International Standard

ISO 4693

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

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

First edition — 1986-11-01

Price based on 8 pages

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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 4693 was prepared by Technical Committee ISO/TC 102, *Iron ores*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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

1 Scope and field of application

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

This method is applicable to a concentration range of 0,003 to 1,0 % (m/m) of copper in natural iron ores, and iron ore concentrates and agglomerates including sinter products.

2 References

ISO 648, *Laboratory glassware — One-mark pipettes.*

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

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

ISO 3082, *Iron ores — Increment sampling and sample preparation — Mechanical method.* [1]

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

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

3 Principle

Decomposition of a test portion by treatment with hydrochloric, nitric and hydrofluoric acids. Evaporation with perchloric acid, dilution and filtration of any insoluble residue.

Measurement of the copper content of the solution by atomic absorption spectrometry using an air-acetylene flame.

4 Reagents

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

NOTE — The distillation apparatus used should not contain any copper, and deionized water should not come into contact with copper tubing or taps.

4.1 Iron metal powder, copper content < 0,001 % (m/m).

4.2 Sodium carbonate (Na_2CO_3), anhydrous.

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

4.4 Nitric acid, ϱ 1,4 g/ml.

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

4.6 Nitric acid, ϱ 1,4 g/ml, diluted 1 + 1.

4.7 Perchloric acid, 60 % (m/m) solution, ϱ 1,54 g/ml, or 70 % (m/m) solution, ϱ 1,67 g/ml.

4.8 Hydrofluoric acid, 40 % (m/m) solution, ϱ 1,13 g/ml or 48 % (m/m) solution, ϱ 1,185 g/ml.

4.9 Background solution.

Dissolve 15 g of iron metal powder (4.1) in 150 ml of hydrochloric acid (4.5). Cool the solution to room temperature, add 10 ml of nitric acid (4.4). Heat carefully to eliminate nitrous gases, add 250 ml of perchloric acid solution (4.7) and evaporate the solution to fumes. Allow to fume for 10 min, cool and dilute to 1 000 ml with water.

4.10 Copper standard solutions.

4.10.1 Stock solution

Dissolve 1,000 g of pure metallic copper in 30 ml of nitric acid solution (4.6), heat to remove nitrous gases, cool and transfer to a 1 000 ml volumetric flask. Dilute to the mark with water and mix.

1 ml of the stock solution contains 1,00 mg of copper.

4.10.2 Standard solution A

Transfer 100 ml of the stock solution (4.10.1) to a 1 000 ml volumetric flask. Dilute to the mark with water and mix.

1 ml of this standard solution contains 0,10 mg of copper.

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1) At present at the stage of draft.

4.10.3 Standard solution B

Transfer 10 ml of the standard solution A (4.10.2) to a 100 ml volumetric flask. Dilute to the mark with water and mix.

1 ml of this standard solution contains 0,010 mg of copper.

5 Apparatus

NOTE — Unless otherwise indicated, any pipettes and volumetric flasks required shall be one-mark pipettes and volumetric flasks complying with the accuracy specifications of ISO 648 and ISO 1042.

Ordinary laboratory equipment and

5.1 Polytetrafluoroethylene (PTFE) beakers, of capacity 150 ml.

5.2 Atomic absorption spectrometer.

The atomic absorption spectrometer used will be satisfactory if it meets the following criteria :

a) *Minimum sensitivity* — the absorbance of the calibration solution of highest copper content (see 7.5.3) when measured in a flame of 10 cm path length is at least 0,3.

b) *Curve linearity* — the slope of the calibration graph covering the top 20 % concentration range (expressed as a change in absorbance) is not less than 0,7 of the value of the slope for the bottom 20 % concentration range determined in the same way.

c) *Minimum stability* — the standard deviation of the absorbance of the calibration solution of highest concentration and the standard deviation of the absorbance of the zero calibration solution, each being calculated from a sufficient number of repetitive measurements, are less than 1,5 % and 0,5 % respectively of the mean value of the absorbance of the calibration solution of highest concentration.

NOTES

1   The use of a strip-chart recorder and/or digital read-out device is recommended to evaluate these criteria and for all subsequent measurements.

2   A background corrector equipped with a hydrogen or a deuterium hollow cathode lamp is advisable for the concentration range of 0,003 to 0,010 % (m/m) of copper.

