

International Standard



3886

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

Iron ores — Determination of manganese content — Periodate spectrophotometric method

Minerais de fer — Dosage du manganèse — Méthode spectrophotométrique au periodate

Second edition — 1986-06-15

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UDC 533.31 : 546.711 : 543.42

Ref. No. ISO 3886-1986 (E)

Descriptors : minerals and ores, iron ores, chemical analysis, determination of content, manganese, spectrophotometric analysis.

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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 3886 was prepared by Technical Committee ISO/TC 102, *Iron ores*.

This second edition cancels and replaces the first edition (ISO 3886-1977), clauses 6, 7 and 8 and annex A of which have been technically revised.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

Iron ores — Determination of manganese content — Periodate spectrophotometric method

1 Scope and field of application

This International Standard specifies a spectrophotometric method using sodium periodate for the determination of the manganese content of iron ores.

This method is applicable to a concentration range of 0,02 to 8 % (*m/m*) of manganese in natural iron ores, and iron ore concentrates and agglomerates including sinter products.

2 References

ISO 648, *Laboratory glassware — One-mark pipettes*.

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

ISO 3081, *Iron ores — Increment sampling — Manual method*.

ISO 3082, *Iron ores — Increment sampling and sample preparation — Mechanical method*.

ISO 3083, *Iron ores — Preparation of samples — Manual method*.

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

3 Principle

Decomposition of a test portion by one of the following methods:

- treatment with hydrochloric, nitric and perchloric acids;
- sintering with sodium peroxide, followed by treatment with hydrochloric and perchloric acids.

Filtration and ignition of the residue, followed by treatment with hydrofluoric and sulfuric acids and fusion with sodium carbonate. Dissolution of the cooled melt in the main solution.

Oxidation of manganese in an aliquot to permanganate ion, using sodium periodate in sulfuric acid - phosphoric acid medium.

Spectrophotometric measurement of the absorbance due to the permanganate ion at a wavelength of about 535 nm.

4 Reagents

During the analysis, use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity, except that water free from organic matter (4.1) shall be used for the spectrophotometric measurement.

4.1 Water, free from organic matter.

Add 20 ml of sulfuric acid (4.9) to 1 litre of water, bring to the boil, add several crystals of sodium periodate, continue boiling for 10 min, then cool.

4.2 Sodium peroxide (Na_2O_2), powder.

NOTE — Sodium peroxide should be kept away from humidity and should be not used once it has begun to agglomerate.

4.3 Sodium carbonate (Na_2CO_3), anhydrous.

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

4.5 Hydrochloric acid, ρ 1,16 to 1,19 g/ml, diluted 1 + 9.

4.6 Nitric acid, ρ 1,4 g/ml.

4.7 Perchloric acid, 60 % (*m/m*) (ρ 1,54 g/ml) or 70 % (*m/m*) (ρ 1,67 g/ml).

4.8 Hydrogen peroxide, 3 % (V/V).

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

4.10 Sulfuric acid, ρ 1,84 g/ml, diluted 1 + 100.

4.11 Hydrofluoric acid, 40 % (m/m) (ρ 1,13 g/ml).

4.12 Sulfuric acid - phosphoric acid mixture.

Pour carefully 100 ml of sulfuric acid (ρ 1,84 g/ml) into about 600 ml of water while stirring, cool, add 150 ml of phosphoric acid (ρ 1,70 g/ml) and dilute to 1 000 ml with water.

4.13 Sodium periodate (NaIO_4) solution, 50 g/l.

4.14 Sodium nitrite (NaNO_2) solution, 10 g/100 ml.

4.15 Manganese, standard solutions.

4.15.1 Stock solution

Dissolve 0,500 g of pure metallic manganese in 20 ml of nitric acid (4.6), add 20 ml of sulfuric acid (4.9) and heat to dense white fumes for about 10 min to expel all oxides of nitrogen. Cool, add about 100 ml of water to dissolve the salt, transfer into a 500 ml volumetric flask, dilute to the mark with water and mix.

1 ml of stock solution contains 1,00 mg of manganese.

4.15.2 Standard solution A

Take 100 ml of stock solution (4.15.1) and dilute to 1 000 ml in a volumetric flask.

1 ml of this standard solution contains 0,100 mg of manganese.

4.15.3 Standard solution B

Take 250 ml of standard solution A (4.15.2) and dilute to 1 000 ml in a volumetric flask.

1 ml of this standard solution contains 0,025 mg of manganese.

