INTERNATIONAL STANDARD

ISO 22682

First edition
2017-08

Iron ores — Determination of trace elements — Plasma spectrometric method

Minerais de fer — Détermination d'éléments traces — Méthode par spectrométrie avec plasma

Reference number
ISO 22682:2017(E)

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see the following URL: www.iso.org/iso/foreword.html.

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

Iron ores — Determination of trace elements — Plasma spectrometric method

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

1 Scope

This document specifies a method for the determination of phosphorus, vanadium, titanium, copper, nickel, chromium, barium and cobalt in iron ores, by inductively coupled plasma atomic emission spectrometry (ICP-AES).

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

Table 1 — Concentration ranges

Element	Concentration range for referee purpose % (mass fraction)	Concentration range for non-referee purpose % (mass fraction)
P	0,000 2 to 0,150	0,000 2 to 0,150
V	0,003 0 to 0,024	0,003 0 to 0,024
Ti	0,015 0 to 0,120	0,015 0 to 0,120
Cu	0,0014 to 0,250	0,001 4 to 0,250
Ni	0,005 0 to 0,090	0,005 0 to 0,090
Cr		0,004 0 to 0,015
Ba		0,002 8 to 0,035
Co		0,002 0 to 0,100

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 — Single-volume pipettes*

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

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

ISO 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*

ISO 11323, *Iron ore and direct reduced iron — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11323 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

4 Principle

The test portion is decomposed with L-ascorbic acid, hydrofluoric acid, concentrated hydrochloric acid, concentrated nitric acid and then evaporated to dryness. The dry mass is dissolved in hydrochloric acid (1 + 1) and the solution is made up to 100 ml.

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

5 Reagents

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

5.1 High-purity iron, metal, of minimum purity grade 99,99 % (mass fraction).

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

5.3 Nitric acid, ρ 1,38 g/ml to 1,4 g/ml

5.4 Hydrofluoric acid, ρ 1,13 g/ml to ρ 1,16 g/ml.

5.5 Sulfuric acid, p.a. grade.

5.6 L-ascorbic acid, $C_6H_8O_6$.

5.7 Stock solutions.

Stock solutions shall be prepared by convenient handling moisture-free high-purity salts, dried until a constant mass and cooled in a desiccator. High-purity metals of minimum purity grade of 99,9 % (mass fraction) can also be used to prepare vanadium, titanium, copper, nickel and chromium stock solutions. Stock solutions may also be prepared by independent laboratories or reagent suppliers.

5.7.1 Phosphorus, 1 000 µg/ml.

Dissolve 4,393 6 g of potassium dihydrogen orthophosphate (KH_2PO_4) 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.

5.7.2 Vanadium, 1 000 µg/ml.

Dissolve 1,000 0 g of high-purity vanadium metal or 2,296 3 g of ammonium metavanadate (NH_4VO_3) in 20 ml of nitric acid (5.3) in a covered tall-form beaker with heating. When dissolution is complete, cool and transfer to a 1 000 ml one mark-volumetric flask, dilute to volume with water and mix.

5.7.3 Titanium, 1 000 µg/ml.

Dissolve 1,000 0 g of high-purity titanium metal in 100 ml of hydrochloric acid (5.2) in a covered tall-form beaker with heating or 4,135 1 g of high-purity ammonium hexafluorotitanate [$(NH_4)_2TiF_6$] in warm distilled water containing drops of hydrofluoridic acid (5.4) in a covered tall-form PTFE beaker. When dissolution is complete, cool and transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

5.7.4 Copper, 1 000 µg/ml.

Dissolve 1,000 0 g of high-purity copper metal in 20 ml of nitric acid (5.3) in a covered tall-form beaker. 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.