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

Copper hollow cathode lamp (mA)	3
Wavelength (nm)	324,7
Air flow rate (l/min)	10
Acetylene flow rate (l/min)	2

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 with 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 sample at 105 ± 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 shall be carried out either by the same operator at a different time or by a different operator including, in either case, appropriate recalibration.

7.2 Safety precautions

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.

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 (see the note).

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 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.

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 would become necessary.

7.4 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, approximately 0,5 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.

7.5 Determination

7.5.1 Decomposition of the test portion

Transfer the test portion (7.4) to a 150 ml PTFE beaker (5.1). Moisten with a few millilitres of water, add 15 ml of hydrochloric acid (4.3), cover with a watch-glass, and heat gently. Increase the heat and digest just below boiling until no further attack is apparent. Add 5 ml of nitric acid (4.4) and heat for 10 min. Remove the watch-glass, add 3 ml of hydrofluoric acid solution (4.8) and heat for a further 10 min.

Wash down the walls of the beaker with water and add 5 ml of perchloric acid solution (4.7). Heat slowly, evaporating until dense white fumes of perchloric acid are evolved. Allow to fume for 2 to 3 min.

Allow the solution to cool, add 50 ml of water and heat gently to dissolve the soluble salts.

Filter the solution through a close-texture paper, collecting the filtrate and washings in a 100 ml volumetric flask. Wash the paper and the residue thoroughly with warm water. Cool the final solution, dilute to the mark with water and mix. (This is the test solution.)

NOTE — If a significant amount of residue remains from the decomposition process or if any residue is suspected to contain a significant amount of copper, such residue shall be examined separately for copper content after ignition, fusion with the sodium carbonate (4.2), and dissolution of the melt in nitric acid diluted 1 + 50. An appropriate blank test solution should also be prepared. The result obtained from a copper determination on any insoluble residue shall be combined with the result obtained for copper in the main test solution.

7.5.2 Treatment of the solution

If the copper content is over 0,2 % (or 0,1 % in the case of instruments with high sensitivity), dilute the test solution as follows : transfer an aliquot (x ml, where x should not be less than 20 ml) to a 100 ml volumetric flask. Add 0,2 (100 − x) ml of background solution (4.9) and dilute to the mark with water and mix. (This is the diluted test solution.) (See the note.) If the copper content is less than 0,2 % (or 0,1 % in the case of instruments with high sensitivity), the absorption measurement of the main solution is carried out without dilution.

When a diluted test solution is to be used, a diluted blank test solution should be prepared as follows : transfer x ml of the blank test solution to a 100 ml volumetric flask, add 0,2 (100 − x) ml of background solution (4.9), dilute to the mark with water and mix.

NOTE — For instruments with high sensitivity this dilution may need to be made if the copper content is between 0,1 and 0,2 % (m/m). If the copper content is between 0,5 and 1 % (m/m) with instruments of high sensitivity the value for x should not be less than 10 ml.

7.5.3 Preparation of the set of calibration solutions

Depending on the expected copper content in the sample, prepare calibration solutions using standard solution A (4.10.2) or standard solution B (4.10.3). For the concentration range of 0,01 to 1 % (m/m) of copper, use standard solution A (4.10.2). For the concentration range of 0,003 to 0,02 % (m/m) of copper, use standard solution B (4.10.3).

Transfer 1,0; 3,0; 5,0; 7,0 and 10,0 ml portions of the appropriate standard solution to 100 ml volumetric flasks and add 20,0 ml of background solution (4.9). Dilute each solution to the mark with water and mix. Prepare a zero calibration solution by transferring 20,0 ml of background solution to a 100 ml volumetric flask. Dilute to the mark with water and mix.

NOTE — The range of copper concentration that can be covered may vary from one instrument to another. Attention should be paid to the minimum performance criteria in 5.2. For instruments with high sensitivity, the calibration series can be prepared using only standard solution B with increases as necessary in the volumes taken.

7.5.4 Adjustment of atomic absorption spectrometer

Set the wavelength for copper (324,7 nm) to obtain minimum absorbance and adjust the read-out to zero absorbance. Light the air-acetylene flame. After 10 min preheating of the burner, aspirate water and, if necessary, readjust the read-out to zero absorbance. Aspirate the calibration solution of highest copper content (7.5.3) and adjust the fuel flow and burner position to obtain maximum absorbance. Check that conditions for zero absorbance have been maintained and evaluate the criteria in 5.2.

