TC 102

International Standard 4687

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Iron ores — Determination of phosphorus content — Molybdenum blue spectrophotometric method

Minerais de fer — Dosage du phosphore — Méthode spectrophotométrique au bleu de molybdène

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Foreword

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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.

International Standard ISO 4687 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
Austria
Canada
China
Czechoslovakia
Egypt, Arab Rep. of
France
Germany, F. R.
India
Italy
Japan
Korea, Dem. P. Rep. of
Poland
Portugal
Romania
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Venezuela

No member body expressed disapproval of the document.

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Iron ores — Determination of phosphorus content — Molybdenum blue spectrophotometric method

1 Scope and field of application

This International Standard specifies a molybdenum blue spectrophotometric method for the determination of phosphorus in iron ores.

This method is applicable to a concentration range of 0,005 to 0,2 % *(m/m)* of phosphorus in natural iron ores, and iron ore concentrates and agglomerates including sinter products.

The arsenic content of the sample does not affect the determination.

2 References

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.*[1]

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

ISO 7764, *Iron ores — Preparation of predried test sample for chemical analysis.*[1]

3 Principle

Decomposition of the test portion, either

a) by sintering with sodium peroxide, followed by treatment with hydrochloric and perchloric acids (this method is recommended for lower-grade ores with a high content of amphoteric elements), or

b) by treatment with hydrochloric, nitric and perchloric acids (this method is recommended for high-grade ores with a low content of gangue).

Dehydration of silica, dilution and filtration, and ignition of the residue. Removal of the silica by evaporation with hydrofluoric and sulfuric acids and fusion with sodium carbonate. Dissolution with hydrochloric acid, and combination with the main solution.

Addition of molybdate to convert the phosphate into molybdophosphate complex and reduction to molybdenum blue with ascorbic acid.

Spectrophotometric measurement of the absorbance of the molybdenum blue complex at a wavelength of approximately 725 nm.

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), powder.

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

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

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

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

4.8 Hydrofluoric acid, ϱ 1,13 g/ml, 40 % *(m/m)* solution, or ϱ 1,185 g/ml, 48 % *(m/m)* solution.

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

4.10 Nitric acid, ϱ 1,4 g/ml.

4.11 Hydrogen peroxide, 3 % *(V/V)*, free from phosphate stabilizer.

Dilute hydrogen peroxide 30 % *(m/m)*, (100 volumes) in the volume ratio of 1 + 9.

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[1] At present at the stage of draft.

4.12 Ascorbic acid ($C_6H_8O_6$), 2 g/l solution.

Prepare this solution fresh on the day of use.

4.13 Sodium disulfite (sodium pyrosulfite), ($Na_2S_2O_5$), 150 g/l solution.

Prepare this solution on the day of use.

4.14 Sodium molybdate, dihydrate ($Na_2MoO_4.2H_2O$), 20 g/l solution.

4.15 Bismuth sulfate [$Bi_2(SO_4)_3$] solution.

Dissolve 4,25 g of bismuth sulfate in 280 ml of the sulfuric acid (4.6) and heat until the salt is dissolved completely. Cool, transfer to a 1 000 ml one-mark volumetric flask, dilute to volume with water, and mix.

1 ml of this solution contains 2,5 mg of bismuth.

This solution can also be prepared using metallic bismuth instead of bismuth sulfate.

4.16 Phosphorus standard solution, containing 0,010 g of P per litre.

Dry potassium dihydrogenorthophosphate (KH_2PO_4) at 110 °C to constant mass and cool in a desiccator. Dissolve 0,220 g of the dried salt in water, transfer to a 500 ml one-mark volumetric flask, dilute to the mark and mix. Transfer 25,0 ml of this solution to a 250 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,010 mg of P.

5 Apparatus

Ordinary laboratory equipment and

5.1 One-mark volumetric flasks of capacity 100 ml, made of borosilicate glass.

5.2 Muffle furnaces, adjustable to 400 ± 20 °C and 800 to 1 000 °C.

5.3 Spectrophotometer, suitable for measurement of absorption in the region of 725 nm.

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 ± 2 °C as specified in ISO 7764. (This is the predried test sample.)

7 Procedure

Carry out the analysis 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, providing 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, approximately 1 g of the predried test sample obtained in accordance with 6.1.

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

7.3 Determination

7.3.1 Decomposition of the test portion

If the decomposition is to be based on alkali sintering, proceed as instructed in 7.3.1.1. If the decomposition is to be based on acid attack, proceed as instructed in 7.3.1.2.

7.3.1.1 Alkali sinter attack

CAUTION — Protective goggles should be used during the following operation.

Place the test portion (7.2) in a 40 ml nickel crucible, add 3 g of the sodium peroxide (4.1), mix well using a nickel spatula, and tamp the mixture. Place the crucible for 1 or 2 min at the entrance of a muffle furnace (5.2), the temperature of which is regulated at 400 ± 20 °C, and then transfer into the closed furnace for about 1 h to effect sintering.