5.7.5 Nickel, 1 000 µg/ml.

Dissolve 1,000 0 g of high-purity nickel metal in 20 ml of nitric acid (5.3) in a covered tall-form beaker with heating. When dissolution is complete, cool and transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

5.7.6 Chromium, 1 000 µg/ml.

Dissolve 1,000 0 g of high-purity chromium metal in 100 ml of nitric acid (5.3) or 7,695 8 g of chromium (III) nitrate nonahydrate [$Cr(NO_3)_3{\cdot}9H_2O$] in 20 ml of nitric acid (5.3) in a covered tall-form beaker with heating. When dissolution is complete, cool and transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

5.7.7 Barium, 1 000 µg/ml.

Dissolve 1,437 0 g of high-purity barium carbonate ($BaCO_3$) in 20 ml of nitric acid (5.3) in a covered tall-form beaker with heating. When dissolution is complete, cool and transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

5.7.8 Cobalt, 1 000 µg/ml.

Dissolve 2,018 2 g of cobalt carbonate ($CoCO_3$) in 20 ml of nitric acid (5.3) in a covered tall-form beaker with heating. When dissolution is complete, cool and transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

5.8 Calibration and reference solutions.

Calibration solutions are defined as the solutions required for the determination of the line peak and background position(s) and 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 five calibration solutions is necessary to cover the concentration ranges given in Table 1. For test samples having narrower concentration ranges, calibration solutions are prepared to cover the region of interest.

In the case of nonlinearity, either a less sensitive line shall be used or appropriate dilutions of sample and calibration solutions shall 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 and acids shall be added (see Note in Table A.1). For each calibration solution, the procedure described in 8.4.1 shall be followed, replacing the test sample with a suitable amount of high-purity iron (5.1).

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

6 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.

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

6.2 Platinum or suitable platinum alloy crucibles, having a minimum volume of 30 ml.

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

6.4 ICP spectrometer.

Any conventional ICP spectrometer, with radial or axial observation path 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 (see 8.4.2.2), carried out prior to the measurements.

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

For the analysis of samples having concentrations in the background equivalent concentration (C_{BE}) 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
P	178,290
V	311,071/309,311/310,230
Ti	334,941/336,120
Cu	327,396/224,700/324,75
Ni	231,604
Cr	267,716
Ba	455,405
Co	228,616/238,892

7 Sampling and samples

7.1 Laboratory sample

For analysis, use a laboratory sample of minus 100 µm 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.

7.2 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.)

For ores having significant content of combined water or oxidizable compounds, an air-equilibrated test sample shall be prepared in accordance with ISO 2596 to determine the dry sample mass using the hygroscopic moisture.

8 Procedure

8.1 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.

8.2 Test portion

Taking several increments, weigh, to the nearest 0,000 1 g, approximately 1,0 g of the predried test sample obtained in accordance with 7.2.

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

8.3 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 7.2.

For the blank test, a suitable amount of high-purity iron (5.1) shall be used in place of the test sample.

The certified reference material shall be of the same type as the sample to be analysed and the properties of the two materials shall 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 9.4.4).

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.

8.4 Determination

8.4.1 Decomposition of the test portion

Transfer the weighed test portion to a 250 ml capacity PTFE Erlenmeyer flask with cover.

Add 0,5 g of L-ascorbic acid (5.6), moisten with water, 5,0 ml of hydrofluoric acid (5.4) and 30 ml of concentrated hydrochloric acid (5.2) and take to a hotplate for 2 h. (The hotplate temperature shall be controlled between 120 °C and 140 °C; if necessary use a thermometer inserted in a beaker containing sulfuric acid.)

Add, after complete dissolution, concentrated nitric acid (5.3) drop by drop until complete oxidation of the sample (approximately 10 ml) and keep heating in the hotplate for 30 min with the cover, and after that time, remove the cover and take to complete dryness.

Recover in 20 ml of hydrochloric acid 1 + 1 (5.2), and take to the hotplate until the dissolution is completed. Filter in white class filter paper.

Transfer the filtrate to a 100 ml volumetric flask. Make up to volume. If necessary, confirm the absence of undecomposed material by transferring the filter to a pre-weighed platinum crucible followed by gentle burn in a Bunsen burner, followed by ashing at 900 °C in a muffle furnace. Confirm absence of residue by taking the difference of crucible masses, before and after the ashing operation.

Carry out also a blank test using all reagents.

8.4.2 Adjustment of spectrometer

8.4.2.1 General

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

The definition of specific ICP components such as type of plasma observation view, torch, nebulizer as well as all instrumental parameters such as plasma power, test sample solution uptake rate, etc., shall be defined during the performance test optimization procedure (see 8.4.2.2), to comply with the performance parameter figures specified in Table 3, and shall remain unchanged thereafter during calibration and analysis.

