

# INTERNATIONAL STANDARD

**ISO**  
**4687-1**

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## **Iron ores — Determination of phosphorus content —**

### **Part 1:**

### **Molybdenum blue spectrophotometric method**

*Minerais de fer — Dosage du phosphore —*

*Partie 1: Méthode spectrophotométrique au bleu de molybdène*



Reference number  
ISO 4687-1:1992(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 voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 4687-1 was prepared by Technical Committee ISO/TC 102, *Iron ores*, Sub-Committee SC 2, *Chemical analysis*.

This first edition of ISO 4687-1 cancels and replaces ISO 4687:1984, which has been technically revised.

ISO 4687 consists of the following parts, under the general title *Iron ores — Determination of phosphorus content*:

- *Part 1: Molybdenum blue spectrophotometric method*

The titrimetric content method will be covered in ISO 4687-2 (at present ISO 2599:1983).

Annex A forms an integral part of this part of ISO 4687. Annexes B and C are for information only.

# Iron ores — Determination of phosphorus content —

## Part 1:

## Molybdenum blue spectrophotometric method

### 1 Scope

This part of ISO 4687 specifies a molybdenum blue spectrophotometric method for the determination of the phosphorus content of iron ores.

This method is applicable to phosphorus contents between 0,003 % (*m/m*) and 2 % (*m/m*) in natural iron ores, iron ore concentrates and agglomerates, including sinter products.

The presence of arsenic, barium or titanium does not affect the result.

### 2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 4687. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 4687 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 648:1977, *Laboratory glassware — One-mark pipettes*.

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

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

Fusion of the test portion in sodium carbonate and sodium tetraborate flux and dissolution of the cooled melt in hydrochloric acid.

Treatment of an aliquot with sodium sulfite and perchloric acid followed by treatment of the phosphorus with molybdate and hydrazine sulfate to form a molybdenum blue complex.

Spectrophotometric measurement of the molybdenum blue complex at an absorption peak wavelength of approximately 820 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 carbonate** ( $\text{Na}_2\text{CO}_3$ ), anhydrous.

**4.2 Sodium tetraborate** ( $\text{Na}_2\text{B}_4\text{O}_7$ ), anhydrous.

**4.3 Hydrochloric acid**,  $\rho$  1,16 g/ml to 1,19 g/ml.

**4.4 Hydrochloric acid**,  $c(\text{HCl}) = 6 \text{ mol/l}$ .

Determine, at ambient temperature, the density of the hydrochloric acid (4.3) and, in accordance with table 1, measure the appropriate volume into a 1 000 ml one-mark volumetric flask. Dilute to volume with water, mix and cool. Readjust the volume and re-mix.

**Table 1 — Preparation of 6 mol/l hydrochloric acid**

| Density<br>g/ml | Hydrochloric acid (4.3) required<br>ml |
|-----------------|----------------------------------------|
| 1,16            | 575                                    |
| 1,17            | 535                                    |
| 1,18            | 500                                    |
| 1,19            | 470                                    |

**4.5 Perchloric acid**,  $\rho$  1,54 g/ml, 60 % (m/m) solution or  $\rho$  1,70 g/ml, 72 % (m/m) solution.

**4.6 Perchloric acid**,  $c(\text{HClO}_4) = 3 \text{ mol/l}$ .

Transfer 250 ml of water to a 1 000 ml one-mark volumetric flask and add 250 ml of 72 % (m/m) perchloric acid (4.5) or 325 ml of 60 % (m/m) perchloric acid (4.5), mix and cool. Dilute to volume with water and mix.

**4.7 Sodium sulfite** ( $\text{Na}_2\text{SO}_3$ ), solution, 100 g/l.

This solution should be prepared freshly on the day of use in a sufficient quantity for the number of tests being made.

**4.8 Hydrazine sulfate** ( $\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{SO}_4$ ), solution 2 g/l.

This solution should be prepared freshly on the day of use in a sufficient quantity for the number of tests being made.

**4.9 Matrix solution.**

Transfer 1,6 g of sodium carbonate (4.1) and 0,8 g of sodium tetraborate (4.2) to a 250 ml beaker and add 40 ml of water. While stirring, add cautiously 70 ml of hydrochloric acid (4.4). Heat to boiling, boil for 1 min, cool and transfer to a 200 ml one-mark volumetric flask. Dilute to volume with water and mix.

