INTERNATIONAL
STANDARD

ISO
13310

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Iron ores — Determination of zinc content — Flame atomic absorption spectrometric method

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

Reference number
ISO 13310:1997(E)

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 voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 13310 was prepared by Technical Committee ISO/TC 102, *Iron ores*, Subcommittee SC 2, *Chemical analysis*.

Together with ISO 13311, it cancels and replaces ISO 8753:1987, of which it constitutes a technical revision.

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

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Iron ores — Determination of zinc content — Flame atomic absorption spectrometric method

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

1 Scope

This International Standard specifies a flame atomic absorption spectrometric method for the determination of the zinc content of iron ores.

This method is applicable to zinc contents between 0,001 % (m/m) and 0,5 % (m/m) in natural iron ores, iron ore concentrates and agglomerates, including sinter products.

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

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

ISO 3081:1986, *Iron ores — Increment sampling — Manual method.*

ISO 3082:1987, *Iron ores — Increment sampling and sample preparation — Mechanical method.*

ISO 3083:1986, *Iron ores — Preparation of samples — Manual method.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 7764:1985, *Iron ores — Preparation of predried test samples for chemical analysis.*

3 Principle

Decomposition of the test portion and removal of silica by treatment with hydrochloric acid and hydrofluoric acid. Oxidation with nitric acid.

Evaporation to dryness, followed by dilution and filtration. Ignition of the residue. Fusion with sodium carbonate. Dissolution of the cooled melt with hydrochloric acid. Reservation of the solution.

Extraction of iron in the filtrate with 4-methyl-2-pentanone. Recovery of zinc extracted. Decomposition of 4-methyl-2-pentanone with nitric acid. Evaporation to dryness and dissolution of salts with the reserved solution and hydrochloric acid.

Aspiration of the solution into the flame of an atomic absorption spectrometer using an air-acetylene burner.

Comparison of absorbance values obtained for zinc with those obtained from the calibration solutions.

4 Reagents

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

4.1 Sodium carbonate (Na_2CO_3), anhydrous.

4.2 4-methyl-2-pentanone (MIBK), high purity.

4.3 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml.

4.4 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 10 + 6.

4.5 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 1 + 1.

4.6 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 2 + 98.

4.7 Nitric acid, ρ 1,4 g/ml.

4.8 Hydrofluoric acid, ρ 1,13 g/ml, 40 % (m/m), or ρ 1,19 g/ml, 48 % (m/m).

4.9 Zinc standard solutions

4.9.1 Zinc stock standard solution

Dissolve 1,000 g of zinc metal [of purity > 99,5 % (m/m)] in 40 ml of hydrochloric acid (4.5). Cool and dilute to 1 000 ml in a one-mark volumetric flask and mix.

1 ml of the stock solution contains 1 000 µg of zinc.

4.9.2 Standard solution

Transfer 10,0 ml of zinc stock standard solution (4.9.1) to a 1 000 ml one-mark volumetric flask. Dilute to volume and mix.

1 ml of this standard solution contains 10 µg of zinc.

5 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

5.1 Polytetrafluoroethylene (PTFE) beaker, of capacity 250 ml, with a PTFE cover.

5.2 Atomic absorption spectrometer, equipped with an air-acetylene burner.

The atomic absorption spectrometer shall meet the following criteria.

WARNING — Follow the manufacturer's instructions for igniting and extinguishing the air-acetylene flame to avoid possible explosion hazards. Wear tinted safety glasses whenever the burner is in operation.

a) *Minimum sensitivity* — the absorbance of the most concentrated calibration solution (see 7.4.4) shall be at least 0,25.

b) *Graph linearity* — 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 of the value of the slope for the bottom 20 % of the concentration range determined in the same way.

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.

NOTES

1 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.

2 Instrument parameters will vary with each instrument. The following parameters were successfully used in several laboratories and they can be used as guidelines.

— Hollow cathode lamp, mA	8
— Wavelength, nm	213,9
— Air flow rate, l/min	14
— Acetylene flow rate, l/min	3

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

6 Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of minus 100 µm particle size which has been taken in accordance with ISO 3081 or ISO 3082 and prepared in accordance with ISO 3082 or ISO 3083. In the case of ores having significant contents of combined water or oxidizable compounds, use a particle size of minus 160 µm.

