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BRITISH STANDARD

BS ISO
11535:2006

Iron ores — Determination of various elements — Inductively coupled plasma atomic emission spectrometric method

ICS 73.060.10

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British Standards

National foreword

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INTERNATIONAL STANDARD

ISO 11535

Second edition
2006-12-15

Iron ores — Determination of various elements — Inductively coupled plasma atomic emission spectrometric method

Minerais de fer — Dosage de divers éléments — Méthode par spectrométrie d'émission atomique avec plasma induit par haute fréquence

Reference number
ISO 11535:2006(E)

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Contents

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Foreword

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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 11535 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 11535:1998), which has been technically revised. It has been updated to alter the manner in which the precision data are presented.

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Iron ores — Determination of various elements — Inductively coupled plasma atomic emission spectrometric method

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

1 Scope

This International Standard specifies a method for the determination of aluminium, calcium, phosphorus, magnesium, manganese, silicon and titanium in iron ores by inductively coupled plasma atomic emission spectrometry (ICP-AES).

This method is applicable to the mass-fraction ranges given in Table 1, in natural iron ores, iron ore concentrates and agglomerates, including sinter products.

Table 1 — Mass-fraction ranges

Element	Range of mass fractions %
Al	0,07 to 3,30
Ca	0,012 to 6,80
Mg	0,008 to 1,90
Mn	0,012 to 1,70
P	0,011 to 1,60
Si	0,44 to 9,40
Ti	0,018 to 0,17

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*

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3 Principle

The test portion is decomposed by fusion in a sodium carbonate/sodium tetraborate flux and the cooled melt is dissolved in hydrochloric acid.

The solution is diluted to volume and measured on an ICP spectrometer. Final results are read from a calibration graph prepared using standard solutions.

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 Iron oxide (Fe_2O_3), of minimum purity 99,99 % (mass fraction).

4.2 Sodium carbonate (Na_2CO_3), anhydrous.

To produce final impurity levels in a solution below the detection limits determined or suggested in the performance test, a high-quality grade is required.

4.3 Sodium tetraborate ($Na_2B_4O_7$), anhydrous.

The same purity criteria as for the sodium carbonate are required.

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

The same purity criteria as for the sodium carbonate are required.

4.5 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 1 + 1.

Add 500 ml of hydrochloric acid (4.4) to 500 ml of water and mix.

4.6 Nitric acid, ρ 1,4 g/ml.

The same purity criteria as for the sodium carbonate are required.

4.7 Stock solutions.

4.7.1 Phosphorus, 1 000 µg/ml.

Dry approximately 10 g of potassium dihydrogen orthophosphate (KH_2PO_4) at 110 °C until a constant mass is reached, and cool in a desiccator. Dissolve 4,393 6 g in about 200 ml of water in a 1 000 ml one-mark volumetric flask. When the dissolution is complete, dilute to volume with water and mix.

4.7.2 Manganese, 1 000 µg/ml.

Dissolve 1,000 0 g of high-purity manganese metal in 20 ml of hydrochloric acid (4.5) in a covered tall-form beaker while heating. When dissolution is complete, cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

4.7.3 Magnesium, 1 000 µg/ml.

Dissolve 1,000 0 g of high-purity magnesium metal in 20 ml of hydrochloric acid (4.5) in a covered tall-form beaker while heating. When dissolution is complete, cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

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4.7.4 Silicon, 1 000 µg/ml.

Accurately weigh 2,139 3 g of pure silicon oxide (finely ground, previously heated at 1 000 °C for 45 min) into a platinum crucible (5.2). Mix with 5 g of sodium carbonate (4.2), and melt in a furnace at 1 000 °C for 15 min. Dissolve the melt in 100 ml of warm water and transfer to a 1 000 ml one-mark volumetric flask; increase the volume to approximately 500 ml with water, add 20 ml of hydrochloric acid (4.5), dilute to volume with water and mix. Store in a polyethylene flask.

4.7.5 Aluminium, 1 000 µg/ml.

Dissolve 1,000 0 g of high-purity aluminium metal in 20 ml of hydrochloric acid (4.5) in a covered tall-form beaker. Add about 4 drops of nitric acid (4.6). When dissolution is complete, add about 20 ml of water and heat to liberate oxides of nitrogen. Cool and transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

4.7.6 Titanium, 1 000 µg/ml.

Dissolve 1,000 0 g of high-purity titanium metal in 100 ml of hydrochloric acid (4.5) in a covered tall-form beaker while heating. When dissolution is complete, cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with hydrochloric acid (4.5) and mix.

4.7.7 Calcium, 1 000 µg/ml.

Dry approximately 10 g of calcium carbonate ($CaCO_3$) at 110 °C until a constant mass is reached, and cool in a desiccator. Dissolve 2,497 2 g in 20 ml of hydrochloric acid (4.5) in a covered tall-form beaker while heating. When dissolution is complete, cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

4.8 Calibration and reference solutions

Calibration solutions are defined as the solutions required for plotting the calibration graphs of the elements analysed. Their concentration ranges in solution, expressed in micrograms per millilitre, are determined with reference to the performance parameter values and the linearity response of the instrument. A minimum of 10 solutions is necessary to cover the mass-fraction ranges given in Table 1. For test samples having narrower concentration ranges, calibration solutions shall be prepared to cover the region of interest. If the element concentration in solution exceeds 5 000 × detection limit (DL), a separate calibration graph shall be prepared to cover the range.

In the case of non-linearity, either a less sensitive line is to be used or appropriate dilutions of sample and calibration solutions are to be carried out.

NOTE For the suggested lines shown in Table 2, the calibration solutions prepared as recommended in Annex A will be in agreement with the performance test figures.

To comply with the requirements of similarity between the test sample and the calibration solutions, iron, flux and acids must be added (see Note 1 to Table A.1). For each calibration solution, the procedure recommended in 7.4.1 is followed, replacing the test sample with the equivalent amount of iron oxide (4.1). Prior to the final dilution to 200 ml, the stock solutions and hydrochloric acid (4.5) are added in sufficient amounts to retain the final acid concentration (40 ml of HCl diluted 1+1) suggested in Annex A.

In addition, to comply with the requirements of similarity, calibration solutions and test samples are prepared from reagents taken from the same containers to minimize purity differences between batches.

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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, and the following.

5.1 Analytical balance, capable of weighing to the nearest 0,000 1 g.

5.2 Platinum or suitable platinum-alloy crucibles, having a minimum volume of 40 ml.

5.3 Bunsen burner, having an appropriate fuel/oxidant ratio to provide a minimum temperature of 500 °C.

5.4 Muffle furnace, to provide a minimum temperature of 1 020 °C.

5.5 Combined hotplate/magnetic stirrer.

5.6 Stirring bars, PTFE-coated, 10 mm long.

5.7 ICP spectrometer.

Any conventional ICP spectrometer may be used, provided that the instrument has been initially set up according to the manufacturer's recommendations, and that it complies with the performance test (7.4.2.2) carried out prior to the measurements.