**4.10 Ammonium heptamolybdate**  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ , solution, 20 g/l.

Dissolve 20 g of ammonium heptamolybdate in 500 ml of water. When dissolved, add slowly, with mixing, 250 ml of 72 % (m/m) perchloric acid (4.5) or 325 ml of 60 % (m/m) perchloric acid (4.5), and cool. Transfer to a 1 000 ml one-mark volumetric flask and dilute to volume with water.

**4.11 Phosphorus**, standard solution, 20  $\mu\text{g/ml}$ .

Dry potassium dihydrogen orthophosphate ( $\text{KH}_2\text{PO}_4$ ) at 110 °C to constant mass and cool in a desiccator. Dissolve 0,219 7 g of the dried salt in water, transfer to a 250 ml one-mark volumetric flask, dilute to volume with water and mix. Transfer

25,0 ml of this solution to a 250 ml one-mark volumetric flask, dilute to volume with water and mix.

## 5 Apparatus

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

**5.1 Platinum or suitable platinum alloy crucibles**, of capacity not less than 25 ml.

**5.2 Muffle furnace**, to provide a temperature of 1 020 °C.

**5.3 Combined magnetic stirrer/hotplate.**

**5.4 Stirring bars**, polytetrafluoroethylene-coated, 10 mm long.

**5.5 Water bath**, at boiling temperature.

**5.6 Spectrophotometer**, suitable for measurement of absorbance at approximately 820 nm.

## 6 Sampling and samples

### 6.1 Laboratory sample

For analysis, use a laboratory sample of minus 10  $\mu\text{m}$  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  $\mu\text{m}$ .

NOTE 1 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 manner that it is representative of the whole contents of the container. Dry the test sample at  $105 \text{ °C} \pm 2 \text{ °C}$  as specified in ISO 7764. (This is the predried test sample.)

## 7 Procedure

### 7.1 Number of determinations

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

NOTE 2 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 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, approximately 0,5 g of the predried test sample obtained in accordance with 6.2.

NOTE 3 The test portion should be taken and weighed quickly to avoid reabsorption of moisture.

## 7.3 Blank test and check test

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

NOTE 4 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 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.

## 7.4 Determination

### 7.4.1 Decomposition of the test portion

Add 0,80 g of sodium carbonate (4.1) to a platinum or platinum alloy crucible (5.1). Transfer the weighed test portion (7.2) to the crucible and mix well using a platinum or stainless-steel rod. Add 0,4 g of sodium tetraborate (4.2) and again mix well, using the metal rod. Place the crucible in a muffle furnace (5.2) set at 1 020 °C, for 30 min.

Remove the crucible from the furnace and gently swirl the melt as it solidifies. Allow to cool.

### 7.4.2 Preparation of the test solution

Place the polytetrafluoroethylene-coated stirring bar (5.4) in the cooled crucible and place the crucible on its side in a 150 ml low-form beaker. Add 25 ml of water and 35 ml of hydrochloric acid (4.4), cover with a watch-glass, place on the magnetic stirrer/hotplate (5.3) and heat with stirring until dissolution of the melt is complete.

NOTE 5 The crucible may need to be rotated to ensure that the solution reaches the whole of the melt.

Cool the solution, remove and rinse the crucible and transfer the solution to a 100 ml one-mark volumetric flask. Dilute to volume with water and mix. (This is the test solution.)

### 7.4.3 Treatment of the test solution

With test samples containing less than 0,2 % (m/m) phosphorus, proceed as specified in 7.4.3.1. With test samples containing more than 0,2 % (m/m) phosphorus, proceed as specified in 7.4.3.2.

#### 7.4.3.1 Phosphorus content below 0,2 % (m/m)

Into two 250 ml tall-form beakers, measure respectively an aliquot of test solution (7.4.2) and an aliquot of blank test solution in accordance with table 2. Add to each the specified volume of matrix solution (4.9) (see table 2).

Prepare an iron compensation solution by measuring into a 250 ml tall-form beaker a corresponding aliquot of test solution (7.4.2) and adding the specified volume of matrix solution (4.9) (see table 2).

