
International Standard



2599

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Iron ores — Determination of phosphorus content — Titrimetric method

Minerais de fer — Dosage du phosphore — Méthode titrimétrique

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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 developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been authorized 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.

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International Standard ISO 2599 was developed by Technical Committee ISO/TC 102, *Iron ores*, and was circulated to the member bodies in June 1982.

It has been approved by the member bodies of the following countries:

Australia	Italy	South Africa, Rep. of
Austria	Japan	Spain
Canada	Korea, Dem. P. Rep. of	Sweden
Czechoslovakia	Korea, Rep. of	United Kingdom
Egypt, Arab Rep. of	Mexico	USA
France	Netherlands	USSR
Germany, F.R.	Poland	Venezuela
India	Portugal	
Iran	Roumania	

The member body of the following country expressed disapproval of the document on technical grounds:

China

This second edition cancels and replaces the first edition (i.e. ISO 2599-1973).

Iron ores — Determination of phosphorus content — Titrimetric method

1 Scope and field of application

This International Standard specifies a titrimetric method for the determination of phosphorus content in iron ores, using hexaammonium heptamolybdate (ammonium molybdate).

This method is applicable to a concentration range of 0,10 to 5,0 % (*m/m*)¹⁾ of phosphorus in natural iron ores, and iron ore concentrates and agglomerates including sinter products.

2 References

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

ISO 3082, *Iron ores — Increment sampling and sample preparation — Mechanical method*.²⁾

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

ISO 7764, *Iron ores — Preparation of predried test samples for chemical analysis*.²⁾

3 Principle

Decomposition of the test portion by treatment with hydrochloric, nitric and perchloric acids. Filtration of the insoluble residue, the filtrate being reserved as the main solution.

Ignition of the residue, treatment with sulfuric and hydrofluoric acids to remove silicon dioxide, fusion with sodium carbonate and leaching of the melt with water. Filtration of the alkaline solution, the residue being discarded.

Acidification of the filtrate from residue treatment with hydrochloric acid, addition of iron(III) chloride and collection of the phosphorus by precipitation with ammonia solution. Dissolution of the precipitate in hydrochloric acid and combination with the main solution. Addition of hydrobromic acid and evaporation to fumes of perchloric acid to expel arsenic.

Dissolution of the salts in water, neutralization of the solution, or an aliquot, with ammonia solution and adjustment of the acidity with nitric acid. Cooling of the solution to 20 °C and reduction of vanadium by iron(II) sulfate. Addition of ammonium molybdate to the cold solution and collection by filtration of the yellow precipitate of ammonium molybdo-phosphate.

Washing free of acid and dissolution in a slight excess of sodium hydroxide, the excess being titrated with nitric acid.

For test portions containing more than 18 mg of titanium, a modified procedure is used (see note 3 to 7.3.1).

4 Reagents

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

4.1 Ammonium nitrate (NH_4NO_3).

4.2 Sodium carbonate (Na_2CO_3), anhydrous.

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

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

4.5 Nitric acid, ρ 1,42 g/ml.

4.6 Nitric acid, ρ 1,4 g/ml diluted 1 + 50.

4.7 Nitric acid, ρ 1,4 g/ml diluted 1 + 5 000.

4.8 Sulfuric acid, ρ 1,84 g/ml.

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

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

1) This method has been tested internationally on samples with phosphorus contents ranging from 0,03 to 1,50 % (*m/m*). See annex B.

2) At present at the stage of draft.

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

4.12 Hydrobromic acid, ρ 1,38 g/ml, 40 % (m/m) solution or ρ 1,48 g/ml, 47 % (m/m) solution.

4.13 Ammonia solution, ρ 0,9 g/ml.

4.14 Hydrogen peroxide, 30 % (m/m) solution, free from phosphate stabilizer.

4.15 Potassium nitrate, 10 g/l solution.

4.16 Ammonium molybdate, solution.

Dissolve 40 g of finely pulverized crystalline ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ in 300 ml of warm water and 80 ml of the ammonia solution (4.13), allow the solution to cool, and add this solution in small portions to 600 ml of nitric acid (1 + 1), while stirring. Add a few milligrams of sodium hydrogen phosphate or ammonium hydrogen phosphate and allow to stand for at least 2 days. Filter before use.

4.17 Iron(III) chloride solution, containing 3 g of Fe per litre.

Dissolve 0,3 g of pure iron, with as small a content of phosphorus as possible, by treatment with hydrochloric acid (4.3), add a few drops of nitric acid (4.5) to oxidize the iron, and boil the mixture to remove chlorine.