Suggested analytical lines are shown in Table 2. These lines were found to be relatively free of significant interferences from the matrix elements, but they shall be carefully evaluated for spectral interference, background and ionization prior to their adoption. Failure to attain the recommended performance parameters may indicate an interference.

For the analysis of samples having concentrations in the background equivalent concentration (BEC) region or lower, as defined in Table 3, careful assessment of the need for background correction for the particular line chosen is recommended prior to calibration and analysis

Table 2 — Suggested analytical lines

Element	Wavelength nm
Al	396,15 or 308,22
Ca	393,36 or 317,93
Mg	279,55 or 279,08
Mn	257,61
P	178,29 [a]
Si	251,61 or 288,16
Ti	334,94 or 336,12

[a] Check and correct, if necessary, for interference by Mn.

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.

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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 C, 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 the 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 of the predried test sample obtained in accordance with 6.2.

The test portion should be taken and weighed quickly to avoid re-adsorption 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 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.

For the blank test, the equivalent amount of pure iron oxide (4.1) shall be used in place of the test sample.

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. Where a certified reference material is not available, a reference material may be used (see 8.4.3).

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

Add 0,80 g of sodium carbonate (4.2) to a platinum or suitable platinum-alloy crucible (5.2), transfer the test portion (7.2) to the crucible and mix well using a platinum or stainless-steel rod. Add 0,40 g of sodium tetraborate (4.3) and repeat the mixing using the metal rod. Pre-fuse the mixture to homogenize it.

The pre-fusion step may be carried out using a bunsen burner having a metallic holder to provide manual agitation. The crucible temperature at this stage should reach the range 350 °C to 450 °C (slightly dull red heat). The mixture melts within 2 min to 3 min without effervescence, and is completely fluid and ready for high-temperature fusion within 5 min.

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After the pre-fusion, place the crucible in a muffle furnace (5.4) set at 1 020 °C for 15 min. Remove the crucible and gently swirl the melt as it solidifies. Allow to cool, then place a PTFE-coated stirring bar in the crucible and place the crucible in a 250 ml low-form beaker. Add 40 ml of hydrochloric acid (4.5) directly to the crucible, and 30 ml of water to the beaker. Cover and heat while stirring on a magnetic stirrer/hotplate (5.5) until dissolution of the melt is complete.

The temperature of the recovery solution should be kept at approximately 70 °C.

NOTE 1 Continuous manual swirling is acceptable as an alternative to magnetic stirring.

Remove and rinse the crucible and stirrer, collecting the washings in the beaker. Cool the solution and immediately transfer it to a 200 ml one-mark volumetric flask. Dilute to volume with water and mix. (This is the test solution.)

NOTE 2 The immediate transfer of the recovered solution to the 200 ml volumetric flask, and the making up to volume, prevent re-precipitation.

NOTE 3 The recommended dilution to 200 ml provides element concentrations in the solution compatible with the performance test figures given in Table 3. Higher dilution rates may be required to cope with instrument linear response at the high concentration ranges. In such situations, the calibration solutions are diluted in the same proportions.

NOTE 4 The use of an internal standard, such as yttrium or scandium, for improvement of the performance figures is not acceptable, and is not necessary if the instrument complies with the performance test figures.

7.4.2 Adjustment of spectrometer

7.4.2.1 General

The ICP spectrometer shall be initially adjusted according to the manufacturer's recommendations and laboratory practice for quantitative analysis.

7.4.2.2 Performance test

The performance test is devised with the purpose of evaluating the ICP performance parameters, to enable all types of spectrometers to perform in equivalent conditions, allowing direct comparison of the data generated.

The test is based on the determination of the following three parameters:

- detection limit (DL);
- background equivalent concentration (BEC):
- short-term precision ($\mathrm{RSDN}_{\mathrm{min}}$).

The definitions of these terms and the procedure for their evaluation are given in Annex B.

The procedure shall be carried out as many times as necessary, with the optimization of the instrument parameters after each round, until the figures obtained are lower than those given in Table 3. For elements present in the sample solutions at concentrations higher than 5 000 × DL, the RSDN is the only performance parameter to be assessed, and the target values are lower than those given in Table 3 for $\mathrm{RSDN}_{\mathrm{min}}$.

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Table 3 — Recommended performance parameters

Element	DL µg/ml	BEC µg/ml	$RSDN_{min}$ %
Al	0,04	2,46	0,87
Ca	0,02	1,04	1,04
Mg	0,03	0,38	0,75
Mn	0,01	0,29	0,89
P	0,07	2,15	1,04
Si	0,07	2,67	0,95
Ti	0,01	0,24	0,78

7.4.3 Measurements

7.4.3.1 Calibration solutions

Aspirate the calibration solutions in order of increasing concentration, starting with the zero calibration solution. Aspirate water between each solution and repeat the measurements at least twice. Take the average of the two readings.

NOTE After initial calibration has been established, a two-point recalibration procedure can be used for routine analysis. In this case, proceed according to 8.3.

7.4.3.2 Test solutions

Immediately after aspiration of the calibration solutions, start running the first test solution, followed by the certified reference material (CRM). Continue aspirating test solutions and CRMs alternately. Aspirate water between each measurement. This procedure should preferably be repeated at least twice.

8 Calculation of results

8.1 Calibration graph

Prepare a calibration graph by plotting the intensity values obtained from the calibration solution against its equivalent element concentration.

Read the intensity values for the test solution and obtain their respective concentration values from calibration graphs.

If spectral interferences are found to exist, corrections have to be carried out in accordance with 8.2.

Calibration graphs are preferably obtained using statistical procedures (e.g. least squares). Computer-assisted spectrometers usually incorporate such a facility. Correlation coefficients and Root Mean Square (RMS) values obtained should be within the laboratory acceptance criteria.

NOTE Calibration-graph drift-correction procedures may be used, provided that they are carried out in accordance with 8.3 immediately before analysis of the test solutions.

8.2 Correction of spectral interference

A correction method for spectral interferences by using synthetic standard solution is recommended. The procedure is described below.

Plot a calibration graph by using binary (iron plus flux and an analyte) synthetic solution series for the analyte interfered element (named “i”). Suggested calibration solutions (Annex A) may be used as long as they are prepared as independent sets of binaries.

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Using the calibration graph for the analyte, determine the apparent content of possible interfering element (named “j”) for the analyte (named “i”) by measuring the intensity of binary (iron plus flux and interfering element named “j”) synthetic solution series.

