25 mg. Fifty millilitres of the reagent are sufficient for the precipitation of 80 mg of aluminium.

Adjust the pH value of the solution to 5,5 with the ammonia solution (4.14), heat the solution at 70 °C for 20 min, then allow to stand for at least 10 min at room temperature. The weighing of the aluminium as the oxinate [up to 5 % (m/m) Al] is described in 7.3.8. The volumetric determination which is intended for aluminium contents up to 2,5 % (m/m), and particularly for aluminium contents less than 0,25 % (m/m), is described in 7.3.9. Ignition of the oxinate precipitate to Al_2O_3 is described in 7.3.10. The weighing of the aluminium in the form of Al_2O_3 is intended for aluminium contents greater than 2,5 % (m/m) and shall always be used for aluminium contents greater than 5 % (m/m).

7.3.8 Gravimetric determination as oxinate

For the gravimetric determination (weighing in the form of aluminium oxinate), filter by means of suction through a glass crucible of medium porosity (5 to 15 µm pore size) which has been dried previously to constant mass.

Wash the precipitate six to eight times with a total of 60 ml of warm water. Discard the filtrate and washings. Dry the crucible at 135 °C for 1,5 h or to constant mass. Cool in a desiccator, weigh as oxinate and calculate the percentage of aluminium from formula (1) in 8.1.1.

7.3.9 Titrimetric determination

For the titrimetric determination, collect the precipitate on a rapid filter paper and wash it with warm water, until the paper is no longer coloured. Wash further with several portions of warm water. Discard the filtrate and washings. Transfer the paper and precipitate to a 300 ml Erlenmeyer flask with a glass stopper. Add 60 ml of water and 40 ml of the hot hydrochloric acid solution (4.2) which has been previously boiled for a few

minutes. Heat the mixture, shaking occasionally to dissolve the aluminium oxinate.

Allow the solution to cool to room temperature and add 3 drops of the indigo carmine indicator solution (4.27). Add drop by drop from a burette the potassium bromate standard solution (4.23), until the colour of the solution changes from blue to yellow. Add an excess of 1 to 3 ml of the potassium bromate standard solution (4.23) and record the total volume added.

Stopper the flask and allow to stand for about 1 min. Add 2 g of potassium iodide crystals and shake the flask to liberate iodine. Wash down the sides of the flask and titrate with the sodium thiosulphate standard volumetric solution (4.24), using the starch solution (4.25) as indicator. The end-point is reached when the violet colour of the solution disappears with a final drop of thiosulphate solution.

Record the volume of the sodium thiosulphate solution used and calculate the percentage of aluminium from formula (2) in 8.1.2.

7.3.10 Gravimetric determination as oxide

If Al_2O_3 is chosen as the final weighing form [aluminium content greater than 2,5 % (m/m)], filter the precipitate obtained in 7.3.7 on a medium-fine paper and wash about 15 times with a maximum of 100 ml of warm water. Discard the filtrate and washings. Place the paper and precipitate in a tared platinum crucible and dry at a temperature below 200 °C.

Then heat at low temperature until the paper is charred. Cover with oxalic acid crystals and ignite to constant mass at 1 100 °C. Cool in a desiccator and weigh as Al_2O_3.

Calculate the percentage of aluminium from formula (3) in 8.1.3.

8 Expression of results

8.1 Calculation of aluminium content

8.1.1 Gravimetric determination as oxinate

The aluminium content, as a percentage by mass, is calculated from the formula

$$\frac{(m_1 - m_2) \times 0{,}058\,73}{m_3} \times \frac{V_1}{V_2} \times 100 \times K \qquad \ldots (1)$$

where

m_1 is the mass, in grams, of the crucible with aluminium oxinate;

m_2 is the tare mass, in grams, of the crucible;

m_3 is the mass, in grams, of the test portion;

V_1 is the volume, in millilitres, of sample solution in accordance with table 1 (7.3.5);

V_2 is the aliquot, in millilitres, of sample solution used for the analysis as indicated in table 1;

K is the conversion factor found from the following formula :

$$K = \frac{100}{100 - A}$$

where A is the hygroscopic moisture content, as a percentage by mass, determined in accordance with ISO 2596.

8.1.2 Titrimetric determination

The aluminium content, as a percentage by mass, is calculated from the formula

$$\frac{(6V_1c_1 - V_2c_2) \times 0{,}002\,249 \times 100 \times K}{m \times S} \qquad \ldots (2)$$

where

V_1 is the volume, in millilitres, of the potassium bromate solution (4.23) consumed;

c_1 is the concentration, in moles per litre, of the potassium bromate solution (4.23);

V_2 is the volume, in millilitres, of the sodium thiosulphate solution (4.24) consumed;

c_2 is the concentration, in moles per litre, of the sodium thiosulphate solution (4.24);

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

S is the volume fraction of the aliquot in table 1 (7.3.5) (a 100 ml aliquot represents 0,4 and a 50 ml aliquot 0,2 of the original sample solution);

K is the conversion factor found from the following formula :

$$K = \frac{100}{100 - A}$$

where A is the hygroscopic moisture content, as a percentage by mass, determined in accordance with ISO 2596.

8.1.3 Gravimetric determination with Al_2O_3 as the weighing form

The aluminium content, as a percentage by mass, is calculated from the formula

$$\frac{(m_1 - m_2) \times 0{,}529\,3 \times 100 \times K}{m_3} \qquad \ldots (3)$$