Allow the solution to cool and dilute with water to 100 ml.

4.18 Iron(II) sulfate solution, 100 g/l.

Dissolve 100 g of iron(II) sulfate heptahydrate ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$) in 1 litre of sulfuric acid (1 + 19).

4.19 Water, free of CO_2 .

Heat distilled or deionized water to the boiling point in a conical flask for 5 min to expel carbon dioxide. Cool, protecting the water in an appropriate way against any pickup of carbon dioxide.

4.20 Sodium hydroxide, standard volumetric solution, $c(\text{NaOH}) = 0,2 \text{ mol/l}$ approx.

Dissolve 8 g of sodium hydroxide in 1 litre of freshly boiled and cooled water (4.19). Standardize this solution with either amidosulfuric acid (sulfamic acid) or potassium hydrogen phthalate.

Dry either potassium hydrogen phthalate or sulfamic acid at $105 \text{ }^\circ\text{C}$ for 1 h and weigh, to the nearest 0,001 g, either approximately 1 g of potassium hydrogen phthalate or approximately 0,5 g of sulfamic acid. Dissolve either material in 50 ml of water free of CO_2 (4.19) and titrate with the sodium hydroxide solution (4.20) using the phenolphthalein solution (4.22) as indicator.

4.21 Nitric acid, standard volumetric solution $c(\text{HNO}_3) = 0,2 \text{ mol/l}$ approx.

Dilute 13 ml of nitric acid (4.5) with water to 1 litre.

Standardize the solution as follows: accurately measure 25 ml of the sodium hydroxide standard volumetric solution (4.20) and titrate with the nitric acid solution, using the phenolphthalein solution (4.22) as indicator.

4.22 3,3-Bis(4-hydroxyphenyl)phthalide (phenolphthalein) solution, 0,1 g/100 ml.

Dissolve 0,10 g of powdered phenolphthalein in 90 ml of ethanol, 95 % (V/V), and dilute with water to 100 ml.

5 Apparatus

Ordinary laboratory apparatus.

6 Sampling and samples

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.

6.1 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 $105 \pm 2 \text{ }^\circ\text{C}$ as specified in ISO 7764. (This is the predried test sample.)

7 Procedure

The analysis shall be carried out generally in duplicate, independently, on one predried test sample.

NOTE — The expression "independently" implies that the repetition of the procedure shall be carried out at a different time and include appropriate recalibration.

7.1 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 6.1.

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.

7.2 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, the amount of the predried test sample (6.1) specified in the table.

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

Table

Phosphorus content	Mass of test portion	Volume of aliquot portion	Volume of ammonium molybdate solution (4.16)
%	g	ml	ml
0,1 up to 0,5	1,0	total	50
0,5 up to 2,5	0,5	total	100
2,5 up to 5,0	0,5	100/250	100

7.3 Determination

7.3.1 Decomposition of the test portion

Place the test portion (7.2) in a 300 ml beaker, add 25 ml of the hydrochloric acid (4.3), cover the beaker with a watch-glass and heat gently to decompose the ore.

NOTES

1 For decomposition of the test portion, place the beaker in a low temperature zone (60 to 100 °C) of the hot-plate to digest the sample for about 1 h, then transfer to a higher temperature zone and heat for about 10 min just below boiling.

2 If a sample obviously contains organic matter, carbonates, or sulfides, and decomposition becomes easier by roasting, place the test portion, accurately weighed, in a porcelain crucible. Cover the crucible and roast at 700 to 750 °C for about 30 min. Allow the crucible to cool to room temperature in a desiccator, wash out the contents of the crucible into a 300 ml beaker, and proceed as directed in 7.3.1.

3 When the test portion contains more than 18 mg of titanium, the following procedure shall be applied:

Place the test portion (7.2) in a platinum crucible lined with 1 g of fused sodium carbonate. Mix the test portion with ten times its mass of fusion mixture (sodium carbonate 10 : sodium nitrate 1) and heat gently at first, then at a higher temperature to complete fusion of the test portion. After cooling, place the crucible together with its contents in a 300 ml beaker, add about 100 ml of warm water and stir gently. Remove the melt from the crucible, rinse the crucible with water and remove.