The relationship between the actual content of interfering element (x_j) and the apparent content of interfering element (x_{ij}) is calculated by the least-squares method.

$$x_{ij} = l_{ij} \cdot x_j + b \tag{1}$$

where

l_{ij} is the coefficient of spectral interference of element (j) for analyte (i) under examination;

b is a constant (negligibly small).

The l_{ij} values are determined for all kinds of interfering elements for the analyte (i).

Being corrected by the interference factor, the actual mass fraction (content) of the analyte is calculated as follows:

— each mass fraction of element, expressed as a percentage, is given by the following equation:

$$x_i = \frac{(\rho_1 - \rho_0) \cdot V}{10^6} \times \frac{100}{m} - \Sigma w_j l_{ij} \tag{2}$$

— or for V = 200 ml,

$$x_i = \frac{(\rho_1 - \rho_0) \cdot 200}{10^6} \times \frac{100}{m} - \Sigma w_j l_{ij} = \frac{(\rho_1 - \rho_0)}{50m} - \Sigma w_j l_{ij} \tag{3}$$

where

x_i is the mass fraction of element (analyte), expressed as a percentage;

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

ρ_1 is the concentration, expressed in micrograms per millilitre, of the analyte in the test portion;

ρ_0 is the concentration, expressed in micrograms per millilitre, of the analyte in the blank test;

w_j is the percentage by mass of the interfering element in the test portion;

l_{ij} is the coefficient of spectral interference of element (j) for analyte (i) under examination, expressed as a percentage by mass, corresponding to 1 % of the interfering element;

V is the final volume of calibration and test solutions (200 ml as recommended in 4.8 and 7.4).

Over-correction of spectral interference is not acceptable. The allowable maximum value for correction is about ten times the repeatability of analyte content under examination. If the correction value is greater than this, the correction for ICP analysis should not be applied.

NOTE 1 If there is no interfering element, the term w_j containing the percentage of interfering element in Equation (2) is equal to zero.

NOTE 2 For the suggested final calibration solution volume V = 200 ml and with no interfering element present, Equation (2) reduces to:

$$x_i = \frac{\rho_1 - \rho_0}{50\,m}$$

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8.3 Standardization of calibration graph (drift correction)

Periodical checking and correction of the calibration graph, if used, shall be carried out as follows.

Take the two calibration solutions that correspond to the lowest and highest analyte content.

At the stage of plotting the calibration graph, measure the intensity of these two calibration solutions and calculate the correction factors α and β as follows:

$$\alpha = \frac{I_{\mathrm{HO}} - I_{\mathrm{LO}}}{I_{\mathrm{H}} - I_{\mathrm{L}}} \tag{4}$$

$$\beta = I_{\mathrm{LO}} - \alpha I_{\mathrm{L}} \tag{5}$$

where

I_{HO} is the initial intensity of the most concentrated calibration solution;

I_{LO} is the initial intensity of the least concentrated calibration solution;

I_{H} is the checked intensity of the most concentrated calibration solution, at a certain interval;

I_{L} is the checked intensity of the least concentrated calibration solution, at a certain interval.

The measured intensity of the test solution shall be corrected using the correction factors α and β, as shown in the following equation:

$$I_{\mathrm{c}} = \alpha I + \beta \tag{6}$$

where

I_{c} is the corrected value of intensity;

I is the measured value of intensity.

The same values for α and β shall be used until the next check is made.

NOTE 1 The frequency of standardization depends upon the characteristics of each instrument. Generally, every 30 min or every 10 to 20 test samples the calibration graph is checked by using the same calibration solutions.

NOTE 2 The corrected value of intensity (I_{c}) is used in determining the analyte content, and this calculation is generally computerized.

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8.4 General treatment of results

8.4.1 Repeatability and permissible tolerances

The precision of this analytical method is expressed by the regression equations given in Table 4.[1]

Table 4 — Regression equations

Element	σ_d	σ_L	R_d	P
Al	$0{,}007\,3X + 0{,}001\,5$	$0{,}018\,9X + 0{,}001\,6$	$0{,}022\,7X + 0{,}004\,2$	$0{,}058\,1X + 0{,}005\,7$
Ca	$0{,}021\,7X^{0{,}627\,2}$	$0{,}053\,5X^{0{,}779\,8}$	$0{,}061\,3X^{0{,}627\,2}$	$0{,}086\,2X^{0{,}596\,8}$
Mg	$0{,}022\,7X$	$0{,}069\,4X^{1{,}129\,7}$	$0{,}064\,3X + 0{,}000\,1$	$0{,}090\,8X^{0{,}868\,2}$
Mn	$0{,}019\,1X + 0{,}000\,3$	$0{,}021\,6X + 0{,}003\,5$	$0{,}053\,9X + 0{,}000\,8$	$0{,}059\,6X + 0{,}003\,9$
P	$0{,}010\,1X^{0{,}618\,5}$	$0{,}004\,5X^{0{,}130\,9}$	$0{,}028\,6X^{0{,}618\,5}$	$0{,}180\,9X^{0{,}006\,49}$
Si	$0{,}015\,3X^{0{,}423\,4}$	$0{,}004\,26X + 0{,}025\,4$	$0{,}043\,4X^{0{,}423\,4}$	$0{,}000\,1X + 0{,}068\,1$
Ti	$0{,}004\,4X^{0{,}406\,9}$	$0{,}003\,03$	$0{,}012\,51X^{0{,}406\,9}$	$0{,}009\,31$

X is the concentration of element in the sample;

σ_d is the independent duplicate standard deviation;

σ_L is the between-laboratories standard deviation;

R_d is the independent duplicate limit;

P is the permissible tolerance between laboratories.

8.4.2 Determination of the analytical result

8.4.2.1 Mean of duplicates

Having computed the independent duplicate results according to Equation (2), compare them with the independent duplicate limit (R_d), using the procedure given in Annex C, and obtain the final laboratory result μ (see 8.4.3).

8.4.2.2 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 8.4.2.1.

Compute the following quantity:

$$\mu_{1,2} = \frac{\mu_1 + \mu_2}{2} \tag{7}$$

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

$\mu_{1,2}$ is the mean of final results.

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[1] Additional information is given in Annexes D and E.

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Substitute $\mu_{1,2}$ for X in the final column of Table 4 and calculate P.

If $|\mu_1 - \mu_2| \leq P$, the final results are in agreement.

8.4.3 Check for trueness

8.4.3.1 The trueness of the analytical method shall be checked by applying it to a certified reference material (CRM) or a reference material (RM) (see 8.4.3.3). Calculate the analytical result (μ) for the RM/CRM using the calculation procedures, and compare it with the certified or reference value A_c. There are two possibilities:

a) $|\mu_c - A_c| \leq C$ in which case the difference between the reported result and the certified/reference value is statistically insignificant.

b) $|\mu_c - A_c| > C$ in which case the difference between the reported result and the certified/reference value is statistically significant.

where

μ_c is the final result for the CRM/RM;

A_c is the certified/reference 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*.