5 Apparatus

5.1 Ordinary laboratory equipment.

Any pipettes and volumetric flasks shall be one-mark pipettes and volumetric flasks complying with the specifications of ISO 648 and ISO 1042.

5.2 Spectrophotometer, suitable for the measurement of absorbance at approximately 535 nm.

6 Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of minus 100 μm particle size which has been taken in accordance with ISO 3081 or ISO 3082 and prepared in accordance with ISO 3082 or ISO 3083. 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

WARNING — Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic matter in general.

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 shall 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 Blank test and check test

In each run, carry out one blank test and one analysis of a certified reference material of the same type of ore in parallel with the analysis of the ore sample(s) under the same conditions. Prepare a predried test sample of the certified reference material as specified in 6.2.

NOTE — 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 would 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 used 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 Calibration

7.3.1 For samples containing more than 0,1 % (m/m) manganese

7.3.1.1 Set of calibration solutions and formation of the absorbing compound

Into a series of five 300 ml beakers, introduce 2,0; 5,0; 10,0; 15,0 and 20,0 ml of manganese standard solution A (4.15.2), add 30 ml of sulfuric acid - phosphoric acid mixture (4.12), and dilute to about 60 ml with water (4.1).

Add 10 ml of sodium periodate solution (4.13), to each solution, cover each beaker with a watch-glass, heat to boiling, and maintain just below boiling point for 10 min after colour development of the permanganate ion. Cool each solution, transfer to a series of five 100 ml volumetric flasks, make up to the mark with water (4.1) and mix.

7.3.1.2 Calibration compensation solution

Prepare a calibration compensation solution according to 7.3.1.1, but omitting the manganese standard solution A.

7.3.1.3 Spectrophotometric measurements

Transfer a part of each solution (7.3.1.1) to a spectrophotometric cell of suitable thickness, and measure the absorbance of each, A_{i1} , where i is 1 to 5 cm optical path length, with the spectrophotometer (clause 5), at the wavelength of maximum absorbance near 535 nm, after having adjusted the instrument to zero absorbance against the calibration compensation solution (7.3.1.2).

Add sodium nitrite solution (4.14), drop by drop, to the solutions in the volumetric flasks, while mixing, until 1 drop in excess decolorizes the pink colour of the permanganate ion; transfer a part of each solution to the corresponding spectrophotometric cell, and measure the absorbances, A_{i2} , as described in the first paragraph.

NOTES

- 1 Increase in the volume of the solution by addition of sodium nitrite solution is disregarded.
- 2 The measurement of absorbance should not be postponed unduly after decoloration of the pink colour of the permanganate ion by sodium nitrite solution, because reoxidation of the manganese ion occurs on standing.

7.3.1.4 Plotting the calibration graph

Plot a calibration graph showing the differences between the absorbances, $A_{i1} - A_{i2}$, of the set of calibration solutions as a function of the quantities of manganese contained in these solutions.

7.3.2 For samples containing less than 0,1 % (m/m) manganese

7.3.2.1 Set of calibration solutions and formation of the absorbing compound

As 7.3.1.1, but using manganese standard solution B (4.15.3) instead of manganese standard solution A.

NOTE — For manganese contents below 0,1 % (m/m), the heating time should be approximately 30 min and, if necessary, water (4.1) should be added to maintain the volume.

7.3.2.2 Calibration compensation solution

Prepare a calibration compensation solution according to 7.3.2.1, but omitting the manganese standard solution B.

7.3.2.3 Spectrophotometric measurements

As 7.3.1.3, but using the solutions from 7.3.2.1.

7.3.2.4 Plotting the calibration graph

See 7.3.1.4.

7.4 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.

NOTE — The test portion should be taken and weighed quickly in order to avoid reabsorption of moisture.

7.5 Determination

7.5.1 Decomposition of the test portion

If the decomposition is to be based on acid attack, proceed as instructed in 7.5.1.1. If the decomposition is to be based on alkali sintering, proceed as instructed in 7.5.1.2.

7.5.1.1 Acid attack

Place the test portion (7.4) in a 300 ml beaker, add 30 ml of hydrochloric acid (4.4), cover the beaker with a watch-glass and heat the solution gently without boiling.

NOTE — For decomposition of the test portion, place the beaker for about 1 h on the low temperature zone (60 to 100 °C) of the hotplate, then transfer to a higher temperature zone and heat for about 10 min at just under boiling point.

Add 5 ml of nitric acid (4.6), 20 ml of perchloric acid (4.7), and 0,2 ml of sulfuric acid (4.9), cover the beaker again with the watch-glass, heat to dense white fumes of perchloric acid and maintain a steady refluxing of acid on the walls of the beaker for about 10 min.

