INTERNATIONAL STANDARD

ISO 5416

Third edition
2006-04-01

Direct reduced iron — Determination of metallic iron — Bromine-methanol titrimetric method

Minerais de fer préréduits — Dosage du fer métallique — Méthode titrimétrique au brome-méthanol

Reference number
ISO 5416:2006(E)

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Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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 5416 was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This third edition cancels and replaces the second edition (ISO 5416:1997), which has been technically revised. It has been updated to alter the manner in which precision data are presented.

Direct reduced iron — Determination of metallic iron — Bromine-methanol titrimetric method

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

1 Scope

This International Standard specifies a titrimetric method for the determination of the mass fraction of metallic iron in reduced iron ores (direct reduced iron: DRI).

This method is applicable to mass fractions of metallic iron between 15 % and 95 % in DRI.

NOTE The term “metallic iron” means those forms of iron not bonded to oxygen or not present as pyrite.

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 385, *Laboratory glassware — Burettes*

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

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

ISO 2596, *Iron ores — Determination of hygroscopic moisture in analytical samples — Gravimetric, Karl Fischer and mass-loss methods*

ISO 2597-1, *Iron ores — Determination of total iron content — Part 1: Titrimetric method after tin(II) chloride reduction*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 10835, *Direct reduced iron and hot briquetted iron — Sampling and sample preparation*

3 Principle

Metallic iron is dissolved by treatment with bromine-methanol solution. The insoluble residue is separated by filtration. The iron in the filtrate is reduced to iron(II), which is titrated with potassium dichromate solution.

NOTE Other metallic elements, such as chromium, cobalt, manganese, nickel and vanadium, are also dissolved by the bromine-methanol solution but, except for vanadium, they do not interfere with the titration procedure.

4 Reagents

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

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

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

4.3 Methanol, Karl Fischer reagent grade, max. 0,1 % H_2O.

4.4 Bromine-methanol solution, 50 ml/l.

Dissolve 5 ml of bromine in 95 ml of methanol (4.3). This solution shall be freshly prepared and used immediately.

WARNING — The preparation of the bromine-methanol solution, and all stages of the procedure where bromine is present, shall be carried out in an efficient fume cupboard.

4.5 Hydrogen peroxide solution, 30 % (V/V).

4.6 Tin(II) chloride solution, 100 g/l.

Dissolve 119 g of tin(II) chloride dihydrate ($SnC1_2 \cdot 2H_2O$), successively in small amounts, with 200 ml of hydrochloric acid (4.1) by warming. Cool, dilute to 1 litre and mix. Add 2 g of coarsely granulated tin and store the solution in a brown bottle.

4.7 Mercury(II) chloride solution, 50 g/l.

Dissolve 50 g of mercury(II) chloride ($HgCl_2$) in 800 ml of hot water. Cool, dilute to 1 litre and mix.

4.8 Sulfuric acid/phosphoric acid mixture.

Add cautiously, while stirring, 150 ml of sulfuric acid (ρ 1,84 g/ml) and 150 ml of phosphoric acid (ρ 1,7 g/ml) to 600 ml of water. Cool, dilute to 1 litre and mix.

4.9 Iron standard solution.

Dissolve 0,800 g of high purity iron(III) oxide ($Fe_2O_3 > 99$ %) in 40 ml of hydrochloric acid (4.1). Dilute to 1 000 ml and mix.

1 ml of this solution contains 0,558 mg of iron.

If the purity of the iron(III) oxide is unknown, the solution should be standardized using a 100 ml aliquot evaporated to a low volume.

4.10 Potassium dichromate, standard volumetric solution, $c(K_2Cr_2O_7) = 0{,}016\ 67$ mol/l.

Pulverize about 6 g of potassium dichromate in an agate mortar, dry at 140 °C to 150 °C for 2 h, then cool to room temperature in a desiccator.

Weigh 4,903 g of the dried material, dissolve in water and transfer to a 1 000 ml volumetric flask. Dilute to volume with water and mix.

