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Iron ores — Determination of nickel — Flame atomic absorption spectrometric method

Minerais de fer — Dosage du nickel — Méthode par spectrométrie d'absorption atomique dans la flamme

Reference number
ISO 15633:2009(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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 15633 was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

Introduction

The objective of a proposed revision of ISO 9685:1991 was to extend the lower limit for a flame atomic absorption spectrometric method determination of both chromium and nickel in iron ores down to 0,001 %. However, due to bias, the method for nickel could not be approved for referee purposes.

The 22nd meeting of ISO/TC 102/SC 2 decided to progress the document as a non-referee method.

Iron ores — Determination of nickel — Flame atomic absorption 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 flame atomic absorption spectrometric method for the determination of the nickel mass fraction of iron ores.

This method is applicable to mass fractions of nickel between 0,001 % and 0,1 % in natural iron ores, iron ore concentrates and agglomerates, including sinter products.

This method is not appropriate for referee purposes.

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*

3 Principle

The test portion of iron ore is decomposed by treatment with hydrochloric and nitric acids.

The major portion of iron in the filtrate is removed by extraction with 4-methylpentan-2-one.

The insoluble residue is ignited and silicon dioxide is removed by evaporation with hydrofluoric and sulfuric acids. The residue is fused with a mixture of sodium carbonate and sodium tetraborate, and then dissolved with hydrochloric acid and combined with the main solution.

The solution is aspirated into the flame of an atomic absorption spectrometer using an air-acetylene burner.

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

4 Reagents

During the analysis, use only reagents of recognized analytical grade, and only water that conforms to grade 2 of ISO 3696.

4.1 Sodium carbonate (Na_2CO_3), anhydrous powder.

4.2 Sodium tetraborate ($Na_2B_4O_7$), anhydrous powder.

4.3 Lithium tetraborate ($Li_2B_4O_7$), anhydrous powder.

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

4.5 Hydrochloric acid, ρ = 1,16 g/ml to 1,19 g/ml, diluted 2 + 1.

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

4.7 Hydrochloric acid, ρ = 1,16 g/ml to 1,19 g/ml, diluted 2 + 100.

4.8 Nitric acid, ρ = 1,4 g/ml.

4.9 Nitric acid, ρ = 1,4 g/ml, diluted 1 + 1.

4.10 Hydrofluoric acid, ρ = 1,13 g/ml, 40 % (mass fraction), or ρ = 1,19 g/ml, 48 % (mass fraction).

4.11 Sulfuric acid, ρ = 1,84 g/ml.

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

4.13 4-Methylpentan-2-one, (methyl isobutyl ketone, MIBK).

4.14 Nickel standard solution A, 100 µg Ni/ml.

Dissolve 0,1 000 g of nickel metal [purity $\geqslant$ 99,9 % (mass fraction)] (see Note to 4.15) in 30 ml of nitric acid (4.9). After cooling, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to volume with water and mix.

4.15 Nickel standard solution B, 10 µg Ni/ml.

Transfer 100,0 ml of nickel standard solution A (4.14) to a 1 000 ml one-mark volumetric flask. Dilute to volume with water and mix.

NOTE The purity of the metals stated on the certificates does not generally take into account the presence of absorbed gases such as oxygen, carbon monoxide, etc.

5 Apparatus

Ordinary laboratory apparatus, including one-mark pipettes and one-mark volumetric flasks complying with the specifications of ISO 648 and ISO 1042, and the following.

5.1 Platinum crucible, of minimum capacity 25 ml.

5.2 Muffle furnace.

5.3 Atomic absorption spectrometer, equipped with an air-acetylene burner.

WARNING — Follow the manufacturer's instructions for igniting and extinguishing the air-acetylene flame to avoid possible explosion hazards. Wear tinted safety glasses whenever the burner is in operation.

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

a) *Minimum sensitivity:* the absorbance of the most concentrated calibration solution (see 7.4.4) is 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) is not 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, are less than 1,5 % and 0,5 %, respectively, of the mean value of the absorbance of the most concentrated 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 vary with each instrument. The following parameters were successfully used in several laboratories and they can be used as guidelines. An air-acetylene flame was used.

Hollow-cathode lamp, mA	10
Wavelength, nm	232,0
Air flow rate, l/min	10
Acetylene flow rate, l/min	2,5

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 < 100 µm particle size which has been taken and prepared in accordance with ISO 3082. In the case of ores containing significant contents of combined water or oxidizable compounds, use a particle size of < 160 µm.

NOTE A guideline on significant contents of combined water and oxidizable compounds is incorporated in ISO 7764.

Ensure that the sample has not been pulverized in a nickel/chromium pot.

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 entire 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 be carried out either by the same operator at a different time or by a different operator including, in either case, appropriate recalibration.

