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Iron ores — Determination of total iron content — Silver reduction titrimetric method

Minerais de fer — Dosage du fer total — Méthode titrimétrique par réduction à l'argent

Reference number
ISO 9508 : 1990 (E)

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.

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 9508 was prepared by Technical Committee ISO/TC 102, *Iron ores.*

Annex A forms an integral part of this International Standard. Annex B is for information only.

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Iron ores — Determination of total iron content — Silver reduction titrimetric method

1 Scope

This International Standard specifies a method, free from mercury pollution, for the determination of total iron content in iron ores by silver reduction and potassium dichromate titration.

The method is applicable to a concentration range of 30 % *(m/m)* to 72 % *(m/m)* of iron in natural iron ores, iron ore concentrates and agglomerates, including sinter products, containing not more than 0,1 % *(m/m)* Cu. Contents of vanadium normally present in iron ores are without effect.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1 : 1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648 : 1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042 : 1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 2596 : 1984, *Iron ores — Determination of hygroscopic moisture in analytical samples — Gravimetric and Karl Fischer methods.*

ISO 3081 : 1986, *Iron Ores — Increment sampling — Manual method.*

ISO 3082 : 1987, *Iron Ores — Increment sampling and sample preparation — Mechanical method.*

ISO 3083 : 1986, *Iron ores — Preparation of samples — Manual method.*

ISO 7764 : 1985, *Iron ores — Preparation of predried test samples for chemical analysis.*

3 Principle

3.1 Fusion decomposition

Fusion of the test portion with sodium peroxide and leaching with water. Dissolution in hydrochloric acid and passing the solution through a silver reductor. Addition of orthophosphoric acid — sulfuric acid mixture and diphenylaminesulfonate indicator and determination of the total iron by titration with a standard solution of potassium dichromate.

3.2 Acid decomposition

Treatment of the test portion with hydrochloric acid. Filtration and ignition of the residue followed by treatment with hydrofluoric and sulfuric acids and fusion with potassium pyrosulfate. Dissolution of the melt in hydrochloric acid, precipitation of iron with ammonia solution and redissolution of the precipitate in hydrochloric acid. Combination of this solution with the main solution and passing this solution through a silver reductor. Addition of orthophosphoric acid-sulfuric acid mixture and diphenylaminesulfonate indicator and determination of the total iron by titration with a standard solution of potassium dichromate.

4 Reagents

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

4.1 Sodium peroxide (Na_2O_2).

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

4.2 Silver powder, 300 µm is suitable.

4.3 Zinc metal rods, about 8 mm in diameter and about 15 cm in length.

4.4 Potassium pyrosulfate ($K_2S_2O_7$), fine powder.

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

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

4.7 Hydrochloric acid, ϱ 1,16 g/ml to 1,19 g/ml, diluted 1 + 11.

4.8 Hydrochloric acid, ϱ 1,16 g/ml to 1,19 g/ml, diluted 1 + 50.

4.9 Nitric acid, ϱ 1,4 g/ml.

4.10 Sulfuric acid, ϱ 1,84 g/ml.

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

4.12 Sulfuric acid, ϱ 1,84 g/ml, diluted 1 + 99.

4.13 Orthophosphoric acid, ϱ 1,7 g/ml.

4.14 Hydrofluoric acid, 40 % (*m*/*m*) solution, (ϱ 1,13 g/ml) or 48 % (*m*/*m*) (ϱ 1,19 g/ml).

4.15 Ammonia solution, ϱ 0,90 g/ml.

4.16 Orthophosphoric acid-sulfuric acid mixture.

To about 600 ml of water add cautiously, while stirring, 150 ml of sulfuric acid (4.10) and 150 ml of orthophosphoric acid (4.13). Cool the solution and dilute with water to 1 litre.

4.17 Iron, standard solution, 0,1 mol/l.

Transfer 5,58 g of pure iron to a 500 ml Erlenmeyer flask and place a small filter funnel in the neck. Add 75 ml of hydrochloric acid (4.5) in small increments and heat until dissolved. Cool and oxidize with 5 ml of hydrogen peroxide (4.15) added in small portions. Heat to boiling and boil to decompose the excess hydrogen peroxide and to remove chlorine.

Transfer to a 1 000 ml volumetric flask and dilute to volume. 1,00 ml of this solution is equivalent to 1,00 ml of the standard potassium dichromate solution.

4.18 Potassium dichromate (99,9 % minimum purity), standard solution, 0,016 67 mol/l.

Weigh accurately 4,904 g of $K_2Cr_2O_7$ (previously ground in an agate mortar and dried for 2 h at 140 °C to 150 °C) into a 250 ml beaker. Dissolve in water and transfer the solution quantitatively into a 1 000 ml one-mark volumetric flask. Make up to volume with water after cooling to 20 °C and mix.

