INTERNATIONAL STANDARD

ISO 11533

Second edition
2009-06-15

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

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

Reference number
ISO 11533:2009(E)

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Published in Switzerland

Contents

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 11533 was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This second edition cancels and replaces the first edition (ISO 11533:1996), which has been technically revised.

Iron ores — Determination of cobalt — 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 problems associated with its use. It is the responsibility of the user of this International Standard 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 mass fraction of cobalt in iron ores.

This method is applicable to a mass-fraction range of 0,000 7 % to 0,06 % of cobalt in natural iron ores, iron ore concentrates and agglomerates, including sinter products.

2 Normative references

The following referenced documents are indispensable for the application 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 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*

3 Principle

A test portion is decomposed by treatment with hydrochloric, nitric, sulfuric and hydrofluoric acids. The solution is evaporated to dryness, then dissolved and filtered.

The residue is ignited, then silica is removed by treatment with hydrofluoric acid and evaporation to dryness. The residue is fused with sodium carbonate. The cooled melt is dissolved with hydrochloric acid, and combined with the original filtrate.

Iron is extracted with isobutyl acetate. The aqueous phase is evaporated to reduced volume, acidified with nitric acid and diluted to volume.

The solution is aspirated into the flame of an atomic absorption spectrometer using an air/acetylene burner.

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

4 Reagents

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

4.1 Sodium carbonate (Na_2CO_3), anhydrous.

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

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

4.4 Nitric acid, ρ 1,4 g/ml.

4.5 Hydrofluoric acid, ρ 1,13 g/ml, 40 % (by mass), or ρ 1,185 g/ml, 48 % (by mass).

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

4.7 Isobutyl acetate.

4.8 Sodium background solution.

Dissolve 15 g of sodium carbonate (4.1) in 50 ml of water. While stirring, slowly add 25 ml of hydrochloric acid (4.2). Warm to eliminate carbon dioxide, then cool. Dilute to 250 ml and mix.

4.9 Cobalt standard solutions.

4.9.1 Stock solution, 1 000 µg Co/ml.

Dissolve 1,000 g of cobalt metal [of purity > 99,5 % (by mass)] by heating in 30 ml of hydrochloric acid (4.2). Add 5 ml of nitric acid (4.4) and heat to expel the oxides of nitrogen. Cool, dilute to 1 000 ml with water in a one-mark volumetric flask and mix.

4.9.2 Standard solution A, 25 µg Co/ml.

Transfer 25 ml of cobalt stock solution (4.9.1) to a 1 000 ml one-mark volumetric flask. Dilute to volume with water and mix.

4.9.3 Standard solution B, 200 µg Co/ml.

Transfer 50 ml of cobalt stock solution (4.9.1) to a 250 ml one-mark volumetric flask. Dilute to volume with water and mix.

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 the following.

5.1 Separating funnels, of capacity 100 ml.

5.2 Platinum crucibles, of capacity 30 ml.

5.3 Atomic absorption spectrometer, equipped with an air/acetylene burner.

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

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

a) **Minimum sensitivity**: the absorbance of the 4 µg/ml cobalt calibration solution, when measured in a flame of 10 cm path length at 240,7 nm, shall be at least 0,20, and the absorbance of the 32 µg/ml cobalt calibration solution, when measured in a flame of 10 cm path length at 252,2 nm, shall be at least 0,60 when scale-expansion facilities are not used.

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 minimum number of 10 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 read-out 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 have been successfully used in several laboratories and they can be used as guidelines. Solutions were aspirated into an air/acetylene flame.

Hollow cathode lamp, mA	7
Wavelength, nm	240,7 252,2
Air flow rate, l/min	20
Acetylene flow rate, l/min	5

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

Criteria b) and c) should be determined separately at wavelengths of 240,7 nm and 252,2 nm.

6 Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of minus 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 minus 160 µm.

NOTE Guidance 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 way that it is representative of the whole contents of the container. Dry the test sample 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 appropriate recalibration in both cases.