8.4.3.2 For a CRM/RM certified by an interlaboratory test programme

$$C = 2\left[\sigma_L^2 + \frac{\sigma_d^2}{n} + V(A_c)\right]^{1/2} \tag{8}$$

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 known to have an unbiased certified value.

8.4.3.3 Acceptance of analytical results for each test sample depends on the acceptance of trueness for the corresponding CRM or RM run immediately after each test solution. Should the CRM or RM result not pass the trueness test, the related test sample result is not acceptable and the entire analytical procedure shall be repeated for this test sample.

8.4.4 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 C, calculated to five decimal places for mass fractions less than 1 % and rounded off to the third decimal place as follows :

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

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b) if the figure in the fifth decimal place is 5 and there is a figure other than 0 in the sixth decimal place, or if the figure in the fifth decimal place is greater than 5, the figure in the fourth decimal place is increased by one;

c) if the figure in the fifth decimal place is 5 and the figure 0 is in the sixth decimal place, the 5 is discarded and the figure in the fourth 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.

For mass fractions greater than 1 %, the result should be calculated to four decimal places and rounded off to the second decimal place.

8.5 Oxide factors

Oxide concentrations may be obtained by multiplying the element mass fractions (contents) by the factors given in Table 5.

Table 5 — Factors for conversion of element contents to oxide contents

Element	Oxide	Conversion factor
Al	Al_2O_3	1,889 5
Ca	CaO	1,399 2
Mg	MgO	1,658 3
Mn	MnO	1,291 2
P	P_2O_5	2,291 4
Si	SiO_2	2,139 3
Ti	TiO_2	1,668 3

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 materials(s).

Annex A

(informative)

Suggested calibration solutions

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Table A.1

	Ca			Mg			Mn			Al			Si			Ti			P			Volume of HCl (4.5)
	ml of solution 1 000 µg/ml	µg/ml	a %	ml of solution 1 000 µg/ml	µg/ml	a %	ml of solution 1 000 µg/ml	µg/ml	a %	ml of solution 1 000 µg/ml	µg/ml	a %	ml of solution 1 000 µg/ml	µg/ml	a %	ml of solution 1 000 µg/ml	µg/ml	a %	ml of solution 1 000 µg/ml	µg/ml	a %	ml
1	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	40,0
2	0,05	0,25	0,01	0,05	0,25	0,01	0,05	0,25	0,01	0,10	0,50	0,02	0,50	2,50	0,10	0,05	0,25	0,01	0,05	0,25	0,01	39.9
3	15,0	75,0	3,00	0,25	1,25	0,05	5,00	25,0	1,00	5,00	25,0	1,00	10,0	50,0	2,00	0,20	1,00	0,40	0,25	1,25	0,05	39,1
4	25,0	125,0	5,00	2,50	12.5	0,50	7,50	37,5	1,50	10,0	50,0	2,00	1,00	5,00	0,20	0,40	2,00	0,08	1,00	5,00	0,20	38,7
5	5,00	25,0	1,00	5,00	25,0	1,00	2,50	12,5	0,50	0,25	1,25	0,05	7,50	37,5	1,50	0,10	0,50	0,02	0,50	2,50	0,10	39,5
6	1,00	5,00	0,20	10,0	50,0	2,00	0,20	1,00	0,04	15,0	75,0	3,00	5,00	25,0	1,00	0,75	3,75	0,150	7,50	37,5	1,50	38,6
7	0,15	0,75	0,03	0,50	2,50	0,10	0,50	2,50	0,10	0,50	2,50	0,10	30,0	150,0	6,00	2,50	0,50	0,10	0,10	0,50	0,02	38,9
8	0,25	1,25	0,05	1,00	5,00	0,20	12,5	62,5	2,50	20,0	100,0	4,00	2,50	12,5	0,50	0,15	0,75	0,03	2,50	12,5	0,50	39,1
9	0,50	2,50	0,10	0,15	0,75	0,03	10,0	50,0	2,00	2,50	12,5	0,50	20,0	100,0	4,00	0,25	1,25	0,05	5,00	25,0	1,00	39,1
10	40,0	200,0	8,00	15,0	75,0	3,00	15,0	75,0	3,00	25,0	125,0	5,00	40,0	200,0	8,00	1,00	5,00	0,20	10,0	50,0	2,00	36,3

NOTE 1 All solutions must contain 0,5 g of Fe_2O_3 (1 750 µg/ml), 1,2 g of flux and sufficient HCl (4.5) to allow a final acid volume of 40 ml.

NOTE 2 Solutions are made up to 200 ml.

NOTE 3 100 µg/ml or 10 µg/ml solutions may be prepared from 1 000 µg/ml stock solutions for convenience and accuracy of additions.

[a] Equivalent concentration in sample.

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Annex B
(normative)

Plasma-spectrometer performance tests

B.1 Purpose

The performance tests given in this annex are intended to provide adequate measurement of the plasma-spectrometer performance regardless of the type of instrument, but allowing for the different operating conditions required for each particular instrument in use, ultimately leading to compatible results generated by plasma spectrometers.

The whole procedure envisages the control of three basic parameters: detection limit (DL), background equivalent concentration (BEC) and short-term precision (RSDN).

For elements present in sample solution at concentrations higher than 5 000 × DL, the RSDN is the only performance parameter to be assessed.

The elements to be investigated will be those given in Table B.1.

Table B.1 — Suggested analytical lines and their estimated detection limit

Element	Wavelength nm	DL µg/ml
Al	396,15/308,22	0,03
Ca	393,36	0,001
Ca	317,93 [a]	0,04
Mg	279,08 [a]	0,1
Mg	279,55	0,008
Mn	257,61	0,01
P	178,29	0,1
Si	251,61/288,16	0,07
Ti	336,1	0,006

[a] Less sensitive lines for higher contents.

B.2 Definitions

B.2.1 Detection limit (DL): The minimum concentration at which the signal that an element generates can be positively recognized above any spurious background signals with a specified degree of certainty; alternatively, the element concentration that produces a signal three times the background standard deviation at the background levels.

B.2.2 Background equivalent concentration (BEC): The concentration of the analyte that yields a net intensity signal equal to the intensity of the background; it is a measure of the sensitivity for a given wavelength.

B.2.3 Short-term precision (RSDN): The relative standard deviation of a series of instrument readings taken at predetermined conditions.

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B.3 Reference solutions

Three reference solutions containing 4 000 µg/ml of sodium carbonate, 2 000 µg/ml of sodium tetraborate, 1 750 µg/ml of iron, in 10 % (by volume) hydrochloric acid and all the elements to be investigated at concentration levels 0 × DL (blank), 10 × DL, and 1 000 × DL should be prepared.

