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International Standard



4690

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## Iron ores — Determination of sulfur content — Combustion method

*Minerais de fer — Dosage du soufre — Méthode par combustion*

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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 preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

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

International Standard ISO 4690 was prepared by Technical Committee ISO/TC 102, *Iron ores*.

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

# Iron ores — Determination of sulfur content — Combustion method

## 1 Scope and field of application

This International Standard specifies a combustion method for the determination of the sulfur content of iron ores.

This method is applicable to a concentration range of 0,002 to 0,25 % (*m/m*) of sulfur in natural iron ores, and iron ore concentrates and agglomerates including sinter products. The results are not affected by the presence of fluoride.

## 2 References

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

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.*<sup>1)</sup>

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

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

## 3 Principle

Mixing of the sample with tungstic oxide and heating at 1 200 °C in a resistance furnace, using nitrogen as a carrier gas.

Absorption of the evolved sulfur dioxide in dilute hydrochloric acid solution containing starch and potassium iodide, and titration of the solution continuously during the evolution with a standard volumetric solution of potassium iodate.

## 4 Reagents

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

**4.1 Magnesium perchlorate** [ $\text{Mg}(\text{ClO}_4)_2$ ], anhydrous, free flowing, particle size 0,5 to 2 mm.

**4.2 Tungsten(VI) oxide** ( $\text{WO}_3$ ).

**4.3 Tin(II) chloride** ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ), particle size 0,5 to 2 mm.

**4.4 Soda-asbestos**, particle size 0,5 to 2 mm.

**4.5 Hydrochloric acid**,  $\rho$  1,16 to 1,19 g/ml, diluted 1 + 66.

**4.6 Potassium iodide** (KI), 3 % (*m/m*) solution.

**4.7 Starch**, 2 % (*m/m*) solution.

Make a suspension of 2,0 g of starch in 10 ml of water, add to 50 ml of boiling water and stir. Cool, dilute to 100 ml and mix.

Prepare this solution immediately prior to use.

**4.8 Potassium iodate** ( $\text{KIO}_3$ ), standard volumetric solution, 0,001 042 mol/l.

NOTE — The potassium iodate should be previously dried for 1 h at 110 °C.

Weigh, to the nearest 0,000 2 g, 0,223 g of dried potassium iodate and dissolve in water. Cool, transfer to a 1 litre volumetric flask, make up to the mark and mix.

1 ml of this standard volumetric solution is equivalent to 0,10 mg of sulfur.

## 5 Apparatus

NOTE — Volumetric flasks shall comply with ISO 1042.

The apparatus is shown in figure 1.

**5.1 Nitrogen supply.**

**5.2 Drying tower**, containing soda-asbestos (4.4) and magnesium perchlorate (4.1).

1) At present at the stage of draft.

**5.3 Flowmeter**, graduated from 0 to 1 l/min.

**5.4 Resistance furnace**, capable of maintaining a temperature of  $1\ 200 \pm 25$  °C.

**5.5 Refractory combustion tube**, capable of withstanding a temperature of  $1\ 200 \pm 25$  °C.

**5.6 Refractory combustion boat** with loose-fitting lid, or a suitable refractory combustion boat capable of accommodating a porous cartridge, as shown in figure 2a) or 2b) respectively. The following dimensions can be used as guidelines.

Combustion boat		Cartridge	
Length	80 mm	Length	50 mm
Width	13 mm	Internal diameter	15 mm
Depth	9 mm		

**5.7 Tin(II) chloride absorption tube**: narrow glass tubing containing approximately 10 g of the solid tin(II) chloride (4.3), suitably plugged with inert wool to prevent the reagent being blown into the absorption vessel. (A U-tube is suitable.) When necessary (see the note) this is inserted in the train at the exit of the combustion tube at point X in figure 1.

NOTE — If the sample is known or thought to contain chloride, for example in the form of sodium chloride, chlorapatite or scapolite, the chlorine formed during combustion of the sample should be removed by passing the gas stream through solid tin(II) chloride in a suitable tube or vessel (5.7) prior to absorption and titration. If numerous samples with chloride contents  $\geq 1$  % (*m/m*) are to be analysed, it is advisable to determine the absorption capacity of the tin(II) chloride to be able to judge the most suitable interval for reagent replacement. In such cases a larger absorption vessel may be preferred.

The tin(II) chloride absorption tube should also be fitted when the chloride content of the test sample is unknown.

**5.8 Cylinder**, 100 ml, tall form, to hold the absorbing solution.

**5.9 Bubbler**, multihole, to reach to the bottom of the cylinder (5.8).

**5.10 Burette**, conforming to ISO 385/1, graduated in divisions of 0,05 ml.

NOTE — For determination of low sulfur contents [ $< 0,005$  % (*m/m*)], alternative titration devices such as a piston burette or a suitable micro-syringe capable of delivering small, precise aliquots of titrant may be used.

## 6 Sampling and samples

### 6.1 Laboratory sample

For analysis, use a laboratory sample of minus 100  $\mu\text{m}$  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 — A guideline on significant contents of combined water and oxidizable compounds is incorporated in ISO 7764.