Allow the beaker to cool, add about 50 ml of warm water and a few drops of hydrogen peroxide (4.8), heat the mixture to dissolve the soluble salts, and boil to decompose the excess of hydrogen peroxide.

Filter the solution through a close-texture paper. Wash the beaker with water, scrubbing the wall with a rubber-tipped glass rod. Wash the residue first with three or four portions of

sulfuric acid (4.10) and then with warm water. Collect the filtrate and washings in a 300 ml beaker and reserve as the main solution. Keep the filter paper with the residue and continue according to 7.5.2.

7.5.1.2 Alkali sinter attack

Place the test portion (7.4) in a 40 ml nickel crucible free of manganese (see note 1), add about 3 g of sodium peroxide powder (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 closed furnace for about 1 h to effect sintering. Take the crucible out of the furnace and cool.

Transfer the sintered mass to a 300 ml beaker, add 30 ml of water (see note 2) and cover the beaker with a watch-glass.

Rinse the crucible first with water and then once with hydrochloric acid (4.5), and add the washings to the bulk solution. Acidify slowly with 30 ml of hydrochloric acid (4.4) and heat the solution gently to decompose the sintered mass. Add 30 ml of perchloric acid (4.7) and 0,2 ml of sulfuric acid (4.9), cover the beaker again with the watch-glass, heat to dense white fumes of perchloric acid and maintain a steady refluxing of acid on the walls of the beaker for about 10 min.

Continue according to 7.5.1.1, starting with "Allow the beaker to cool, ...".

NOTES

- 1 An alkali-resistant alumina crucible free of manganese may be used in place of a nickel crucible.
- 2 If the volume of water added is insufficient, bumping may occur on subsequent heating. Therefore the volume, for safety, may be increased up to 100 ml.

7.5.2 Treatment of the residue

Place the residue from 7.5.1 with the filter in a platinum crucible, dry, ash the paper, and finally ignite at 950 to 1 050 °C. Allow the crucible to cool, then moisten the residue with sulfuric acid (4.9). Add 5 to 15 ml of hydrofluoric acid (4.11), depending on the silica content, heat gently to expel silica, and fume off sulfuric acid. Allow the crucible to cool, add 2 g of sodium carbonate (4.3), and heat, gently at first, then finally to dull red, to fuse the residue.

Allow the melt to cool, place the crucible in the beaker containing the main solution from 7.5.1, and heat gently to dissolve the melt. Take out the crucible and rinse it with water.

7.5.3 Treatment of the test solution

Evaporate the solution to approximately 50 ml. Cool to room temperature, transfer directly, or filter if necessary, into a 100 ml volumetric flask for manganese contents less than 4,0 % (m/m), or a 500 ml volumetric flask for manganese contents between 4,0 and 8,0 % (m/m), and dilute with water to the mark, shaking at intervals.

7.5.4 Spectrophotometric measurements

7.5.4.1 Formation of the absorbing compound

Transfer to a 300 ml beaker an aliquot of the solution from 7.5.3, chosen in accordance with table 1, and add 30 ml of sulfuric acid - phosphoric acid mixture (4.12). Dilute to about 60 ml with water.

Table 1 — Aliquots

Expected manganese content % (m/m)	Aliquots
0,02 up to 0,1	take a 25,0 ml aliquot out of 100 ml
0,1 up to 1,0	take a 20,0 ml aliquot out of 100 ml
1,0 up to 2,0	take a 10,0 ml aliquot out of 100 ml
2,0 up to 4,0	take a 5,0 ml aliquot out of 100 ml
4,0 up to 8,0	take a 10,0 ml aliquot out of 500 ml

Add 10 ml of sodium periodate solution (4.13), cover the beaker with a watch-glass, heat to boiling, and maintain just below boiling point for 10 min after colour development of the permanganate ion. Cool the solution, transfer to a 100 ml volumetric flask, make up to the mark with water (4.1) and mix.

NOTE — For manganese contents below 0,1 % (m/m), the heating time should be approximately 30 min and, if necessary, water (4.1) should be added to maintain the volume.

7.5.4.2 Spectrophotometric measurements

Transfer a part of the solution into a spectrophotometric cell with a suitable thickness, and measure the absorbance, A_1 , with the spectrophotometer (5.2), at a wavelength of the maximum absorption located near 535 nm, after having adjusted the instrument to zero absorbance against water (4.1).

