

International Standard



5418

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Iron ores — Determination of copper content — 2,2'-Biquinolyl spectrophotometric method

Minerais de fer — Dosage du cuivre — Méthode spectrophotométrique à la biquinoléine-2,2'

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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 developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been authorized 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.

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.

International Standard ISO 5418 was developed by Technical Committee ISO/TC 102, *Iron ores*, and was circulated to the member bodies in November 1981.

It has been approved by the member bodies of the following countries :

Australia	Germany, F.R.	Romania
Austria	India	South Africa, Rep. of
Brazil	Italy	Spain
Canada	Japan	Sweden
China	Korea, Dem. P. Rep. of	Thailand
Czechoslovakia	Mexico	United Kingdom
Egypt, Arab Rep. of	Netherlands	USA
France	New Zealand	Venezuela

No member body expressed disapproval of the document.

Iron ores — Determination of copper content — 2,2'-Biquinolyl spectrophotometric method

1 Scope and field of application

This International Standard specifies a 2,2'-biquinolyl spectrophotometric method for the determination of copper in iron ores.

This method is applicable to a concentration range of 0,004 to 0,8 % (m/m) of copper in natural iron ores, and iron ore concentrates and agglomerates including sinter products.

2 References

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.*¹⁾

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 about 545 nm.

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.

1) At present at the stage of draft.

4.1 Sodium carbonate (Na_2CO_3), anhydrous.

4.2 Iron(III) oxide.

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

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

4.5 Hydrochloric acid, ρ 1,16 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, 60 % (m/m), ρ 1,54 g/ml, or 70 % (m/m), ρ 1,67 g/ml.

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

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

4.11 Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), 200 g/l solution.

Prepare this solution at the time of use.

4.12 *N,N*-Dimethylformamide [$\text{HCON}(\text{CH}_3)_2$].

Take care not to inhale toxic fumes.

4.13 2,2'-Biquinolyl ($\text{C}_{18}\text{H}_{12}\text{N}_2$) 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

Dissolve 0,500 g of copper metal (99,9 %) in 20 ml of the nitric acid solution (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 the mark with water and mix.

1 ml of this solution contains 1,00 mg of Cu.

4.14.2 Standard solution B

Take 25,0 ml of standard solution A (4.14.1) and dilute to the mark in a 500 ml one-mark volumetric flask.

1 ml of this solution contains 0,05 mg of Cu.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Spectrophotometer, suitable for measurement of absorbance in the region of 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 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 $105 \pm 2^\circ\text{C}$ as specified in ISO 7764. (This is the predried test sample.)

7 Procedure

7.1 Number of determinations

Carry out the analysis generally in duplicate, independently, on one predried test sample.

NOTE — The expression "independently" implies that the repetition of the procedure shall be carried out at a different time and include 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.

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.

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.

7.3 Test portion

Weigh, to the nearest 0,000 2 g, approximately 0,5 or 1 g of the test sample (see table 1 in 7.4.4), obtained in accordance with 6.2.

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

7.4 Determination

7.4.1 Decomposition of the test portion

Place the test portion (7.3) in a 250 ml beaker (tall form) and moisten with 5 ml of water. Add 20 ml of the 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 the nitric acid (4.6) followed by 10 ml of the perchloric acid (4.8) and 0,2 ml of the sulfuric acid (4.9), cover the beaker with a watch glass and heat until perchloric acid fumes are evolved. Continue the heating for a further 3 to 5 min.

Allow the beaker to cool and add 20 ml of the hydrochloric acid solution (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 the hydrochloric acid solution (4.5) (use 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.

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. Allow the crucible to cool, moisten the residue with a few drops of water, and add 5 drops of the sulfuric acid solution (4.9) and 5 ml of the 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 the sodium carbonate (4.1). Heat gently for several minutes, then at 900 to $1\,000^\circ\text{C}$ until decomposition of the residue is complete.

NOTE — With a large amount of residue, additional sodium carbonate may be required. If so, the amount of sodium carbonate taken in 7.5 must 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 7.4.4 (table 1), dilute to the mark with water and mix (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 :

Test solution : 5 ml of the ascorbic acid solution (4.11);
25 ml of the 2,2'-biquinolyl solution (4.13).

Reference solution: 5 ml of the ascorbic acid solution (4.11);
25 ml of the *N,N*-dimethylformamide (4.12).