8.4.2.2 Performance test

The performance test is devised with the purpose of optimizing the ICP spectrometer to carry out the analysis with adequate sensitivity and precision. Target values for these figures, called method performance parameters are listed in Table 3.

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

— detection limit (L_D);

— background equivalent concentration (C_{BE});

— short-term precision ($\sigma_{r,N\min}$).

The definitions of these terms and the procedure for their evaluation shall be as described in Annex B.

The procedure shall be carried out as many times as necessary, with the optimization of the instrument parameters after each turn, until the figures obtained are equal or lower than those given in Table 3.

Table 3 — Recommended performance parameters

Element	λ nm	Adopted C_{BE} µg/ml	Adopted L_D µg/ml	$\sigma_{r,N\min}$ %
P	178,287	0,86	0,025	2
V	310,230	0,44	0,021	2
Ti	334,941	0,12	0,003	2
Cu	324,75	0,28	0,003	2
Ni	231,604	0,53	0,016	2
Cr	267,716	0,25	0,007	2
Ba	455,403	0,06	0,002	2
Co	228,616	0,30	0,020	5

8.4.2.3 Measurements

8.4.2.3.1 Calibration solutions

Prepare a series of at least five calibration solutions plus a blank, all containing the equivalent of 6 000 µg/ml of iron (Fe), from 0,6 g of high-purity iron (5.1) portions, following exactly the decomposition of the test portion procedure described in 8.4.1. Add convenient amounts of each single element stock solutions (5.7.1 to 5.7.8) to cover the required analytical range. A suggested set of calibration solutions is given in Annex A.

Aspirate the calibration solutions in order of increasing concentration, starting with the blank (zero) calibration solution.

Aspirate water between each solution and repeat the measurements at least twice. Take the average of the readings.

If saturation of detector(s) occurs while running the most concentrated calibration solutions, establish the limit of linearity range of the curve and either choose a less sensitive line from this limit or conveniently dilute these calibration standards, plotting a new specific calibration curve to cover this high range of concentration, adding, if necessary, new calibration solutions, to comply with a required minimum of five points per curve.

For the concentration ranges covered by this procedure, it is necessary to verify if the chosen lines need background correction. This correction is performed by means of careful choice of their background position(s) prior to calibration and analysis. To assess the background position(s) all the 5 calibration solutions, the NFe solution (to be used for assessment of interferences and contamination of reagents) and a typical test sample, submitted to dissolution according to 8.4.1, should be scanned around the chosen lines. Except for the NFe calibration solution, scanned to test for eventual reagents contamination, all others should present background levels not significantly different from the test solution, indicating that matrix matching, in terms of viscosity and surface tension has been achieved.

After initial calibration has been established, a two-point recalibration procedure can be used for routine analysis. In this case, proceed according to 9.3.

8.4.2.3.2 Test solutions

Immediately after aspiration of the calibration solutions, commence 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.

9 Calculation of results

9.1 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 shall be carried out in accordance with 9.2.

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 shall be within the laboratory acceptance criteria.

Calibration-graph drift-correction procedures may be used, provided that they are carried out in accordance with 9.3 immediately before analysis of the test solutions.

9.2 Correction of spectral interference

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

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

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 reagents and interfering element named "j") synthetic solution series.

The relationship between actual content of interfering element (x_j) and apparent content of interfering element (x_{ij}) is calculated by the least-squares method, as shown by Formula (1):

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

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 analyte (i).

Being corrected by the interference factor, the actual mass fraction (content) of the analyte is calculated as one of the following.

a) Each element content, expressed as a percentage by mass, is given by Formulae (2) and (3):

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

b) For V = 100 ml:

$$x_i = \frac{\left(\rho_1 - \rho_0\right) \times 100}{10^6} \times \frac{100}{m} - \sum w_j \, l_{ij} = \frac{\left(\rho_1 - \rho_0\right)}{100\, m} - \sum w_j \, l_{ij} \tag{3}$$

where

x_i is the element (analyte) content expressed as a percentage by mass;

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;

V is the final volume of calibration and test solutions (100 ml as suggested in 8.4).

