BRITISH STANDARD

BS ISO
4688-1:2006

Iron ores — Determination of aluminium —

Part 1: Flame atomic absorption spectrometric method

ICS 73.060.10

National foreword

This British Standard reproduces verbatim ISO 4688-1:2006 and implements it as the UK national standard. It supersedes BS 7020-8.2:1993 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee ISE/58, Iron ores, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Summary of pages

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Iron ores — Determination of aluminium —

Part 1: Flame atomic absorption spectrometric method

Minerais de fer — Dosage de l'aluminium —

Partie 1: Méthode par spectrométrie d'absorption atomique dans la flamme

Reference number
ISO 4688-1:2006(E)

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Foreword

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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 4688-1 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 4688-1:1992), which has been technically revised. It has been updated to alter the manner in which precision data are presented.

ISO 4688 consists of the following parts, under the general title *Iron ores — Determination of aluminium* :

— *Part 1: Flame atomic absorption spectrometric method*

Iron ores — Determination of aluminium —

Part 1:
Flame atomic absorption spectrometric method

WARNING — This part of ISO 4688 may involve hazardous materials, operations and equipment. This part of ISO 4688 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 4688 to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This part of ISO 4688 specifies a flame atomic absorption spectrometric method for the determination of the mass fraction of aluminium in iron ores.

This method is applicable to mass fractions of aluminium between 0,1 % and 5,0 % 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 7764, *Iron ores — Preparation of predried test samples for chemical analysis*

3 Principle

The test portion is decomposed by treatment with hydrochloric acid and a small amount of nitric acid.

The mixture is evaporated to dehydrate silica, followed by dilution and filtration.

The residue is ignited and silica is removed by evaporation with hydrofluoric and sulfuric acids. The residue is then fused with sodium carbonate and the cooled melt is dissolved in the filtrate.

The solution obtained is aspirated into the flame of an atomic absorption spectrometer using a dinitrogen oxide/acetylene burner.

The absorbance values obtained for aluminium are compared with those obtained from the calibration solutions.

4 Reagents

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

4.1 Sodium carbonate (Na_2CO_3), anhydrous.

4.2 Hydrochloric aid, ρ 1,19 g/ml.

4.3 Nitric acid, ρ 1,4 g/ml.

4.4 Hydrochloric acid, ρ 1,19 g/ml, diluted 1 + 9.

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

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

4.7 Background solution

Dissolve 10 g of high purity iron [minimum purity 99,9 % (mass fraction)] of mass fraction of aluminium less than 0,002 %, in 50 ml of hydrochloric acid (4.2) and oxidize by adding nitric acid (4.3) drop by drop.

Evaporate until a syrupy consistence is obtained. Add 20 ml of hydrochloric acid (4.2) and dilute to 200 ml with water. Dissolve 17 g of sodium carbonate (4.1) in water and add it to the iron solution. Transfer the solution to a 1 000 ml one-mark volumetric flask and dilute to volume with water.

4.8 Aluminium standard solution, 500 µg Al/ml.

Dissolve 0,5 000 g of high purity aluminium [minimum purity 99,9 % (mass fraction)] in 25 ml of hydrochloric acid (4.2). Cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

4.9 Aluminium calibration solutions

Transfer 2,0 ml; 5,0 ml; 10,0 ml; 20,0 ml; 40,0 ml; and 50,0 ml portions of aluminium standard solution (4.8) to 200 ml volumetric flasks. Dilute to about 100 ml. Add 6 ml of hydrochloric acid (4.2) and 60 ml of background solution (4.7) to each flask. Prepare a zero aluminium calibration solution by transferring 60 ml of the background solution to a 200 ml volumetic flask, and add 6 ml of hydrochloric acid (4.2). Dilute all the solutions to 200 ml with water and mix. (For an atomic absorption spectrometer having high sensitivity, smaller portions of the standard solution may be used.)

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 Platinum crucible, of capacity 30 ml.

5.2 Muffle furnace, capable of maintaining a temperature of approximately 1 100 °*C*.

5.3 Atomic absorption spectrometer, equipped with a dinitrogen oxide/acetylene burner.

WARNING — Follow the manufacturer's instructions for igniting and extinguishing the dinitrogen oxide/acetylene flame to avoid possible explosion hazards. Wear tinted safety glasses whenever the flame is burning.