4.11 Sodium diphenylamine sulfonate, 2 g/l solution.

Dissolve 0,2 g of sodium diphenylamine sulfonate ($C_6H_5NHC_6H_4SO_3Na$) in 100 ml of water. Store the solution in a brown glass bottle.

5 Apparatus

Ordinary laboratory apparatus, including one-mark pipettes and one-mark volumetric flasks complying with the specifications of ISO 648 and ISO 1042 respectively, and the following

5.1 Burette, complying with the specifications of ISO 385.

5.2 Conical flask, of capacity 100 ml, diameter 50 mm to 60 mm, without concave base, for dissolving the sample. A watch-glass or reflux condenser is required if working outside a fume cupboard.

5.3 Magnetic stirrer (rotational frequency 200 min^{-1} to 400 min^{-1}), magnetic stirring bar without pivot ring, polytetrafluoroethylene (PTFE) coated; diameter 5 mm, length 40 mm.

5.4 Filtering apparatus, with glass-fibre filters or plastics micro-filters 1), in either case with a pore size of less than 1 µm.

6 Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of minus 160 µm particle size which has been taken and prepared in accordance with ISO 10835.

6.2 Preparation of test samples

Thoroughly mix the laboratory sample using non-magnetic materials. Taking multiple increments with a non-magnetic spatula, extract a test sample of not less than 25 g in such a manner that it is representative of the whole contents of the container. Prepare an air-equilibrated test sample in accordance with ISO 2596.

7 Procedure

7.1 Number of determinations

Carry out the analysis at least in duplicate in accordance with Annex A, independently, on one air-equilibrated 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 Test portion

Taking several increments using a non-magnetic spatula, weigh, to the nearest 0,000 2 g, approximately 0,50 g of the air-equilibrated test sample (6.2).

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 DRI shall be carried out in parallel with the analysis of the sample(s) under the same conditions. A test sample of the certified reference material shall be prepared as specified in 6.2.

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1) PVC filters or PVF filters.

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.

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 DRI at the same time, the analytical value of one certified reference material may be used.

7.4 Determination of hygroscopic moisture content

Determine the hygroscopic moisture content in accordance with ISO 2596, simultaneously with the taking of the test portion (7.2) for the determination of the mass fraction of metallic iron.

7.5 Determination

7.5.1 Dissolution of metallic iron

Place the test portion (7.2) in a thoroughly dry 100 ml conical flask (5.2), add 50 ml of bromine-methanol solution (4.4), cover with a watch-glass, or fit a reflux condenser, and stir continuously with the magnetic stirrer for 30 min (see the next paragraph) at a temperature of 20 °C. Filter immediately through a glass-fibre filter or plastics microfilter (5.4) under suction and collect the filtrate in a suction filter flask. Wash the filter with methanol (4.3) (e.g. six times with 5 ml portions) until the washings are colourless (free from bromine), then wash a further three times with water to remove the methanol. Transfer the solution to a 600 ml beaker, washing with water.

A dissolution time of 30 min is usually adequate. To ensure complete dissolution, two different dissolution times should be used. If 30 min has been taken for the first test portion, the replicate test portion should be digested for twice this time, i.e. 60 min. This procedure should be repeated, increasing the digestion time until agreement is reached between replicate determinations.

7.5.2 Determination of metallic iron

Add 20 ml of sulfuric acid (4.2) to the total filtrate, heat the solution cautiously until fumes of sulfuric acid appear, then continue the heating until strong fuming takes place. Remove from the hotplate, cool and add 10 ml of hydrogen peroxide solution (4.5). Evaporate until sulfuric acid fumes again evolve. Cool and repeat the oxidation with hydrogen peroxide (bromides and methanol are to be completely removed). Add some water, rinsing the walls of the beaker, and heat again until fuming takes place. Cool, carefully add about 140 ml of water and 25 ml of hydrochloric acid (4.1) and boil until all salts are redissolved.

For mass fractions of metallic irons greater than 50 %, cool the solution, transfer quantitatively to a 200 ml volumetric flask, dilute to volume and mix. Measure a 100,0 ml aliquot into a 600 ml beaker, add 10 ml of hydrochloric acid (4.1) and proceed from the addition of tin(II) chloride.