#### 7.4.3.2 Phosphorus content above 0,2 % (m/m)

Prepare a diluted test solution and a diluted blank test solution as follows: into two 100 ml one-mark volumetric flasks, measure 10,0 ml aliquots of test solution (7.4.2) and blank test solution respectively. Dilute to volume with matrix solution (4.9) and mix.

Into two 250 ml tall-form beakers, measure respectively an aliquot of diluted test solution and an aliquot of diluted blank test solution in accordance with table 2. Add to each the specified volume of matrix solution (4.9) (see table 2).

**Table 2 — Aliquots of test solution or diluted test solution**

| Phosphorus content of test sample                                                                                                                                                          | Aliquot of test solution (7.4.2) | Aliquot of diluted test solution (7.4.3.2) | Matrix solution (4.9) |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------|--------------------------------------------|-----------------------|
| % (m/m)                                                                                                                                                                                    | ml                               | ml                                         | ml                    |
| 0,003 to 0,1                                                                                                                                                                               | 20,0                             |                                            | 0                     |
| 0,05 to 0,2                                                                                                                                                                                | 10,0                             |                                            | 10,0                  |
| 0,2 to 1                                                                                                                                                                                   |                                  | 20,0                                       | 0                     |
| 0,5 to 2                                                                                                                                                                                   |                                  | 10,0                                       | 10,0                  |
| NOTE — The overlap in concentration ranges allows the value for the content obtained to differ from the value expected. Normally the first range specified in the table should be adopted. |                                  |                                            |                       |

**7.4.4 Spectrophotometric measurement**

Add 15 ml of sodium sulfite solution (4.7) to the solutions obtained in either 7.4.3.1 or 7.4.3.2. Mix, cover and allow to stand at room temperature for 2 min. Transfer to a water bath at boiling temperature (5.5) immersing the beakers to the solution level, heat for 10 min and remove the beakers from the bath.

Add stirring rods and, mixing after each addition, add, except to the iron compensation solution 25 ml of perchloric acid (4.6), 20 ml of water and 10,0 ml of ammonium heptamolybdate solution (4.10) (see notes 6 and 7).

**NOTES**

6 With the iron compensation solution, increase the volume of perchloric acid (4.6) from 25 ml to 35 ml, add 20 ml of water, but omit the addition of ammonium heptamolybdate solution (4.10).

7 For convenience, a premixed stock of perchloric acid (4.6) and water in the ratio of 25 ml to 20 ml may be prepared in sufficient quantity for the required number of tests in the series. To provide for the seven tests required in a normal test and calibration series, add 200 ml of perchloric acid (4.6) to 160 ml of water and mix thoroughly. Use 45 ml of this diluted perchloric acid-water mixture in place of the specified separate additions of perchloric acid (4.6) and water.

Add 2,0 ml of hydrazine sulfate solution (4.8), mix and transfer to a water bath at boiling temperature (5.5), immersing the beaker to the solution level, and heat at the maximum temperature of the bath for 20 min. Cool in a water bath, transfer to a 100 ml one-mark volumetric flask, dilute to volume with water and mix (see note 8).

Measure the absorbances of the solutions in 10 mm cells at a peak absorbance in the vicinity of 820 nm using water as the reference solution, and correct the value obtained for the test solution or diluted test solution with the value obtained for the blank test

or diluted blank test as appropriate (see note 9). If an iron compensation test has been conducted (see 7.4.3.1), subtract the absorbance value obtained from the corrected absorbance of the test solution.

**NOTES**

8 Stability of the colour for at least 5 h has been confirmed.

9 If the absorbance value obtained for the blank test is greater than 0,025, purer reagents should be used.

**7.4.5 Preparation of the calibration graph****7.4.5.1 Preparation of calibration stock solution, 5 µg/ml**

Transfer 0,8 g of sodium carbonate (4.1) and 0,4 g of sodium tetraborate (4.2) to a 250 ml beaker and add 30 ml of water. While stirring, add cautiously 35 ml of hydrochloric acid (4.4). Cover, heat to boiling, boil for 1 min and cool. Add 25,0 ml of phosphorus standard solution (4.11), mix and transfer to a 100 ml one-mark volumetric flask. Dilute to volume with water and mix.