Over-correction of spectral interference is not acceptable. The allowable maximum value for correction is about 10 times the repeatability of analyte content under examination.

If the correction value is greater than this, the correction for ICP analysis shall not be applied.

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

NOTE 2 With the suggested final calibration solution volume V = 100 ml and no interfering element present, Formula (2) reduces to

$$x_i = \frac{(\rho_1 - \rho_0)}{100\ m}$$

9.3 Standardization of calibration graph (drift correction)

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

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

b) 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 shown by Formulae (4) and (5):

$$\alpha = \frac{I_{HO} - I_{LO}}{I_H - I_L} \quad (4)$$

$$\beta = I_{LO} - \alpha\, I_L \quad (5)$$

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.

c) The measured intensity of the test solution shall be corrected using the correction factors α and β, as shown by Formula (6):

$$I_C = \alpha\, I + \beta \quad (6)$$

where

I_C is the corrected value of intensity;

I is the measured value of intensity.

d) 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, for 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.

9.4 General treatment of results

9.4.1 Repeatability and permissible tolerances

The precision of this analytical method is expressed by the regression formulae given in Table 4.

NOTE Additional information is given in Annex D.

Table 4 — Regression formulae

Element	σ_d	σ_L	R_d	P
P	0,000 39 + 0,032 57 X	0,000 51 + 0,034 74 X	0,001 10 + 0,092 12 X	0,001 14 + 0,081 00 X
V	0,000 17 + 0,041 78 X	0,000 41 + 0,027 53 X	0,000 48 + 0,118 17 X	0,001 18 + 0,117 23 X
Ti	0,000 27 + 0,035 78 X	−0,000 09 + 0,054 70 X	0,000 76 + 0,101 20 X	0,000 16 + 0,171 15 X
Cu	0,000 05 + 0,059 74 X	0,000 14 + 0,023 57 X	0,000 14 + 0,168 97 X	0,000 42 + 0,105 36 X
Ni	0,001 6	0,000 08 + 0,161 38 X	0,004 5	0,000 37 + 0,257 36 X
Cr	$0{,}0120\ 3\ X^{0{,}602\ 75}$	0,000 25 + 0,096 95 X	0,034 026 X 0,602 75	0,000 67 + 0,389 81 X
Ba	0,000 28 + 0,046 40 X	0,000 37 + 0,043 27 X	0,000 79 + 0,131 23 X	0,001 16 + 0,121 90 X
Co	0,000 15 + 0,037 14 X	0,000 16 + 0,203 46 X	0,000 42 + 0,105 05 X	0,000 49 + 0,137 54 X

Key

X concentration of element in the sample

σ_d independent duplicate standard deviation

σ_L between-laboratories standard deviation

R_d independent duplicate limit

P permissible tolerance between laboratories

9.4.2 Determination of analytical result

9.4.2.1 Mean of duplicates

Having computed the independent duplicate results according to Formula (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 9.4.4).

9.4.2.2 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 described in 9.4.2.

9.4.2.3 Computation

Compute using Formula (7):

$$\mu_{12} = \frac{\mu_1 + \mu_2}{2} \tag{7}$$

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

μ_{12} is the mean of final results.

Substitute μ_{12} 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.

9.4.3 Check for trueness

9.4.3.1 The trueness of the analytical method shall be checked by applying it to a certified reference material (CRM) or a reference material (RM). The procedure is the same as that described above. After confirmation of the precision, the final laboratory result is compared with the reference or certified value A_c. There are two possibilities:

a) $|\mu_c - A_c| \leq C$, 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.

9.4.3.2 C shall be calculated as shown by Formula (8):

$$C = 2\sqrt{\frac{s_{Lc}^2 + \frac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_d^2}{n}} \quad (8)$$

where

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 carried out on the CRM/RM;

σ_L and σ_d are as defined in 9.4.1.

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

— if there are sufficient data to enable the between-laboratories standard deviation to be estimated, delete the expression s^2_{Wc} / n_{Wc} and regard s_{Lc} as the standard deviation of the laboratory means;

— if the certification has been made by only one laboratory or if the interlaboratory results are missing, use the condition shown by Formula (9):

$$C = 2\sqrt{2\,\sigma_L^2 + \frac{\sigma_r^2}{n}} \tag{9}$$

CRMs certified by only one laboratory should be avoided unless it is known to have an unbiased certified value.