DL values for the preparation of reference solutions may be either laboratory-established figures or the estimated values given in Table B.1.

For each order of magnitude, the respective increments in concentration for each element are added to the same volumetric flask. Alternatively, a stock solution containing all seven elements at a concentration twice that required for the most concentrated solution should be prepared; from that, tenfold dilution aliquots are added to the flux, iron and acid solutions previously contained in each of the three volumetric flasks.

B.4 Procedure (to be carried out for each element investigated)

The plasma spectrometer shall be initially adjusted according to the manufacturer's recommendations and the laboratory practice for quantitative analysis. Aspirate the blank and take 10 intensity readings. Repeat the operation for the other two reference solutions.

Calculate the slopes of the analytical graphs using the equation:

$$M = C_2 / \left(I_2 - I_\mathrm{b} \right) \tag{B.1}$$

where

M is the slope of the analytical graph;

C_2 is the concentration of the second reference solution, one degree of magnitude higher than the detection limit;

I_2 is the average of 10 gross intensity readings of the second reference solution;

I_b is the average of 10 intensity readings of the blank solution.

Determine the DL from the equation

$$\mathrm{DL} = 3 s_\mathrm{b} M \tag{B.2}$$

where

DL is the detection limit, in micrograms per millilitre;

s_b is the standard deviation of 10 blank intensity readings.

Calculate the BEC from the equation

$$\mathrm{BEC} = M \left(I_\mathrm{b} \right) \tag{B.3}$$

where BEC is the background equivalent concentration, in micrograms per millilitre.

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Calculate, for reference solution 3, the net average intensity (IN_3) determined from the difference of the gross average intensity (I_3) and the average blank intensity I_b, i.e.

$$\mathrm{IN}_3 = I_3 - I_\mathrm{b} \tag{B.4}$$

where IN_3 is the net average intensity for the reference solution (1 000 × DL).

The $\mathrm{RSDN}_\mathrm{min}$ is estimated from reference solution 3 containing the elements present at the concentration 1 000 × DL.

Calculate the relative standard deviation of the net intensity for reference solution 3 (1 000 × DL).

$$\mathrm{RSDN}_\mathrm{min} = \frac{\sqrt{s_3^2 + s_\mathrm{b}^2}}{\mathrm{IN}_3} \times 100 \tag{B.5}$$

where s_3 is the standard deviation of the 10 intensity readings for reference solution 3.

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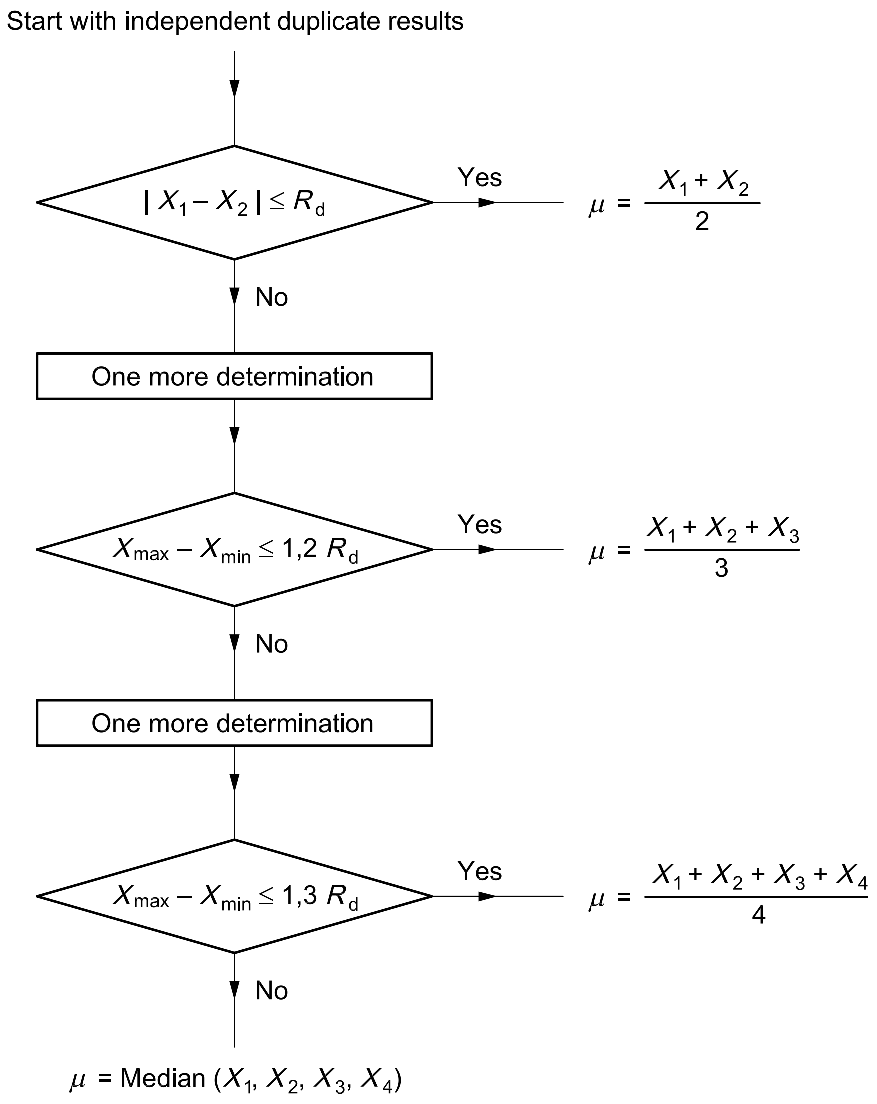
Annex C
(normative)

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



R_d: as defined in 8.4.1.

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Annex D
(informative)

Derivation of repeatability and permissible tolerance equations

The equations in 8.4.1 were derived from the results of international trials carried out in 1993/1994 on eight iron ore samples, involving eight laboratories in two countries.

A graphical treatment of the precision data is given in Annex E.

The test samples are listed in Table D.1.