7.2 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, in order 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 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.

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 8.2.4).

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.

7.4 Determination

7.4.1 Decomposition of the test portion

Transfer the test portion (7.2) to a 250 ml tall-form beaker. Moisten with a few millilitres of water. Add 25 ml of hydrochloric acid (4.4), cover with a watch-glass, and heat for about 1 h on a hotplate adjusted to give a temperature of 100 °C in a test beaker containing a similar volume and depth of sulfuric acid (4.11).

If the amount of insoluble reside is high, continue heating on a higher temperature zone of the hotplate without boiling the solution.

After heating, the volume of the solution should have decreased to about 10 ml.

Add 5 ml of nitric acid (4.8) and 0,2 ml of sulfuric acid (4.12), digest for about 15 min and evaporate the solution almost to dryness.

If the test sample contains significant barium content, the addition of sulfuric acid (4.12) should be omitted.

Be sure to cover with a watch-glass, in order to prevent sublimation of chlorides. During evaporation, shift the glass slightly.

Add 20 ml of hydrochloric acid (4.6), and heat to dissolve the salts. Cool, wash the watch-glass and the walls of the beaker, and filter the solution through a close-texture filter paper containing filter pulp (0,3 g to 0,4 g dry mass) into a 200 ml beaker. Carefully remove all adhering particles with a rubber-tipped glass rod or piece of moistened filter paper, and transfer to the filter, washing the paper with warm hydrochloric acid (4.7) until it is visibly free from iron, and again wash the paper with three or four portions of warm water. Reserve the filtrate and washings in the 200 ml beaker as the main solution. Transfer the filter paper and residue to a platinum crucible (5.1).

7.4.2 Removal of iron

Heat the main solution and evaporate almost to dryness. Dissolve the salts in 15 ml of hydrochloric acid (4.5) and transfer to a 200 ml separating funnel. Rinse the beaker with 20 ml of hydrochloric acid (4.5) and transfer the washings to the funnel.

Add 50 ml of 4-methylpentan-2-one (4.13) to the funnel and shake it for 1 min. Allow the two layers to separate and drain the lower aqueous layer into the original 200 ml beaker. Wash the organic layer by adding 10 ml of hydrochloric acid (4.5) to the funnel and shaking it for 30 s. Allow the two layers to separate and drain the lower aqueous layer into the 200 ml beaker to combine with the first aqueous layer. Discard the organic layer.

Heat the solution gently and expel almost all of the 4-methylpentan-2-one in the solution. Then add 5 ml of nitric acid (4.8) and evaporate to dryness. Dissolve the salts in 20 ml of hydrochloric acid (4.6).

7.4.3 Treatment of the residue

Dry and burn off the filter paper in the platinum crucible (5.1) at a low temperature (500 °C to 800 °C), and ignite the residue. Cool, moisten with 1 to 2 drops of water and add 3 drops of sulfuric acid (4.11) and 5 ml of hydrofluoric acid (4.10). Evaporate slowly to expel silicon dioxide and continue heating to remove the sulfuric acid. Ignite at 800 °C for several minutes and then cool. Add 1,2 g of a mixture of 0,8 g of sodium carbonate (4.1) and 0,4 g of sodium tetraborate (4.2) to the residue and mix. Heat gently for several minutes, then heat at 1 000 °C for 15 min in a muffle furnace (5.2) or over a pressurized air burner for a time sufficient to produce a clear melt.

Lithium tetraborate (4.3) may be used instead of sodium tetraborate (4.2). In this case, sodium tetraborate should be replaced with lithium tetraborate in the calibration solutions (7.4.4) and the flame-setting solutions (7.4.5).

Allow the crucible to cool, add 10 ml of hydrochloric acid (4.6) and heat gently to dissolve the melt. Combine this solution with the main solution from 7.4.2, heat to remove carbon dioxide and cool.

For samples containing a mass fraction of more than or equal to 0,01 % nickel, transfer to a 100 ml one-mark volumetric flask quantitatively, dilute to volume with water and mix. (This is the test solution.)

For samples containing a mass fraction of less than 0,01 % nickel, transfer to a 50 ml one-mark volumetric flask quantitatively, dilute to volume with water and mix. (This is the test solution.)

7.4.4 Preparation of the calibration solutions

Introduce into a series of six 200 ml beakers, 30 ml of hydrochloric acid (4.6), 0,2 ml of sulfuric acid (4.12) and a mixture of 0,8 g of sodium carbonate (4.1) and 0,4 g of sodium tetraborate (4.2). Heat to remove carbon dioxide and cool.