9.4.4 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 fourth 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.

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 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 shall be calculated to four decimal places and rounded off to the second decimal place.

9.5 Oxide factors

Oxide concentrations may be obtained by multiplying the element concentrations by the factors given in Table 5.

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

Element	Oxide	Conversion factor
P	P_2O_5	2,291 4
Ti	TiO_2	1,668 3
Ba	BaO	1,116 5

10 Test report

The test report shall include the following information:

a) the name and address of the testing laboratory;

b) the date of issue of the test report:

c) a reference to this document, i.e. ISO 22682;

d) the details necessary for the identification of the sample;

e) the result of the analysis;

f) the reference number of the result;

g) any characteristics noticed during the determination, and any operations not specified in this document which may have had an influence on the result, for either the test sample or the certified reference material(s).

Annex A
(informative)

Suggested calibration solutions

Table A.1 — Suggested calibration solutions

	Solution Nfe[a]		Branco K		Solution A		Solution B		Solution C		Solution D		Solution E	
	µg/ml	µg/g	µg/ml	µg/g	µg/ml	µg/g	µg/ml	µg/g	µg/ml	µg/g	µg/ml	µg/g	µg/ml	µg/g
P	0,5	50	0	0	0,5	50	1,0	100	10	1 000	5,0	500	20	2 000
V	0,1	10	0	0	0,1	10	0,5	50	5,0	500	10	1 000	40	4 000
Ti	0,5	50	0	0	0,5	50	1,0	100	10	1 000	5,0	500	20	2 000
Cu	0,1	10	0	0	0,1	10	0,5	50	1,0	100	3,0	300	6,0	600
Ni	0,2	20	0	0	0,2	20	1,0	100	0,5	50	3,0	300	6,0	600
Cr	0,1	10	0	0	0,1	10	1,0	100	0,5	50	2,0	200	6,0	600
Ba	0,5	50	0	0	0,5	50	1,0	100	5,0	500	10	1 000	80,0	8 000
Co	0,1	10	0	0	0,1	10	1,0	100	0,5	50	2,0	200	6,0	600
Fe[b]	0	0	6 000	60 %	6 000	60 %	6 000	60 %	6 000	60 %	6 000	60 %	6 000	60 %

NOTE 1 Values, in µg/g, refer to a 1:100 sample-to-final-volume ratio.

NOTE 2 Multi-element solutions tend to deteriorate after very short time of use. Phosphorus, in particular, may be seriously affected. Separate phosphorus (or any other element) single element calibration solutions can be used, as long as they all have the proper amount of iron and reagents included. It is advisable to prepare fresh solutions whenever required, or carry out periodic verification tests to confirm the integrity of the stored solutions.

[a] To be used only for assessment of interferences and contamination of reagents.

[b] From 0,6 g of high-purity iron (5.1) for a suggested 100 ml volume of prepared calibration solution.

Annex B
(normative)

Plasma spectrometer performance tests

B.1 Purpose

The performance tests given in this annex are intended to provide means to optimize the ICP spectrometer through the adequate measurement of its performance for the method in question, 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 (L_D), background equivalent concentration (C_{BE}) and short-term precision (σ_r).

The elements to be investigated and figures to be achieved for optimum performance are given in Table 3.

B.2 Terms and definitions

B.2.1 Detection limit (L_D)

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 (C_{BE})

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 (σ_r)

The relative standard deviation of a series of instrument readings taken at predetermined conditions expressed as a percentage of the average intensity.

B.3 Reference solutions

To perform this test, use the three calibration solutions defined in Annex A: the blank solution, solution A (containing the minimum concentration range established in Table 1), and solution B.

B.4 Procedure (to be carried out for all elements)

The procedure shall be as follows.

