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

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

Reference number
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Foreword

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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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 5416 was prepared by Technical Committee ISO/TC 102, *Iron ores*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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

1 Scope and field of application

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

This method is applicable to a concentration range of 15 to 95 % (m/m) of metallic iron in DRI.

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

2 References

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 and Karl Fischer methods.*

ISO 2597, *Iron ores — Determination of total iron content — Titrimetric methods.*

ISO 3081, *Iron ores — Increment sampling — Manual method.*

ISO 3082, *Iron ores — Increment sampling and sample preparation — Mechanical method.*

ISO 3083, *Iron ores — Preparation of samples — Manual method.*

3 Principle

Dissolution of metallic iron by treatment with bromine-methanol solution. Separation of the insoluble residue by filtration. Reduction of the iron in the filtrate to iron(II) followed by titration 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 distilled water or water of equivalent purity.

4.1 Hydrochloric acid, ϱ 1,16 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 must 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 100 g of tin(II) chloride ($SnCl_2 \cdot 2H_2O$) 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 in 800 ml of hot water. Cool, dilute to 1 litre and mix.

4.8 Sulfuric acid-phosphoric acid mixture.

Add cautiously and with 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 litre and mix.

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

NOTE — 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 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 to 150 °C for 2 h then cool to room temperature in a desiccator.

Weigh 4,904 g of the dried material, dissolve in water and transfer to a 1 000 ml volumetric flask. Dilute to the mark with water and mix.

4.11 Sodium diphenylamine sulfonate solution, 2 g/l.

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

5 Apparatus

5.1 Ordinary laboratory apparatus.

Any pipettes and volumetric flasks required shall be one-mark pipettes and volumetric flasks complying with the specifications of ISO 648 and ISO 1042. The burette required shall comply with the specifications of ISO 385.

5.2 Conical flask, capacity 100 ml, diameter 50 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 to 400 min^{-1}), magnetic stirring bar without pivot ring, PTFE coated; diameter 5 mm, length 40 mm.

5.4 Filtering apparatus, with glass fibre filters or plastic 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.

NOTE — There is no International Standard for sampling and sample preparation of direct reduced iron, and the application of ISO 3081, ISO 3082 and ISO 3083, which cover the sampling and sample preparation of iron ores, is recommended for materials suitably stabilized against oxidation.

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 shall be 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 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 clause 6.

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 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.

7.3 Determination of hygroscopic moisture content

Determine the hygroscopic moisture content in accordance with ISO 2596, simultaneously with the taking of the test portion (7.4) for the determination of metallic iron content.

7.4 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 (clause 6).

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1) PVC filters or PVF filters.

7.5 Determination

7.5.1 Dissolution of metallic iron

Place the test portion (7.4) 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 note below) at a temperature of 20 °C. Filter immediately through a glass fibre filter or plastic 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 in order to remove the methanol. Transfer the solution to a 600 ml beaker, washing with water.

NOTE — A dissolution time of 30 min is usually adequate. In order 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 shall be digested for twice this time, i.e. 60 min. This procedure shall 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 to strong fuming. 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 to fuming. Cool, carefully add about 140 ml of water and 25 ml of hydrochloric acid (4.1) and boil until all salts are redissolved.

NOTE — For metallic iron contents 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 the tin(II) chloride solution (4.6) to the boiling solution dropwise with 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 the 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 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 metallic iron content

Calculate the metallic iron content, as a percentage by mass, to three decimal places using the equation

$$\text{Fe (metallic) } \% \ (m/m) = \frac{(V - V_0) \times 0{,}558\,5 \times F}{m} \times \frac{100}{100 - A} \qquad \ldots (1)$$

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 note to 7.5.2);

A is the hygroscopic moisture content, 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:[1]

$$r = 0{,}000\,9X + 0{,}452\,4 \qquad \ldots (2)$$

$$P = 0{,}009\,7X + 0{,}911\,2 \qquad \ldots (3)$$

$$\sigma_r = 0{,}000\,3X + 0{,}163\,2 \qquad \ldots (4)$$

$$\sigma_L = 0{,}003\,6X + 0{,}308\,9 \qquad \ldots (5)$$

where

X is the metallic iron content, as a percentage by mass, of the test sample, calculated as follows:

— for the within-laboratory equations (2 and 4), the arithmetic mean of the duplicate values;

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

— for the between-laboratories equations (3 and 5), the arithmetic mean of the final results (8.2.3) of the two laboratories;

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

P is the permissible tolerance between laboratories;

σ_r is the within-laboratory standard deviation;

σ_L is the between-laboratories standard deviation.

8.2.2 Acceptance of analytical values

The result obtained for the certified reference material shall be such that the difference between this result and the certified 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:

$$|A_c - A| \leqslant 2\sqrt{\frac{s_{Lc}^2 + \frac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_r^2}{n}} \qquad \ldots (6)$$

where

A_c is the certified value;

A is the result, or the mean of results, obtained for the certified 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 condition (6) is satisfied, i.e. 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 DRI.

