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Iron ores — Determination of calcium — Flame atomic absorption spectrometric method

Minerais de fer — Dosage du calcium — Méthode par spectrométrie d'absorption atomique dans la flamme

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This fourth edition cancels and replaces the third edition (ISO 10203:2015), of which it constitutes a minor revision with the following changes:

- in 5.11, minor editorial/grammatical amendments have been incorporated;
- in 6.1, “with a lid” has been inserted after “crucible”;
- in 6.3 b), “the ratio between” has been inserted before “the slope” and minor editorial/grammatical amendments have been incorporated;
- in 7.2, reference to ISO 2596 has been incorporated and 7.2 has been rearranged in a more appropriate layout/format;
- in 8.2, reference to ISO 2596 has been incorporated;
- “predried” has been deleted where it is inappropriate in 8.1, 8.2, and 8.3.2;
- some references to the reagents in 8.4.2, 8.4.3, and Table 2 have been corrected;
- in the last line of 9.2.3, the formula has been corrected from $\left|\mu_1 - A_c\right| \leq P$ to $\left|\mu_1 - \mu_2\right| \leq P$;
- in 9.2.4, Formula (7) and the relevant descriptions have been modified to harmonize this subclause across all International Standards for which ISO/TC 102/SC 2 is responsible.

Iron ores — Determination of calcium — Flame atomic absorption spectrometric method

WARNING — This document might involve hazardous materials, operations, and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this document to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This document specifies a flame atomic absorption spectrometric method for the determination of the mass fraction of calcium in iron ores.

This method is applicable to mass fractions of calcium between 0,010 % and 8,00 % in natural iron ores, iron ore concentrates, and agglomerates, including sinter products.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 648, *Laboratory glassware — Single-volume pipettes*

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

ISO 2596, *Iron ores — Determination of hygroscopic moisture in analytical samples — Gravimetric, Karl Fischer and mass-loss methods*

ISO 3082, *Iron ores — Sampling and sample preparation procedures*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 7764, *Iron ores — Preparation of predried test samples for chemical analysis*

ISO 80000-1:2009, *Quantities and units — Part 1: General*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

4 Principle

The test portion is decomposed by the treatment with hydrochloric acid and a small amount of nitric acid, and then evaporated to dehydrate silica, followed by dilution and filtration.

The residue is ignited and silica is removed by evaporation with hydrofluoric and sulfuric acids. The residue is fused with sodium carbonate and the cooled melt is dissolved in the filtrate.

The solution obtained is aspirated into the flame of an atomic absorption spectrometer using a dinitrogen oxide-acetylene burner.

The absorbance values obtained for calcium are compared with those obtained from calibration solutions.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and only water that complies with Grade 2 of ISO 3696.

5.1 **Sodium carbonate**, (Na_2CO_3), anhydrous.

5.2 **Hydrochloric acid**, (ρ 1,19 g/ml).

5.3 **Hydrochloric acid**, ρ 1,19 g/ml, diluted 1 + 9.

5.4 **Nitric acid**, ρ 1,4 g/ml.

5.5 **Hydrofluoric acid**, ρ 1,13 g/ml, 40 % (mass fraction) or ρ 1,185 g/ml, 48 % (mass fraction).

5.6 **Sulfuric acid**, ρ 1,84 g/ml, diluted 1 + 1.

5.7 **Pure iron**, minimum purity 99,9 % (mass fraction), of mass fraction of calcium less than 0,000 2 %.

5.8 Background solution.

Dissolve 5,0 g pure iron (5.7) in 50 ml of hydrochloric acid (5.2) and oxidize by adding nitric acid (5.4) drop by drop. Evaporate until a syrupy consistency is obtained. Add 20 ml of hydrochloric acid (5.2) and dilute to 200 ml with water. Dissolve 17 g of sodium carbonate (5.1) in water, add carefully to the iron solution, and heat to remove carbon dioxide. Transfer the cooled solution to a 1 000 ml one-mark volumetric flask, dilute to volume with water, and mix.

5.9 Lanthanum chloride solution.

Dissolve 50 g of lanthanum chloride ($LaCl_3 \cdot 7H_2O$) (of mass fraction of calcium less than 0,002 %) in 50 ml of hydrochloric acid (5.2) and 300 ml of hot water. Cool and dilute to 1 l.

5.10 **Calcium standard solution**, 25 µg Ca/ml.

Dissolve 1,248 7 g of dried calcium carbonate ($CaCO_3$) [minimum purity 99,9 % (mass fraction), dried at 105 °C for 1 h] in 100 ml of hydrochloric acid (5.2), diluted 1 + 3. When dissolved, cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water, and mix. Transfer 10 ml of this solution to a 200 ml one-mark volumetric flask, dilute to volume with water, and mix.