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.

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.

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 both cases, no significant changes in the analytical procedure will become necessary.

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 the reagents used are from the same reagent bottles.

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.

7.4 Determination

7.4.1 Decomposition of the test portion

Transfer the test portion (7.2) to a 250 ml beaker. Moisten with a few millilitres of water, add 50 ml of hydrochloric acid (4.2), cover with a watch-glass, and heat at 95 °C for 1 h.

If after this digestion the amount of insoluble residue is high, raise the hotplate temperature to about 105 °C and continue heating, avoiding boiling.

Add 5 ml of nitric acid (4.4) and 0,5 ml of sulfuric acid (4.6) and heat at 105 °C for 15 min. Displace the watch-glass to provide a gap of approximately 5 mm, and add 1 ml of hydrofluoric acid (4.5). Evaporate to dryness and heat for a further 15 min.

Add 20 ml of hydrochloric acid (4.3) and heat gently to dissolve the soluble salts. Wash the watch-glass and wall of the beaker. Filter through a close-texture filter paper (maximum diameter 11 cm) into a 250 ml beaker. Remove all adhering particles from the beaker with a rubber-tipped rod, and wash the paper and residue with several minimum volumes of warm hydrochloric acid (4.3) until the paper is free from iron stain, then wash thoroughly with warm water. Retain the filtrate.

7.4.2 Treatment of residue

Place the paper and residue in a platinum crucible (5.2). Evaporate most of the water from the filter paper by placing the crucible on a hotplate for approximately 20 min. Char the paper at 600 °C for 30 min, then ignite at 850 °C for 60 min. Cool and add 5 ml of hydrofluoric acid (4.5) and 0,5 ml of sulfuric acid (4.6). Evaporate to dryness on a hotplate at 200 °C. Add 300 mg of sodium carbonate (4.1) and fuse at 900 °C for 30 min. Dissolve the cooled melt by warming with 10 ml of hydrochloric acid (4.3) on a hotplate.

7.4.3 Treatment of combined filtrate and washings

Evaporate the filtrate (7.4.1) and washings to between 5 ml and 10 ml.

Add 20 ml of hydrochloric acid (4.2). Add the processed residue solution (7.4.2), using 2 ml of hydrochloric acid (4.3) from the jet of a wash bottle to rinse out the crucible.

Transfer to a separating funnel (5.1), using 5 ml to 7 ml of hydrochloric acid (4.3) from the jet of a wash bottle. Add 25 ml of isobutyl acetate (4.7) and shake vigorously for 1 min. Allow the layers to separate, then run the lower aqueous layer into a 250 ml beaker until 0,5 ml of the aqueous layer remains. Add 5 ml of hydrochloric acid (4.2) and allow 1 ml to flow through the stopcock. Shake vigorously for 30 s, allow the layers to separate, then run all of the lower aqueous layer into the beaker. Discard the organic layer containing the extracted iron.

Rinse the aqueous solution back into the separating funnel, using 2 ml of hydrochloric acid (4.3) from the jet of a wash bottle, and repeat the isobutyl acetate extraction step described above.

Evaporate the beaker containing the aqueous phase to approximately 5 ml.

Rinse the walls of the beaker with 5 ml of water. Add 5 ml of nitric acid (4.4). Transfer to a 50 ml volumetric flask and dilute to volume with water.

7.4.4 Preparation of the set of calibration solutions

Prepare a range of calibration solutions to suit the expected mass fraction of cobalt in the sample. For the mass-fraction range of 0,000 7 % to 0,010 0 % of cobalt, use standard solution A (4.9.2). For the mass-fraction range of 0,010 0 % to 0,06 % of cobalt, use standard solution B (4.9.3).