NOTE — The mixture should not reach its melting point. Should this occur, repeat the operation at a lower temperature.

Remove the crucible from the furnace and cool to room temperature.

Place the crucible containing the sintered mass in a 600 ml beaker (low form), cover the beaker with a watch-glass, and add carefully 200 ml of water, 50 ml of the hydrochloric acid (4.3) and 25 ml of the perchloric acid (4.7). When the sintered mass has been substantially dissolved from the crucible, remove the crucible and rinse with water and the hydrochloric acid (4.5), if necessary detaching any undissolved material adhering to the walls of the crucible with a rubber-tipped glass rod. Place the beaker on a hot-plate, and heat the solution gently to dissolve the soluble salts.

Add 0,2 ml of the sulfuric acid (4.6) to prevent titanium precipitation. Remove the cover partially from the beaker and heat until dense white fumes of perchloric acid appear. Cover the beaker completely and continue heating to maintain a steady refluxing of acid on the walls of the beaker for about 10 min.

Allow the beaker to cool and add 25 ml of the hydrochloric acid (4.4). Stir and heat gently to dissolve the soluble salts. Add about 30 ml of water.

Filter the solution through a close-texture paper, collecting the filtrate in a 500 ml beaker. Rinse the beaker with water using a rubber-tipped glass rod and transfer the residue quantitatively to the paper. Wash the paper and residue three to four times with the hot hydrochloric acid (4.5), and finally with hot water. Reserve the filtrate and washings as the main solution.

NOTE — Washing should be conducted thoroughly to remove all residual perchloric acid from the filter paper.

Retain the filter paper and residue, and continue according to 7.3.2.

7.3.1.2 Acid attack

Place the test portion (7.2) in a 400 ml beaker (low form) and moisten with 5 ml of water. Add 50 ml of the hydrochloric acid (4.3), cover with a watch-glass, and heat until decomposition is substantially complete.

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

Add 5 ml of the nitric acid (4.10), and then, carefully, 25 ml of the perchloric acid (4.7). Add 0,2 ml of the sulfuric acid (4.6) to prevent titanium precipitation. Remove the cover partially from the beaker and heat until dense white fumes of perchloric acid appear. Cover the beaker completely and continue heating to maintain a steady refluxing of acid on the walls of the beaker for about 10 min. Allow the beaker to cool and add 25 ml of the hydrochloric acid (4.4). Stir and heat gently to dissolve the soluble salts. Add about 30 ml of water.

Filter the solution through a close-texture paper with ashless filter pulp, collecting the filtrate in a 500 ml beaker. Rinse the beaker with water using a rubber-tipped glass rod, and transfer the residue quantitatively to the paper. Wash the paper and residue three to four times with the hot hydrochloric acid (4.5), and finally with hot water. Reserve the filtrate and washings as the main solution.

NOTE — Washing should be conducted thoroughly to remove all residual perchloric acid from the filter paper.

Retain the filter paper and residue, and continue according to 7.3.2.

7.3.2 Treatment of the residue

Transfer the filter paper and residue from 7.3.1.1 or 7.3.1.2 to a platinum crucible. Dry, ash the filter paper, and ignite at 800 to 900 °C in a muffle furnace (5.2).

Allow the crucible to cool, and moisten the residue with a few drops of water. Add 5 drops of the sulfuric acid (4.6) and, depending on the silica content, 5 to 15 ml of the hydrofluoric acid (4.8). Evaporate carefully in a fume cupboard to dryness to expel silica and sulfuric acid. Allow the crucible to cool, add 2 g of the sodium carbonate (4.2), and heat, gently at first, then finally at 900 to 1 000 °C to fuse the residue completely.

NOTE — With a large amount of residue, a further addition of sodium carbonate might be necessary.

Allow the crucible to cool, then transfer it to a 250 ml beaker (low form) containing 100 ml of water and 10 ml of the hydrochloric acid (4.3). Heat gently to dissolve the cooled melt, then remove the crucible and rinse with water.

Combine the solution from 7.3.2 with the main solution from 7.3.1.1 or 7.3.1.2 and evaporate the resultant solution to about 150 ml. Cool to room temperature, transfer to a 200 ml one-mark volumetric flask (5.1), and dilute to volume with water and mix (the test solution).

7.3.3 Treatment of the test solution

Transfer 20,0 ml of the test solution (corresponding to approximately 100 mg of the test portion) to a 250 ml beaker, and add 1 ml of the perchloric acid (4.7) and 5 ml of the hydrobromic acid (4.9). Heat the solution until dense white fumes of perchloric acid are evolved, then cool and add 50 ml of water.

