INTERNATIONAL STANDARD

ISO 5418-2

First edition
2006-12-01

Iron ores — Determination of copper —

Part 2:
Flame atomic absorption spectrometric method

Minerais de fer — Dosage du cuivre —

Partie 2: Méthode par spectrométrie d'absorption atomique dans la flamme

Reference number
ISO 5418-2:2006(E)

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Published in Switzerland

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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 5418-2 was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This first edition cancels and replaces ISO 4693:1986, which has been technically revised. It has been updated to alter the manner in which precision data are presented.

ISO 5418 consists of the following parts, under the general title *Iron ores — Determination of copper*:

— *Part 1: 2,2′-Biquinolyl spectrophotometric method*

— *Part 2: Flame atomic absorption spectrometric method*

Iron ores — Determination of copper —

Part 2:
Flame atomic absorption spectrometric method

WARNING — This part of ISO 5418 may involve hazardous materials, operations and equipment. This part of ISO 5418 does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this part of ISO 5418 to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This part of ISO 5418 specifies a flame atomic absorption spectrometric method for the determination of the mass fraction of copper in iron ores.

This method is applicable to a mass-fraction range of 0,004 % to 0,8 % of copper in natural iron ores, and 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 — One-mark 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 and hydrofluoric acids. The solution is evaporated with perchloric acid and diluted, and any insoluble residue is filtered.

The copper concentration of the solution is measured by atomic absorption spectrometry using an air-acetylene flame.

4 Reagents

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

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**, mass fraction of copper $< 0,001$ %.

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

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

4.4 **Hydrochloric acid**, ρ 1,16 g/m/l to 1,19 g/ml, diluted 1 + 2.

4.5 **Nitric acid**, ρ 1,4 g/ml.

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 power (4.1) in 150 ml of hydrochloric acid (4.4). Cool the solution to room temperature and add 10 ml of nitric acid (4.5). Heat carefully to eliminate nitrous gases, add 250 ml of perchloric acid solution (4.7) and evaporate the solution until it 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 dilute nitric acid (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 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.

4.10.3 Standard solution B

Transfer 10 ml of 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

Ordinary laboratory equipment, including pipettes and volumetric flasks complying with the accuracy specifications of ISO 648 and ISO 1042, and the following.

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

5.2 Atomic absorption spectrometer.

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.

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 concentration (see 7.4.3), 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.

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

NOTE 1 A background corrector equipped with a hydrogen or a deuterium hollow-cathode lamp is advisable for the mass-fraction range of 0,003 % to 0,010 % of copper.

NOTE 2 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 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 A guideline on significant contents of combined water and oxidizable compounds is given 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 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 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 last paragraph of this subclause).

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.

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.

7.3 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.

The test portion should be taken and weighed quickly to avoid reabsorption of moisture.

7.4 Determination

7.4.1 Decomposition of the test portion

Transfer the test portion (7.3) 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 (4.5) and heat for 10 min. Remove the watch-glass, add 3 ml of hydrofluoric acid (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 (4.7). Heat slowly, evaporating until dense white fumes of perchloric acid are evolved. Allow to fume for 2 min 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 volume with water and mix. (This is the test solution.)

If a significant amount of residue remains from the decomposition process, or if any residue is suspected to contain a significant amount of copper, examine such residue separately for mass fraction of copper 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 is then combined with the result obtained for copper in the main test solution.

7.4.2 Treatment of the solution

If the mass fraction of copper is greater than 0,2 % (or 0,1 % in the case of instruments having 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), dilute to volume with water and mix. (This is the diluted test solution.) (See the last paragraph of this subclause.) If the mass fraction of copper is less than 0,2 % (or 0,1 % in the case of instruments having high sensitivity), the absorption measurement of the main solution is carried out without dilution.

If 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 volume with water and mix.

For instruments having high sensitivity, this dilution may need to be made if the mass fraction of copper is between 0,1 % and 0,2 %. If the mass fraction of copper is between 0,5 % and 1 % with instruments of high sensitivity, the value for x should not be less than 10 ml.

7.4.3 Preparation of the set of calibration solutions

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

Transfer 1,0 ml, 3,0 ml, 5,0 ml, 7,0 ml 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 volume 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 volume with water and mix.

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 having high sensitivity, the calibration series can be prepared using only standard solution B with increases, as necessary, in the volumes taken.

7.4.4 Adjustment of atomic absorption spectrometer

Set the wavelength for copper (324,7 nm) to obtain minimum absorbance and adjust the readout to zero absorbance. Light the air-acetylene flame. After 10 min of preheating the burner, aspirate water and, if necessary, readjust the readout to zero absorbance. Aspirate the calibration solution of highest copper concentration (7.4.3) 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 concentration to establish that the absorbance reading is not drifting, and set the reading for water to zero absorbance.

7.4.5 Atomic absorption measurements

Aspirate the calibration solutions and the test or diluted test solution in 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.

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.

8 Expression of results

8.1 Calculation of mass fraction of copper

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

$$w_{\mathrm{Cu}} = \frac{\rho_{\mathrm{Cu}} \times 100}{m_1 \times 10\,000}$$

$$= \frac{\rho_{\mathrm{Cu}}}{m_1 \times 100} \qquad (1)$$

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 a 100 ml volume of the test solution or diluted test solution. [$m_1 = m_2 \times x/100$, where m_2 is the mass, in grams, of the test portion and x is an aliquot, in millilitres, taken in 7.4.2. When no dilution has been made, $x = 100$.]