Transfer 2 ml; 4 ml; 6 ml and 8 ml portions of the appropriate standard solution to 50 ml one-mark volumetric flasks. Add 5 ml of sodium background solution (4.8), 5 ml of nitric acid (4.4) and 5 ml of hydrochloric acid (4.3). Dilute each solution to volume with water and mix. Prepare a zero calibration solution by transferring 5 ml of sodium background solution (4.8), 5 ml of nitric acid (4.4) and 5 ml of hydrochloric acid (4.3) to a 50 ml one-mark volumetric flask. Dilute to volume with water and mix.

The range of cobalt that can be covered may vary from instrument to instrument. Attention should be paid to the minimum criteria given in 5.3. For instruments having high sensitivity, smaller aliquots of the standard solutions can be used. In this situation, the concentrations in Table 1 will have to be adjusted accordingly.

7.4.5 Adjustment of atomic absorption spectrometer

Set the wavelength for cobalt (240,7 nm for a mass fraction of cobalt less than 0,010 0 %, 252,2 nm for a mass fraction of cobalt range 0,010 0 % to 0,06 %) to obtain minimum absorbance. Fit the correct burner and, in accordance with the manufacturer's instructions, light the air/acetylene flame. After 10 min of preheating the burner, adjust the fuel and burner to obtain maximum absorbance while aspirating the calibration solution with the highest concentration (see 7.4.4), and evaluate the criteria in 5.3.

Aspirate water and the calibration solution to verify that the absorbance reading is not drifting, 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 absorbance readings when stable responses are obtained.

Repeat the measurements at least twice more, and average the readings. 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 cobalt (see Table 1).

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

Table 1 — Calibration solutions

Solution number	Standard solution A (4.9.2) ml	Standard solution B (4.9.3) ml	Concentration of cobalt µg/ml
0	0	0	0
1	2	—	1
2	4	—	2
3	6	—	3
4	8	—	4
5	—	2	8
6	—	4	16
7	—	6	24
8	—	8	32

8 Expression of results

8.1 Calculation of mass fraction of cobalt

The mass fraction of cobalt, w_{Co}, expressed as a percentage to six decimal places, is calculated from Equation (1):

$$w_{\mathrm{Co}} = \frac{\rho_{\mathrm{Co}} \times 50}{1\,000\,000 \times m} \times 100 = \frac{\rho_{\mathrm{Co}}}{200 \times m} \tag{1}$$

where

ρ_{Co} is the concentration, in micrograms per millilitre, of cobalt in the test solution;

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

8.2 General treatment of results

8.2.1 Repeatability and permissible tolerances

The precision of this analytical method is expressed by the following equations:

$$R_{\mathrm{d}} = 0{,}053\,2X + 0{,}000\,3 \tag{2}$$

$$P = 0{,}101\,8X + 0{,}000\,4 \tag{3}$$

$$\sigma_{\mathrm{d}} = 0{,}018\,8X + 0{,}000\,1 \tag{4}$$

$$\sigma_{\mathrm{L}} = 0{,}032\,5X + 0{,}000\,1 \tag{5}$$

where

X is the mass fraction of cobalt, expressed as a percentage, of the predried test sample, calculated as follows:

- within-laboratory Equations (2) and (4): the arithmetic mean of the duplicate values;
- between-laboratories Equations (3) and (5): the arithmetic mean of the final results (8.2.5) of the two laboratories.

σ_d is the independent duplicate standard deviation;

σ_L is the between-laboratories standard deviation;

R_d is the independent duplicate limit;

P is the permissible tolerance between laboratories.

Additional information is given in Annexes B and C.

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:

$$\mu_{1,2} = \frac{\mu_1 + \mu_2}{2} \tag{6}$$

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

$\mu_{1,2}$ is the mean of the final results.

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

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.

Certified reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35:2006, *Reference materials — General and statistical principles for certification*.

C shall be calculated as follows:

$$C = 2\sqrt{\frac{s_c^2}{N_c} + \sigma_L^2 + \frac{\sigma_d^2}{n}} \tag{7}$$

where

s_c is the standard deviation of laboratory means (each value for calculating the standard deviation is the average value in each certifying laboratory) of the CRM/RM;

N_c is the number of certifying laboratories;

n is the number of replicate determinations carried out on the CRM/RM.

