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Iron ores — Determination of titanium — Diantipyrylmethane spectrophotometric method

Minerais de fer — Dosage du titane — Méthode spectrophotométrique au diantipyrylméthane

Reference number
ISO 4691:2009(E)

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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 4691 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 4691:1985), which has been technically revised.

Iron ores — Determination of titanium — Diantipyrylmethane spectrophotometric 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 spectrophotometric method using diantipyrylmethane for the determination of the mass fraction of titanium in iron ores.

This method is applicable to a mass-fraction range of 0,02 % to 4,0 % of titanium in natural iron ores, and iron ore concentrates and agglomerates including sinter products.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 648, *Laboratory glassware — Single-volume pipettes*

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

ISO 3082, *Iron ores — Sampling and sample preparation procedures*

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

3 Principle

The test portion is decomposed by one of the following methods.

a) By treatment with hydrochloric, nitric and sulfuric acids, filtration and ignition of the residue, followed by treatment with hydrofluoric and sulfuric acids and fusion with potassium disulfate. Dissolution of the melt in the main solution.

b) By sintering with sodium peroxide, followed by treatment with hydrochloric and sulfuric acids, filtration and ignition of the residue, followed by treatment with hydrofluoric and sulfuric acids and fusion with potassium disulfate. Dissolution of the melt in the main solution.

c) By fusion with a sodium tetraborate/sodium carbonate mixture, followed by treatment with hydrochloric acid. Not applicable to samples containing more than 8 % (by mass) silicon.

Reduction of the iron with ascorbic acid. Colour development with diantipyrylmethane, and measurement of the absorbance at approximately 385 nm.

4 Reagents

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

4.1 Potassium disulfate ($K_2S_2O_7$).

4.2 Sodium peroxide (Na_2O_2), fine powder.

4.3 Sodium tetraborate ($Na_2B_4O_7$), anhydrous.

4.4 Sodium carbonate (Na_2CO_3), anhydrous.

4.5 Fusion mixture: 1 part by mass of the sodium tetraborate (4.3) mixed with 1 part by mass of the sodium carbonate (4.4) and stored in a closed vessel.

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

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

4.8 Hydrochloric acid, ρ 1,16 to 1,19 g/ml, diluted 1 + 4.

4.9 Nitric acid, ρ 1,4 g/ml.

4.10 Hydrofluoric acid, ρ 1,13 g/ml, 40 % (by mass) solution.

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

4.12 Sulfuric acid, ρ 1,84 g/ml, diluted 1 + 9.

4.13 Sulfuric acid, ρ 1,84 g/ml, diluted 2 + 98.

4.14 Diantipyrylmethane, solution, 15 g/l.

Dissolve 15 g of diantipyrylmethane monohydrate ($C_{23}H_{24}O_2N_4 \cdot H_2O$) in about 300 ml of water and 30 ml of sulfuric acid (4.11) and dilute with water to 1 litre. If a residue remains in the solution, filter off the residue. Store the solution in a brown bottle.

4.15 Ascorbic acid, 100 g/l solution.

The solution should be freshly prepared.

4.16 Ammonium iron(III) sulfate, 100 g/l solution.

Dissolve 100 g of ammonium iron(III) sulfate in 500 ml of water acidified with 5 ml of sulfuric acid (4.11). Dilute to 1 litre and mix.

4.17 Titanium, standard solution corresponding to 0,1 mg Ti/ml.

Weigh 0,167 g of titanium dioxide (TiO_2) calcined previously at 900 to 950 °C for about 40 min in a platinum crucible and fuse with 3 to 4 g of the potassium disulfate (4.1) at a temperature of 650 to 700 °C until a clear melt is obtained. After cooling, place the crucible in a 100 ml beaker, add 50 to 60 ml of sulfuric acid (4.12) and dissolve the cooled melt with moderate heating. After washing the platinum crucible with sulfuric acid (4.12), transfer the solution to a 1 000 ml volumetric flask, dilute with sulfuric acid (4.12) to volume and mix.