NOTE 1 A report of the international trials and a statistical analysis of the results (Documents ISO/TC 102/SC 2N 1213, September 1994) is 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 D.1 — Mass fraction of elements in test samples

Sample	**Mass fraction of element, %**						
	Al	**Ca**	**Mg**	**Mn**	**P**	**Si**	**Ti**
Schefferville	0,514	0,029	0,021	0,791	0,055	3,780	0,027 0
Euro standard 678-1	0,273	3,995	0,593	0,076	1,612	1,735	0,131
Andalussa	0,761	4,087	0,273	1,725	0,011	2,637	0,033 9
Carol Lake	0,069	0,358	0,220	0,115	0,005 0	2,004	0,012 7
Aglorundo Hemantitowo	0,742	0,234	0,175	0,032	0,025	9,388	0,033 2
IRSID 609-1	2,257	6,870	1,921	0,456	0,608	7,841	—
Geothite material	3,36	0,003	0,008	0,017	0,178	0,444	0,175
Titaniferous Itabirite material	2,428	0,007	0,014	0,011	0,341	0,544	0,134

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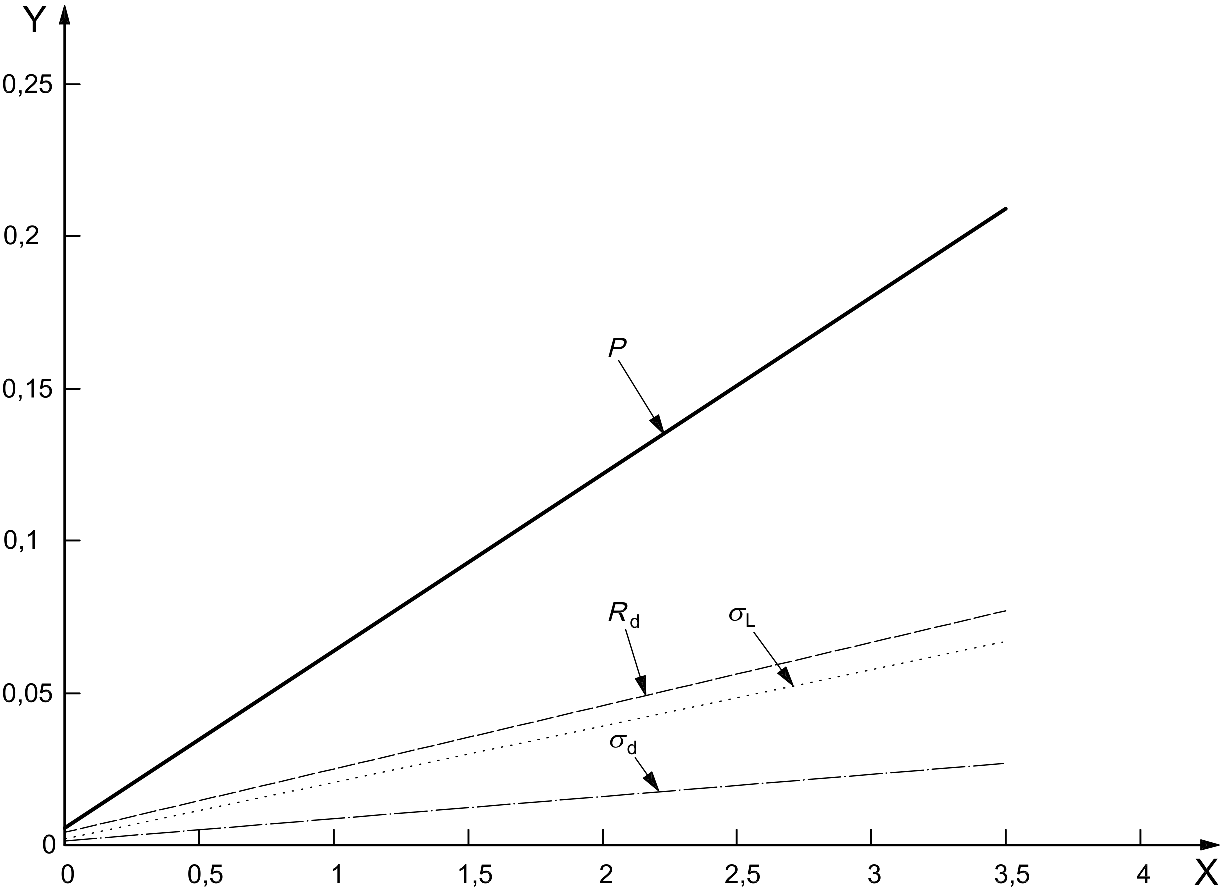
Annex E
(informative)

Precision data obtained by international analytical trials

NOTE Figures E.1 to E.7 are graphical representations of the equations in 8.4.1.



Key

X mass fraction of aluminium, %

Y precision, %

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

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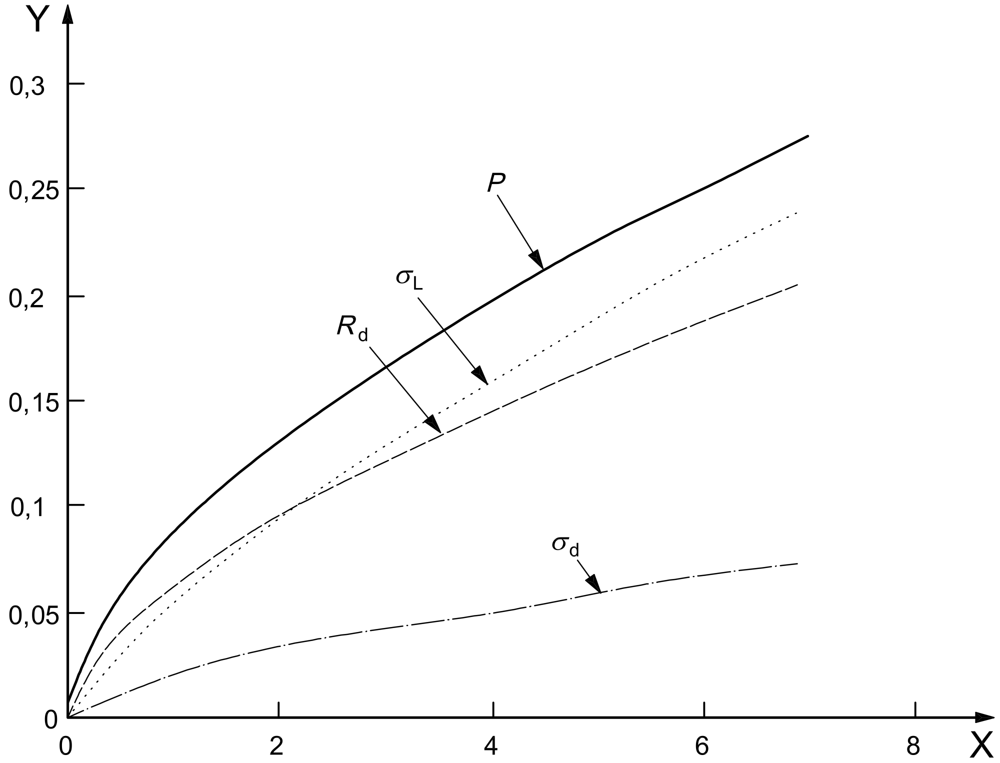
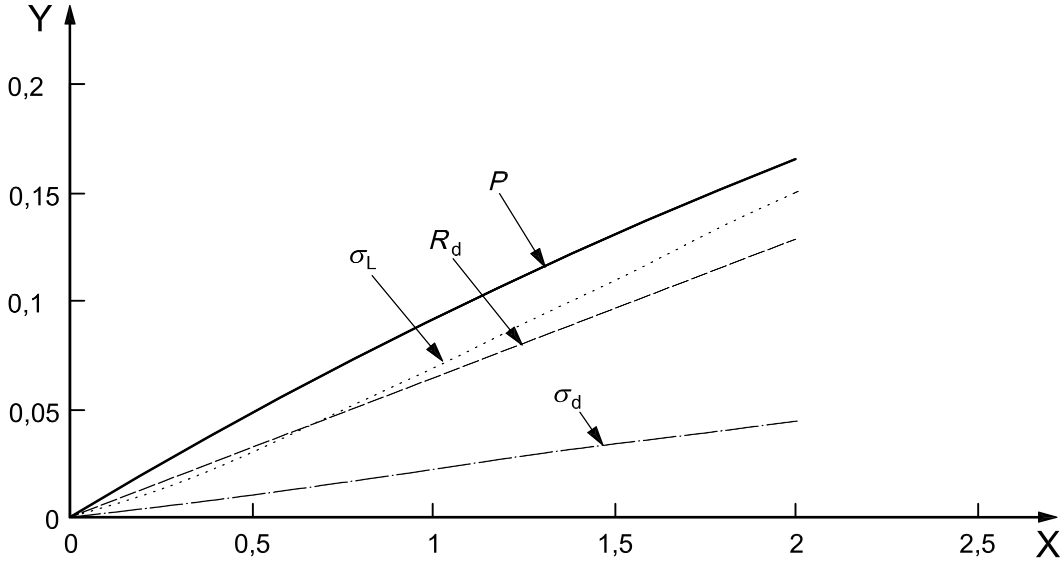


