INTERNATIONAL STANDARD

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Iron ores — Determination of acid-soluble iron(II) content — Titrimetric method

Minerais de fer — Dosage du fer(II) soluble dans l'acide — Méthode titrimétrique

Reference number
ISO 9035 : 1989 (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 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 9035 was prepared by Technical Committee ISO/TC 102, *Iron ores.*

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

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INTERNATIONAL STANDARD **ISO 9035 : 1989 (E)**

Iron ores — Determination of acid-soluble iron(II) content — Titrimetric method

1 Scope

This International Standard specifies a method for the determination of iron(II) content in natural and processed iron ores containing from 1 % to 25 % acid-soluble iron(II) and only traces of metallic iron. This method is specifically limited for use in conjunction with the reducibility test methods specified in ISO 4695 or ISO 7215.

This method is not applicable to ores containing more than 0,3 % (m/m) sulfur (as sulfide) and/or 5 % (m/m) free carbon. Experiments have shown that the acid-insoluble residue can be neglected, especially as regards the needs of the reducibility test methods concerned and the precision obtainable.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1 : 1984, *Laboratory glassware — Burettes — Part 1 : General requirements.*

ISO 4695 : 1984, *Iron ores — Determination of reducibility.*

ISO 4791-1 : 1985, *Laboratory apparatus — Vocabulary relating to apparatus made essentially from glass, porcelain or vitreous silica — Part 1 : Names for items of apparatus.*

ISO 7215 : 1985, *Iron ores — Determination of relative reducibility.*

ISO 7764 : 1985, *Iron ores — Preparation of predried test samples for chemical analysis.*

3 Principle

Dissolution with hydrochloric acid in an inert atmosphere, addition of a mixture of sulfuric and phosphoric acid and dilution with water. Determination of the iron(II) content by titration with potassium dichromate standard solution using sodium diphenylaminesulfonate as indicator.

4 Reagents

During the analysis, use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity.

NOTE — The water used for the procedure should be de-oxygenated by boiling.

4.1 Sodium carbonate (Na_2CO_3) or **sodium hydrogen carbonate** ($NaHCO_3$).

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

NOTE — This reagent should be de-oxygenated by purging with either nitrogen or argon, or by heating for a short time.

4.3 Hydrofluoric acid, 40 % (m/m), ϱ 1,13 g/ml or 48 % (m/m), ϱ 1,16 g/ml.

4.4 Sodium carbonate or **sodium hydrogen carbonate,** saturated solution, at ambient temperature.

4.5 Sulfuric acid - phosphoric acid mixture.

To 300 ml of water, add cautiously 150 ml of sulfuric acid (ϱ 1,84 g/ml), with constant stirring . After cooling, add 150 ml of phosphoric acid (ϱ 1,71 g/ml). Cool and dilute with water to 1 000 ml.

4.6 Nitrogen (99,99 % N_2) or **argon** (optional).

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

Dissolve 4,904 g of pulverized potassium dichromate (dried at 140 °C to 150 °C for 2 h and cooled to room temperature in a desiccator) in water and dilute to a volume of 1 000 ml after cooling to 20 °C.

4.8 Sodium diphenylaminesulfonate solution.

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

NOTES

1) Alternatively, an equivalent quantity of indicator in pellet form may be used.

2) Barium diphenylaminesulfonate may be used instead of sodium diphenylaminesulfonate.

5 Apparatus

Ordinary laboratory apparatus, and

5.1 **Conical flask,** of capacity 500 ml.

5.2 **Göckel safety trap** (see ISO 4791-1) or an apparatus with a feed tube for inert gas.

NOTE — Alternatively, a slit rubber valve (Bunsen valve) may be used, but its efficiency depends on the length of the slit and the quality and flexibility of the rubber tubing.

5.3 **Burette,** class B, conforming with ISO 385-1.

6 Sampling and samples

6.1 Laboratory sample

Crush and pulverize the whole of one of the test portions for the reducibility test, which has been reserved for chemical analysis, down to minus 100 µm particle size. 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 using non-magnetic materials. Taking multiple increments with a non-magnetic spatula, 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 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 Check test

In each run, 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.

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.

NOTES

1 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.