For CRMs certified by only one laboratory, C shall be calculated as follows:

$$C = \sqrt{2\sigma_L^2 + \frac{\sigma_d^2}{n}} \tag{8}$$

A CRM certified by only one laboratory 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 six decimal places and rounded off to the fourth decimal place as follows:

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

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

c) when the figure in the fifth decimal place is 5 and the figure 0 is in the sixth decimal place, the 5 is discarded and the figure in the fourth 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

The oxide factor, expressed as a percent, is given by the following equation:

$$w_{CoO} = 1{,}271 w_{Co} \tag{9}$$

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) a reference to this International Standard;

d) details necessary for the identification of the sample;

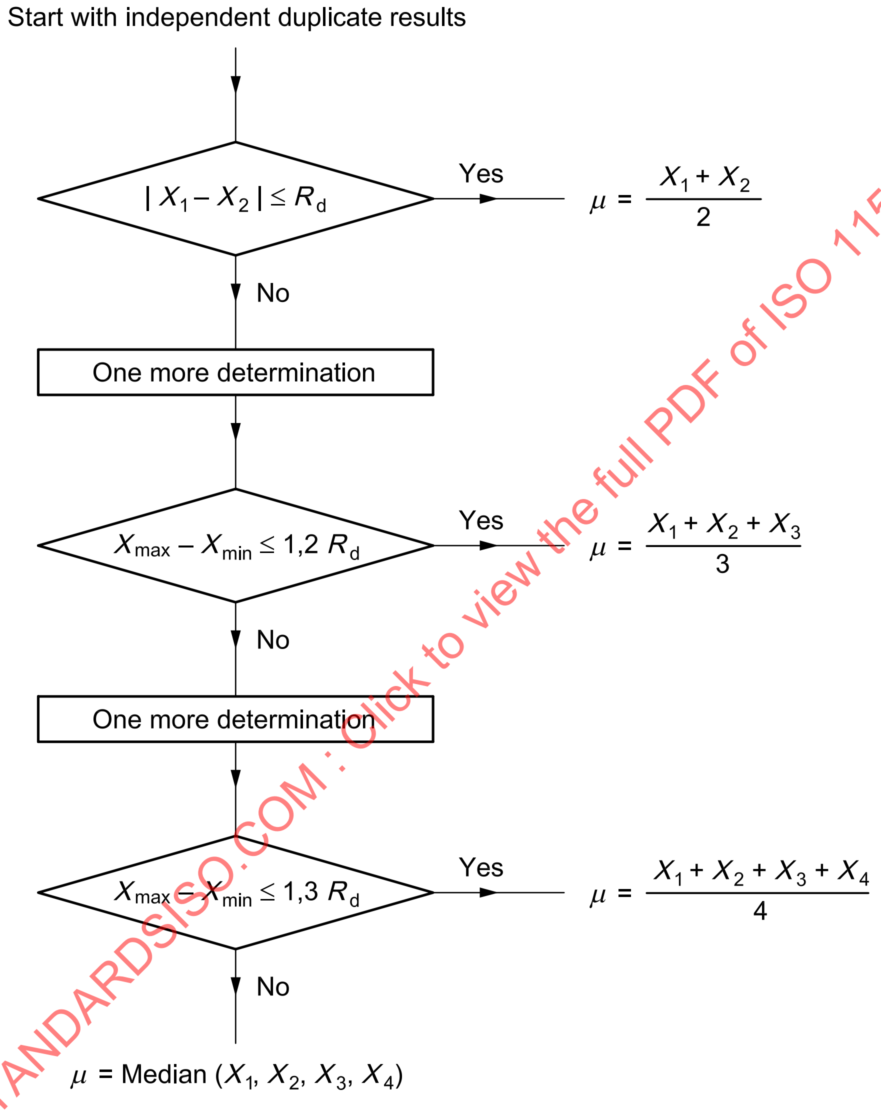
e) result of the analysis;

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