**7.4.5.2 Calibration**

Transfer to each of four 250 ml tall-form beakers 0 ml; 5,0 ml; 10,0 ml and 20,0 ml of phosphorus calibration stock solution (7.4.5.1). Add to the first three beakers respectively 20,0 ml; 15,0 ml and 10,0 ml of matrix solution (4.9), then continue with the procedure specified in 7.4.4.

Measure the absorbance of each solution using water as the reference and correct the values with the value for the zero phosphorus solution. Plot the net absorbances against the mass of phosphorus in micrograms to three significant figures.

NOTE 10 The absorbance value obtained for the 100 µg of phosphorus calibration can be expected to be  $0,870 \pm 0,03$ .

**8 Expression of results****8.1 Calculation of phosphorus content**

The phosphorus content,  $w_p$ , as a percentage by mass, is calculated to six decimal places for contents below 0,1 %, to five decimal places for contents between 0,1 % and 1 % and to four decimal places for contents above 1 %, using the equation

$$w_p = \frac{m_1 f}{100 m_0 V} \quad \dots (1)$$

where

$m_0$  is the mass, in grams, of the test portion (7.3);

- $m_1$  is the mass of phosphorus, in micrograms, contained in the aliquot taken in 7.4.3 and determined from the calibration graph;
- $f$  is the dilution factor ( $f = 10$  when diluted test solution as specified in 7.4.3.2 is used, otherwise  $f = 1$ );
- $V$  is the volume of aliquot taken in 7.4.3, in millilitres.

NOTE 11 If the arsenic content of the sample is greater than 100 µg/g and more than twice the phosphorus content, correct the phosphorus value by subtracting 1 % of the arsenic content from the calculated phosphorus content.

## 8.2 General treatment of results

### 8.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed by the following regression equations<sup>1)</sup>:

$$r = 0,020\ 6\ X + 0,000\ 9 \quad \dots (2)$$

$$P = 0,067\ 3\ X - 0,001\ 4$$

(minimum value: 0,001 3) ... (3)

$$\sigma_r = 0,007\ 3\ X + 0,000\ 3 \quad \dots (4)$$

$$\sigma_L = 0,023\ 2\ X - 0,000\ 6$$

(minimum value: 0,000 4) ... (5)

where

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

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

$r$  is the permissible tolerance within a laboratory (repeatability);

$P$  is the permissible tolerance between laboratories;

$\sigma_r$  is the within-laboratory standard deviation;

$\sigma_L$  is the between-laboratories standard deviation.

NOTE 12 The minimum values are the actual precision values, obtained in the international test programme, for the lowest concentration test samples. Such values are required where the application of the linear regression equation would produce negative precision values at very low concentration levels.

### 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 certified value of the 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 in both 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 certified 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  $n = 1$ );

$\sigma_L$  and  $\sigma_r$  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

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

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 13 The following procedure should be used when the information on the reference material certificate is incomplete:

- if there are insufficient 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;
- 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 case its use is unavoidable, use the condition

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

### 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 six decimal places for contents of phosphorus lower than 0,1 % (m/m), to five decimal places for contents between 0,1 % (m/m) and 1 % (m/m) and to four decimal places for contents above 1 % (m/m).

For contents of phosphorus lower than 0,1 % (m/m), the value calculated to six decimal places is rounded off to the fourth decimal place as follows:

- when the figure in the fifth decimal place is less than 5, it is discarded and the figure in the fourth decimal place is kept unchanged;
- when the figure in the fifth decimal place is 5 and there is a figure other than 0 in the sixth decimal place, or when the figure in the fifth decimal

place is greater than 5, the figure in the fourth decimal place is increased by one;

- when the figure in the fifth decimal place is 5 and the figure 0 is in the sixth decimal place, the 5 is discarded and the figure in the fourth 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.

In a similar manner, with the ordinal numbers decreased by one, the value for contents of phosphorus between 0,1 % (m/m) and 1 % (m/m) is rounded off to the third decimal place and with the ordinal numbers decreased by two, the value for contents of phosphorus above 1 % (m/m) is rounded off to the second decimal place.