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

6.2 Preparation of predried test samples

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a manner that it is representative of the whole contents of the container. Dry the test samples at 105 °C ± 2 °C as specified in ISO 7764. (This is the predried test sample.)

7 Procedure

7.1 Number of determinations

Carry out the analysis at least in duplicate in accordance with annex A, independently, on one predried test sample.

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.

7.2 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, approximately 2 g of the predried test sample obtained in accordance with 6.2.

NOTE — The test portion should be taken and weighed quickly in order to avoid reabsorption of moisture.

7.3 Blank test and check test

In each run, one blank test and 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 predried test sample of the certified reference material shall be prepared as specified in 6.2.

NOTE — 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 become necessary.

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 are from the same reagent bottles.

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.

7.4 Determination

7.4.1 Decomposition of the test portion

Transfer the test portion (7.2) to a 250 ml PTFE beaker (5.1). Moisten with a few millilitres of water, add 40 ml of hydrochloric acid (4.3) and 10 ml of hydrofluoric acid (4.8), and cover with a PTFE cover. Heat on a hotplate at 100 °C, then increase the heat to 200 °C. Evaporate to dryness. Add 5 ml of nitric acid (4.7) and evaporate to nearly 1 ml. Dissolve the salts with 10 ml of hydrochloric acid (4.3) and evaporate to dryness again.

Dissolve the salts with 5 ml of hydrochloric acid (4.3). Add 10 ml of water and filter through a close-texture paper into a 250 ml beaker. Remove all adhering particles from the beaker with a rubber-tipped rod, wash with hydrochloric acid (4.6) until the paper is free from iron stains, and wash the paper three times with hot water. Reserve the residue and combined filtrate and washings.

7.4.2 Treatment of residue

Place the paper and residue in a platinum crucible, dry and char the paper at a low temperature and ignite in a muffle furnace at 550 °C. Add 0,5 g of sodium carbonate (4.1) and fuse over a Bunsen burner (about 900 °C to 1 000 °C) until a clear melt is obtained. Dissolve the cooled melt with 5 ml of hydrochloric acid (4.5), heat to remove carbon dioxide and reserve the solution.

7.4.3 Treatment of combined filtrate and washings

Evaporate the filtrate and washings (7.4.1) just to dryness. Dissolve the salts with 20 ml of hydrochloric acid (4.4), and transfer to a 200 ml separating funnel. Rinse the beaker with 20 ml of hydrochloric acid (4.4) and combine these washings with the main solution. Add 50 ml of 4-methyl-2-pentanone (4.2) and shake thoroughly for 1 min. Allow the layers to separate, then run the lower aqueous solution into a 250 ml beaker. Wash the organic phase by extracting with 10 ml of hydrochloric acid (4.4), and transfer the washings to the beaker.

Heat the solution gently and expel almost all of the 4-methyl-2-pentanone in the solution. Then add 5 ml of nitric acid (4.7) and evaporate to dryness. Dissolve the salts with 15 ml of hydrochloric acid (4.5). Combine this solution with the reserved solution from 7.4.2.

Transfer the solution to a 50 ml one-mark volumetric flask, and dilute to volume with water and mix. Depending on the concentration (see table 1), use the solution for atomic absorption measurement either without dilution or as specified. If dilution is required, transfer the appropriate aliquot to a 250 ml beaker. Add the amount of sodium carbonate (4.1) and hydrochloric acid (4.5) indicated in table 1. Heat the solution to remove carbon dioxide. Cool and dilute to 100 ml in a one-mark volumetric flask with water. (See the note to table 1.) (This solution is the final test solution.)

Table 1 — Dilution guide for test solution1)

Expected content, w, of zinc in sample % (m/m)	Aliquot ml	Mass of sodium carbonate (4.1) to be added g	Volume of hydrochloric acid (4.5) to be added ml
$0{,}001 < w_{Zn} \leqslant 0{,}006$	—	—	—
$0{,}006 < w_{Zn} \leqslant 0{,}02$	25	0,75	30
$0{,}02 < w_{Zn} \leqslant 0{,}06$	10	0,9	36
$0{,}06 < w_{Zn} \leqslant 0{,}12$	5	0,95	38
$0{,}12 < w_{Zn} \leqslant 0{,}3$	2	0,98	39
$0{,}3 < w_{Zn} \leqslant 0{,}5$	1	0,99	40

1) Dilution shown will provide concentrations of zinc falling within the range of the calibration solutions (7.4.4). For instruments having high sensitivity, smaller portions of the test solution may be preferable. For 1 ml or 2 ml of aliquot, make a preliminary dilution to avoid dilution error. Treat the blank test solution similarly.