Heat the contents of the beaker to boiling to dissolve soluble salts and filter off any insoluble residue through a medium-texture filter paper. Wash the residue thoroughly with sodium carbonate solution (2 %) and discard the residue. Transfer the filtrate and washings to a 500 ml

beaker, add the hydrochloric acid (4.3) until the solution is acid and boil it to remove carbon dioxide.

After cooling, add 10,0 ml of the iron(III) chloride solution (4.17) and add the ammonia solution (4.13) in small portions and while stirring, until the solution is slightly alkaline, to precipitate iron hydroxide and iron phosphate. Boil the solution for about 2 min, remove from the source of heat, allow the precipitate to settle, filter through a rapid filter paper, wash with hot water and discard the filtrate and washings.

Pour about 10 ml of the warm hydrochloric acid (4.4) onto the filter paper to dissolve the precipitate and wash with hot water. Collect the solution and washings in a 300 ml beaker, add 15 ml of the perchloric acid (4.10), evaporate the solution to about 30 ml and continue from the addition of 5 ml of the hydrobromic acid (4.12) in 7.3.2, fifth paragraph.

Add 5 ml of the nitric acid (4.5) and 15 ml of the perchloric acid (4.10), cover the beaker and heat to dense white fumes of perchloric acid. Maintain a steady refluxing of the acid on the walls of the beaker for about 10 min. Allow the beaker to cool, add about 50 ml of warm water and heat to dissolve soluble salts.

Filter the solution through a close-texture paper and wash the residue three to five times with the nitric acid (4.6) and finally with hot water until free from acid, receiving the filtrate and washings in a 300 ml beaker. Evaporate the filtrate by gently heating and reserve as the main solution.

7.3.2 Treatment of the residue

While the main solution is evaporating, place the filter paper and residue in a platinum crucible, dry, char the paper and finally ignite at 750 to 800 °C. Cool the crucible, moisten the residue with a few drops of the sulfuric acid (4.9), add 5 ml of the hydrofluoric acid (4.11) and evaporate to remove silicon dioxide and sulfuric acid. Cool the crucible, add 3 g of the sodium carbonate (4.2) and fuse until a clear melt is obtained.

Cool the crucible, place it in a 300 ml beaker, add 100 ml of water and heat to disintegrate the melt and to dissolve all soluble salts. Remove and rinse the crucible. Filter the alkaline solution through a medium-texture paper and wash with warm water, collecting the filtrate and washings in a 300 ml beaker. Discard the residue.

Add the hydrochloric acid (4.3) to the filtrate until it is acid, boil to remove carbon dioxide, cool, and add 10,0 ml of the iron(III) chloride solution (4.17). Add the ammonia solution (4.13) in small portions and while stirring, until the solution is slightly alkaline (indicator paper), to precipitate iron hydroxide and iron phosphate. Boil the solution for about 2 min, then remove from the source of heat. Allow the precipitate to settle, filter through a rapid filter paper and wash with hot water. Discard the filtrate.

Place the beaker containing the main solution from 7.3.1 under the funnel. Dissolve the precipitate by pouring onto the paper about 10 ml of hydrochloric acid (4.4). Wash with warm water.

Evaporate the combined solutions to about 30 ml, add 5 ml of the hydrobromic acid (4.12) and continue to evaporate, in the uncovered beaker, to dense white fumes of perchloric acid. Cool, add 20 ml of water and again evaporate to dense white fumes of perchloric acid. Cover the beaker and maintain a steady refluxing of the acid on the wall of the beaker for

10 min. Cool, add about 50 ml of water and warm to dissolve the salts. If a precipitate of silica appears here, filter the solution into a 500 ml Erlenmeyer flask and wash eight times with warm nitric acid (4.6).

If the entire solution is to be used for the analysis, leave the filtrate in the 500 ml Erlenmeyer flask. If an aliquot is to be used, transfer to a 250 ml volumetric flask, dilute to volume and mix. Transfer an aliquot, according to the table, to a 500 ml Erlenmeyer flask.

7.3.3 Precipitation and treatment of precipitate

7.3.3.1 Evaporate by heating or dilute with water to about 60 ml and cool to room temperature. Add ammonia solution (4.13) until a small precipitate of iron(III) hydroxide persists after shaking or stirring. Add nitric acid (4.5) until the precipitate just dissolves and then 5 ml in excess.

NOTE — If a precipitate of manganese dioxide remains here, add a small amount of the ammonium iron(II) sulfate crystals or a few drops of hydrogen peroxide (4.14), to reduce and dissolve manganese, then boil the solution to oxidize excess of iron(II) or to remove the excess of hydrogen peroxide and cool.