Key

X mass fraction of calcium, %

Y precision, %

Figure E.2 — Least-squares fit of precision against X for calcium



Key

X mass fraction of magnesium, %

Y precision, %

Figure E.3 — Least-squares fit of precision against X for magnesium

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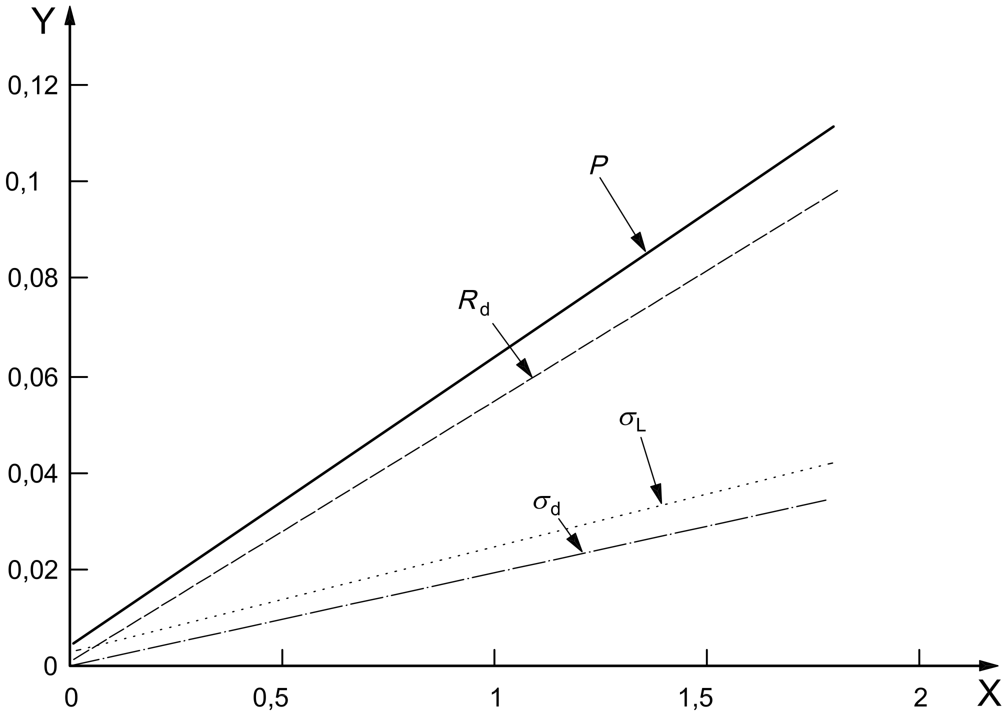

Key

X mass fraction of manganese, %

Y precision, %

Figure E.4 — Least-squares fit of precision against X for manganese

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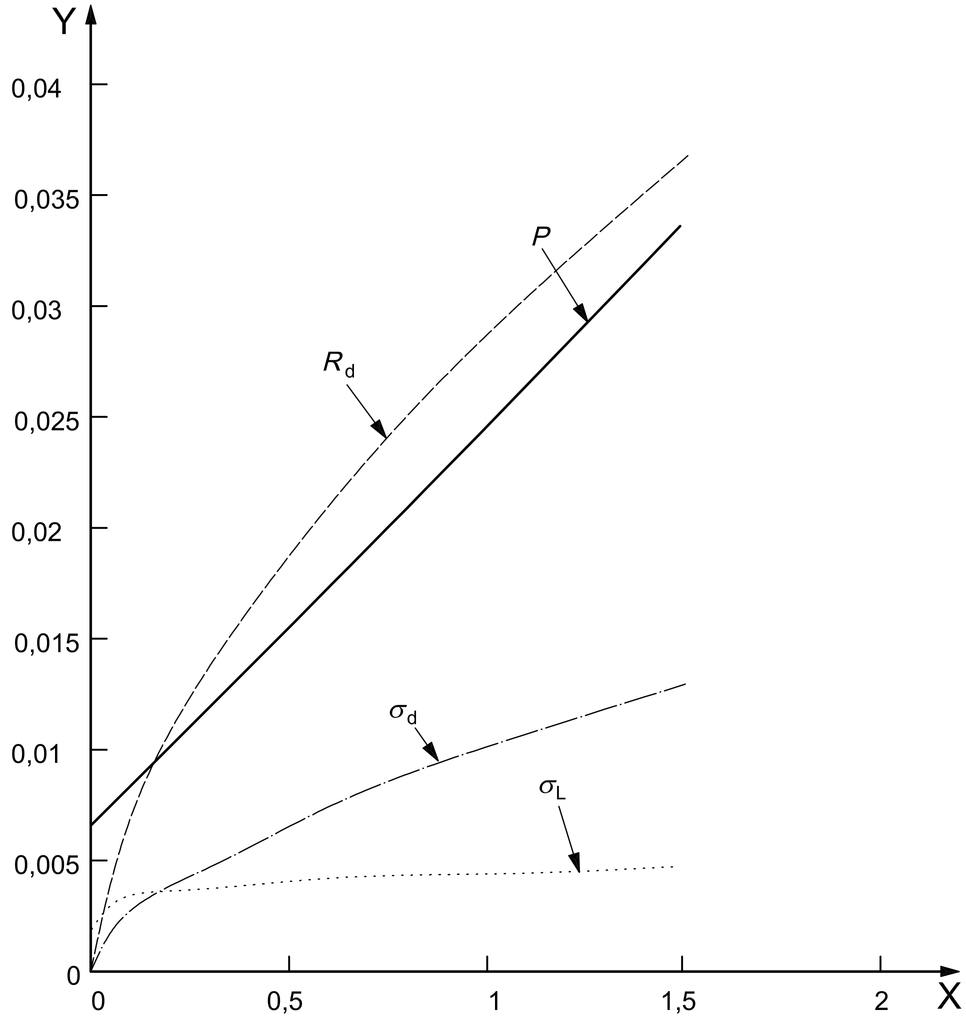