The atomic absorption spectrometer used in this method shall meet the following criteria.

a) Minimum sensitivity: the absorbance of the most concentrated aluminium calibration solution (4.9) shall be at least 0,3.

b) Graph linearity: the slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) shall not be less than 0,7 of the value of the slope for the bottom 20 % of the concentration range determined in the same way.

c) Minimum stability: the standard deviation of the absorbance of the most concentrated calibration solution and that of the zero calibration solution, each being calculated from a sufficient number of repetitive measurements, shall be less than 1,5 % and 0,5 %, respectively, of the mean value of the absorbance of the most concentrated calibration solution.

The use of a strip-chart recorder and/or digital readout device is recommended to evaluate criteria a), b) and c) and for all subsequent measurements.

NOTE Instrument parameters may vary with each instrument. The following parameters were successfully used in several laboratories and they can be used as guidelines. Solutions were aspirated into a dinitrogen oxide/acetylene flame of a premix burner.

Aluminium hollow cathode lamp, mA 25

Wavelength, nm 396,2

Dinitrogen oxide flow rate, l/min 13,8

Acetylene flow rate, l/min 6,6

In systems where the values shown above for gas flow rates do not apply, the ratio of the gas flow rates may still be a useful guideline.

6 Sampling and samples

6.1 Laboratory sample

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 way 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, in either case, appropriate recalibration.

7.2 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, approximately 1 g of the predried test sample obtained in accordance with 6.2.

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

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 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 that 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

Transfer the test portion (7.2) to a 250 ml beaker. Moisten with a few millilitres of water, add 25 ml of hydrochloric acid (4.2), cover with a watch-glass and heat gently. Increase the heat and digest just below boiling, until no further attack is apparent. Add 2 ml of nitric acid (4.3) and digest for several minutes. Remove the watch-glass and evaporate the solution to dryness. Heat the salts on the hot-plate at 105 °C to 110 °C for 30 min. Add 5 ml of hydrochloric acid (4.2), cover the beaker with a watch-glass, and warm for several minutes. Add 50 ml of water, heat to boiling, wash the watch-glass and the walls of the beaker, and filter the solution through a medium-texture paper into a 250 ml beaker. Carefully remove all adhering particles with a rubber-tipped rod or moistened filter paper. Wash three times with hydrochloric acid (4,4), then with hot water until the filter paper is free of iron. Transfer the paper and residue to a platinum crucible (5.1). Evaporate the filtrate to about 100 ml and retain it.

7.4.2 Treatment of the residue

Ignite the paper and residue in the platinum crucible (5.1) at a low temperature (500 °C to 800 °C). Cool, moisten with a few drops of water, add 3 or 4 drops of sulfuric acid (4.6) and 10 ml of hydrofluoric acid (4.5), Evaporate slowly to expel silica and then fume to remove the excess sulfuric acid. Ignite at about 700 °C. Add 1,0 g of sodium carbonate (4.1) to the residue (see Note), cover the crucible, and fuse over a burner or in a muffle furnace (5.2) until a clear melt is obtained (at about 1 100 °C for 15 min).

NOTE If difficulties are experienced with the fusion, 2 g of sodium carbonate (4.1) may be used, with a doubled volume of hydrochloric acid (4.2). In this case, prepare the background solution (4.7) with doubled quantities of sodium carbonate and hydrochloric acid.

7.4.3 Preparation of the test solution

Dissolve the cooled melt in the retained filtrate (see 7.4.1), then remove and wash in the crucible and cover (see next paragraph).

If the solution is cloudy at this stage, indicating the presence of substantial amounts of hydrolysed titanium, it should be filtered prior to the transfer to the 200 ml volumetric flask.

Transfer the solution to a 200 ml one-mark volumetric flask, dilute to volume with water and mix. Use this solution (the test solution) directly for the atomic absorption measurements, if the mass fraction of aluminium in the test sample is between 0,1 % and 2,5 %. For mass fractions of aluminium greater than 2,5 %, transfer a 40 ml aliquot to a 200 ml one-mark volumetric flask (see next paragraph), add 50 ml of background solution (4.7) and 4 ml of hydrochloric acid (4.2). Dilute to volume with water and mix. (This solution is the diluted test solution).