NOTE Include the result obtained for a copper determination made on any insoluble residue (see 7.4.1).

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]

$$R_{\mathrm{d}} = 0{,}018\,7X^{0{,}5024} \qquad (2)$$

$$P = 0{,}046\,6X^{0{,}5700} \qquad (3)$$

$$\sigma_{\mathrm{d}} = 0{,}006\,6X^{0{,}5024} \qquad (4)$$

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

$$\sigma_L = 0{,}015\,6X^{0{,}5828} \qquad (5)$$

where

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

- for the within-laboratory Equations (2) and (4); the arithmetic mean of the duplicate values;
- for the between-laboratories Equations (3) and (5); the arithmetic mean of the final results (see 8.2.3) 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 (2), compare them with the independent duplicate limit (R_d), using the procedure given in Annex A, and obtain the final laboratory result μ_c (see 8.2.5).

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 same procedure as described in 8.2.2.

Compute the following quantity:

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

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 the final results.

Substitute μ_{12} for X in Equation (3) and calculate P.

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) (see the last paragraph of 7.2). Calculate the analytical result (μ_c) for the RM/CRM using the procedures in 8.1 and 8.2.1 to 8.2.3, and compare it 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 analytical result for the CRM/RM;

A_c is the certified/reference 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*.

For a CRM/RM certified by an interlaboratory test programme

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

where

$V(A_c)$ is the variance of the certified/reference value A_c (= 0 for a CRM/RM certified by only one laboratory);

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

CRMs certified by only one laboratory should be avoided, unless they are 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, is calculated to five decimal places and rounded off to the third decimal place as follows:

a) where 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) where 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) where 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

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

$$w_{\mathrm{CuO}} = 1{,}251\,8\; w_{\mathrm{Cu}}$$

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 part of ISO 5418;

d) details necessary for the identification of the sample;

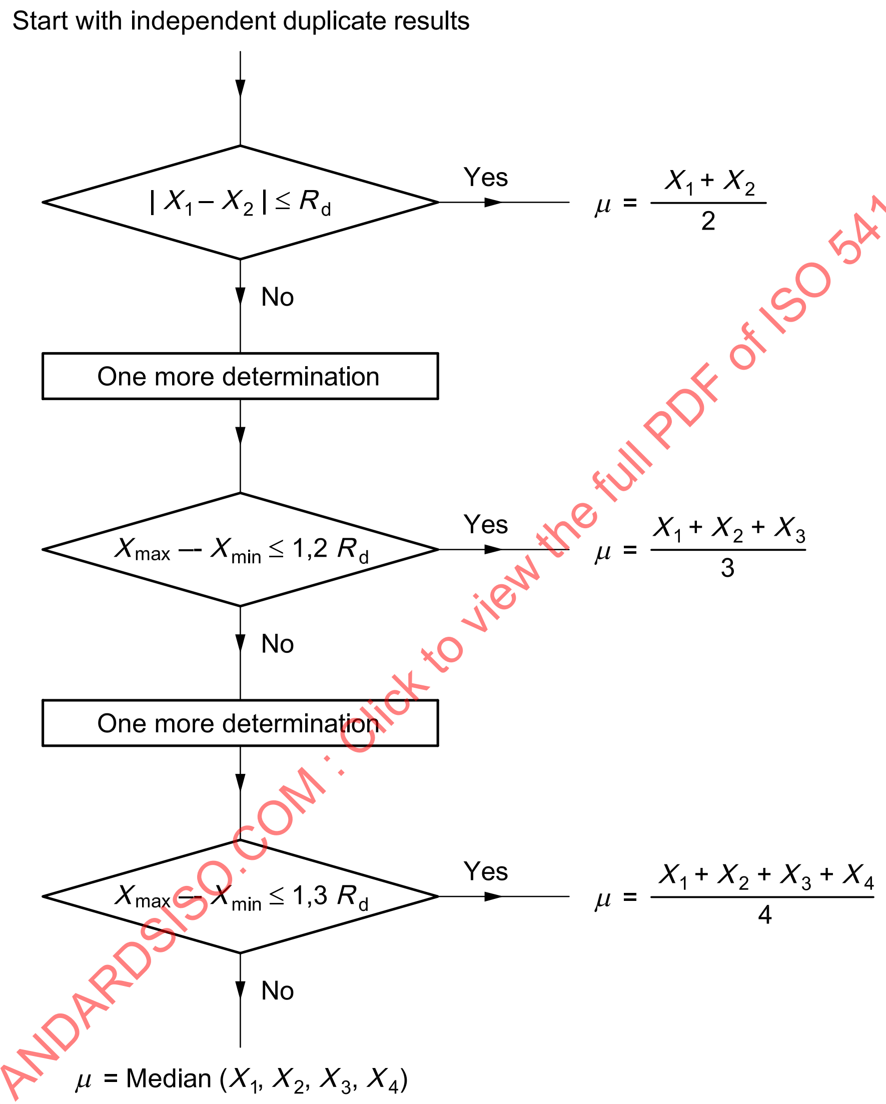
e) result of the analysis;

f) reference number of the result;

g) any characteristics noticed during the determination and any operations not specified in this part of ISO 5418 which may have had an influence on the result, either for the test sample or for 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.