INTERNATIONAL STANDARD

ISO 5418-1

First edition
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Iron ores — Determination of copper content —

Part 1:
2,2′-Biquinolyl spectrophotometric method

Minerais de fer — Dosage du cuivre —

Partie 1: Méthode spectrophotométrique à la biquinoléine-2,2′

Reference number
ISO 5418-1:1994(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 5418-1 was prepared by Technical Committee ISO/TC 102, *Iron ores*, Subcommittee SC 2, *Chemical analysis*.

This first edition cancels and replaces ISO 5418:1984, of which it constitutes a technical revision.

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

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

— *Part 2: Flame atomic absorption spectrometric method*

Annex A forms an integral part of this part of ISO 5418. Annexes B and C are for information only.

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Iron ores — Determination of copper content —

Part 1:
2,2′-Biquinolyl spectrophotometric method

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1 Scope

This part of ISO 5418 specifies a 2,2′-biquinolyl spectrophotometric method for the determination of the copper content of iron ores.

This method is applicable to copper contents between 0,004 % (*m/m*) and 0,8 % (*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 part of ISO 5418. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 5418 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 by treatment with hydrochloric, nitric and perchloric acids.

Dehydration of silica, dilution and filtration. Ignition of the residue, treatment with hydrofluoric and sulfuric acids, and fusion with sodium carbonate. Dissolution of the cooled melt in the filtrate.

Reduction of copper(II) with ascorbic acid. Addition of 2,2′-biquinolyl in the presence of *N,N*-dimethylformamide to form the red-violet complex of copper(I).

Spectrophotometric measurement of the absorbance of the coloured complex at a wavelength of approximately 545 nm.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and water that complies with grade 3 of ISO 3696.

NOTE 1 The distillation apparatus used should not contain any copper, and deionized water should not come into contact with copper tubing or taps.

4.1 Sodium carbonate (Na_2CO_3), anhydrous powder.

4.2 Iron(III) oxide, minimum purity: 99,9 % (*m/m*), copper content less than 0,000 2 % (*m/m*).

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 1 + 2.

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

4.6 Nitric acid, ρ 1,4 g/ml.

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

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

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

4.10 Hydrofluoric acid, ρ 1,13 g/ml, 40 % (*m/m*), or ρ 1,85 g/ml, 48 % (*m/m*).

4.11 Ascorbic acid ($C_6H_8O_6$), solution, 200 g/l.

Prepare this solution at the time of use.

4.12 *N,N*-Dimethylformamide [$HCON(CH_3)_2$].

WARNING — Take care not to inhale toxic fumes.

4.13 2,2′-Biquinolyl ($C_{18}H_{12}N_2$), solution.

Dissolve 0,15 g of 2,2′-biquinolyl in 250 ml of *N,N*-dimethylformamide. Protect the solution from light and store in a brown bottle.

4.14 Copper standard solutions.

4.14.1 Standard solution A, 1 000 µg Cu/ml.

Dissolve 0,500 g of copper metal [of minimum purity 99,9 % (*m/m*)] in 20 ml of dilute nitric acid (4.7) in a 250 ml tall-form beaker. After elimination of the nitrous fumes by boiling, cool, transfer to a 500 ml one-mark volumetric flask, dilute to volume with water and mix.

4.14.2 Standard solution B, 50 µg Cu/ml.

Transfer 25,0 ml of standard solution A (4.14.1) to a 500 ml one-mark volumetric flask and dilute to volume with water.

5 Apparatus

Ordinary laboratory equipment, including one-mark pipettes and one-mark volumetric flasks complying with the specifications of ISO 648 and ISO 1042 respectively (unless otherwise indicated), and

5.1 Platinum crucible, of capacity 25 ml to 30 ml.

5.2 Muffle furnace, suitable for heating at 1 000 °C.

5.3 Spectrophotometer, suitable for measurement of absorbance at approximately 545 nm.

6 Sampling and samples

6.1 General

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 2 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 °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 3 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 either case.

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7.2 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, approximately 0,5 g or 1 g of the predried test sample (see table 1) obtained in accordance with 6.2.

NOTE 4 The test portion should be taken and weighed quickly, to avoid reabsorption of moisture.

Table 1 — Measurement guide for test solution

Copper content of test sample % (*m/m*)	Mass of test portion g	Volumetric flask ml	Cell cm
0,004 to 0,05	1,0	50	5
0,05 to 0,4	0,5	100	2
0,4 to 0,8	0,5	100	1

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 5 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 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

Place the test portion (7.2) in a 250 ml tall-form beaker, and moisten with 5 ml of water. Add 20 ml of hydrochloric acid (4.3), cover the beaker with a watch glass, and heat the solution gently without boiling until decomposition of the test portion is complete. Add 5 ml of nitric acid (4.6), followed by 10 ml of perchloric acid (4.8) and 0,2 ml of sulfuric acid (4.9). Cover the beaker with a watch glass, and heat until perchloric acid fumes are evolved. Continue heating for a further 3 min to 5 min.