For instruments having high sensitivity, smaller portions of the test solution may be preferable. In this case, the amounts of background solutions (4.7) and hydrochloric acid (4.2) should be adjusted.

Transfer a 40 ml aliquot of blank test solution to a 200 ml volumetric flask. Add 50 ml of background solution (4.7) and 4 ml of hydrochloric acid (4.2). Dilute to volume with water and mix. (This solution is the diluted blank test solution.) (See next paragraph.)

The test solution should be measured together with the blank test solution, and the diluted test solution with the diluted blank test solution.

7.4.4 Adjustment of the atomic absorption spectrometer

Set the wavelength for aluminium (396,2 nm) to obtain minimum absorbance. Fit the correct burner for dinitrogen oxide and, in accordance with the manufacturer's instructions, light the flame. After 10 min of preheating the burner, adjust the fuel flow and burner to obtain maximum absorbance while aspirating the calibration solution of highest mass fraction of aluminium (4.9). Then evaluate the criteria in 5.3.

Aspirate water and the calibration solution of highest mass fraction of aluminium, to establish that the absorbance reading is not drifting, and then set the reading for water to zero absorbance.

7.4.5 Atomic absorption measurements

Aspirate the aluminium calibration solutions (4.9) and test solutions (see 7.4.3) in order of increasing absorption, starting with the zero calibration solution and the blank test or diluted blank test solutions. When a stable response is obtained for each solution, record the readings. Aspirate the test solutions or diluted test solutions at the appropriate points in the calibration series and record the readings. Aspirate water between each calibration solution and test solution.

Repeat the measurements at least twice.

If necessary, convert the average of the readings for each calibration solution to absorbance. Obtain the net absorbance of each calibration solution by subtracting the average absorbance of the zero calibration solution. In a similar manner, obtain the net absorbance of the test solution, or that of the diluted test solution, by subtracting the absorbance of the blank test solution, or that of the diluted blank test solution, respectively.

Prepare a calibration graph by plotting the net absorbance values of the calibration solutions against the mass concentration of aluminium, in micrograms per millilitre. (The test solution, or in the case of a dilution, the diluted test solution, is the final test solution.)

Convert the net absorbance value of the final test solution to micrograms of aluminium per millilitre by means of the calibration graph.

8 Expression of results

8.1 Calculation of mass fraction of aluminium

The mass fraction of aluminium, w_{Al}, expressed as a percentage, is calculated to four decimal places using the equation:

$$w_{Al} = \frac{\rho_{Al} \times 200}{m \times 10\,000} = \frac{\rho_{Al}}{m \times 50} \quad (1)$$

where

ρ_{Al} is the mass concentration, in micrograms per millilitre, of aluminium in the final test solution;

m is the mass, in grams, of sample contained in 200 ml of the final test solution.

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)] ;

$$R_d = 0{,}082\,5\,X^{0{,}5242} \quad (2)$$

$$P = 0{,}122\,3\,X^{0{,}5938} \quad (3)$$

$$\sigma_d = 0{,}029\,1\,X^{0{,}5242} \quad (4)$$

$$\sigma_L = 0{,}036\,3\,X^{0{,}6101} \quad (5)$$

where

X is the mass fraction of aluminium, expressed as a percentage, in the pre-dried 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_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.

1) Addition information is given in Annexes B and C.

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, and obtain the final laboratory result μ_c (see 8.2.5).

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:

$$\mu_{12} = \frac{\mu_1 + \mu_2}{2} \tag{6}$$

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.

Substitute μ_{12} for X in Equation (3) and calculate P.

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) (see second paragraph of 7.3). Calculate the analytical result (μ_c) for the RM/CRM using the procedures in 8.1 and 8.2, and compare it 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 analytical result for the certified reference material;

A_c is the certified/reference value for the CRM/RM;

C is a value dependent on the type of CRM/RM used.

NOTE 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

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

where

$V(A_c)$ is the variance of the certified value A_c (= 0 for a CRM certified by only one laboratory);

n is the number of replicate 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.