Heat to boiling to facilitate dissolution of the salts and to eliminate chlorine compounds, and evaporate to about 30 ml.

NOTE — If a precipitate of manganese dioxide appears at this stage, dissolve it by dropwise addition of hydrogen peroxide (4.11). Boil the solution for about 5 min to decompose the excess peroxide.

7.3.4 Spectrophotometric measurements

Transfer the solution to a 100 ml one-mark volumetric flask (5.1) and rinse the beaker with water. (The total volume shall not exceed 60 ml.) Add 10 ml of the sodium pyrosulfite solution (4.13), and place in a boiling water bath for exactly 5 min.

Add 10 ml of the bismuth solution (4.15), and cool to 30 to 35 °C. Using a pipette, add 10 ml of the sodium molybdate solution (4.14) into the centre of the solution without allowing it to contact the inner walls of the flask, mix and then immediately add 10 ml of the ascorbic acid solution (4.12). Dilute to the mark with water, and mix (final test solution).

Allow to stand for 25 min, then measure the absorbance of the test solution and the blank test solution against water in cuvettes of suitable path length.

NOTE — Usually, 1 cm optical path length will be preferred. If the absorbance value is less than 0,05, a 2 cm cuvette is recommended. If necessary, correct absorbance readings to a path length of 1 cm. Correct the absorbance of the test solution with the absorbance of the blank test.

The portion of the absorption curve suitable for measurement is located at approximately 725 nm.

7.4 Plotting of the calibration curve

Transfer suitable increments (0 to 20,0 ml) of the phosphorus standard solution (4.16) to 250 ml beakers.

Add 0,02 ml of the sulfuric acid (4.6), 1 ml of the perchloric acid (4.7) and 5 ml of the hydrobromic acid (4.9) in this order, and mix. Heat the solutions until dense white fumes of perchloric acid appear, then cool to room temperature and add 40 ml of water. Transfer the solutions to 100 ml one-mark volumetric flasks (5.1), rinsing the beakers with water, but keeping the final volume below 60 ml.

Add 10 ml of the sodium pyrosulfite solution (4.13), then proceed with the formation and subsequent spectrophotometric measurement of the molybdenum blue complex as indicated in 7.3.4 but with measurement of the absorbances against water. *Correct the absorbances with the absorbance of the zero* calibration solution and prepare the calibration curve by plotting the relationship between absorbances and the quantity of phosphorus in milligrams.

8 Expression of results

8.1 Calculation of phosphorus content

The phosphorus content, as a percentage by mass, is calculated to five decimal places using the equation

$$w_{\mathrm{P}}\,(\%) = \frac{m_2 \times 10 \times 10^{-3}}{m_1} \times 100$$

$$= \frac{m_2}{m_1}$$

where

m_1 is the mass, in grams, of the test portion (7.2);

m_2 is the mass of phosphorus, in milligrams, contained in the final test solution in 7.3.4 determined by using the calibration curve and corrected for the blank value.

8.2 General treatment of results

8.2.1 Repeatability and reproducibility

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

$$r = 0{,}024\,6\,X + 0{,}003\,0$$

$$p = 0{,}029\,9\,X + 0{,}011\,2$$

$$\sigma_{\mathrm{r}} = 0{,}008\,9\,X + 0{,}001\,1$$

$$\sigma_{\mathrm{L}} = 0{,}009\,1\,X + 0{,}004\,0$$

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 phosphorus content, as a percentage by mass, of the test sample :

within-laboratory equations — the arithmetic mean of the duplicate values,

between-laboratory equations — the arithmetic mean of the final results (8.2.3) of the two laboratories.

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 significance of the difference :

$$|A_{\mathrm{c}} - A| \leqslant 2\sqrt{\frac{S_{\mathrm{Lc}}^2 + \dfrac{S_{\mathrm{Wc}}^2}{n_{\mathrm{Wc}}}}{N_{\mathrm{c}}} + \sigma_{\mathrm{L}}^2 + \frac{\sigma_{\mathrm{r}}^2}{n}}$$

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;

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

n_{Wc} is the average number of replicate determinations in the certifying laboratories;

N_c is the number of certifying laboratories;

σ_L and σ_r are as defined in 8.2.1;

n is the number of replicate determinations on the reference material (in most cases $n = 1$).

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}^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

$$|A_c - A| \leqslant 2\sqrt{2\sigma_L^2 + \frac{\sigma_r^2}{n}}$$

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 five decimal places, and rounded off to the third decimal place as follows :

a) when 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) when the figure in the fourth decimal place is 5 and there are figures other than 0 in the fifth decimal place, or when the figure in the fourth decimal place is greater than 5, the figure in the third decimal place is increased by one;

c) when the figure in the fourth decimal place is 5 and there are no figures other than 0 in the fifth decimal place, the 5 is discarded and the figure in the third decimal place is kept unchanged if it is 0, 2, 4, 6 or 8 and is increased by one if it is 1, 3, 5, 7 or 9.