Transfer corresponding amounts of blank test solution to a 250 ml beaker, and add the same volume of sodium carbonate (4.1) and hydrochloric acid (4.5) as used for the test solution. Heat the solution to remove carbon dioxide. Cool and dilute to 100 ml in a one-mark volumetric flask with water and mix. (This solution is the diluted blank test solution.)

7.4.4 Preparation of the set of zinc calibration solutions

Transfer 1,0 g of sodium carbonate (4.1) to each of six 250 ml beakers. Add 20 ml of hydrochloric acid (4.3) and appropriate aliquots of zinc standard solution (4.9.2) as listed in table 2. Heat the solution to remove carbon dioxide. Cool and dilute to 100 ml in a one-mark volumetric flask.

NOTE — The range of zinc that can be covered may vary from instrument to instrument. Attention should be paid to the minimum criteria given in 5.2. For instruments having high sensitivity, smaller aliquots of the standard solutions can be used.

Table 2 — Calibration solutions

Solution number	Standard solution (4.9.2) ml	Zinc concentration µg/ml
0	0	0
1	5	0,5
2	10	1
3	15	1,5
4	20	2
5	25	2,5

7.4.5 Adjustment of atomic absorption spectrometer

Set the wavelength for zinc (213,9 nm) to obtain minimum absorbance. Fit the correct burner and, in accordance with the manufacturer's instructions, light the appropriate flame. After preheating of the burner for 2 min, adjust fuel and burner to obtain maximum absorbance while aspirating the most concentrated calibration solution (see 7.4.4), and evaluate the criteria in 5.2.

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.

7.4.6 Atomic absorption measurements

Aspirate the calibration solutions and the final test solution in order of increasing absorption, starting with the diluted blank test solution and the zero calibration solution, with the final test solution being aspirated at the proper point in the series. Aspirate water between each solution and record the readings when stable responses are obtained.

Repeat the measurements at least twice more. If necessary, convert the average of the readings for each solution to absorbance. Obtain the net absorbance of each calibration solution by subtracting the absorbance of the zero calibration solution. Similarly, obtain the net absorbance of the final test solution by subtracting the absorbance of the diluted blank test solution.

Prepare a calibration graph by plotting the net absorbance values of the calibration solutions against the concentrations, in micrograms per millilitre, of zinc.

Convert the net absorbance values of the final test solution to micrograms of zinc per millilitre by means of the calibration graph.

8 Expression of results

8.1 Calculation of zinc content

The zinc content, w_{Zn}, expressed as a percentage by mass, is calculated to five decimal places using the equation

$$w_{\mathrm{Zn}} = \frac{\rho V}{m_1 \times 10\,000} \qquad \ldots (1)$$

where

ρ is the concentration, in micrograms per millilitre, of zinc in the final test solution;

V is the volume, in millilitres, of final test solution;

m_1 is the mass of sample, in grams, in the final test solution, taking account of any preliminary dilution that may have been made.

$$m_1 = \frac{m \times V_1}{50}$$

where

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

V_1 is the volume, in millilitres, of the aliquot taken in 7.4.3 (see table 1). When no dilution has been made, $V_1 = 50$.

8.2 General treatment of results

8.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed by the following regression equations[1]:

$$R_d = 0,041\,5\,X + 0,001\,1 \qquad \ldots (2)$$

$$P = 0,104\,8\,X + 0,003\,0 \qquad \ldots (3)$$

$$\sigma_d = 0,014\,7\,X + 0,000\,4 \qquad \ldots (4)$$

$$\sigma_L = 0,035\,5\,X + 0,001\,0 \qquad \ldots (5)$$

where

X is the zinc content, expressed as a percentage by mass, of the predried test sample, calculated as follows:

- for the within-laboratory equations (2, 4), the arithmetic mean of the duplicate values;
- for the between-laboratories equations (3, 5), the arithmetic mean of the final results (8.2.5) of the two laboratories;

R_d is the independent duplicate limit;

P is the permissible tolerance between laboratories;

σ_d is the independent duplicate standard deviation;

σ_L is the between-laboratories standard deviation.