When the range of the two values for the test sample is outside the limit for r calculated according to equation (2) in 8.2.1, one or more additional tests shall be carried out in accordance with the flowsheet presented in annex A, simultaneously with an analysis of a certified reference material of the same type of DRI.

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 should be used when the information on the reference material certificate is incomplete:

a) 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;

b) if the certification has been made by only one laboratory or if the interlaboratory results are missing, it is advisable not to use this material for this purpose. In case its use is unavoidable, use the formula

$$|A_c - A| \leqslant 2\sqrt{2\sigma_L^2 + \frac{\sigma_r^2}{n}} \qquad \ldots (7)$$

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

c) when the figure in the second decimal place is 5 and there is no figure other than 0 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;

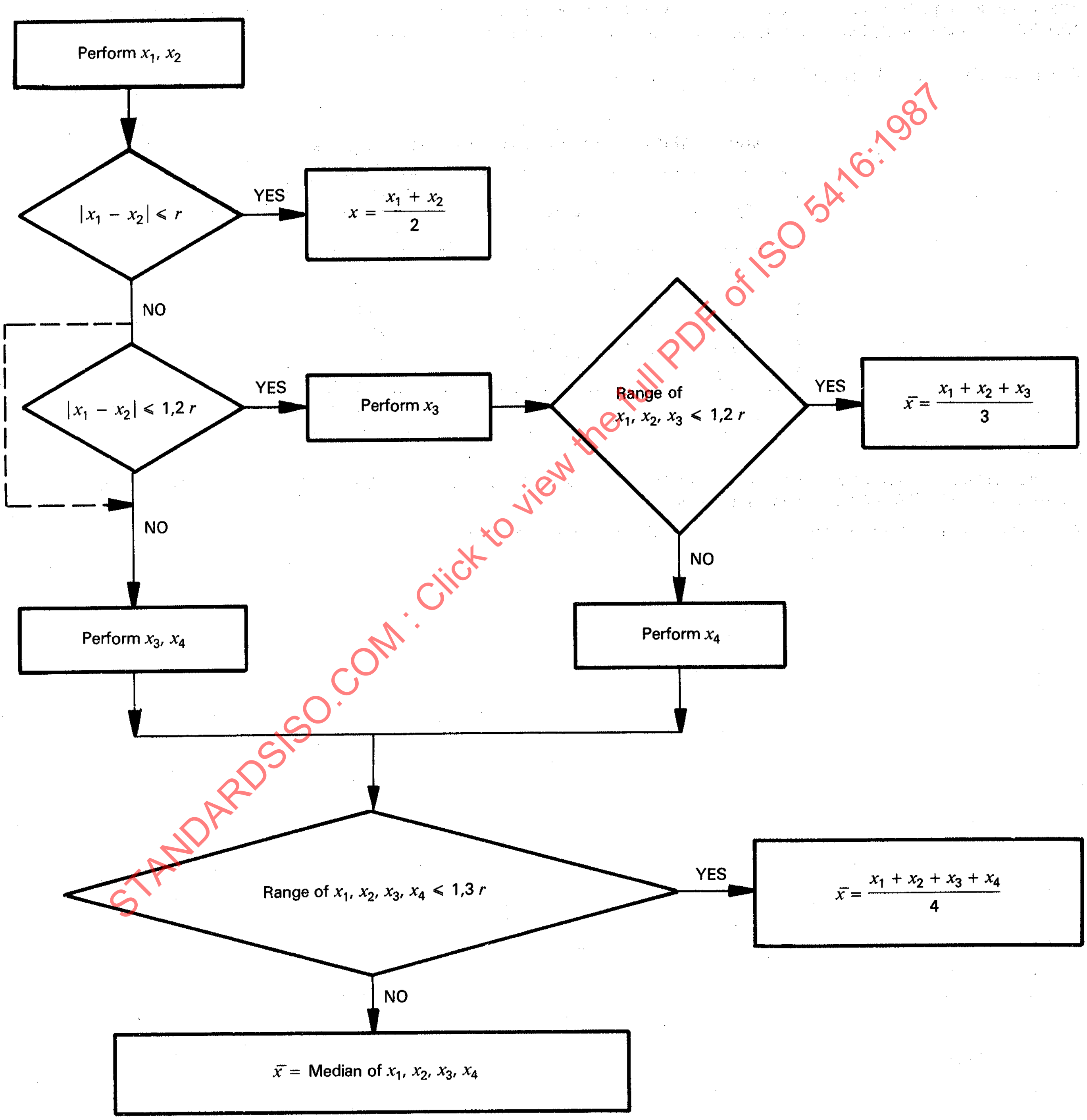
f) reference number of the result;

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

Annex A

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

(This annex is an integral part of the standard.)



r is as defined in 8.2.1.