Add 3 g of the ammonium nitrate (4.1), shake to dissolve and dilute to about 100 ml. Cool to 20 °C, then add 5 ml of the iron(II) sulfate solution (4.18) to reduce the vanadium.

7.3.3.2 Precipitate the phosphorus by the addition of the amount of the ammonium molybdate solution (4.16) specified in the table. Stopper and shake the flask vigorously for 10 min and allow to stand for 1 h or until the ammonium molybdo-phosphate precipitate has settled completely.

NOTE — If the phosphorus content is small it may be necessary to allow the solution to stand for 4 h or overnight for complete settling.

7.3.3.3 Collect the precipitate on a small, close texture paper or on a filtering tube containing paper pulp and wash the flask and the precipitate with nitric acid (4.6) until iron ion is no longer detected in the washings. Further wash the flask three times and the precipitate five times with the dilute nitric acid (4.7).

NOTE — The yellow precipitate tends to climb; hence, when washing the precipitate, the jet of the wash solution should be directed to the top of the paper and spirally downward.

Wash the flask three times with the potassium nitrate wash solution (4.15) and the precipitate until the washings are free from acid as shown by an indicator test.

7.3.4 Titration

Return the precipitate with the filter paper to the original flask, add 50 ml of the cold freshly boiled water (4.19) and shake to disintegrate the paper. Add a slight measured excess of the sodium hydroxide standard volumetric solution (4.20) and

shake the mixture to dissolve the yellow precipitate. Add a few drops of the phenolphthalein indicator (4.22), dilute to about 150 ml with the water (4.19) and titrate the excess sodium hydroxide with the nitric acid standard volumetric solution (4.21), until the red colour of the solution disappears with a final drop of the titrant.

8 Expression of results

8.1 Calculation of phosphorus content

The analytical values obtained shall first be corrected with the blank value and then the phosphorus content w_p of each analysis shall be calculated as a percentage by mass to four decimal places using the following equation:

$$w_p (\%) = \frac{c_1 V_1 - c_2 V_2}{m} \times 0,001\,347 \times 100$$

where

c_1 is the concentration, in moles per litre, of sodium hydroxide standard volumetric solution (4.20);

c_2 is the concentration, in moles per litre, of nitric acid standard volumetric solution (4.21);

V_1 is the volume, in millilitres, of sodium hydroxide standard volumetric solution (4.20), taken in 7.3.4;

V_2 is the volume, in millilitres, of nitric acid standard volumetric solution (4.21), used for the titration in 7.3.4;

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

0,001 347 is the mass, in grams, of phosphorus corresponding to 1,00 ml of sodium hydroxide solution, $c(\text{NaOH}) = 1,000 \text{ mol/l}$.

8.2 General treatment of results

8.2.1 Repeatability and reproducibility

The precision of this analytical method is expressed by the following regression formulae¹⁾:

$$r = 0,019\,8X + 0,009\,4$$

$$P = 0,089\,1X + 0,007\,4$$

$$\sigma_r = 0,007\,0X + 0,003\,4$$

$$\sigma_L = 0,031\,5X + 0,001\,9$$

where

X is the phosphorus content, as a percentage by mass, of the test sample;

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.

1) Additional information is given in annexes B and C.

8.2.2 Acceptance of analytical values

The result obtained for the 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 formula may be used to test the significance of the difference:

$$|A_c - A| \leq 1,96 \sqrt{\frac{S_{Lc}^2 + \frac{S_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_r^2}{n}}$$

where

A_c is the certificate 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 the left-hand side of the formula 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 calculated according to the equation for r in 8.2.1, 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 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, delete the expression S_{Wc}/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 following condition:

$$|A_c - A| \leq 1,96 \sqrt{2 \sigma_L^2 + \frac{\sigma_r^2}{n}}$$

8.2.3 Calculation of final result

The final result is the arithmetic mean of the acceptable analytical values for the test sample 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 second 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 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 is increased by one if it is 1, 3, 5, 7 or 9.