2 The certified reference material is used only to validate the performance of the analytical procedure and expressly not to standardize the potassium dichromate solution.

7.3 Test portion

Taking several increments, using a non-magnetic spatula, weigh to the nearest 0,000 2 g approximately 0,5 g of the predried test sample obtained in accordance with 6.2.

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

7.4 Decomposition

Transfer the predried test portion (7.3) to a dry 500 ml conical flask (5.1) and add 1 g to 2 g of solid sodium hydrogen carbonate or sodium carbonate (4.1) and 30 ml of hydrochloric acid (4.2). For ores with high silica contents [i.e. $\geqslant 5\ \%\ (m/m)$ SiO_2], add a few drops of hydrofluoric acid (4.3). Immediately close the flask with a Göckel safety trap (5.2) which contains sodium hydrogen carbonate or sodium carbonate solution (4.4) or is to be flushed with nitrogen or argon (4.6) at 0,5 l/min during the decomposition. Heat the flask on a heating plate at a temperature of about 90 °C until complete decomposition of the test portion.

NOTE — The decomposition time should not exceed 60 min. Normally a decomposition time of 30 min is sufficient. In order to ensure the complete decomposition of the sample, a duplicate determination may be performed using twice the decomposition time, provided that this time does not exceed 60 min.

When the closed flask has cooled, remove the valve and wash away the iron chlorides adhering to the stem of the valve with water.

7.5 Titration

Add 30 ml of sulfuric acid — phosphoric acid mixture (4.5) to the solution, dilute with water to about 300 ml and add about 5 to 6 drops of sodium diphenylaminesulfonate solution (4.8) as an indicator. Titrate immediately with the potassium dichromate standard solution (4.7) until the colour of the solution changes from green to bluish green to violet with the last drop of the titrant.

NOTE — The ambient temperature of the potassium dichromate solution should be noted. If it differs by more than 2 °C from the temperature at which it was prepared, make the appropriate volumetric correction : 0,02 % relative for each 1 °C of difference, i.e. the titre should be decreased when the ambient temperature during the titration is higher than the temperature during preparation of the standard volumetric solution.

8 Expression of results

8.1 Calculation of iron(II) content

The iron(II) content, expressed as a percentage by mass, is calculated to three decimal places using the equation

$$\text{Fe(II)}\ \%\ (m/m) = \frac{V \times 0{,}558\,5}{m} \qquad \ldots (1)$$

where

V is the volume, in millilitres, of potassium dichromate solution (4.7) required for sample analysis;

m is the mass, in grams, of the predried sample;

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]:

$$r = 0{,}015\,3\,X + 0{,}060\,0 \qquad \ldots (2)$$

$$P = 0{,}021\,5\,X + 0{,}180\,6 \qquad \ldots (3)$$

$$\sigma_r = 0{,}005\,4\,X + 0{,}021\,2 \qquad \ldots (4)$$

$$\sigma_L = 0{,}006\,6\,X + 0{,}062\,7 \qquad \ldots (5)$$

where

X is the iron(II) content, as a percentage by mass, of the 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 (8.2.3) 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 certified reference material is statistically insignificant. For a certified 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 condition may be used to test the significance of the difference :

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

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 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 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.

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

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 $s_{\mathrm{Wc}}^2/n_{\mathrm{Wc}}$ 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 inter-laboratory results are missing, it is advisable that this material not be used in the application of the standard. In case its use is unavoidable, use the formula

$$|A_{\mathrm{c}} - A| \leqslant 2\sqrt{2\sigma_{\mathrm{L}}^2 + \frac{\sigma_{\mathrm{r}}^2}{n}} \qquad \ldots (7)$$

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 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 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;