Add sodium nitrite solution (4.14), drop by drop, to the solution in the volumetric flask, while mixing, until 1 drop in excess decolorizes the pink colour of the permanganate ion; transfer a part of this solution to the same spectrophotometric cell, and measure the absorbance, A_2 , as described in the first paragraph. Rinse the spectrophotometric cell carefully after each measurement.

NOTES

- 1 Increase in the volume in the solution by addition of sodium nitrite solution is disregarded.
- 2 The measurement of absorbance should not be postponed unduly after decoloration of the pink colour of the permanganate ion by sodium nitrite solution, because reoxidation of the manganese ion occurs on standing.

Determine the quantity of manganese from the difference between these absorbances, $A_1 - A_2$, by using the calibration graph prepared as instructed, specified in 7.3.1.4 or 7.3.2.4.

8 Expression of results

8.1 Calculation of manganese content

Calculate the manganese content, w_{Mn} (%), expressed as a percentage by mass, to four decimal places using the equation

$$w_{\text{Mn}} (\%) = \frac{m_1 V_0}{m_0 V_1} \times 100 \quad \dots (1)$$

where

m_0 is the mass, in grams, of the test portion (7.4);

m_1 is the mass, in grams, of manganese in the aliquot of sample solution in table 1, after correction for the blank value (7.2), obtained from the calibration graph;

V_0 is the total volume, in millilitres, of the test solution depending on the manganese content (7.5.3);

V_1 is the volume, in millilitres, taken as an aliquot from table 1.

The manganese content shall be expressed to the fourth decimal place.

8.2 General treatment of results

8.2.1 Precision

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

$$r = 0,014 \, 0X + 0,003 \, 7 \quad \dots (2)$$

$$P = 0,039 \, 7X + 0,012 \, 7 \quad \dots (3)$$

$$\sigma_r = 0,004 \, 9X + 0,001 \, 3 \quad \dots (4)$$

$$\sigma_L = 0,013 \, 6X + 0,004 \, 3 \quad \dots (5)$$

where

r is the permissible tolerance within laboratory (repeatability);

P is the permissible tolerance between laboratories;

σ_r is the within-laboratory standard deviation;

σ_L is the between-laboratories standard deviation;

X is the manganese content, expressed as a percentage by mass, of the test sample, calculated as follows:

- for the within-laboratory equations (2 and 4), the arithmetic mean of the duplicate values;
- for the between-laboratory equations (3 and 5), the arithmetic mean of the final results (8.2.3) of the two laboratories.

See annexes B and C.

8.2.2 Acceptance of analytical values

The result obtained for the certified reference material shall be such that the difference between this result and the certificate value of the reference material is statistically insignificant. For a reference material that has been analysed by at least 10 laboratories using method(s) that are comparable both in accuracy and precision with this method, the following condition may be used to test the significance of the difference:

$$|A_c - A| \leq 2 \sqrt{\frac{s_{Lc}^2 + \frac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_r^2}{n}} \quad \dots (6)$$

where

A_c is the certified value;

A is the result or the mean of results obtained for the reference material;

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 on the reference material (in most cases $n = 1$);

σ_L and σ_r are as defined in 8.2.1.

If condition (6) is satisfied (i.e. if the left-hand side is less than or equal to the right-hand side), then the difference, $|A_c - A|$, is statistically insignificant; otherwise it is statistically significant.

When the difference is significant, the analysis shall be repeated, simultaneously with an analysis of the test sample. If the difference is again significant, the procedure shall be repeated using a different certified reference material of the same type of ore.

When the range of the two values for the test sample is outside the limit for r calculated according to equation (2) in 8.2.1, one or more additional tests shall be carried out in accordance with the flowsheet presented in annex A, simultaneously with an analysis of a certified reference material of the same type of ore.

Acceptability of the results for the test sample shall in each case be subject to the acceptability of the results for the certified reference material.

NOTE — The following procedure shall be used when the information on the reference material certificate is incomplete:

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

- b) if the certification has been made by only one laboratory or if the interlaboratory results are missing, use the formula

$$|A_c - A| \leq 2 \sqrt{2\sigma_L^2 + \frac{\sigma_r^2}{n}} \quad \dots (7)$$

8.2.3 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 four decimal places and rounded off to the second decimal place as follows:

- when the figure in the third decimal place is less than 5, it is discarded and the figure in the second decimal place is kept unchanged;
- when the figure in the third decimal place is 5 and there is a figure other than 0 in the fourth decimal place, or when the figure in the third decimal place is greater than 5, the figure in the second decimal place is increased by one;
- when the figure in the third decimal place is 5 and there is no figure other than 0 in the fourth decimal place, the 5 is

discarded and the figure in the second decimal place is kept unchanged if it is 0, 2, 4, 6 or 8 and increased by one if it is 1, 3, 5, 7 or 9.

