INTERNATIONAL STANDARD

ISO 5418-1

Second edition
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Iron ores — Determination of copper —

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 5418-1:2006(E)

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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 5418-1 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 5418-1:1994), 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 1:
2,2′-Biquinolyl spectrophotometric 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 2,2′-biquinolyl spectrophotometric method for the determination of copper in iron ores.

This method is applicable to mass fractions of copper between 0,005 % and 0,77 % 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 — 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

The test portion is decomposed by treatment with hydrochloric, nitric and perchloric acids.

Silica is dehydrated and the solution is diluted and filtered. The residue is ignited, treated with hydrofluoric and sulfuric acids, and fused with sodium carbonate. The cooled melt is dissolved in the filtrate.

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

The absorbance of the coloured complex is measured spectrophotometrically 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.

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 % (mass fraction), mass fraction of copper less than 0,000 2 %.

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, 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 1,185 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°% (mass fraction)] 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 the following.

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 an absorbance of 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 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 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 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.

7.2 Test portion

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

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

Table 1 — Measurement guide for test solution

Mass fraction of copper in test sample %	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.

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 at between 900 °C and 1 000 °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 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:

- 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 acid 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 calibration curve

Weigh 0,5 g or 1,0 g portions of iron(III) oxide (4.2) in accordance with 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) in accordance with 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 solution 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 Calibration solution No. 1 (without addition of copper) is used as a blank solution for mass fractions of copper between 0,004 % and 0,05 %, and calibration solution No. 5 (without addition of copper) is used for mass fractions of copper between 0,05 % and 0,8 %.

The ranges of mass fractions of copper 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 A	ml B	**Cu** mg	**Cu** %
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 mass fraction of copper

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

$$w_{\mathrm{Cu}} = \frac{m_1 f}{100 m_0 V} \tag{1}$$

where

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

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]:

$$\sigma_d = 0{,}009\,5X^{05779} \qquad (2)$$

$$\sigma_L = 0{,}013\,3X^{0{,}5201} \qquad (3)$$

$$R_d = 0{,}026\,8X^{0{,}5779} \qquad (4)$$

$$P = 0{,}042\,5X^{0{,}5305} \qquad (5)$$

where

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;

X is the mass fraction of copper, 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 (see 8.2.3) of the two laboratories.

8.2.2 Determination of analytical result

Having computed the independent duplicate results in accordance with 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 same procedure as described in 8.2.2.

Compute the following quantities:

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

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

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

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 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 CRM/RM;

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.*

For a CRM/RM certified by an interlaboratory test programme

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

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, 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, 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;

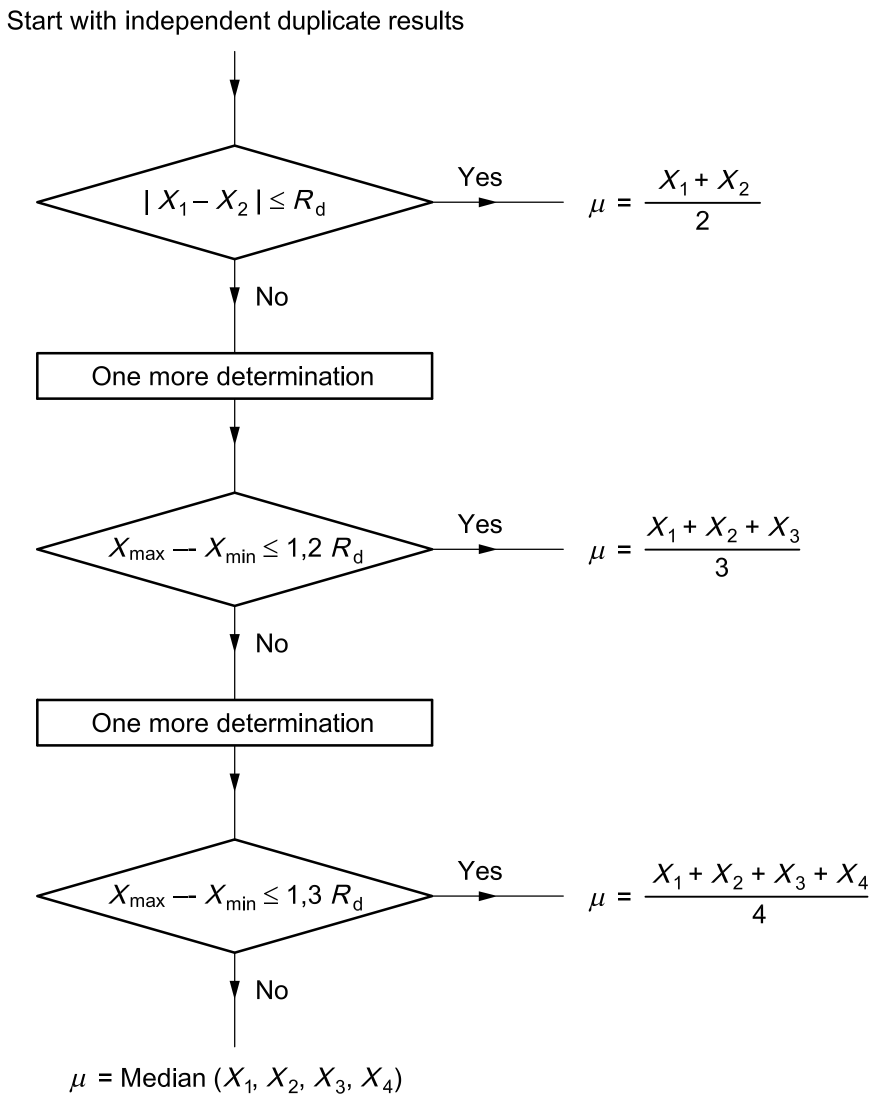
e) result of the analysis;