8.3 Oxide factor

$$w_{P_2O_5} (\%) = 2,291 4 w_P (\%)$$

9 Test report

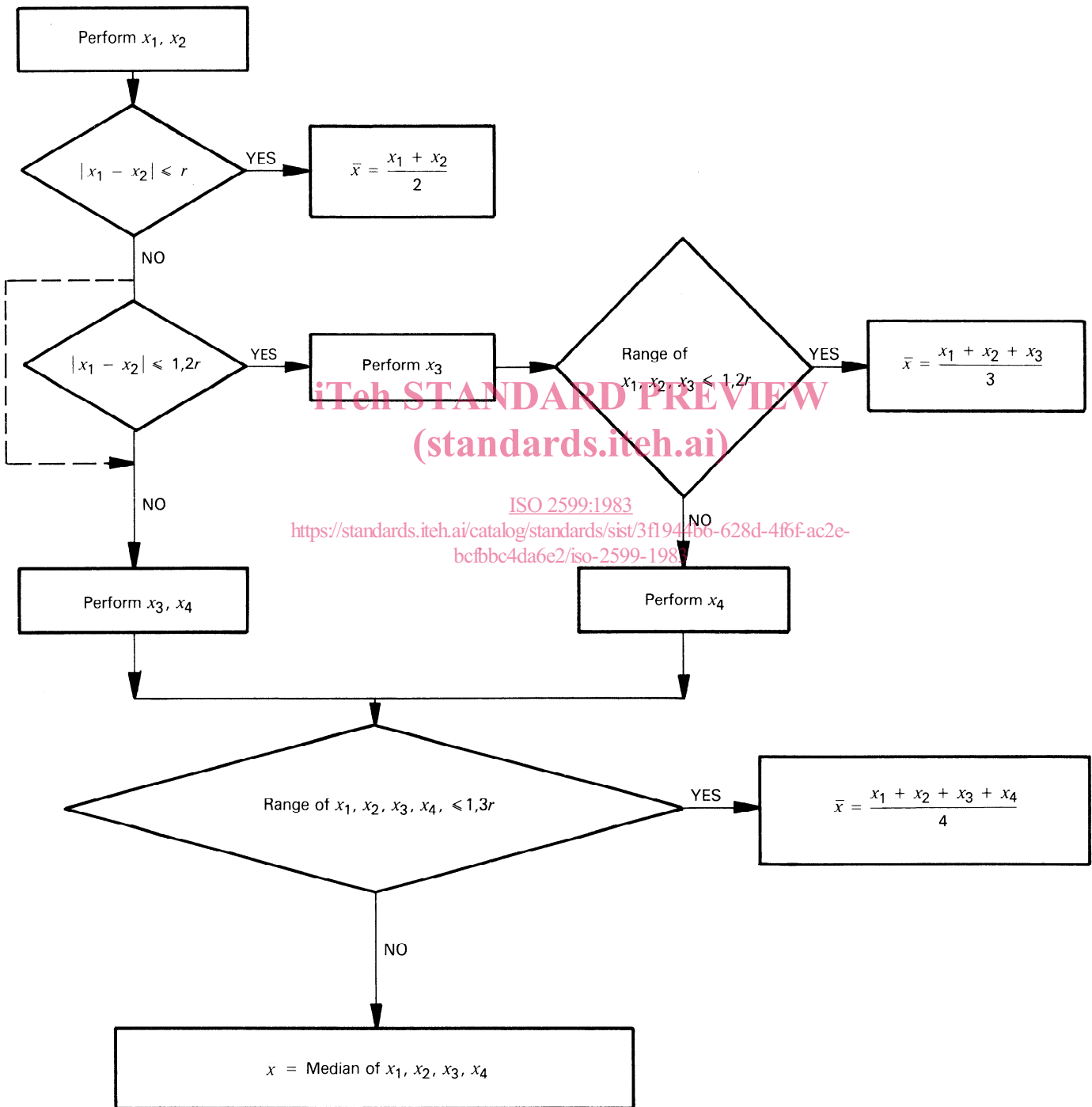
The test report shall include the following information:

- 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

(An integral part of the Standard.)



r: as defined in 8.2.1.

Annex B

Derivation of repeatability and permissible tolerance equations

(This annex is for information only, and is not an integral part of the Standard.)

The regression formulae in 8.2.1 have been derived from the results of international analytical trials carried out in 1967/1968 on 5 ore samples involving 23 laboratories. The results of the trials were reported in document ISO/TC 102/SC 2 N 149E, January, 1969.

Graphical treatment of the precision data is given in annex C.

The test samples used were :

Sample	P content [% (m/m)]
Krivoj Rog	0,031
Marcona	0,040
British Sinter	0,529
Minette	0,665
Sweden-7	1,505

NOTE — The statistical analysis has been performed in accordance with the principles embodied in ISO 5725.

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