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

Blank test solution : 5 ml of the ascorbic acid solution (4.11); 25 ml of the 2,2'-biquinolyl solution (4.13).

Blank reference solution : 5 ml of the ascorbic acid solution (4.11); 25 ml of the *N,N*-dimethylformamide (4.12).

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

7.4.4 Spectrophotometric measurement

Using cuvettes 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 to obtain the value to be used in 8.1.

Table 1 — Measurement guide for the test solution

Copper content of test sample (%) Cu	Mass of test portion g	Volumetric flask ml	Cuvette 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

7.5 Preparation of calibration curve

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

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

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

Allow to cool and add 20 ml of the hydrochloric acid (4.4). Add carefully 1 g of the 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 50 ml one-mark volumetric flasks, and solutions Nos. 5 to 11 into 100 ml one-mark volumetric flasks. Dilute to the mark with water and mix.

Continue as indicated in 7.4.3 and 7.4.4. Plot the relationship between quantity of copper and absorbance to calculate the slope factor (*Z*).

NOTE — Calibration solution No. 1 (without addition of copper) is used as a blank solution for the range of 0,004 to 0,05 % (*m/m*) of copper, while calibration solution No. 5 (without addition of copper) is used for the range of 0,05 to 0,8 % (*m/m*) of copper.

The ranges of copper content 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 solution

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, as a percentage by mass, is given by the formula

$$w_{\text{Cu}} (\%) = \frac{E \times Z}{m \times 10}$$

where

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

E is the absorbance of the test solution measured against the reference solution, corrected by the blank value and reduced to an optical pathlength of 1 cm;

Z is the slope factor of the calibration curve in either

$$\frac{\text{mg Cu in 100 ml}}{\text{absorbance/cm}} \quad \text{or} \quad \frac{\text{mg Cu in 50 ml}}{\text{absorbance/cm}}$$

8.2 General treatment of results

8.2.1 Repeatability and reproducibility

The precision of this analytical method is expressed by the following regression formulae:¹⁾

$$r = 0,027 4 X + 0,002 6$$

$$P = 0,046 5 X + 0,004 2$$

$$\sigma_r = 0,009 7 X + 0,000 9$$

$$\sigma_L = 0,014 9 X + 0,001 3$$

where

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

P is the permissible tolerance between laboratories (reproducibility);

σ_r is the within laboratory standard deviation;

σ_L is the between laboratories standard deviation;

X is the copper content, expressed as a percentage by mass, of the test sample :

— within-laboratory equations — the arithmetic mean of the duplicate values;

— between-laboratory equations — the arithmetic mean of the final results (8.2.3) of the two laboratories.

8.2.2 Acceptance of analytical values

The result obtained for the reference material shall be such that the difference between this result and the certificate 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 formula may be used to test the significance of the difference:

$$|A_c - A| < 2 \sqrt{\frac{S_{Lc}^2 + \frac{S_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_r^2}{n}}$$

where

A_c is the certificate value;

A is the result or the mean of results obtained for the 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 the left-hand side of the formula 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 values for the test sample is outside the limit calculated according to the equation for r in 8.2.1, an analysis shall be carried out in accordance with the flowsheet presented in annex A, simultaneously with an analysis of a certified reference material of the sample 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 shall be used when the information on the reference material certificate is incomplete:

- 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;
- if the certification has been made by only one laboratory or if the interlaboratory results are missing, use the formula

$$|A_c - A| < 2 \sqrt{2 \sigma_L^2 + \frac{\sigma_r^2}{n}}$$

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

8.2.3 Calculation of final result

The final result is the arithmetic mean of the acceptable analytical values for the test sample 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 no figure other than 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

$$w_{\text{CuO}} (\%) = 1,2518 w_{\text{Cu}} (\%)$$

9 Test report

The test report shall include the following information :