The arithmetic mean of the acceptable analytical values, calculated to the fourth decimal place, is rounded off to the second decimal place as follows:

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

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

c) where the figure in the third decimal place is 5 and the figure 0 is in the fourth decimal place, the 5 is discarded and the figure in the second 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

The oxide factor, expresses as a percent, is given by the following equation:

$$w_{Al_2O_3} = 1{,}889\,5\ w_{Al} \qquad (7)$$

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 part of ISO 4688;

d) details necessary for the identification of the sample;

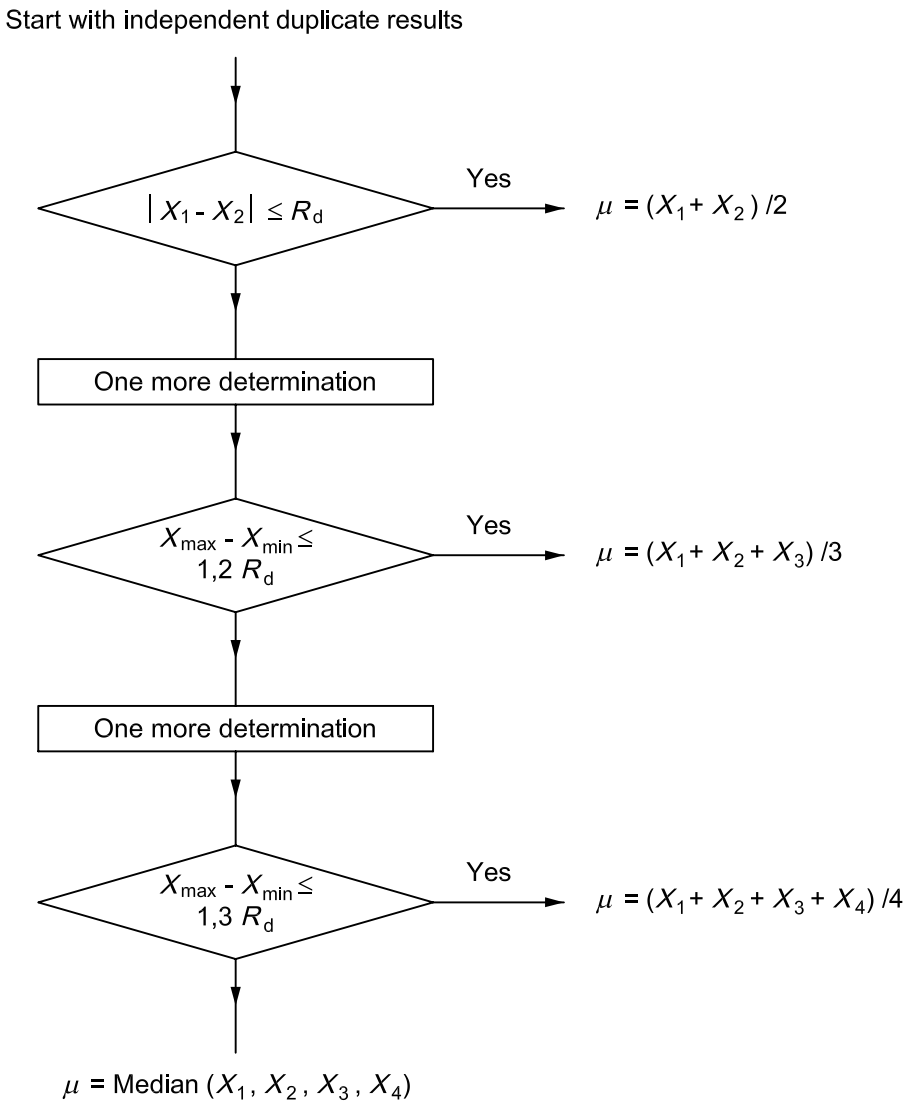
e) results of the analysis;

f) reference number of the result;

g) any characteristic noticed during the determination, and any operation not specified in this part of ISO 4688 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



Annex B
(informative)

Derivation of repeatability and permissible tolerance equations

The equations in 8.2.1 were derived from the results of international analytical trails carried out in 1971 to 1973 on six iron ore samples, involving 38 laboratories in 12 countries.

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

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

NOTE 1 A report of the international trials and a statistical analysis of the results (Documents ISO/TC 102/SC 2 N 237, January 1972 and N 335, January 1974) 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*.