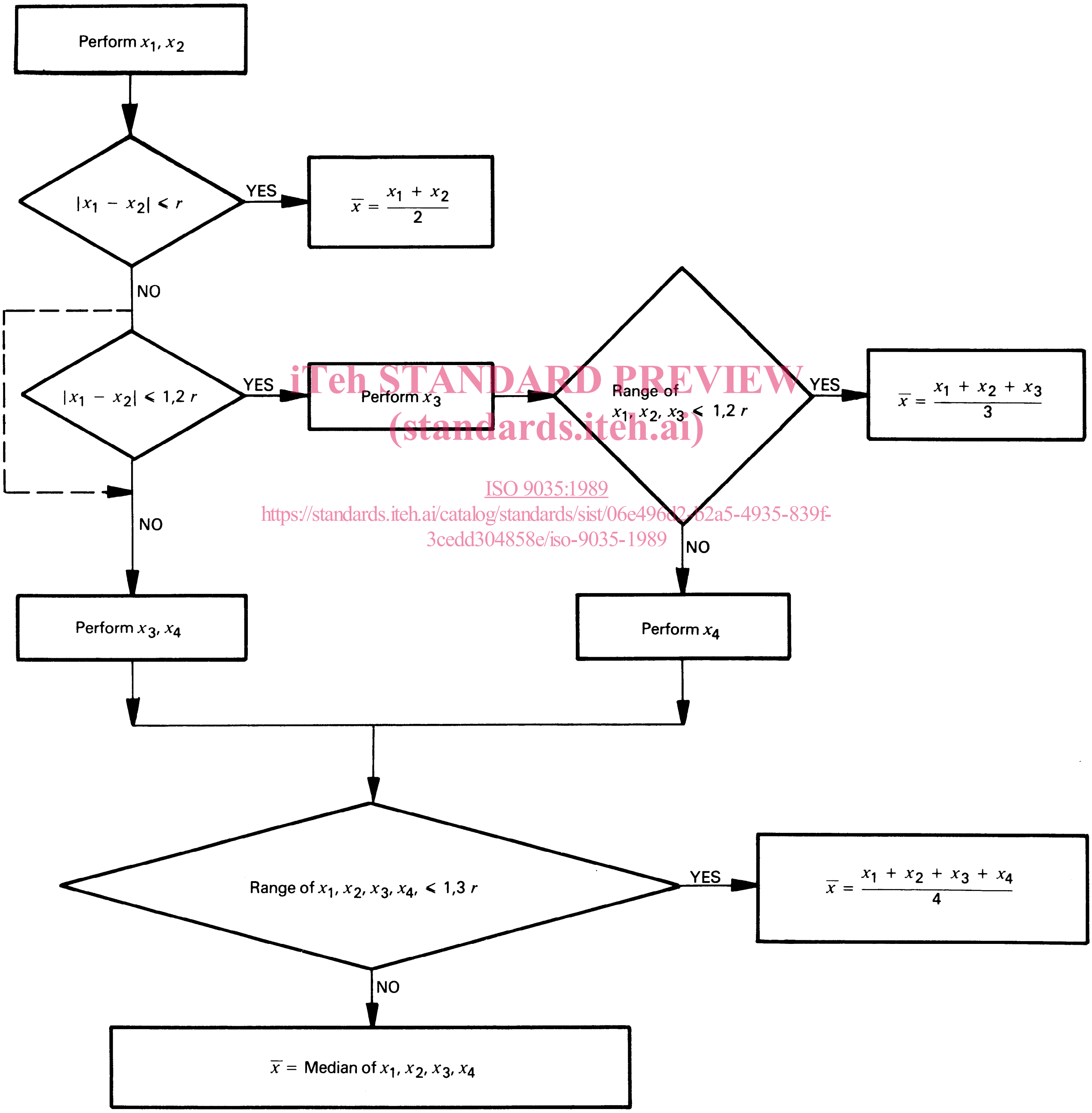
e) results of the analysis;

f) reference number of the result;

g) any characteristics noticed during the determination and any operation 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
(normative)

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



r : 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 1983 on four iron ore samples (see table B.1) involving 18 laboratories in seven countries.