Repeat the aspiration of water and the calibration solution of highest copper content to establish that the absorbance reading is not drifting, and set the reading for water to zero absorbance.

7.5.5 Atomic absorption measurements

Aspirate the calibration solutions and the test or diluted test solution in the order of increasing absorption, starting with the zero calibration solution and the blank test or diluted blank test solution. When a stable response is obtained for each solution, record the readings. Aspirate water between each calibration and test solution. Repeat the measurements at least twice more.

If necessary, convert the average of the readings for each calibration solution to absorbance. Obtain the net absorbance of each calibration solution by subtracting the average absorbance of the zero calibration solution. In a similar manner, obtain the net absorbance of the test solution or diluted test solution by subtracting the absorbance of the blank test or diluted blank test solution.

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

Convert the net absorbance value of the test solution or diluted test solution to micrograms of copper per millilitre by means of the calibration graph.

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8 Expression of results

8.1 Calculation of copper content

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

$$w_{Cu} (\%) = \frac{\varrho_{Cu} \times 100}{m_1 \times 10\,000}$$

$$= \frac{\varrho_{Cu}}{m_1 \times 100} \qquad \ldots (1)$$

where

ϱ_{Cu} is the concentration, in micrograms per millilitre, of copper in the test solution or diluted test solution;

m_1 is the mass, in grams, of the test portion in 100 ml volume of the test solution or diluted test solution. [$m_1 = m_2 x/100$, where m_2 is the mass, in grams, of the test portion and x is an aliquot, in millilitres, taken in 7.5.2. When no dilution has been made, $x = 100$.]

NOTE — Include the result obtained for a copper determination made on any insoluble residue (7.5.1).

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]

$r = 0,029\,8\,X + 0,001\,0 \qquad \ldots (2)$

$P = 0,066\,8\,X + 0,004\,0 \qquad \ldots (3)$

$\sigma_r = 0,010\,5\,X + 0,000\,4 \qquad \ldots (4)$

$\sigma_L = 0,022\,4\,X + 0,001\,4 \qquad \ldots (5)$

where

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

— within-laboratory equations (2, 4); the arithmetic mean of the duplicate values;

— between-laboratories equations (3, 5); the arithmetic mean of the final results (8.2.3) of the two laboratories;

r is the permissible tolerance within a laboratory (repeatability);

P is the permissible tolerance between laboratories;

σ_r is the within-laboratory standard deviation;

σ_L is the between-laboratories standard deviation.

8.2.2 Acceptance of analytical values

The result obtained for the certified reference material shall be such that the difference between this result and the certified value of the reference material is statistically insignificant. For a reference material that has been analysed by at least 10 laboratories using method(s) that are comparable both in accuracy and precision with this method, the following conditions may be used to test the significance of the difference :

$$|A_c - A| \leqslant 2 \sqrt{\frac{s_{Lc}^2 + \frac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_r^2}{n}} \qquad \ldots (6)$$

where

A_c is the certified value;

A is the result or the mean of results obtained for the certified reference material;

s_{Lc} is the between-laboratories standard deviation of the certifying laboratories;

s_{Wc} is the within-laboratory standard deviation of the certifying laboratories;

n_{Wc} is the average number of replicate determinations in the certifying laboratories;

N_c is the number of certifying laboratories;

n is the number of replicate determinations on the reference material (in most cases $n = 1$);

σ_L and σ_r are as defined in 8.2.1.

If condition (6) is satisfied, i.e. if the left-hand side is less than or equal to the right-hand side, then the difference $|A_c - A|$ is statistically insignificant; otherwise, it is statistically significant.

When the difference is significant, the analysis shall be repeated, simultaneously with an analysis of the test sample. If the difference is again significant, the procedure shall be repeated using a different certified reference material of the same type of ore.

When the range of the two values for the test sample is outside the limit for r calculated according to equation (2) in 8.2.1, one or more additional tests shall be carried out in accordance with the flowsheet presented in annex A, simultaneously with an analysis of a certified reference material of the same type of ore.

Acceptability of the results for the test sample shall in each case be subject to the acceptability of the results for the certified reference material.