1 ml of this standard solution contains 0,1 mg of titanium.

4.18 Titanium, standard solution corresponding to 20 mg Ti/l.

Pipette a 50 ml aliquot of the titanium standard solution (4.17) into a 250 ml volumetric flask, dilute with sulfuric acid (4.12) to volume and mix.

1 ml of this standard solution contains 0,02 mg of titanium.

5 Apparatus

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

5.1 Spectrophotometer, suitable for the measurement of absorbance at a wavelength of 385 nm, together with 10 mm cells.

6 Sampling and samples

6.1 Laboratory samples

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 with significant contents of combined water or oxidizable compounds, use a particle size of minus 160 µm.

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

6.2 Preparation of predried test samples

Thoroughly mix the laboratory sample 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 ± 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 both cases, appropriate recalibration.

7.2 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 both cases, no significant changes in the analytical procedure will become necessary.

When 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 are from the same reagent bottles.

When the analysis is carried out on several samples of the same type of ore at the same time, the analytical value of one certified reference material may be used.

7.3 Test portion

Taking several increments, weigh, to the nearest 0,000 1 g, approximately the amount of the predried test sample (6.2) in accordance with Table 1.

Table 1 — Test portion

Ti mass fraction w_{Ti} %	**Mass of test portion** g	**Aliquot** (7.4.2) ml
$0{,}02 \leqslant w_{\mathrm{Ti}} < 0{,}1$	0,5	30,0
$0{,}1 < w_{\mathrm{Ti}} < 0{,}3$	0,5	20,0
$0{,}3 < w_{\mathrm{Ti}} < 1{,}0$	0,5	5,0
$1{,}0 < w_{\mathrm{Ti}} \leqslant 4{,}0$	0,13	5,0
NOTE The test portion should be taken and weighed quickly in order to avoid reabsorption of moisture.		

7.4 Determination

7.4.1 Decomposition of the test portion

If the decomposition is to be based on acid attack, proceed as instructed in 7.4.1.1. If it is to be based on alkali sintering, proceed as instructed in 7.4.1.2, and if it is to be based on alkali fusion, proceed as instructed in 7.4.1.3, respectively.

7.4.1.1 Acid attack

Place the test portion (7.3) in a 300 ml beaker, moisten with a few drops of water, add 30 ml of hydrochloric acid (4.6), cover with a watch-glass, and heat gently to decompose. Add 5 ml of nitric acid (4.9) and 10 ml of sulfuric acid (4.11), remove the watch-glass, heat cautiously until dense white fumes are obtained, and continue heating for about 10 min. Allow the beaker to cool, add 20 ml of hydrochloric acid (4.7) and about 50 ml of water, and heat to dissolve the soluble salts.

Filter the solution through a medium-texture filter paper, scrub the wall of the beaker with a rubber-tipped glass rod, and transfer the residue to the filter paper. Wash the residue two or three times with hot sulfuric acid (4.13) and two or three times with hot water. Collect the filtrate and washings in a 300 ml beaker and reserve as the main solution.

Place the filter paper and the residue in a platinum crucible, dry, char, ignite and cool. Moisten the residue in the crucible with sulfuric acid (4.11), add 5 ml of hydrofluoric acid (4.10) and heat gently to expel the silicon tetrafluoride and sulfuric acid. Allow the crucible to cool, add about 2 g of potassium disulfate (4.1), cover with a platinum lid and heat, gently at first, then finally until dull red heat to fuse the residue.

NOTE If it is necessary for complete fusion, the amount of potassium disulfate can be increased to 5 g altogether.

After cooling, transfer the crucible and lid to the 300 ml beaker containing the main solution, heat to dissolve the cooled melt, and take out the crucible and lid after washing with water. Transfer the solution to a 200 ml volumetric flask, dilute to volume with water and mix.

7.4.1.2 Alkali sintering

Place the test portion in a nickel crucible, add 3 g of sodium peroxide (4.2), mix well using a platinum or nickel spatula, and tamp the mixture. Place the crucible for 1 or 2 min at the entrance of a muffle furnace, the temperature of which is regulated at 400 ± 20 °C, and then into the furnace for about 1 h to effect sintering. Take the crucible out of the furnace and cool it. Transfer the sintered mass to a 300 ml beaker, cover the beaker with a watch-glass and add about 30 ml of water.