Annex B

Derivation of repeatability and permissible tolerance equations

(For information only — not an integral part of the standard.)

The regression equations in 8.2.1 were obtained by statistical evaluation of the results of international analytical trials carried out in 1976-77 on 6 samples of DRI (see table below), involving 40 laboratories in 12 countries.

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

Table — Metallic iron contents of the test samples

Sample	Country	Metallic iron content [% (m/m)]
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

NOTES

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 either from the secretariat of ISO/TC 102/SC 2 or from ISO/TC 102.

2 The statistical analysis was performed in accordance with the principles embodied in ISO 5725.

Annex C

Precision data obtained by international analytical trial

(For information only — Not an integral part of the standard.)

NOTE — This figure is a graphical presentation of the equations in 8.2.1.

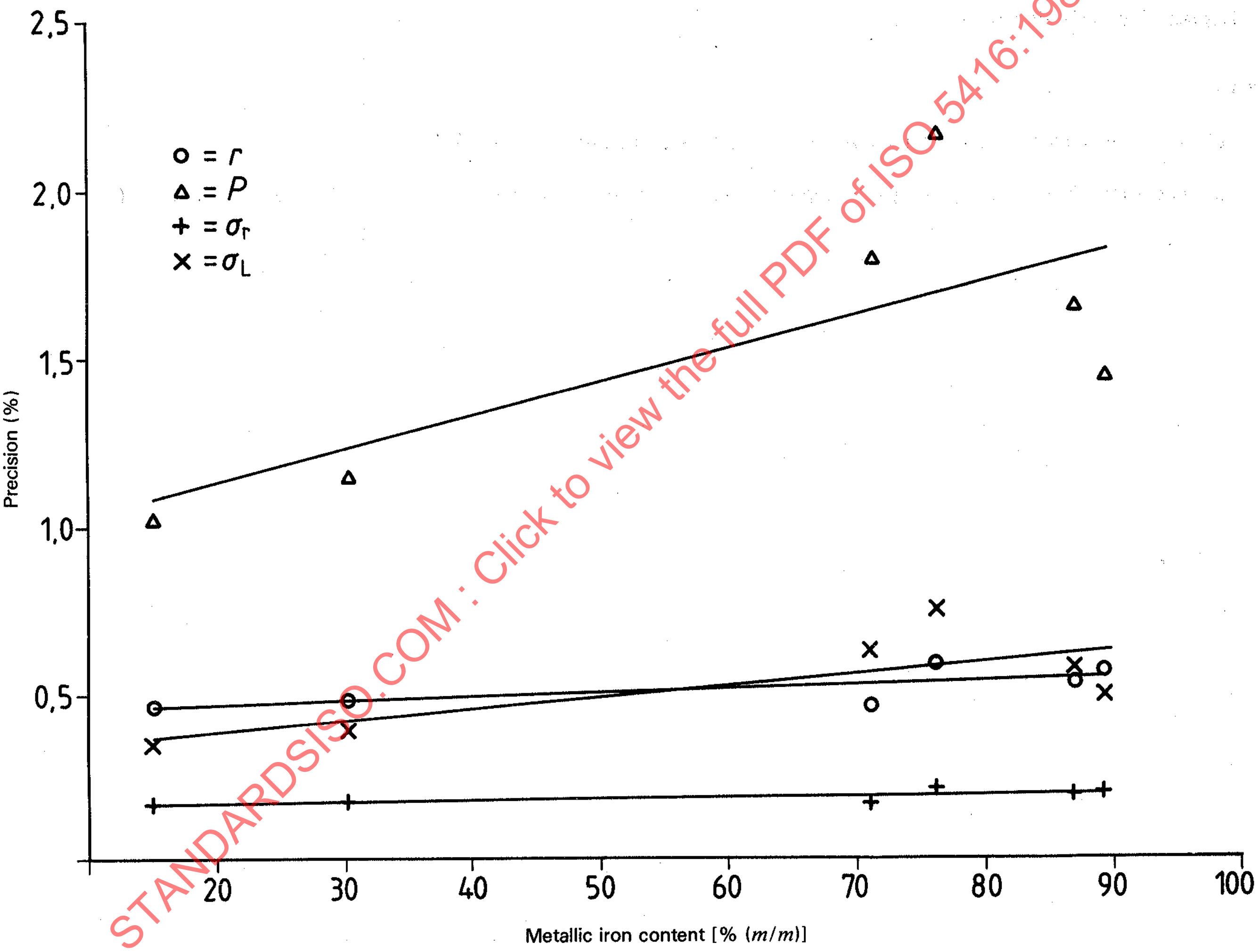


Figure — Least-squares fit of precision against X for metallic iron