NOTES

1 The volumetric flask should previously be calibrated by weighing the mass of water contained at 20 °C and converting to volume.

2 Record on the stock bottle the temperature at which this dilution was made (20 °C).

4.19 Sodium diphenylaminesulfonate indicator, solution 0,2 g/100 ml.

Dissolve about 0,2 g of sodium diphenylaminesulfonate ($C_6H_5NHC_6H_4SO_3Na$) in a small volume of water and dilute to 100 ml. Store the solution in a brown glass bottle.

5 Apparatus

NOTE — The pipette and volumetric flask specified should conform with ISO 648 and ISO 1042 respectively.

Ordinary laboratory apparatus, and

5.1 Zirconium or vitreous carbon crucible, capacity 50 ml.

5.2 Burette, class A, conforming with ISO 385-1.

5.3 Silver reductor.

5.3.1 Preparation of column

NOTE — Care should be taken not to let the column run dry. Always maintain about 1 cm of hydrochloric acid above the silver powder.

5.3.1.1 Use of commercially-available silver powder

Use a glass column (diameter 2 cm and length 25 cm) fitted with a stopcock and a reservoir cup (about 100 ml capacity, diameter 4 cm and length 9 cm). Place glass wool very lightly above the stopcock. Fill column with hydrochloric acid (4.7). Place approximately 125 g of silver powder (4.2) into a 150 ml beaker and add hydrochloric acid (4.7). Transfer the silver powder into the column using hydrochloric acid (4.7), avoiding the entrapment of air. Pass about 100 ml of hydrochloric acid (4.7) through the column. Place glass wool very lightly above the silver powder. The silver reductor is now ready.

NOTE — The height of silver in the column is about 17 cm and is adequate for at least 18 samples prior to regeneration. The flow rate is 30 ml to 40 ml per min.

5.3.1.2 Use of precipitated silver

Dissolve 100 g silver nitrate in 400 ml of water in a 600 ml beaker. Add 10 ml of nitric acid (4.9). Place two zinc metal rods (4.3) crosswise in the solution and leave for 4 hours or overnight. Wash the precipitated silver thoroughly by decantation using sulfuric acid (4.12). A glass column (diameter 2 cm of and length 25 cm) fitted with a stopcock and reservoir cup (about 100 ml capacity, diameter 4 cm and length 9 cm) is used. Pack glass wool lightly above the stopper. Transfer the washed, precipitated silver into the column using sulfuric acid (4.12) and avoiding the entrapment of any air.

Wash the column with hydrochloric acid (4.7) several times (150 ml is sufficient) at a flow rate of 30 ml to 35 ml per min (the length of the silver column should be about 17 cm). Place glass wool very lightly above the silver powder. The silver reductor is now ready.

5.3.2 Regeneration

With the passage of iron(III), the silver in the reductor darkens at the very top, forming a greyish ring which extends downwards. When this ring extends down to about 10 cm, the column should be regenerated as follows.

a) Drain the solution, leaving about 1 cm on the top, and wash with 150 ml of sulfuric acid (4.12), again leaving the level of sulfuric acid (4.12) in the column about 1 cm above the silver.

b) Gently rest two zinc rods (4.3) in contact with the silver in the column.

NOTE 1

Passing 50 ml of sulfuric acid (4.12) through the column accelerates the regeneration.

c) Leave overnight and then remove the zinc rods.

NOTE 2

If the flow is slow, remove the silver and the glass wool from the column and repack as in 5.3.1.1. Ensure that new glass wool is placed very lightly to maintain a flow rate of 30 ml to 35 ml per min.

d) Wash the column several times by passing about 150 ml of hydrochloric acid (4.7) at a rate of 30 ml to 35 ml per min. The column is now ready for re-use.

NOTE 3

The regeneration can be accomplished by emptying the contents into a beaker with zinc rods (4.3) and repacking as in 5.3.1.1.

5.4 Platinum crucible.

Platinum crucibles should be precleaned, before use, to avoid iron contamination.

5.5 Weighing spatula of a non-magnetic material or demagnetized stainless steel.

6 Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of less than 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 less than 160 µm.

NOTES

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

2 If the determination of total iron relates to a reducibility test, prepare the laboratory sample by crushing and pulverizing, to less than 100 µm particle size, the whole of one of the reducibility test portions which has been reserved for chemical analysis. In the case of ores with significant contents of combined water or oxidizable compounds, use a particle size of less than 160 µm.