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

b) Define the analytical lines and measure only the peak absolute intensities (without background subtraction).

c) Aspirate the blank and take 10 peak intensity readings.

d) Repeat the operation for the other two reference solutions.

e) Calculate the slopes of the analytical graphs using Formula (B.1):

$$M = \frac{C_2}{\bar{I}_2 - \bar{I}_B} \quad \text{(B.1)}$$

where

M is the slope of analytical graph;

C_2 is the concentration of the calibration solution B;

$\bar{I}_2$ is the average of 10 gross peak intensity readings of calibration solution B;

$\bar{I}_B$ is the average of 10 intensity readings at peak position of blank solution.

f) Determine L_D from Formula (B.2):

$$L_D = 3\, s_b\, M \quad \text{(B.2)}$$

where

L_D is the detection limit, in micrograms per millilitre;

s_b is the standard deviation of 10 intensity readings for the blank solution.

g) Calculate C_{BE} from Formula (B.3):

$$C_{BE} = M \times \bar{I}_B \quad \text{(B.3)}$$

where C_{BE} is the background equivalent concentration, in micrograms per millilitre.

h) For the calibration solution A, calculate the net average intensity determined from the difference of the gross average peak intensity and the average blank intensity, as shown by Formula (B.4):

$$\bar{I}_{net} = \bar{I}_A - \bar{I}_B \quad \text{(B.4)}$$

where

$\bar{I}_{net}$ is the net average intensity;

$\bar{I}_A$ is the gross average peak intensity;

$\bar{I}_B$ is the average blank intensity.

i) $\sigma_{r,Nmin}$ is estimated from the calibration solution A. Calculate the relative standard deviation of the net intensity for the calibration solution A, shown by Formula (B.5):

$$\sigma_{r,Nmin} = \frac{\sqrt{\sigma_A^2 + \sigma_b^2}}{\bar{I}_{net}} \times 100 \quad \text{(B.5)}$$

where

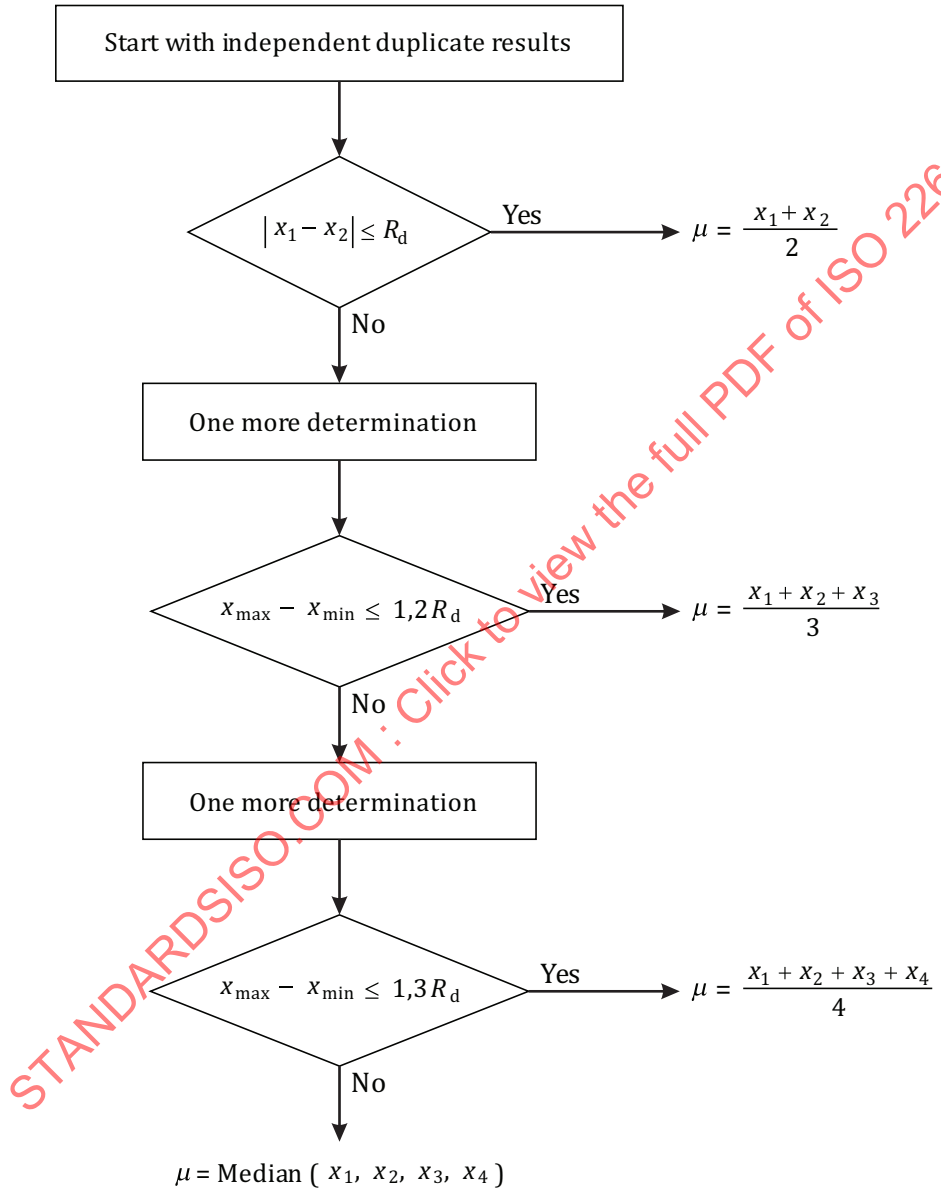
σ_A is the standard deviation of 10 intensity readings for reference solution A;