Key

X mass fraction of phosphorus, %

Y precision, %

Figure E.5 — Least-squares fit of precision against X for phosphorus

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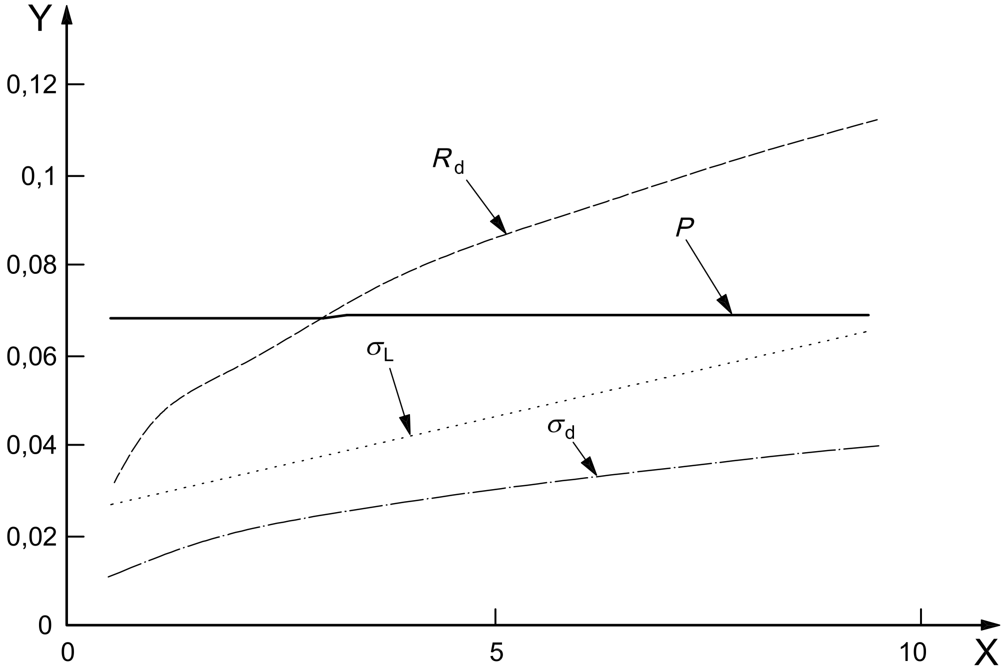

Key

X mass fraction of silicon, %

Y precision, %

Figure E.6 — Least-squares fit of precision against *X* for silicon

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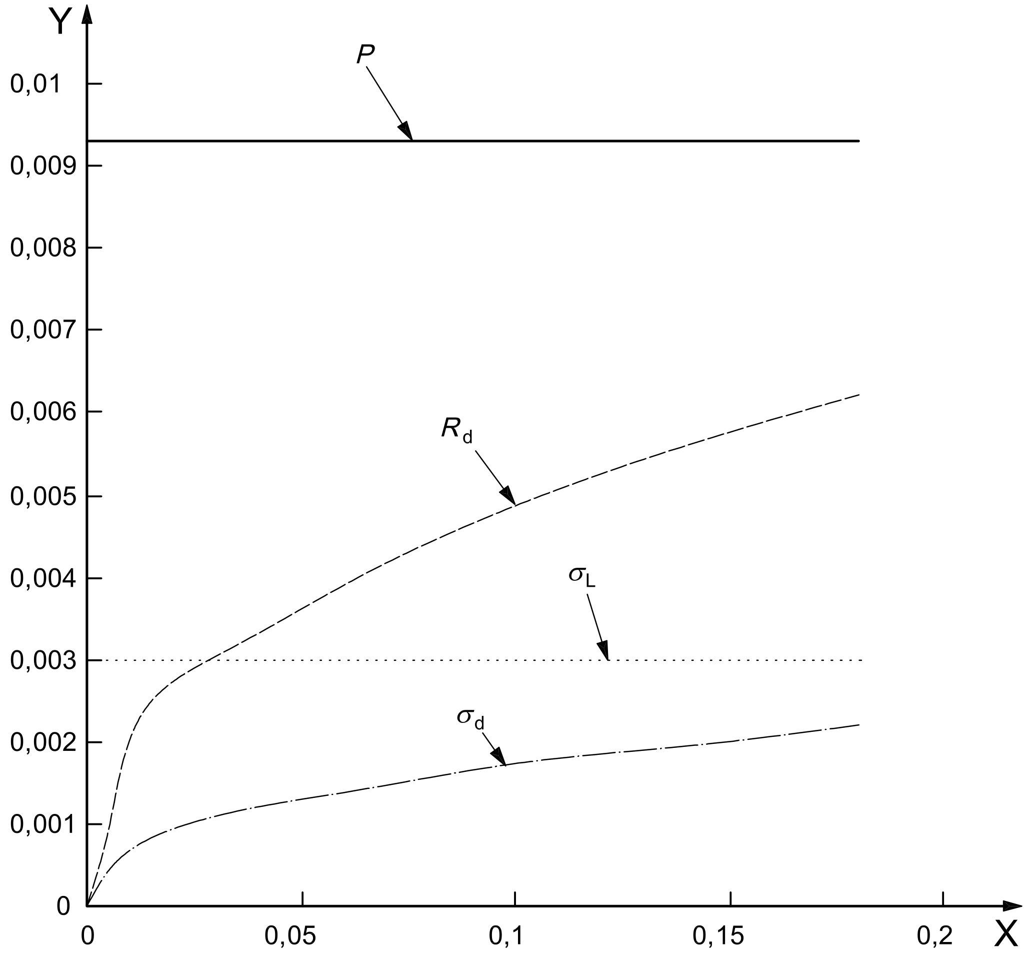

Key

X mass fraction of titanium, %

Y precision, %

Figure E.7 — Least-squares fit of precision against X for titanium

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