6.2 Preparation of test samples

Depending on the ore type, proceed in accordance with either 6.2.1 or 6.2.2.

6.2.1 Ores with significant contents of combined water or oxidizable compounds

Prepare an air-equilibrated test sample in accordance with ISO 2596 with the following types of ores:

a) processed ores containing metallic iron;

b) natural or processed ores in which the sulfur content is higher than 0,2 % (m/m);

c) natural or processed ores in which the content of combined water is higher than 2,5 % (m/m);

6.2.2 Ores outside the scope of 6.2.1

Prepare a predried test sample as follows.

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a manner that it is representative of the whole contents of the container. Dry the test sample at 105 °C ± 2 °C as specified in ISO 7764. (This is the predried test sample.)

7 Procedure

7.1 Number of determinations

Carry out the analysis at least in duplicate in accordance with annex A, independently, on one test sample (6.2).

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 appropriate recalibration in each case.

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) and under the same conditions. A test sample of the certified reference material shall be prepared in the manner appropriate to the type of ore involved (see 6.2). (See note 1 below.)

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.

NOTES

1 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 would become necessary.

2 The certified reference material is used only to validate the performance of the analytical procedure and expressly not to standardize the potassium dichromate solution.

7.3 Determination of hygroscopic moisture content

When the ore type conforms to the specifications of 6.2.1, determine the hygroscopic moisture content in accordance with ISO 2596, simultaneously with the taking of the test portion (7.4) for the determination of the iron content.

7.4 Test portion

Taking several increments, weigh to the nearest 0,000 2 g, approximately 0,3 g of the test sample (6.2) using a non-magnetic spatula (5.5).

NOTE — When predried test samples are being used, the test portion should be taken and weighed quickly on the day of predrying to avoid re-absorption of moisture.

7.5 Determination

7.5.1 Decomposition

7.5.1.1 Fusion decomposition

Transfer 2 g of sodium peroxide (4.1) into a dry zirconium or vitreous carbon crucible (5.1). Add the test portion (7.4) to the crucible and mix the contents with a dry stainless steel spatula.

Fuse over a Meker burner at low heat, swirling the crucible until the melt is cherry red and clear. Remove the crucible from the heat and swirl it until melt solidifies on the crucible wall.

NOTE — If spattering occurs in the early stages of fusion, repeat the test, placing the crucible in a muffle furnace at 500 °C for 10 min to 15 min prior to fusion.

Allow the crucible to cool in air for 1 min to 2 min and place it in a dry 250 ml beaker. Pour about 10 ml of water into the crucible, and cover the beaker with a watch glass. After effervescence has ceased, empty the contents of the crucible into the beaker and wash the crucible with 15 ml to 20 ml of water. Introduce 10 ml of hydrochloric acid (4.5) via the crucible into the beaker and rinse the crucible with water. Boil the solution in the beaker for 3 min to 4 min. Wash the sides of the beaker and watch glass with water and continue boiling for about 30 s. Cool, dilute the solution to about 60 ml with water and follow the procedure specified in 7.5.2.

7.5.1.2 Acid decomposition

Place the test portion (7.4) in a 250 ml beaker, add 20 ml of hydrochloric acid (4.5), cover the beaker with a watch glass, and heat the solution gently without boiling, to decompose the ore.

NOTE — Boiling is avoided to prevent volatilisation of iron(III) chloride.

Wash the watch glass with a jet of water, and dilute to 50 ml with warm water. Filter the insoluble residue on a close-textured paper. Wash the residue with warm hydrochloric acid (4.8) until the yellow colour of iron(III) chloride is no longer observed. Then wash with warm water six to eight times. Collect the filtrate and washings in a 400 ml beaker.

Place the filter paper and residue in a platinum crucible (5.4), dry and ignite at 750 °C to 800 °C. Allow the crucible to cool, moisten the residue with sulfuric acid (4.11), add about 5 ml of hydrofluoric acid (4.14) and heat gently to remove silica and sulfuric acid. Add 2 g of potassium pyrosulfate (4.4) to the cold crucible, heat gently at first then strongly until a clear melt is obtained. Cool, place the crucible in a 250 ml beaker, add about 25 ml of water and about 5 ml of hydrochloric acid (4.5) and warm to dissolve the melt. Remove and wash the crucible.

Adjust the solution to slight alkalinity with ammonia solution (4.15). Heat to coagulate the precipitate, filter on a coarse-textured paper, and wash several times with hot water. Discard the filtrate.