5.11 Calcium calibration solutions.

Using pipettes, transfer 2,0 ml, 5,0 ml, 10,0 ml, 15,0 ml, and 20,0 ml portions of calcium standard solution (5.10) to 200 ml volumetric flasks (Clause 6). Add 6 ml of hydrochloric acid (5.2), 60 ml of background solution (5.8), and 40 ml of lanthanum chloride solution (5.9) to each flask. Dilute the solution to volume with water and mix. Prepare a zero calcium calibration solution by transferring 60 ml of the background solution to a 200 ml volumetric flask. Then add 6 ml of hydrochloric acid (5.2) and 40 ml of lanthanum chloride solution (5.9). Dilute the solution to volume with water and mix.

6 Apparatus

Ordinary laboratory apparatus, including one-mark pipettes and one-mark volumetric flasks complying with the specifications of ISO 648 and ISO 1042, respectively, and the following.

All glassware, volumetric flask lids, and the platinum crucibles shall first be washed in hydrochloric acid (diluted 1 + 1) and then in water.

6.1 Platinum crucible with a lid, of minimum capacity 30 ml.

6.2 Muffle furnace, capable of maintaining a temperature of approximately 1 100 °C.

6.3 Atomic absorption spectrometer, equipped with a dinitrogen oxide/acetylene burner.

WARNING — Follow the manufacturer's instructions for igniting and extinguishing the dinitrogen oxide-acetylene flame to avoid possible explosion hazards. Wear tinted safety glasses whenever the flame is burning.

The atomic absorption spectrometer used in this method shall meet the following criteria.

a) Minimum sensitivity: The absorbance of the most concentrated calcium calibration solution (see 5.11) shall be at least 0,3.

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

c) Minimum stability: The standard deviation of the absorbance of the most concentrated calibration solution and that of the zero calibration solution, each being calculated from a sufficient number of repetitive measurements, shall be less than 1,5 % and 0,5 %, respectively, of the mean value of the absorbance of the most concentrated calibration solution.

The use of a strip chart recorder and/or digital readout device is recommended to evaluate criteria a), b), and c) and for all subsequent measurements.

NOTE Instrument parameters can vary with each instrument. The following parameters were successfully used in several laboratories and they can be used as guidelines. Solutions were aspirated into a dinitrogen oxide-acetylene flame of a premix burner.

In systems where the values shown below for gas flow rates do not apply, the ratio of the gas flow rates may still be a useful guideline.

— Hollow cathode lamp, mA	15
— Wavelength, nm	422,7
— Dinitrogen oxide flow rate, l/min	13,8
— Acetylene flow rate, l/min	6,6

7 Sampling and samples

7.1 Laboratory sample

For analysis, use a laboratory sample of −100 μm particle size which has been taken and prepared in accordance with ISO 3082. In the case of ores having significant contents of combined water or oxidizable compounds, use a particle size of −160 μm.

NOTE A guideline on significant contents of combined water and oxidizable compounds is incorporated in ISO 7764.

7.2 Preparation of predried test samples

7.2.1 General

Depending on the ore type, proceed in accordance with either 7.2.2 or 7.2.3.

7.2.2 Method specified in ISO 2596

This method is applicable to all types of ores.

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a way that it is representative of the whole contents of the container. Bring the test sample into equilibrium with the laboratory atmosphere in accordance with ISO 2596.

7.2.3 Method specified in ISO 7764

This method is not applicable to the following types of ores:

a) processed ores containing metallic iron (direct-reduces iron);

b) natural or processed ores in which the sulfur content is higher than 0,2 %;

c) natural or processed ores in which the content of combined water is higher than 2,5 % by mass.

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a way that it is representative of the whole contents of the container.

8 Procedure

8.1 Number of determinations

Carry out the analysis at least in duplicate in accordance with Annex A, independently, on one test sample (see 7.2).

NOTE 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 is carried out either by the same operator at a different time or by a different operator including, in either case, appropriate recalibration.

8.2 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, approximately the amount of the air-equilibrated test sample obtained in accordance with 7.2.2 specified in Table 1. Concurrently, determine the hydroscopic moisture content in accordance with ISO 2596 and calculate the dried mass of the test portion.

Where the test sample is obtained in accordance with 7.2.3, transfer the test portion specified in Table 1 to a weighing bottle, then dry at 105 °C ± 2 °C and determine the dried mass of the test portion to the nearest 0,000 2 g in accordance with ISO 7764.

Table 1 — Mass of test portion

Expected mass fraction of calcium in sample, w_{Ca} Mass fraction %	**Mass of test portion** g
$0{,}010 \le w_{\text{Ca}} \le 4{,}00$	0,5
$4{,}00 < w_{\text{Ca}} \le 8{,}00$	0,2

8.3 Blank test and check test

8.3.1 Blank test

8.3.1.1 Preparation of blank test solution

Using pure iron (5.7) with a 60 % mass of the test portion in place of the test portion, carry out the same procedure described in 8.4.1 to 8.4.3 as the test portion in parallel with it.

8.3.1.2 Measurement of blank value

Carry out in accordance with 8.4.5.

Where 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 that the reagents used are from the same reagent bottles.