Allow the beaker to cool and add 20 ml of hydrochloric acid (4.4). Boil for 1 min to remove chlorine, and dilute with 10 ml of water.

Filter the solution through a medium-texture filter paper, collecting the filtrate in a 300 ml beaker. Wash the paper with hydrochloric acid (4.5), using as small a volume as possible, until the yellow colour due to iron(III) can no longer be detected. Finally, wash with hot water until the washings are free from acid. Reserve the filtrate and washings as the main solution. Transfer the filter paper containing the residue to a platinum crucible (5.1).

7.4.2 Treatment of the residue

Dry and burn off the filter paper at a low temperature, and ignite the residue at about 800 °C in a muffle furnace (5.2). Allow the crucible to cool, moisten the residue with a few drops of water, and add 5 drops of sulfuric acid (4.9) and 5 ml of hydrofluoric acid (4.10).

Heat gently in a fume cupboard to volatilize silica as the tetrafluoride, and evaporate the sulfuric acid to dryness. Finally, heat the crucible at a high temperature for several seconds to ensure complete removal of sulfuric acid. Allow to cool and add 1 g of sodium carbonate (4.1). Heat gently for several minutes, then heat at between 900 °C and 1 000 °C until decomposition of the residue is complete.

NOTE 6 With a large amount of residue, additional sodium carbonate may be required. If so, the amount of sodium carbonate added in 7.5 will have to be increased correspondingly.

Allow the crucible to cool and transfer it to the beaker containing the main solution from 7.4.1, heating gently to dissolve the melt. Remove the crucible and rinse with water. Evaporate the solution as necessary and cool to room temperature. Transfer to a 50 ml or 100 ml one-mark volumetric flask, as indicated in table 1, dilute to volume with water and mix. (This is the test solution.)

7.4.3 Treatment of the test solution

Transfer 10,0 ml aliquots of the solution from 7.4.2 to two 50 ml one-mark volumetric flasks. Add the following reagents, mixing well after each addition:

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— for the test solution, 5 ml of ascorbic acid solution (4.11) and 25 ml of 2,2′-biquinolyl solution (4.13);

— for the reference solution, 5 ml of ascorbic acid solution (4.11) and 25 ml of *N*,*N*-dimethylformamide (4.12).

Similarly, transfer 10 ml aliquots of the blank test solution to two 50 ml one-mark volumetric flasks. Add the following reagents, mixing well after each addition:

— for the blank test solution, 5 ml of ascorbic acid solution (4.11) and 25 ml of 2,2′-biquinolyl solution (4.13);

— for the blank reference solution, 5 ml of ascorbic solution (4.11) and 25 ml of *N*,*N*-dimethylformamide (4.12).

Dilute each solution to volume with water, mix and stand the flasks in a water bath at approximately 20 °C for 5 min. Adjust to volume, if necessary, mix, allow to stand for 10 min and measure.

7.4.4 Spectrophotometric measurement

Using cells of suitable optical pathlength (see table 1), measure the absorbance of the test solution against the reference solution. The wavelength of maximum absorption is approximately 545 nm.

Similarly, measure the absorbance of the blank test solution against the blank reference solution under the same conditions.

Correct the absorbance value of the test solution with the absorbance value obtained for the blank test solution.

7.5 Preparation of the calibration curve

Weigh 0,5 g or 1,0 g portions of iron(III) oxide (4.2) according to table 2, transfer to 250 ml tall-form beakers, and dissolve in 20 ml of hydrochloric acid (4.3).

Add increments of copper standard solution A (4.14.1) or B (4.14.2) according to table 2.

Add 5 ml of nitric acid (4.6), 0,2 ml of sulfuric acid (4.9) and 10 ml of perchloric acid (4.8) to each beaker. Heat until perchloric acid fumes are evolved and continue heating for 3 min to 5 min.

Allow to cool and add 20 ml of hydrochloric acid (4.4). Carefully add 1 g of sodium carbonate (4.1), boil for 1 min to remove chlorine and carbon dioxide, and cool to room temperature.

Transfer solutions Nos. 1 to 4 to four 50 ml one-mark volumetric flasks, and solutions Nos. 5 to 11 to seven 100 ml one-mark volumetric flasks. Dilute to volume with water and mix.