Place the beaker containing the main solution under the funnel and dissolve the precipitate on the filter paper by pouring over it 10 ml of hot hydrochloric acid (4.6). Wash the filter, first six to eight times with warm hydrochloric acid (4.8), then twice with hot water. Dilute to about 240 ml with water and follow the procedure specified in 7.5.2.

7.5.2 Reduction of iron

Place a 600 ml beaker containing 10,00 ml of standard potassium dichromate solution (4.18), 25 ml of mixed acid solution (4.16) and 25 ml of water, under the silver reductor. Pass the test solution through the silver reductor at a rate of 35 ml per min, retaining about 1 cm above the top of the silver. Rinse the reservoir and column 2 to 3 times with hydrochloric acid (4.7) and drain the rinsings. Finally pass 150 ml of hydrochloric acid (4.7) through at a rate of 35 ml per min, to elute the reduced iron completely from the silver reductor, leaving 1 cm of the acid above the top of the silver.

NOTE — Care should be taken not to let the column run dry.

7.5.3 Titration

To the reduced iron and washings in the 600 ml beaker add 5 to 6 drops of sodium diphenylaminesulfonate indicator solution (4.19). Titrate immediately with standard potassium dichromate solution (4.18) to a permanent violet end point. The end point is discernible to within 0,02 ml. Include in the titre the 10,00 ml added in 7.5.2.

NOTE — The ambient temperature of the potassium dichromate solution should be noted. If this differs by more than 1 °C from the temperature at which it was prepared (20 °C), make the appropriate volumetric correction: 0,02 % relative for each 1 °C of difference. For example, the titre should be decreased when the ambient temperature during the titration is higher than the temperature during preparation of the standard volumetric solution. A correction for the temperature difference, if any, is essential.

7.5.4 Blank test

Determine the blank test value (7.2) using the same amounts of all reagents and following all the steps of the procedure. Immediately before reduction (7.5.2), add by means of a one-mark pipette, 1,00 ml of iron standard solution (4.17) and titrate the solution as described in 7.5.3. Record the volume of this titration as (V_0). The blank test value of this titration (V_2) is calculated as: $V_2 = V_0 - 1{,}00$.

NOTES

1 In the absence of iron, the sodium diphenylaminesulfonate indicator does not react with the dichromate solution. The addition of the iron solution is therefore necessary to promote indicator response in the blank solution and thus allow a suitable correction for the blank in terms of its equivalent in millilitres of the potassium dichromate standard solution.

2 The one-mark pipette should previously be calibrated by weighing the mass of water delivered and converting to volume.

8 Expression of results

8.1 Calculation of total iron content

The total iron content, w_{Fe}, as a percentage by mass is calculated to four decimal places from the following equation:

$$w_{Fe} = \frac{V_1 - V_2}{m} \times 0{,}005\,584\,7 \times 100 \times K \qquad \ldots (1)$$

where

V_1 is the volume, in millilitres, of potassium dichromate standard solution (4.18) used for the titration of the test sample;

V_2 is the volume, in millilitres, of potassium dichromate standard solution used for the titration in the blank test, corrected for the iron added in 7.5.4;

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

0,005 584 7 is a multiple of the atomic mass of iron;

K is 1,00 for predried test samples (6.2.2), and for air-equilibrated test samples (6.2.1) is the conversion factor found from the equation

$$K = \frac{100}{100 - A} \qquad \ldots (2)$$

where A is the hygroscopic moisture content, as a percentage by mass, determined in accordance with ISO 2596.

8.2 General treatment of results

8.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed in table 1[1].

Table 1 — Precision

	Acid decomposition	Fusion decomposition
r	0,209	0,216
P	0,282	0,325
σ_r	0,074	0,076
σ_L	0,085	0,105

r is the permisible tolerance within a 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.

8.2.2 Acceptance of analytical values

The result obtained for the certified reference material (7.2) shall be such that the difference between this result and the certified value of the certified reference material is statistically insignificant. For a certified 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:

$$|A_c - A| \leqslant 2\sqrt{\frac{s_{Lc}^2 + \frac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_r^2}{n}} \qquad \ldots (3)$$

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.

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[1] Additional information is given in annex B.

If condition (3) 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 insignifiant; 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 material of the same type of ore.

When the range of the two values for the test sample is outside the value for r in table 1, an analysis 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 should be used when the information on the reference material certificates is incomplete:

a) if there are sufficient data to enable the between-laboratories standard deviation to be estimated, delete the expression $s_{\mathrm{Wc}}^2/n_{\mathrm{Wc}}$ 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, it is advisable that this material not be used in the application of the standard. In the case that its use is unavoidable, use the formula

$$|A_c - A| < 2\sqrt{2\sigma_L^2 + \frac{\sigma_r^2}{n}} \qquad \ldots (12)$$

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:

a) 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;

b) 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;

c) when the figure in the third decimal place is 5 and there is the figure 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 is increased by one if it is 1, 3, 5, 7 or 9.