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, 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.

Annex B
(informative)

Derivation of repeatability and permissible tolerance equations

The equations in 8.2.1 were derived from the results of international analytical trials carried out in 1972 and 1973 on five ore samples, involving 37 laboratories in eight countries.

The graphical treatment of the precision data is given in Annex C.

The test samples used are listed in Table B.1.

Table B.1 — Mass fractions of copper in test samples

Sample	Mass fraction of copper %
Malmberget concentrate	0,001 2
Kiruna R	0,011 5
Roasting residue	0,067 7
Russian pyrite ashes	0,376
Forsbo	0,772

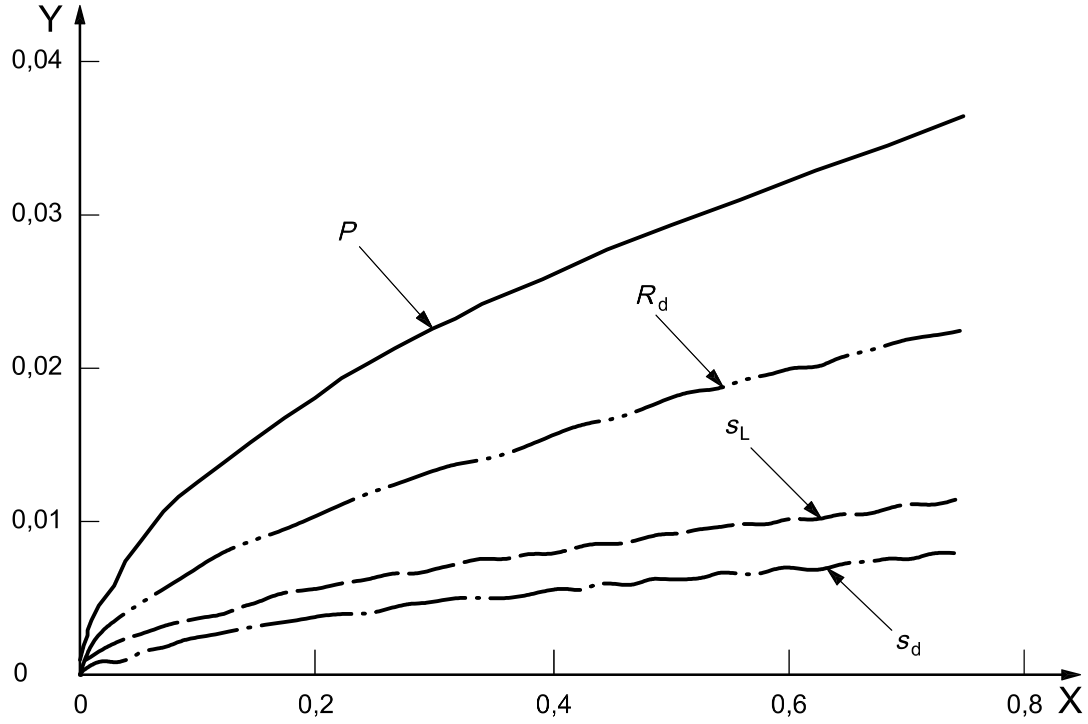
NOTE 1 A report of the international trials and a statistical analysis of the results (Document ISO/TC 102/SC 2 N313 E, October 1973) are available from the Secretariat of ISO/TC 102/SC 2.

NOTE 2 The statistical analysis was performed in accordance with the principles embodied in ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*.

Annex C
(informative)

Precision data obtained by international analytical trials

NOTE Figure C.1 is a graphical presentation of the equations in 8.2.1.



Key

X Mass fraction of copper, %

Y Precision, %

Figure C.1 — Least-squares fit of precision against X for copper

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