8.3 Oxide factor

$$w_{\text{MnO}} (\%) = 1,2912 w_{\text{Mn}} (\%)$$

9 Test report

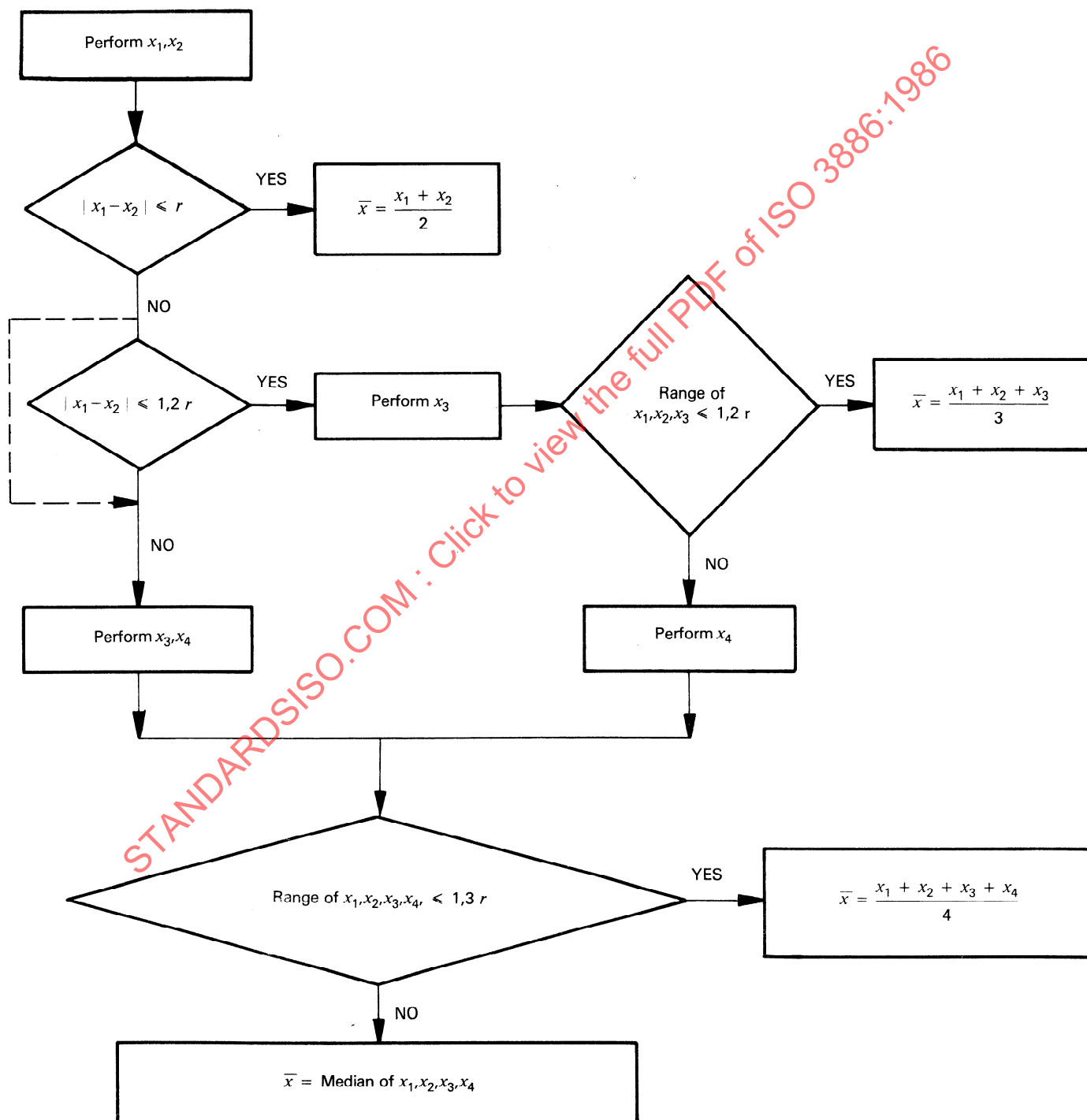
The test report shall include the following information:

- reference to this International Standard;
- details necessary for the identification of the sample;
- result of the analysis;
- reference number of the result;
- 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

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

(This annex is an integral part of the standard.)

 r is as defined in 8.2.1.