NOTE 1 If the volume of water added is insufficient, bumping can occur on subsequent heating. As a safety precaution, the volume can be increased up to 100 ml.

Rinse the crucible first with water and then once with hydrochloric acid (4.8), and add the washings to the mass in the beaker. Acidify slowly with 30 ml of hydrochloric acid (4.6), cover the beaker with a watch-glass and heat the solution gently to decompose the excess peroxide. Remove the watch-glass, add 10 ml of sulfuric acid (4.11), heat cautiously to dense white fumes and continue heating for about 10 min. Allow the beaker to cool, add 20 ml of hydrochloric acid (4.7) and about 50 ml of water, and heat to dissolve the soluble salts.

Filter the solution through a medium-texture filter paper, scrub the wall of the beaker with a rubber-tipped glass rod, and transfer the residue to the filter paper. Wash the residue two or three times with hot sulfuric acid (4.13) and two or three times with hot water. Collect the filtrate and washings in a 300 ml beaker and reserve this as the main solution.

Place the filter paper and the residue in a platinum crucible, dry, char, ignite and cool. Moisten the residue in the crucible with sulfuric acid (4.11), add 5 ml of hydrofluoric acid (4.10) and heat gently to expel the silicon tetrafluoride and sulfuric acid. Allow the crucible to cool, add about 2 g of the potassium disulfate (4.1), cover with a platinum lid and heat, gently at first, then finally until dull red heat to fuse the residue.

NOTE 2 If it is necessary for complete fusion, the amount of potassium disulfate can be increased to 5 g altogether.

After cooling, transfer the crucible and lid to the 300 ml beaker containing the main solution, heat to dissolve the cooled melt, and take out the crucible and lid after washing with water. Transfer the solution to a 200 ml volumetric flask, dilute to volume with water and mix.

7.4.1.3 Alkali fusion

Mix the test portion with 5 g of fusion mixture (4.5) in a platinum crucible, cover with a platinum lid, heat gently, and, after melting, fuse at a temperature of 1 000 to 1 050 °C for about 10 min. Remove from the heat and swirl cautiously to cause the cooling melt to solidify in a thin layer on the wall of the crucible. Allow the crucible to cool, then place the crucible and lid and the contents in a 300 ml beaker and add 100 ml of hydrochloric acid (4.8). Dissolve the melt, take out the crucible and lid and wash the contents into the beaker.

Transfer the solution to a 200 ml volumetric flask, dilute to volume with water and mix.

7.4.2 Spectrophotometric determination

Pipette an aliquot, given in Table 1, of the test solution and the blank solution, respectively, into 100 ml volumetric flasks, add 5 ml of ammonium iron(III) sulfate solution (4.16), add 10 ml of the ascorbic acid solution (4.15) and shake. Add 15 ml of hydrochloric acid (4.7) and 30 ml of diantipyrylmethane solution (4.14), dilute to volume with water and mix. (This is the final test solution.)

Allow to stand for at least 20 min and measure the absorbance at a wavelength of approximately 385 nm in a 10 mm cell using the blank test solution as a reference.

NOTE 1 20 mm cells can be used, If necessary, for test solutions of lowest titanium contents.

When the fusion decomposition is applied to samples containing more than 1 % (by mass) silicon, the test solution, after colour development and just before measuring the absorbance, should be filtered to remove possible precipitates of silica.

NOTE 2 The colour is stable for at least 24 h.

Determine the concentration, expressed in micrograms per millilitre, of titanium from the absorbance using the calibration graph prepared as instructed in 7.4.3.