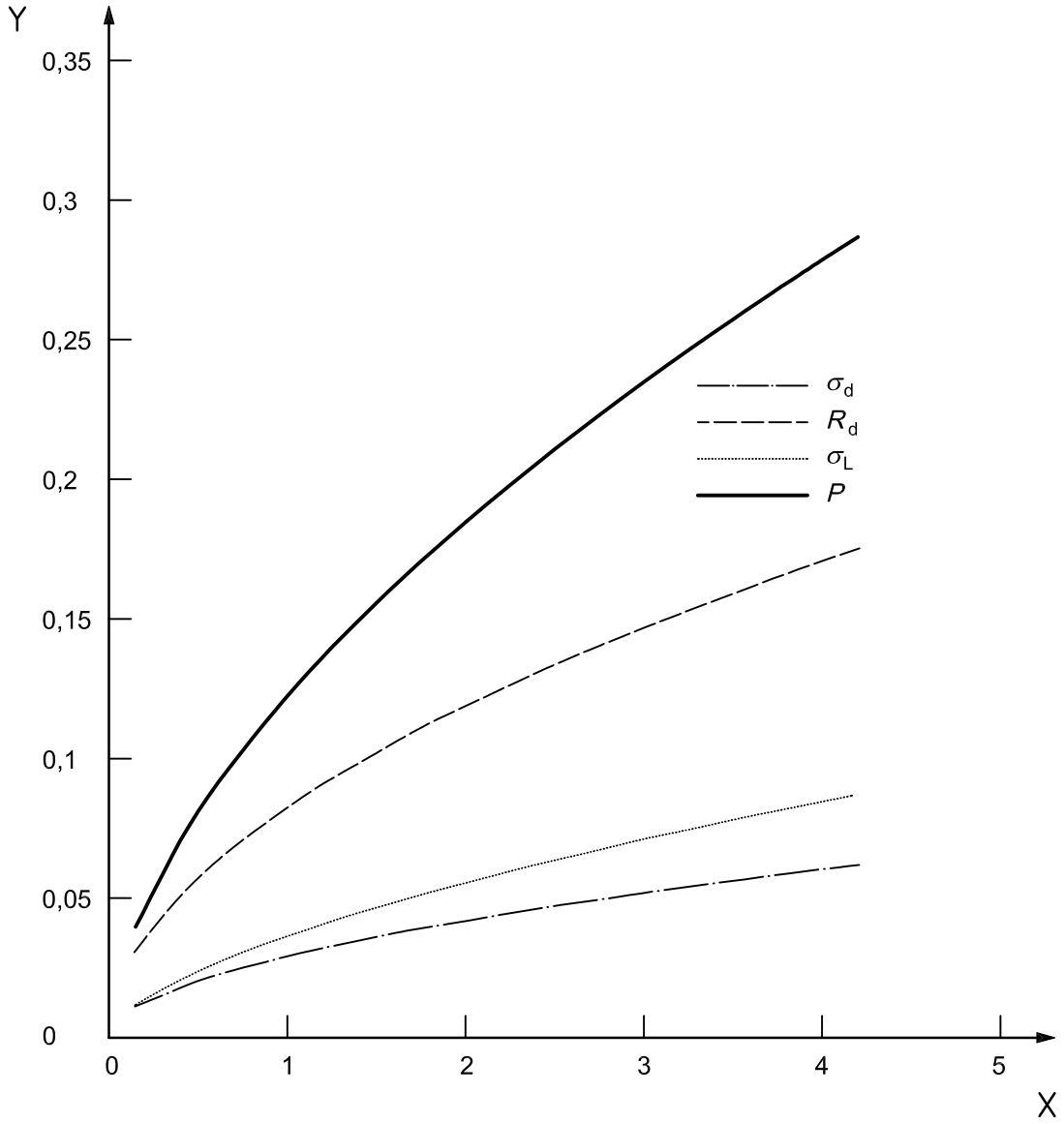
Table B.1 — Mass fractions of aluminium in test samples

Sample	Mass fraction of aluminium %
Canadian ore	0,18
Sweden-7 ore	0,28
CSR ore (Krivoi Rog)	0,89
Phillipine iron sand	1,47
Minette ore	2,13
72-8	4,14

Annex C
(informative)

Precision data obtained by international analytical trials

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



Key

Y Precision, %

X Mass fraction of aluminium, %

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

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