### 8.3 Oxide factor

The oxide factor is given by the following equation:

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

### 9 Test report

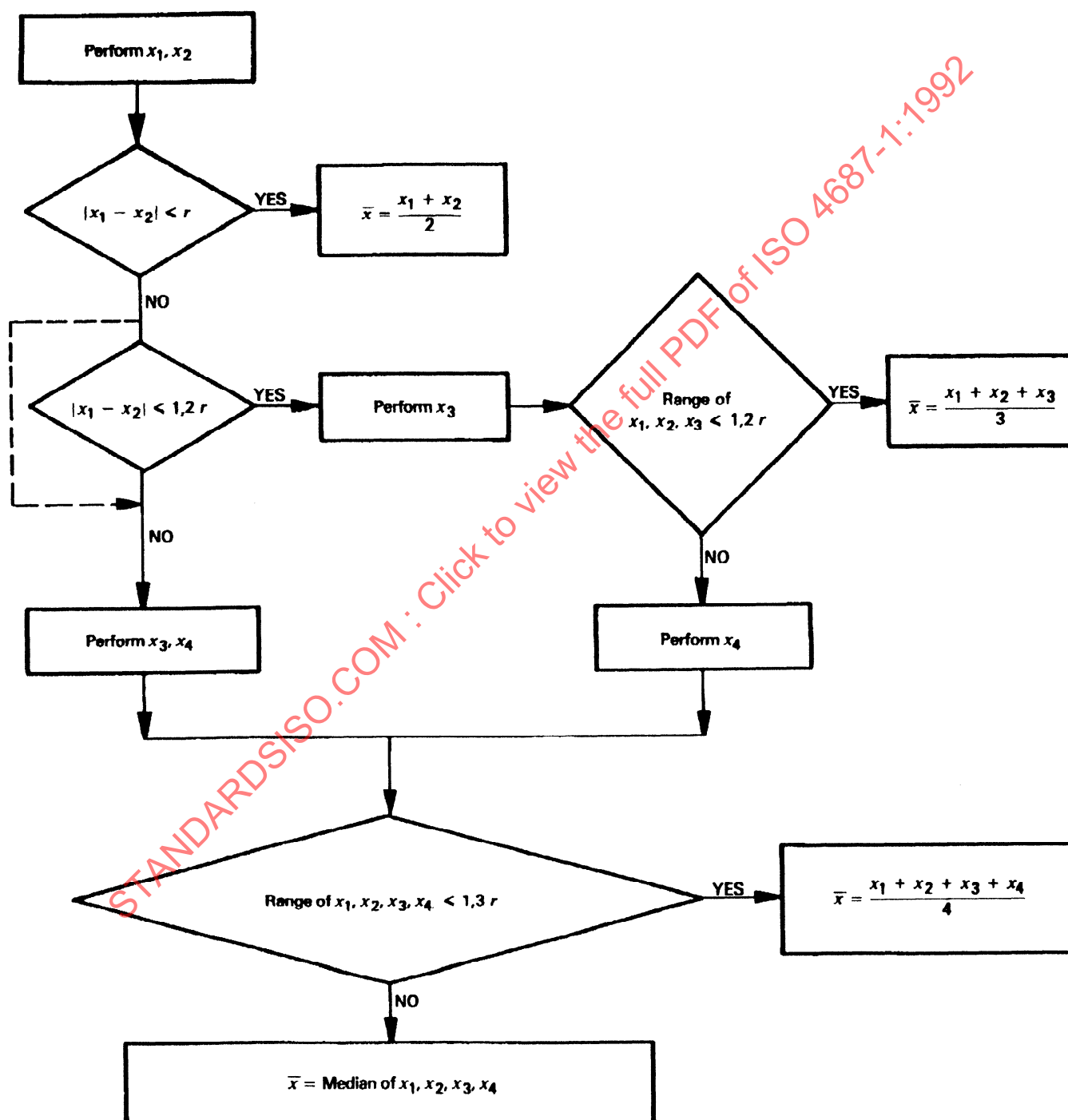
The test report shall include the following information:

- name and address of the testing laboratory;
- date of issue of the test report;
- reference to this part of ISO 4687;
- 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 part of ISO 4687 which may have had an influence on the result, either for the test sample or for the certified reference material(s).

# Annex A

(normative)

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



$r$  : as defined in 8.2.1.