8.2.2 Determination of analytical result

Having computed the independent duplicate results according to equation (1), compare them with the independent duplicate limit (R_d), using the procedure given in annex A.

8.2.3 Between-laboratories precision

Between-laboratories precision is used to determine the agreement between the final results reported by two laboratories. The assumption is that both laboratories followed the procedure described in 8.2.2.

Compute the following quantity:

$$\mu_{12} = \frac{\mu_1 + \mu_2}{2} \qquad \ldots (6)$$

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

μ_{12} is the mean of final results.

If $|\mu_1 - \mu_2| \leqslant P$ (see 8.2.1), the final results are in agreement.

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[1] Additional information is given in annexes B and C.

8.2.4 Check for trueness

The trueness of the analytical method shall be checked by applying it to a certified reference material (CRM) or a reference material (RM). The procedure is the same as that described above. After confirmation of the precision, the final laboratory result is compared with the reference or certified value A_c. There are two possibilities:

a) $|\mu_c - A_c| \leqslant C$ in which case the difference between the reported result and the reference/certified value is statistically insignificant.

b) $|\mu_c - A_c| > C$ in which case the difference between the reported result and the reference/certified value is statistically significant.

where

μ_c is the final result for the certified reference material;

A_c is the reference/certified value for the CRM/RM;

C is a value dependent on the type of CRM/RM used.

NOTE 1 Certified reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35:1989, *Certification of reference materials — General and statistical principles.*

For a CRM certified by an interlaboratory test programme

$$C = 2\left[\sigma_L^2 + \frac{\sigma_d^2}{n} + V(A_c)\right]^{1/2}$$

where $V(A_c)$ is the variance of the certified value A_c.

For a CRM certified by only one laboratory

$$C = 2\left[\sigma_L^2 + \frac{\sigma_d^2}{n}\right]^{1/2}$$

NOTE 2 This type of CRM should be avoided unless it is known to have an unbiased certified value.

8.2.5 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 five decimal places and rounded off to the third decimal place as follows:

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

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

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

8.3 Oxide factor

w_{ZnO} [% (m/m)] = 1,244 7 w_{Zn} [% (m/m)]

9 Test report

The test report shall include the following information:

a) name and address of the testing laboratory;

b) date of issue of the test report;

c) reference to this International Standard;

d) details necessary for the identification of the sample;

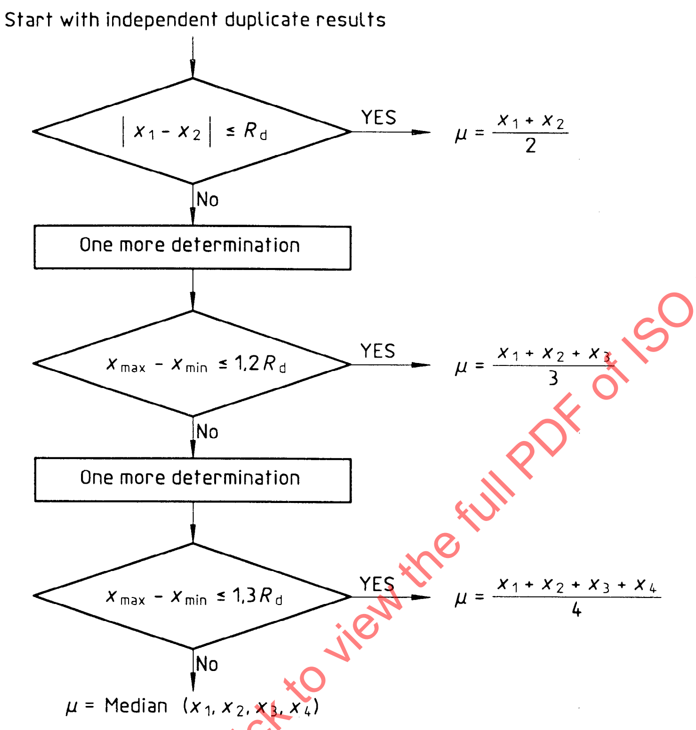
e) result of the analysis;

f) reference number of the result;

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

Annex A
(normative)

Flowsheet of the procedure for the acceptance of analytical values for test samples



R_d: as defined in 8.2.1.