7.4.3 Preparation of calibration graph

Put 0,0; 1,0; 3,0; 5,0; 7,0 and 10,0 ml of the titanium standard solution (4.18) into six 100 ml volumetric flasks, add 5 ml of the ammonium iron(III) sulfate solution (4.16) and 10 ml of the ascorbic acid solution (4.15), and shake. Add 15 ml of hydrochloric acid (4.7) and 30 ml of the diantipyrylmethane solution (4.14) to each flask, dilute to volume with water and proceed as instructed in 7.4.2. Plot the relationship between the concentration, expressed in micrograms per millilitre, of titanium and the absorbance to prepare the calibration graph.

8 Expression of results

8.1 Calculation of mass fraction of titanium

The mass fraction of titanium, w_{Ti}, expressed as a percentage, is calculated to five decimal places for mass fractions lower than 1 %, and to four decimal places for mass fractions higher than 1 %, using the following equation:

$$w_{\mathrm{Ti}} = \frac{\rho_{\mathrm{Ti}} \times 100}{m_1 \times 1\,000\,000} \times 100 = \frac{\rho_{\mathrm{Ti}}}{100 m_1} \qquad (1)$$

where

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

m_1 is the mass, in grams, of sample represented in the 100 ml of final test solution calculated from the equation

$$m_1 = \frac{m_{\mathrm{o}} \times V}{200}$$

in which

m_{o} is the mass of the test portion (see Table 1);

V is the volume of the aliquot (see Table 1).

8.2 General treatment of results

8.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed by the following regression equations[1]:

Acid attack

$$\sigma_{\mathrm{d}} = 0{,}009\,6X + 0{,}000\,8 \qquad (2)$$

$$\sigma_{\mathrm{L}} = 0{,}018\,5X + 0{,}000\,8 \qquad (3)$$

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

$$R_d = 0{,}027\,0X + 0{,}002\,2 \tag{4}$$

$$P = 0{,}055\,4X + 0{,}002\,8 \tag{5}$$

Alkali sintering

$$\sigma_d = 0{,}007\,3X + 0{,}000\,5 \tag{6}$$

$$\sigma_L = 0{,}016\,2X + 0{,}001\,1 \tag{7}$$

$$R_d = 0{,}020\,8X + 0{,}001\,3 \tag{8}$$

$$P = 0{,}048\,5X + 0{,}003\,2 \tag{9}$$

Alkali fusion

$$\sigma_d = 0{,}011\,3X + 0{,}000\,6 \tag{10}$$

$$\sigma_L = 0{,}016\,5X + 0{,}001\,3 \tag{11}$$

$$R_d = 0{,}032\,0X + 0{,}001\,6 \tag{12}$$

$$P = 0{,}055\,1X + 0{,}003\,9 \tag{13}$$

where

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;

X is the mass fraction of titanium, expressed as a percentage, of the predried test sample, calculated as follows:

- within-laboratory Equations (2), (4), (6), (8) and (10): the arithmetic mean of the duplicate values;
- between-laboratories Equations (3), (5), (7), (9) and (11): the arithmetic mean of the final results (8.2.5) of the two laboratories.

8.2.2 Determination of analytical result

Having computed the independent duplicate results according to Equation (1), compare them with the independent duplicate limit (R_d), using the procedure given in Annex A.

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 quantities:

$$\mu_{12} = \frac{\mu_1 + \mu_2}{2} \tag{14}$$

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 the final results.

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 the second paragraph of 7.2). 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 final result for the CRM/RM;
A_c	is the reference/certified 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.*

For a CRM/RM certified by an interlaboratory test programme, C shall be calculated as follows:

$$C = 2\sqrt{\frac{s_c^2}{N_c} + \sigma^2{}_L + \frac{\sigma_d^2}{n}}$$

where

s_c	is the standard deviation of laboratory means (each data value for calculating the standard deviation is the average data value in each certifying laboratory) of the CRM/RM;
N_c	is the number of certifying laboratories;
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.