Using pipettes or burettes, add 0 ml, 1,0 ml, 3,0 ml, 5,0 ml, 7,0 ml and 10,0 ml of nickel standard solution A (4.14) for samples containing 0,01 % to 0,1 % nickel, or nickel standard solution B (4.15) for samples containing 0,001 % to 0,01 % nickel.

Transfer to six 100 ml one-mark volumetric flasks for samples containing 0,01 % to 0,1 % nickel or 50 ml one-mark volumetric flasks for samples containing 0,001 % to 0,01 % nickel, respectively, dilute to volume with water and mix. These calibration solutions cover the nickel concentration ranges 0 µg/ml to 10 ug/ml in the case of standard solution A, or 0 µg/ml to 2 µg/ml in the case of standard solution B.

7.4.5 Adjustment of the atomic absorption spectrometer

Optimize the response of the instrument as specified in 5.3. Set the wavelength at 232,0 nm to obtain minimum absorbance and adjust the readout to zero absorbance. Light the air-acetylene flame. After 10 min of preheating the burner, aspirate water and, if necessary, readjust the readout to zero absorbance. Aspirate the calibration solution of highest nickel content (7.4.4) and adjust the fuel flow and burner position to obtain maximum absorbance.

Check that the conditions for zero absorbance have been maintained and evaluate the criteria in 5.3.

Repeat the aspiration of water and the calibration solution of highest nickel content to establish that the absorbance reading is not drifting. Set the reading for water to zero absorbance.

7.4.6 Atomic absorption measurements

Aspirate the calibration solutions (7.4.4) and the test solution (7.4.3) in order of increasing absorption, starting with the zero calibration solution (7.4.4) and the blank test solution. When a stable response has been obtained for each solution, record the readings. Aspirate water between each calibration and test solution.

Correct the absorbance values obtained for the calibration solutions by subtracting the absorbance of the zero calibration solution, and prepare a calibration graph by plotting the net absorbance values against micrograms of nickel per millilitre. If the graph is substantially linear, subtract the absorbance obtained for the blank test from the absorbance obtained for the test solution and, using the graph, convert the net absorbance to micrograms of nickel per millilitre.

If any curvature obtained approaches the limit specified in 5.3 b), replot the graph using uncorrected values for all solutions and establish the concentration of the zero calibration solution from the intercept of the graph on the negative side of the concentration axis. Add this value to the nominal concentration values of the calibration solutions and replot the graph to pass through the origin. Determine from the graph the concentration of nickel, in micrograms per millilitre, in the blank test and test solutions respectively, and correct the concentration of the test solution with the concentration of the blank test.

8 Expression of results

8.1 Calculation of mass fraction of nickel

The mass fraction of nickel, w_{Ni}, expressed as a percentage by mass, is calculated to five decimal places, using the following equations:

For $< 0{,}01$ % (mass fraction) of nickel content,

$$w_{\mathrm{Ni}}\,\% = \frac{\rho_{\mathrm{Ni}} \times 50}{m \times 10^{6}} \times 100 = \frac{\rho_{\mathrm{Ni}} \times 0{,}005}{m} \qquad (1)$$

For $\geqslant 0{,}01$ % (mass fraction) of nickel content,

$$w_{\mathrm{Ni}}\,\% = \frac{\rho_{\mathrm{Ni}} \times 100}{m \times 10^{6}} \times 100 = \frac{\rho_{\mathrm{Ni}} \times 0{,}01}{m} \qquad (2)$$

where

w_{Ni} is the mass fraction (%) of nickel in the test portion;

ρ_{Ni} is the concentration, in micrograms per millilitre, of nickel in the final test solution;

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

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. See Annexes B and C.

$$R_\mathrm{d} = 0{,}004\,3X^{0{,}3051} \tag{3}$$

$$P = 0{,}021\ 5X^{0{,}4977} \tag{4}$$

$$\sigma_\mathrm{d} = 0{,}0015X^{0{,}3051} \tag{5}$$

$$\sigma_\mathrm{L} = 0{,}007\,6X^{0{,}5242} \tag{6}$$

where

X is the concentration of nickel in the sample, expressed as mass fraction (%), and is calculated as follows:

- for the within-laboratory Equations (3) and (5), the arithmetic mean of the duplicate values,
- for the between-laboratories Equations (4) and (6), the arithmetic mean of the final results (8.2.5) 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.

8.2.2 Determination of analytical result

Having computed the independent duplicate results according to Equation (1) or (2), compare them with the independent duplicate limit (R_d), using the procedure given in Annex A, Figure A.1, and obtain the final laboratory result μ (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 procedure described in 8.2.2.

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 the final results.

Substitute $\mu_{1,2}$ for X in Equation (4) 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 CRM/RM 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 CRM;

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.