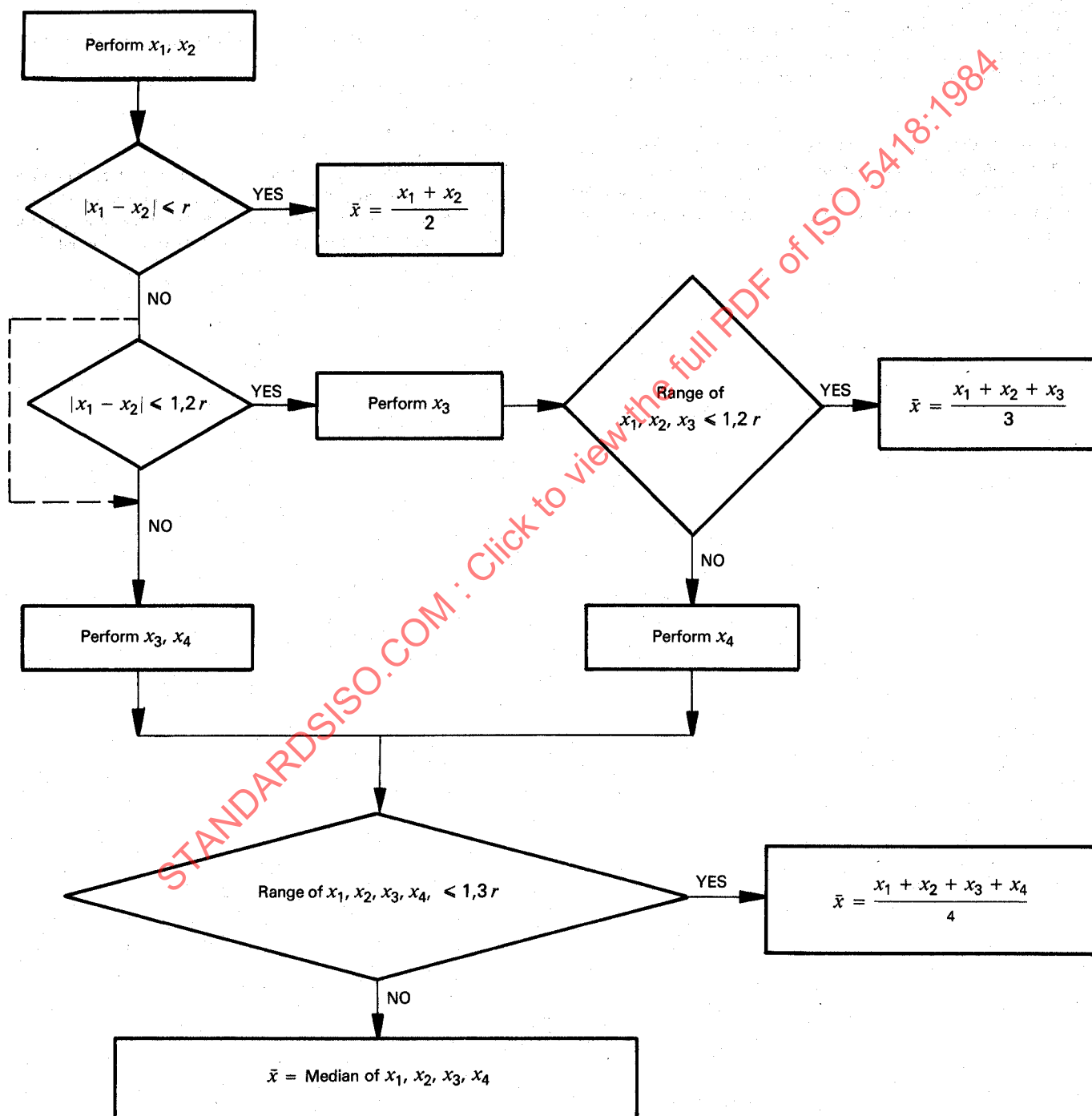
- a) reference to this International Standard;
- b) details necessary for the identification of the sample;
- c) result of the analysis;
- d) reference number of the result;
- e) any characteristics noticed during the determination, and any operations not specified in this International Standard which may have had an influence on the result, either for the test sample or the certified reference material(s).

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Annex A

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

(An integral part of the Standard.)

 r as defined in 8.2.1.

Annex B

Derivation of repeatability and permissible tolerance equations

(Information only — not in an integral part of the Standard.)

The regression formulae in 8.2.1 have been derived from the results of international analytical trials carried out in 1972/1973 on 5 iron ore samples, involving 37 laboratories in 8 countries. The results of the trials were reported in document ISO/TC 102/SC 2 N 313E, October 1973.

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

The test samples used were:

Sample	Cu content [% (m/m)]
Malmberget concentrate	0,002
Kiruna R	0,012
Roasting residue	0,067
Russian pyrite ashes	0,37
Forsbo	0,77

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