For CRMs certified by only one laboratory, C shall be calculated as follows:

$$C = \sqrt{2\sigma_{\mathrm{L}}^2 + \frac{\sigma_{\mathrm{r}}^2}{n}}$$

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

8.2.5 Calculation of final result

The final result is the arithmetic mean of the acceptable analytical values for the test sample, or as otherwise determined by the operations specified in Annex A, calculated to five decimal places for mass fractions of titanium less than 1 % and to four decimal places for mass fractions greater than 1 % rounded to the third decimal place 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 one;

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, 6, or 8 and is increased by one if it is 1, 3, 5, 7, or 9.

In a similar manner, with the ordinal numbers decreased by one, the value for mass fractions of titanium greater than 1 % is rounded to the second decimal place.

8.3 Oxide factor

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

$$w_{\mathrm{TiO_2}} = 1{,}668 w_{\mathrm{Ti}}$$

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) a reference to this International Standard;

d) details necessary for the identification of the sample;

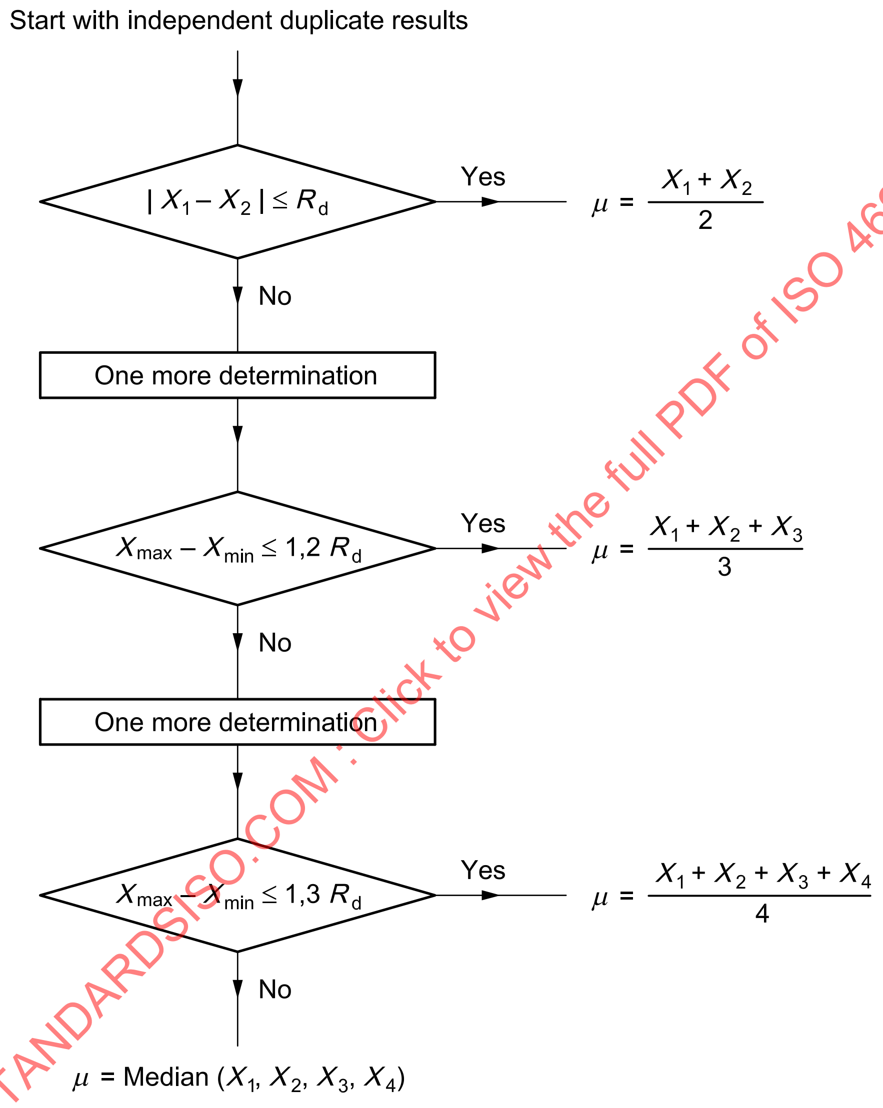
e) result of the analysis;

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 material(s).

Annex A
(normative)

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



R_d: as defined in 8.2.1.