σ_b is the standard deviation of 10 intensity readings for the blank solution;

$\bar{I}_{net}$ is the net average intensity for calibration solution A.

Annex C
(normative)

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



Key

R_d permissible tolerance within a laboratory (repeatability), as defined in 9.4.1

Figure C.1 — Flowchart of the procedure for the acceptance of analytical values for test samples

Annex D
(informative)

Derivation of repeatability and permissible tolerance formulae

The formulae in 9.4.1 were derived from the results of international trials carried out in 2013 on 22 iron ore samples, involving eight laboratories in three countries.

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 2 N 2059) 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 TCR 04 and TCR 05.

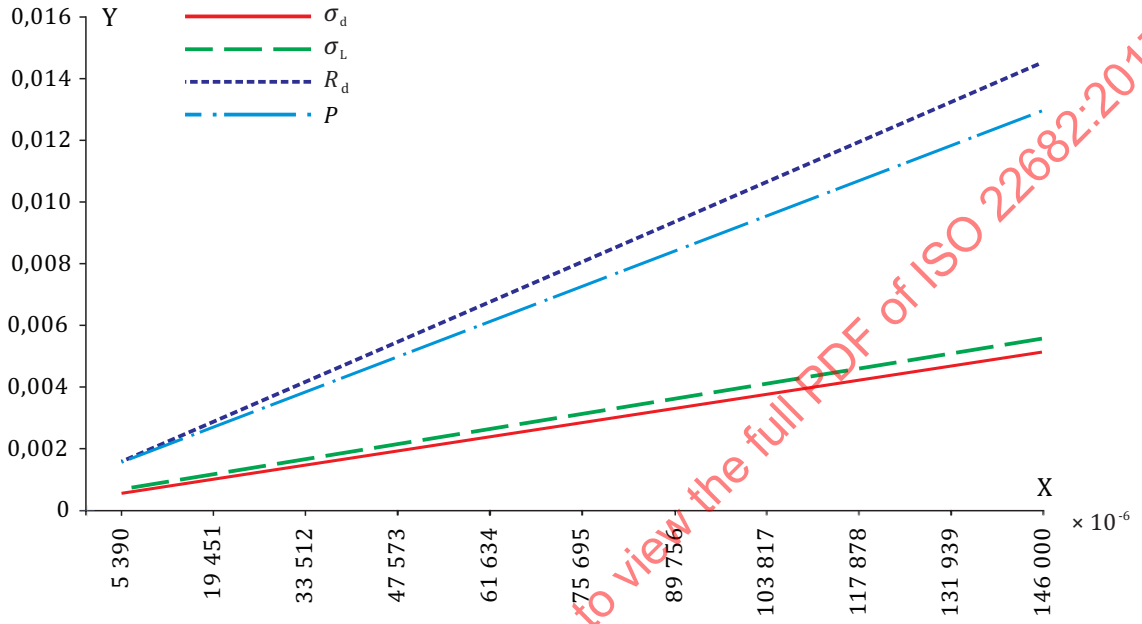
Table D.1 — Element contents of test samples