8.3.2 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) under the same conditions. A test sample of the certified reference material shall be prepared as specified in 7.2. The certified reference material should be of the same type as the sample to be analysed and the properties of the two materials should be sufficiently similar to ensure that, in either case, no significant changes in the analytical procedure will become necessary.

Where 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.

8.4 Determination

8.4.1 Decomposition of the test portion

Transfer the test portion (see 8.2) to a 250 ml beaker. Moisten with a few millilitres of water, add 25 ml of hydrochloric acid (5.2), cover with a watch-glass, and heat gently. Increase the heat and digest just below boiling, until no further attack is apparent. Add 2 ml of nitric acid (5.4) and digest for several minutes. Remove the watch-glass and evaporate the solution until dry. Heat the salts on a hot-plate at 105 °C to 110 °C for 30 min. Add 5 ml of hydrochloric acid (5.2), cover the beaker with a watch-glass, and warm for several minutes. Add 50 ml of water, stirring to avoid the hydrolysis of titanium, and heat to boil. Wash the watch-glass and the walls of the beaker and filter the solution through a medium-texture paper containing some filter pulp into a 250 ml beaker. Carefully remove all adhering particles with a rubber-tipped glass rod or moistened filter paper and transfer to the filter, washing three times with dilute hydrochloric acid (5.3), then with hot water until the filter paper is free of iron. Transfer the paper and residue to a platinum crucible (6.1).

Evaporate the filtrate to about 100 ml and retain it.

The filter paper shall first be washed several times in warm hydrochloric acid (diluted 1 + 2), then in warm water after being attached to the funnel.

8.4.2 Treatment of the residue

Ignite the filter paper and residue in a platinum crucible (6.1) at a low temperature (500 °C to 800 °C). Cool, moisten with a few drops of water, and add three or four drops of sulfuric acid (5.6) and 10 ml of hydrofluoric acid (5.5).

Evaporate slowly to expel silica and then fume to remove the excess sulfuric acid. Ignite at about 700 °C. Add 1,0 g of sodium carbonate (5.1) to the residue (see note), cover the crucible, and fuse over a burner or in a muffle furnace (6.2) until a clear melt is obtained (at about 1 100 °C for 15 min).

NOTE If difficulties are experienced with the fusion, 2 g of sodium carbonate (5.1) can be used, in which case, it is advisable to double the amount of sodium carbonate and the volume of hydrochloric acid (5.2) in the background solution (5.8).

8.4.3 Preparation of the test solution

Dissolve the cooled melt in the retained filtrate (see 8.4.1), then remove and wash the crucible and cover (see next paragraph).

If the solution is cloudy at this stage, indicating the presence of substantial amounts of hydrolyzed titanium, it should be filtered prior to the transfer to the 200 ml volumetric flask.

Transfer the solution to a 200 ml one-mark volumetric flask.

When the mass fraction of calcium in sample is expected to be ≤0,10 %, add 40 ml of lanthanum chloride solution (5.9), dilute to volume with water, and mix. This solution is the final test solution for the low Ca sample.

When the mass fraction of calcium in sample is expected to be >0,10 %, dilute to volume with water and mix.

Transfer an appropriate aliquot of this solution (see Table 2) to a 200 ml one-mark volumetric flask and add 40 ml of lanthanum chloride solution (5.9). Add the amount of background solution (5.8) and hydrochloric acid (5.2) indicated in Table 2, dilute to volume with water, and mix (see last paragraph). This solution is the final test solution for the high Ca sample.

The dilutions shown in Table 2 will provide mass concentrations of calcium falling within the range of the calibration solutions. For instruments having high sensitivity, smaller portions of the test solution may be preferable. Avoid aliquot portions of less than 2 ml by making a preliminary dilution. Treat the blank test solution similarly.

Table 2 — Dilution guide for test solution

Expected mass fraction of calcium in sample, w_{Ca} %	**Aliquot** ml	**Equivalent mass of sample** g	**Background solution (5.8) to be added** ml	**Hydrochloric acid (5.2) to be added** ml
$0,10 < w_{Ca} \leq 1,00$	20	0,05	55	5
$1,00 < w_{Ca} \leq 4,00$	5	0,012 5	60	6
$4,00 < w_{Ca} \leq 8,00$	5	0,005	60	6

8.4.4 Adjustment of the atomic absorption spectrometer

Set the wavelength for calcium (422,7 nm) to obtain minimum absorbance. Fit the correct burner and, in accordance with the manufacturer's instructions, light the appropriate flame. After 10 min of preheating the burner, adjust the fuel flow and burner to obtain maximum absorbance while aspirating the calibration solution of highest mass fraction of calcium (see 5.11). Then evaluate the criteria in 6.3.

When the sensitivity of the instrument is too high to meet the criteria, it is permitted to set analytical conditions by which the absorbance is not the maximum. In this case, the criteria in 6.3 shall be met and the conditions shall not be changed during the measurements of all solutions prepared in each independent analysis.

Aspirate water and the calibration solution to establish that the absorbance reading is not drifting and then set the initial reading for water to zero absorbance.