Continue as indicated in 7.4.3 and 7.4.4. Plot the relationship between the mass of copper and absorbance.

NOTE 7 Calibration solution No. 1 (whitout addition of copper) is used as a blank solution for copper contents between 0,004 % (*m/m*) and 0,05 % (*m/m*), and calibration solution No. 5 (without addition of copper) is used for copper contents between 0,05 % (*m/m*) and 0,8 % (*m/m*).

The ranges of copper contents relate to a mass of test portion of either 1 g or 0,5 g under the conditions given in table 1.

Table 2 — Calibration solutions

Solution No.	Mass of iron(III) oxide g	Volume of copper standard solution ml		Cu mg	Cu %
		A	B		
1	1,0	0	0	0	0
2	1,0		1,0	0,05	0,005
3	1,0		5,0	0,25	0,025
4	1,0		10,0	0,50	0,050
5	0,5		0	0	0
6	0,5		5,0	0,25	0,05
7	0,5		10,0	0,50	0,10
8	0,5		20,0	1,00	0,20
9	0,5	2,0		2,00	0,40
10	0,5	3,0		3,00	0,60
11	0,5	4,0		4,00	0,80

8 Expression of results

8.1 Calculation of copper content

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

$$w_{Cu} = \frac{m_1 f}{100 m_0 V} \quad \ldots (1)$$

where

m_0 is the mass, in grams, of the test portion;

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m_1 is the mass of copper, in micrograms, contained in the aliquot taken in 7.4.3 and determined from the calibration graph;

f is the dilution factor ($f = 0,5$ if a 1 g test portion is used, otherwise $f = 1$);

V is the volume of aliquot taken in 7.4.3, in millilitres.

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]:

$$\sigma_d = 0,009\ 7\ X + 0,000\ 9 \quad \ldots (2)$$

$$\sigma_L = 0,014\ 9\ X + 0,001\ 3 \quad \ldots (3)$$

$$R_d = 0,027\ 4\ X + 0,002\ 6 \quad \ldots (4)$$

$$P = 0,046\ 5\ X + 0,004\ 2 \quad \ldots (5)$$

where

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;

X is the copper content, expressed as a percentage by mass, 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.

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 described in annex A.

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

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 quantities:

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

$$P = 0,046\ 5\ \mu_{12} + 0,004\ 2 \quad \ldots (7)$$

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 $|\mu_1 - \mu_2| \leqslant P$, 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 in 8.2.3. 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 8 Certified reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35: 1988, *Certification of reference materials — General and statistical principles.*

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For a CRM certified by an interlaboratory test programme:

$$\sigma_d = 0{,}009\ 7\ \mu_c + 0{,}000\ 9 \quad \ldots (8)$$

$$\sigma_L = 0{,}014\ 9\ \mu_c + 0{,}001\ 3 \quad \ldots (9)$$

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

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 9 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) 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 where 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 is given by the following equation:

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

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 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, for either the test sample or the certified reference material(s).

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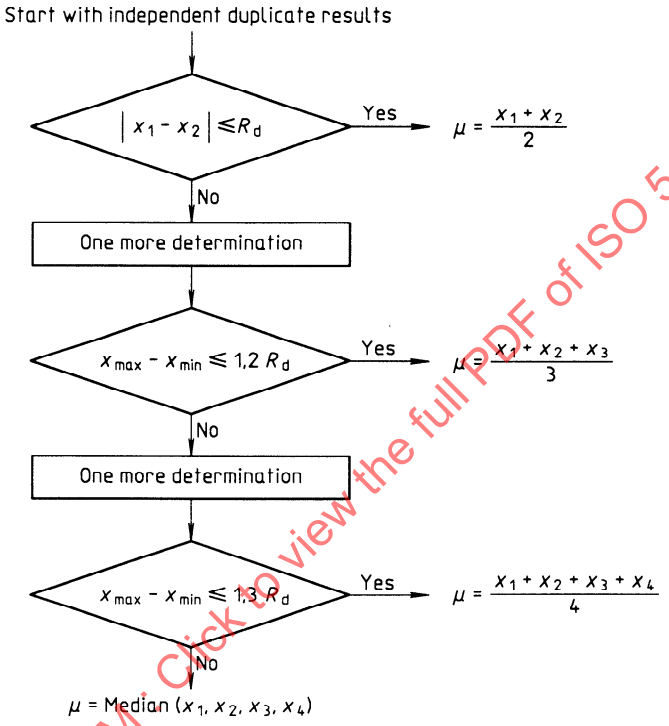
Annex A
(normative)

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



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