Add tin(II) chloride solution (4.6) to the boiling solution, drop by drop while stirring, until the solution is just colourless, then add 2 drops in excess. Rinse the walls of the beaker and cool quickly, dilute with water to 300 ml and add 15 ml of mercury(II) chloride solution (4.7). Wait for about 5 min until slight turbidity appears, add 25 ml of sulfuric acid/phosphoric acid mixture (4.8) and 1,0 ml of sodium diphenylamine sulfonate solution (4.11), and titrate with potassium dichromate solution (4.10) until one drop produces a change in colour from green to purple.

7.5.3 Blank test

Determine the blank test value in the same manner, using all reagents but adding 10 ml of standard iron solution (4.9) in place of the test portion. Add the standard iron solution after the addition of the 25 ml of hydrochloric acid (end of paragraph 1 in 7.5.2). Then continue as described in the third paragraph of 7.5.2.

Subtract 1,00 ml from the volume of potassium dichromate solution required for the titration of the blank test solution (0,50 ml in the case of an aliquot of test solution being used). The result is the blank test value to be subtracted from the titration value obtained in 7.5.2 (see 8.1) for the test portion.

8 Expression of results

8.1 Calculation of mass fraction of metallic iron

The mass fraction of metallic iron w_{MFe}, expressed as a percentage, is calculated to three decimal places using the equation

$$w_{\mathrm{MFe}} = \frac{(V - V_0) \times 0{,}558\,5 \times F}{m} \times \frac{100}{100 - A} \qquad (1)$$

where

V is the volume, in millilitres, of potassium dichromate solution required for the sample analysis;

V_0 is the corrected volume, in millilitres, of potassium dichromate solution required for the determination of the blank test value;

m is the mass, in grams, of the air-equilibrated test portion;

F is the dilution factor, if applicable (see second paragraph of 7.5.2);

A is the hygroscopic moisture content, expressed as a percentage by mass, of the air-equilibrated test sample determined in accordance with ISO 2596;

0,558 5 is a multiple of the atomic mass of iron.

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: [2)]

$$R_{\mathrm{d}} = 0{,}495 \qquad (2)$$

$$P = 0{,}006\,7\,X + 0{,}925\,1 \qquad (3)$$

$$\sigma_{\mathrm{d}} = 0{,}175 \qquad (4)$$

$$\sigma_{\mathrm{L}} = 0{,}002\,4\,X + 0{,}308\,0 \qquad (5)$$

where

X is the mass fraction of metallic iron, expressed as a percentage, of the 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 (8.2.5) of the two laboratories;

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2) Additional information is given in Annexes B and C.

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 (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 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 final results.

If $|\mu_1 - \mu_2| \leqslant P$ (see 8.2.1), 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 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.

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 certified by an interlaboratory test programme

$$C = 2\left[\sigma_{\mathrm{L}}^{2} + \frac{\sigma_{\mathrm{d}}^{2}}{n} + V(A_{\mathrm{c}})\right]^{1/2}$$

where

$V(A_{\mathrm{c}})$ is the variance of the certified value A_{c}.(= 0 for a CRM certified by only one laboratory);

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

A CRM certified by only one laboratory 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 three decimal places, and rounded off to the first decimal place as follows:

a) if the figure in the second decimal place is less than 5, it is discarded and the figure in the first decimal place is kept unchanged;

b) if the figure in the second decimal place is 5 and there is a figure other than 0 in the third decimal place, or if the figure in the second decimal place is greater than 5, the figure in the first decimal place is increased by one;

c) if the figure in the second decimal place is 5 and the Figure 0 is in the third decimal place, the 5 is discarded and the figure in the first 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.