NOTE — The following procedure should be used when the information on the reference material certificate is incomplete :

a) if there are sufficient data to enable the between-laboratories standard deviation to be estimated, delete the expression s_{Wc}^2/n_{Wc} and regard s_{Lc} as the standard deviation of the laboratory means;

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1) Additional information is given in annex B and annex C.

b) if the certification has been made by only one laboratory or if the interlaboratory results are missing, use the following condition :

$$|A_c - A| \leqslant 2 \sqrt{2\sigma_L^2 + \frac{\sigma_r^2}{n}} \qquad \ldots (7)$$

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

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

c) when the figure in the fourth decimal place is 5 and there is the figure 0 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

$$w_{CuO} (\%) = 1{,}251\,8\ w_{Cu} (\%)$$

9 Test report

The test report shall include the following information :

a) reference to this International Standard;

b) details necessary for the identification of the sample;

c) 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 result either for the test sample or the certified reference material(s).
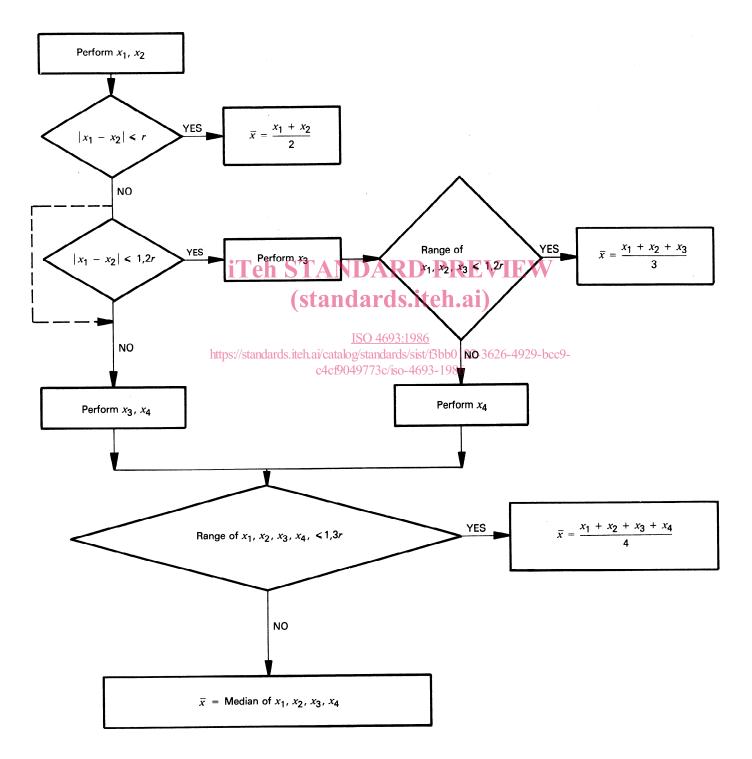
Annex A

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

(This annex forms an integral part of this International Standard.)

Perform x_1, x_2

$|x_1 - x_2| < r$ — YES → $\bar{x} = \dfrac{x_1 + x_2}{2}$

NO

$|x_1 - x_2| < 1{,}2r$ — YES → Perform x_3 → Range of x_1, x_2, x_3 $< 1{,}2r$ — YES → $\bar{x} = \dfrac{x_1 + x_2 + x_3}{3}$

NO

NO

Perform x_3, x_4

Perform x_4

Range of x_1, x_2, x_3, x_4, $< 1{,}3r$ — YES → $\bar{x} = \dfrac{x_1 + x_2 + x_3 + x_4}{4}$

NO

$\bar{x}$ = Median of x_1, x_2, x_3, x_4

r : as defined in 8.2.1.

Annex B

Derivation of repeatability and permissible tolerance equations

(This annex is for information only, and is not an integral part of this International Standard.)

The regression equations in 8.2.1 have been derived from the results of international analytical trials carried out in 1972/1973 on five iron ore samples involving 45 laboratories in nine countries.

Graphical treatment of the precision data is given in annex C.

The test samples used were :

Sample	Copper content [% (m/m)]
Malmberget concentrate (72-1)	0,001
Kiruna R (72-2)	0,011
Roasting residue (Purpurerz) (72-3)	0,072
Russian pyrite cinder (Russ Abbrände) (72-4)	0,380
Forsbo ore (72-5)	0,787

NOTES

1   A report of the international trial and a statistical analysis of the results (Document ISO/TC 102/SC 2 N 306E, May 1973) is available from either the Secretariat of ISO/TC 102/SC 2 or the Secretariat of ISO/TC 102.

2   The statistical analysis has been performed in accordance with the principles embodied in ISO 5725.