Table B.1 — Acid-soluble iron(II) contents of the test samples

Sample	Fe(II) content [% (m/m)]
Malmberget BF pellets	0,7
Malmberget hematite fines	6,1
Svappavaara martite fines	13,5
Malmberget magnetite fines	22,6

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

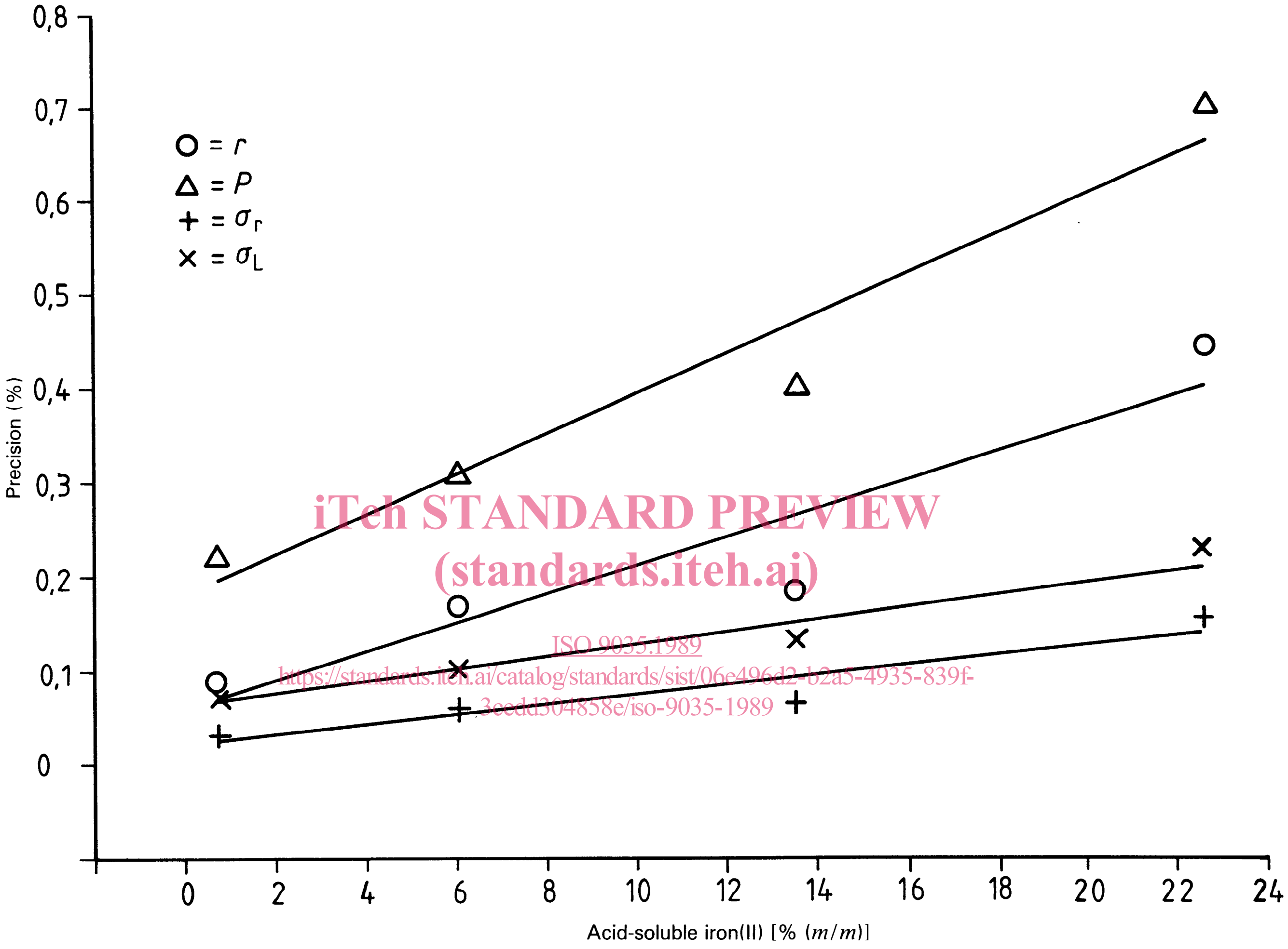
NOTES

1 A report of the international trial and a statistical analysis of the results (Document ISO/TC 102/SC 2 N 758E, August 1984) is available from either the secretariat of ISO/TC 102/SC 2 or the secretariat of ISO/TC 102.

2 The statistical analysis has been performed in accordance with the principles embodied in ISO 5725 : 1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

Annex C
(informative)

Precision data obtained by international analytical trial



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

Figure C.1 — Least-squares fit of precision against X for acid-soluble iron(II)