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 International Standard;

d) details necessary for the identification of the sample;

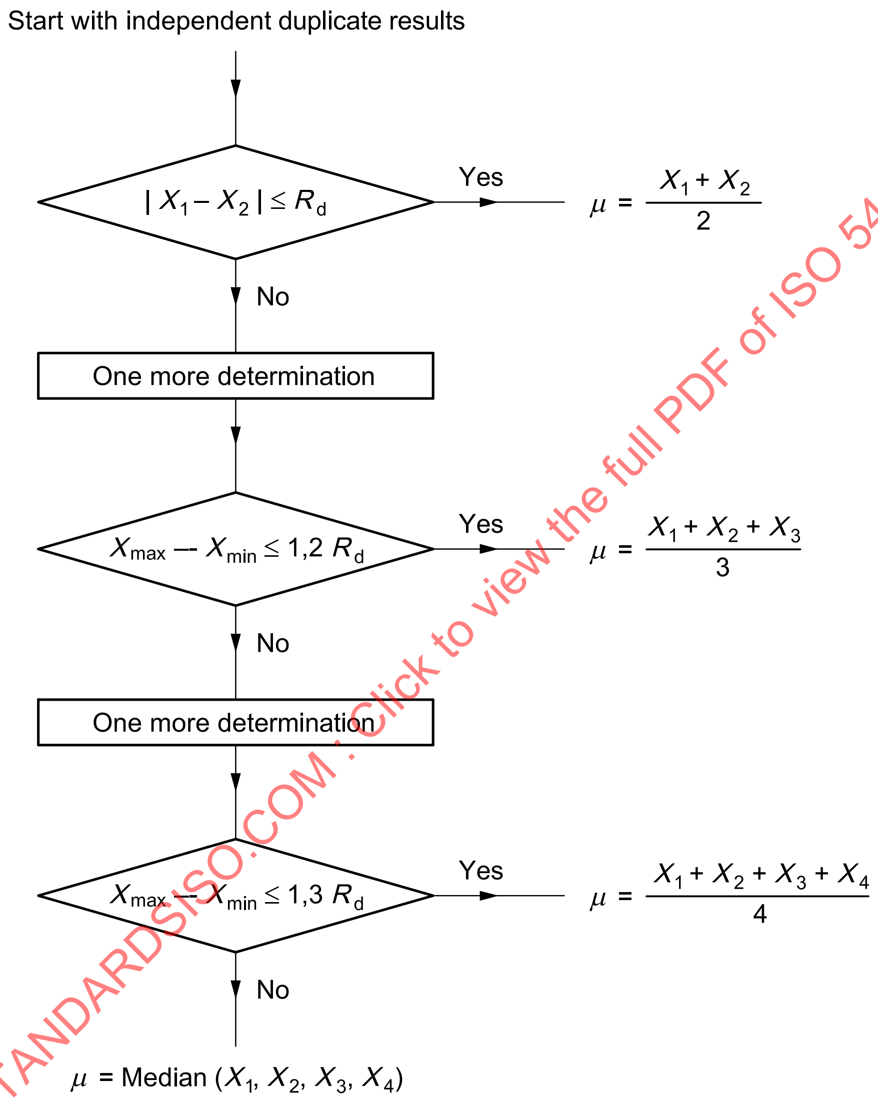
e) result of the analysis;

f) reference number of the result;

g) any characteristics noticed during the determination, and any operations not specified in this International Standard, 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 is as defined in 8.2.1.

Annex B
(informative)

Derivation of repeatability and permissible tolerance equations

The regression equations in 8.2.1 were obtained by statistical evaluation of the results of international analytical trials carried out in 1976 and 1977 on six samples of DRI, involving 40 laboratories in 12 countries.

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

The samples used are listed in Table B.1.