8.3 Oxide factor

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

9 Test report

The test report shall include the following information :

a) reference to this International Standard;

b) details necessary for the identification of the sample;

c) result of the analysis;

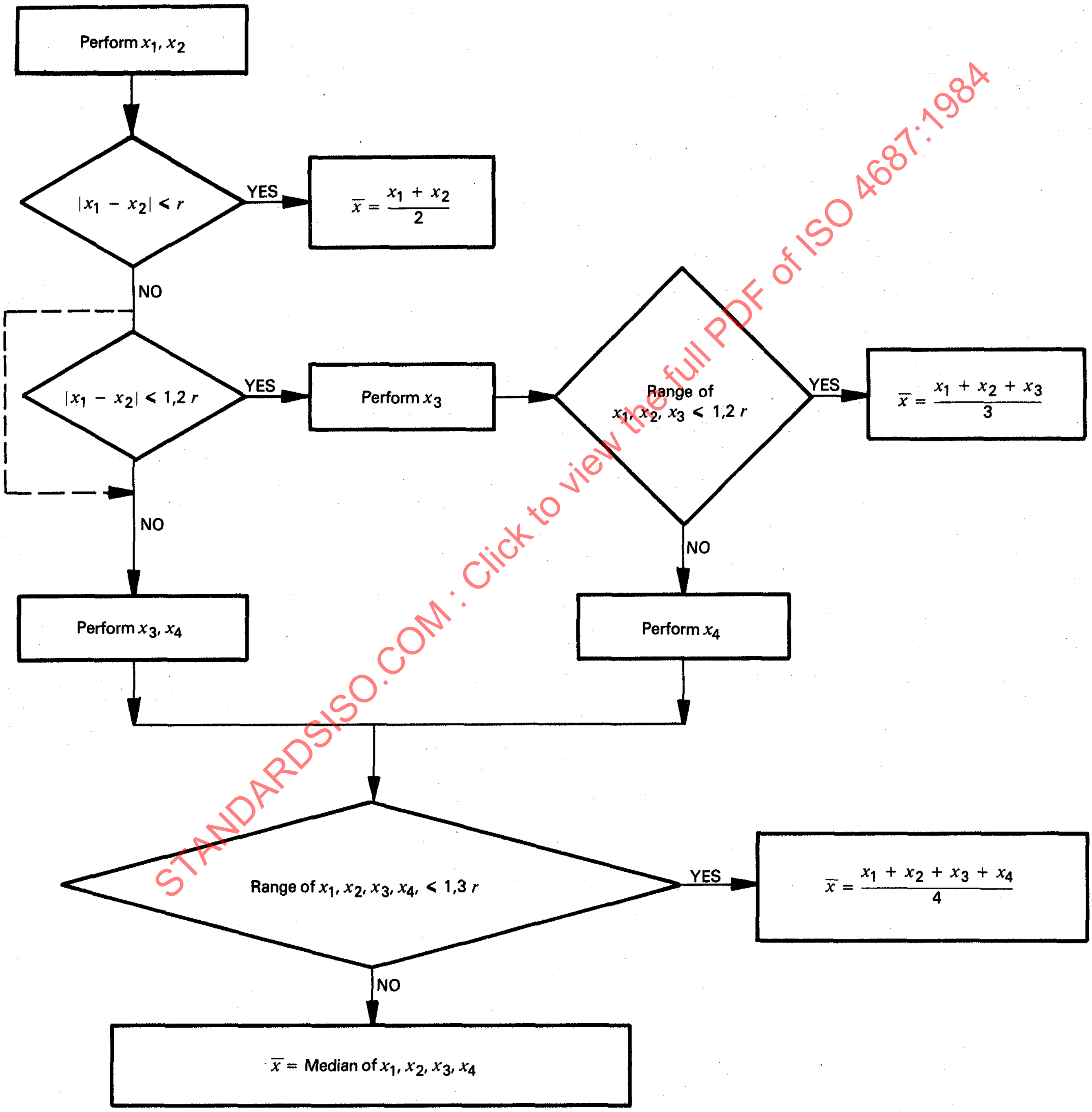
d) reference number of the result;

e) 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 forms 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 given for information only and does not form an integral part of the standard.)

The regression equations in 8.2.1 have been derived from the results of international analytical trials carried out in 1970/1971 on 5 ore samples involving 18 laboratories in 8 countries. The results of the trials were reported in document ISO/TC 102/SC 2 N 224 F, June 1971.

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

The test samples used were :

Sample	**P content** [% (m/m)]
Swedish ore	0,008
Krivoj Rog	0,031
Palabora	0,059
Philippine Iron Sand	0,114
British Sinter	0,534

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