8.3 Oxide factors

$w_{\mathrm{Fe_2O_3}} = 1{,}430\ w_{\mathrm{Fe}}$

$w_{\mathrm{FeO}} = 1{,}286\ w_{\mathrm{Fe}}$

$w_{\mathrm{Fe_3O_4}} = 1{,}382\ w_{\mathrm{Fe}}$

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;

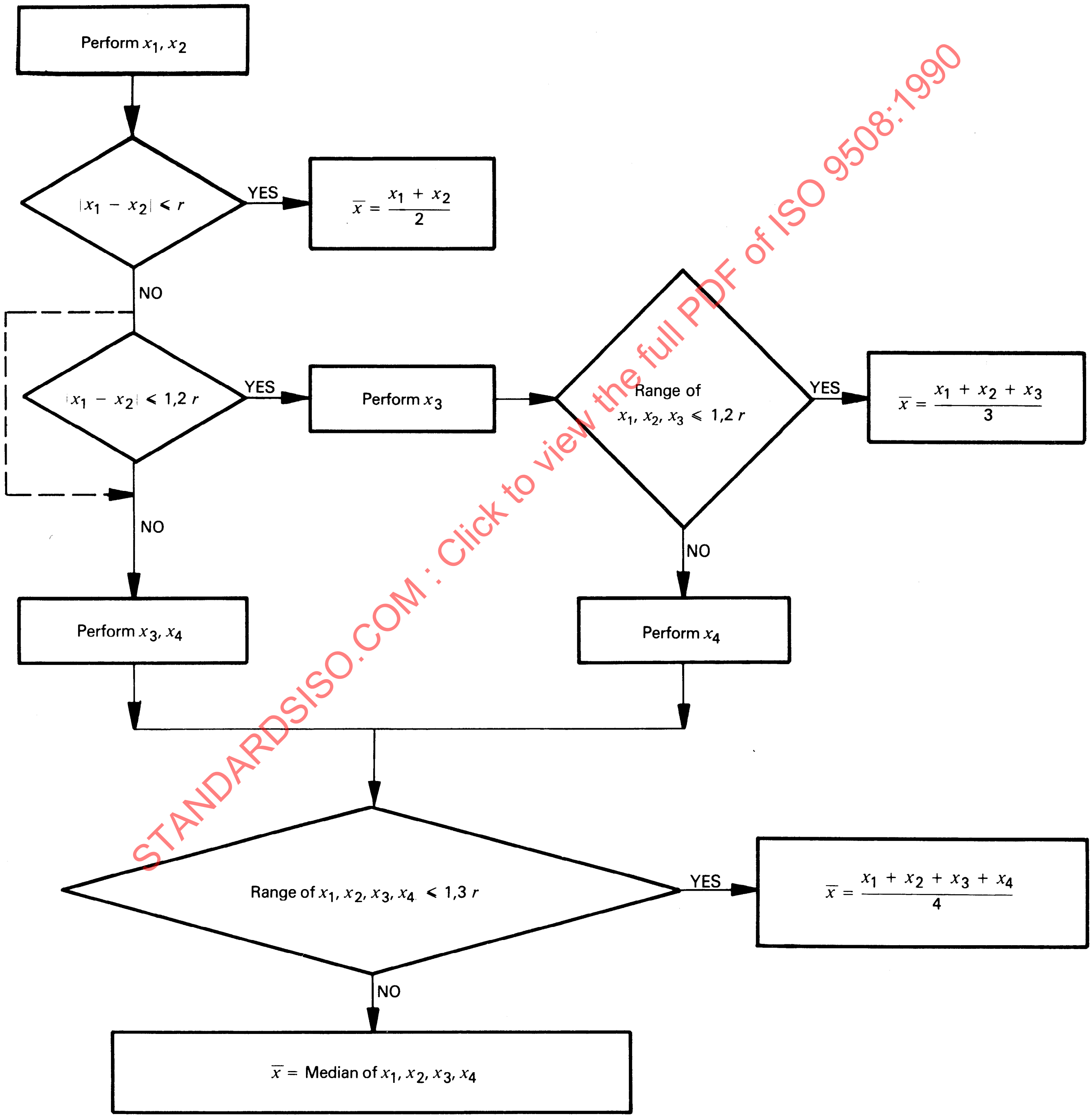
e) result of the analysis;

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 results, 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



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r: see table 1.