Table B.1 — Mass fractions of metallic iron of test samples

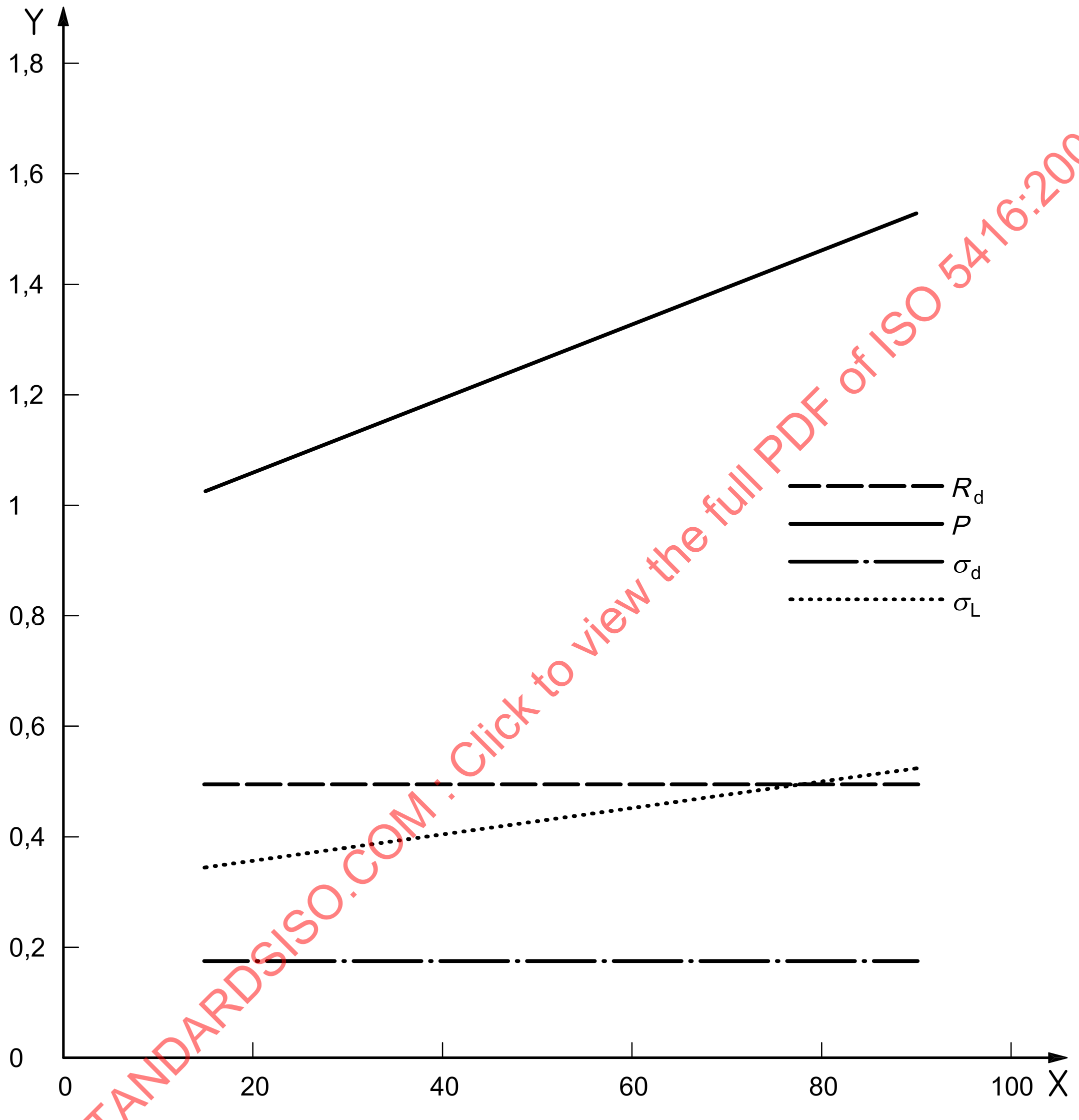
Sample	Country	Mass fractions of metallic iron %
76-25	New Zealand	15,1
76-26	Sweden	30,3
76-27	Brazil	71,0
76-28	Germany	86,8
76-29	U.S.A.	76,1
76-30	Canada	89,1

NOTE 1 A report of the international trials and a statistical analysis of the results (Document ISO/TC 102/SC 2 N 502E, June 1978) is available from either the Secretariat of ISO/TC 102/SC 2 or the Secretariat of ISO/TC 102.

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 metallic iron, %

Y precision, %

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