For a CRM certified by an interlaboratory test programme

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

where

$V(A_c)$ is the variance of the certified 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;

σ_d is the independent duplicate standard deviation;

σ_L is the between-laboratories standard deviation.

If the certification has been made by only one laboratory or if the interlaboratory results are missing, it is advisable that this material not be used in the application of the standard. In case its use is unavoidable, substitute σ_L^2 for $V(A_c)$.

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, calculated to five decimal places and rounded off to the third decimal place according to Rule A in ISO 31-0:1992, B.3 as follows.

a) Where the figure in the fourth decimal place is less than 5, it is discarded and the figure in the third decimal place is kept unchanged.

b) Where the figure in the fourth decimal place is 5 and there is a figure other than 0 in the fifth decimal place, or where the figure in the fourth decimal place is greater than 5, the figure in the third decimal place is increased by 1.

c) Where the figure in the fourth decimal place is 5 and the figure 0 is in the fifth decimal place, the 5 is discarded and the figure in the third 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 mass fraction of nickel oxide is calculated using the following equation:

$$w_{\mathrm{NiO}}(\%) = 1{,}272\,5\ w_{\mathrm{Ni}}\ (\%)$$

9 Test report

The test report shall include the following information:

a) name and address of the testing laboratory;

b) date of issue of the test report;

c) reference to this International Standard;

d) details necessary for the identification of the sample;

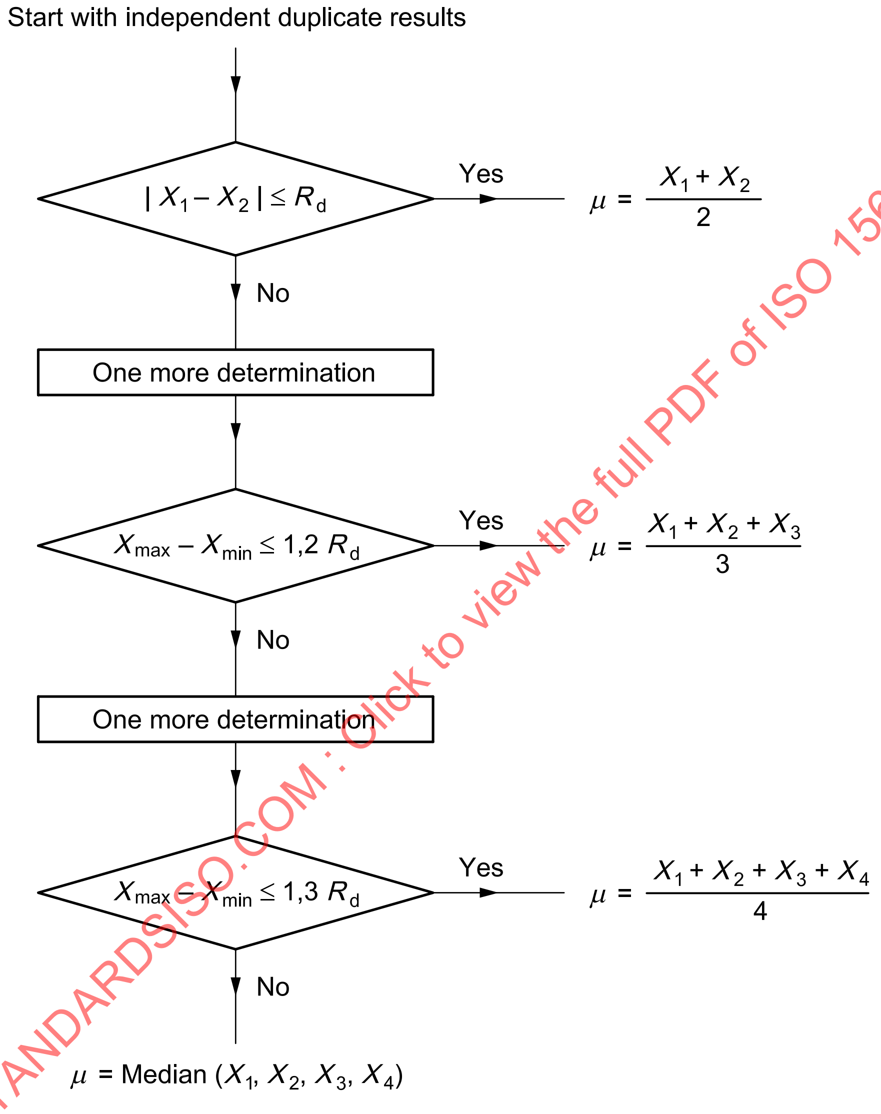
e) result of the analysis;

f) reference number of the result;

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

Annex A
(normative)

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



NOTE R_d as defined in 8.2.1.

Figure A.1 — Procedure for acceptance of analytical values