Sample	Element content, %							
	P	V	Ti	Cu	Ni	Cr	Ba	Co
LA 01 Ouro Preto Iron Ore BR	0,049 46	0,002 84	0,019 30	0,001 430	0,001 726	0,007 73	0,006 54	0,001 326
LA 02 Ouro Preto Pellet BR	0,030 30	0,003 46	0,070 2	0,000 679	0,001 069	0,013 56	0,006 37	0,000 760
LB 01 Nova Lima Iron Ore BR	0,048 83	0,006 42	0,038 11	0,000 382	0,000 829	0,008 25	0,004 59	0,000 46
LB 02 Nova Lima Pellet BR	0,048 41	0,003 11	0,058 86	0,000 720	0,001 162	0,012 62	0,005 53	0,000 622
LC 01 Itabirito Iron Ore BR	0,035 97	0,001 84	0,025 76	0,000 714	0,001 59	0,005 68	0,014 5	0,000 873
LE Barao de Cocais Iron Ore BR	0,012 951	0,004 38	0,024 10	0,000 31	0,000 369	0,002 42	0,000 46	0,000 300
LE 02 Barao de Cocais Iron Ore BR	0,028 73	0,004 78	0,026 89	0,000 543	0,000 867	0,002 40	0,016 01	0,006 74
LF 01 Belo Vale Iron Ore BR	0,054 29	0,002 77	0,026 68	0,000 845	0,001 762	0,001 50	0,008 67	0,000 911
LF 02 Belo Vale Iron Ore BR	0,028 63	0,001 37	0,025 17	0,000 807	0,000 912	0,001 43	0,012 60	0,000 617
LG 01 South Africa Iron Ore	0,146 0	0,002 44	0,065 2	0,001 751	0,000 965	0,002 22	0,006 44	0,000 587
LG 02 South Africa Iron Ore	0,020 35	0,002 97	0,035 48	0,000 532	0,001 798	0,002 70	0,002 08	0,001 375
LG 03 South Africa Iron Ore	0,136 7	0,002 25	0,054 44	0,000 794	0,000 735	0,002 50	0,007 49	0,000 295
LG 04 South Africa Iron Ore	0,047 81	0,002 20	0,060 9	0,001 268	0,002 06	0,004 11	0,002 43	0,000 737
LH 01 Iron Ore BR	0,036 90	0,001 24	0,014 16	0,000 337	0,000 476	0,000 94	0,002 85	0,000 270
LH 02 Iron Ore Geological sample BR	0,005 39	0,023 72	0,118 7	0,211 1	1,607	0,793	0,033 33	0,096 7
LI 01 Iron Ore BR	0,057 8	0,001 25	0,025 12	0,000 660	0,000 825	0,001 06	0,002 01	0,000 428
LJ 01 Anchieta Pellet BR	0,043 80	0,001 93	0,024 72	0,000 507	0,000 716	0,006 54	0,003 28	0,000 437
LJ 02 Mariana Pelletfeed BR	0,038 57	0,001 71	0,016 06	0,000 372	0,000 643	0,004 91	0,002 24	0,000 338
LL 01 Vitoria Iron Ore BR	0,027 12	0,003 83	0,024 41	0,000 496	0,000 830	0,002 82	0,004 52	0,004 33
LL 02 Vitoria Pellet BR	0,026 86	0,005 37	0,049 05	0,000 495	0,000 777	0,016 33	0,005 22	0,001 849
LM 01 Itaúna Iron Ore BR	0,037 68	0,003 81	0,037 49	0,000 975	0,002 16	0,005 69	0,001 47	0,000 616
LO 01 Iron Ore ITAK-024	0,062 76	0,003 93	0,111 1	0,002 399	0,001 109	0,004 49	0,005 12	0,000 511

Annex E
(informative)

Precision data obtained by international analytical trials

Figure E.1 is a graphical representation of the formulae for phosphorus (P) given in 9.4.1.



Key

X P content, in %

Y precision, in %

Figure E.1 — Least squares fit of precision against phosphorus