### 6.2 Preparation of predried test samples

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a manner that it is representative of the whole contents of the container. Dry the test sample at  $105 \pm 2$  °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 predried test sample.

NOTE — The expression "independently" means that the second and any subsequent result is not affected by the previous result(s). For this particular analytical method this condition implies that the repetition of the procedure shall be carried out either by the same operator at a different time or by a different operator, including in either case, appropriate recalibration.

### 7.2 Blank test and check test

In each run, 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 — 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 are from the same reagent bottles.

When the analysis is carried out on several samples of the same type of ore at the same time, the analytical value of one certified reference material may be used.

### 7.3 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.

#### NOTES

- For samples containing less than 0,005 % (*m/m*) sulfur, 1 g of sample can be taken, provided that the combustion boat or cartridge used will accommodate the increased bulk of sample plus tungsten(VI) oxide. If this is not possible, see the note to 5.10.
- The test portion should be taken and weighed quickly in order to avoid reabsorption of moisture.

## 7.4 Determination

**7.4.1** Place the test portion (7.3) in a small weighing bottle containing 1,0 g of tungsten(VI) oxide (4.2) and mix thoroughly.

Transfer 80 ml of hydrochloric acid (4.5), 1 ml of potassium iodide solution (4.6) and 1 ml of starch solution (4.7) to the absorption cylinder (5.8) and place in position at the end of the combustion train. Adjust the nitrogen flow rate to 150 to 200 ml/min and titrate the absorbing solution with potassium iodate solution (4.8) until the colour of the solution is pale blue.

NOTE — A few drops of the potassium iodate solution (4.8) should be sufficient.

**7.4.2** Transfer the mixture of test portion and tungsten(VI) oxide (4.2) to a refractory combustion boat fitted with a loose-fitting lid (5.6) and insert into the hot zone of the furnace at 1 200 °C.

NOTE — Alternatively, the mixture of test portion and tungsten(VI) oxide (4.2) can be placed inside a porous cartridge which is placed in a refractory combustion boat [figure 2 b)].

**7.4.3** Leave the boat standing in the hot zone for approximately 1 min and then pass nitrogen at a flow rate of 150 to 200 ml/min through the furnace. With the nitrogen flowing continuously, titrate the absorbing solution with the potassium iodate solution (4.8) so as to keep the solution just blue in colour.

NOTE — Titration should be carried out during the evolution of sulfur gases to prevent sulfur dioxide being swept out of solution by the flow of carrier gas. It may be necessary to reduce the gas flow to 150 ml/min when titrating samples of high sulfur content. A faster flow rate of 300 ml/min may be necessary when analysing samples of very low sulfur content to ensure complete transfer of evolved sulfur gases into the absorbing solution.

**7.4.4** Continue to pass nitrogen through the apparatus for at least 5 min or until the absorbing solution remains permanently blue, whichever involves the longer time.

### NOTES

1 If the sample contains large amounts of combined water, a film of moisture may appear on the inside of the apparatus. This should be completely vaporized before completion of the test.

2 For samples of normal sulfur content, combustion times of 4 to 8 min are usually sufficient. With samples of high sulfur content, however, it may be necessary to increase combustion times to 10 min or more to ensure complete extraction of sulfur from the sample.

**7.4.5** Wash the inside of the bubbler several times by repeatedly releasing the inlet bung to the combustion tube (so as to allow the absorbant to flow back up the bubbler) and then replacing the bung to restore the nitrogen flow through the apparatus. Finally, titrate the solution to a pale blue end-point and record the volume of potassium iodate solution (4.8) used.

Record also the volume of potassium iodate solution (4.8) used in the blank test.

NOTE — If high blanks occur [ $>$  the equivalent of 0,001 5 % ( $m/m$ ) in the test sample], this may be due to the presence of sulfur compounds either in the tungsten(VI) oxide or in the refractory boats/porous cartridges used. Tungsten(VI) oxide (4.2) can be pretreated by heating for 2 h at a temperature of 800 °C, whilst the blank in the combustion boats/cartridges can be reduced by allowing them to stand overnight in a suitable furnace at a temperature of 1 200 °C and then storing in a desiccator prior to use. Such pre-treatment of tungsten(VI) oxide and the combustion boats is also required when the sulfur content of the test sample is less than 0,01 % ( $m/m$ ).

## 8 Expression of results

### 8.1 Calculation of sulfur content

The sulfur content,  $w_S$ , is calculated as a percentage by mass, to five decimal places for contents higher than 0,01 % and to six decimal places for contents lower than 0,01 %, using the equation

$$w_S (\%) = \frac{V_1 - V_2}{m \times 100} \quad \dots (1)$$

where

$V_1$  is the volume, in millilitres, of standard volumetric potassium iodate solution (4.8) used in the titration of the test portion;

$V_2$  is the volume, in millilitres, of standard volumetric potassium iodate solution (4.8) used in the blank titration;

$m$  is the mass, in grams, of the test portion (7.3).

### 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>

$$r = 0,040 1 X + 0,001 3 \quad \dots (2)$$

$$P = 0,090 1 X + 0,001 3 \quad \dots (3)$$

$$\sigma_r = 0,014 5 X + 0,000 5 \quad \dots (4)$$

$$\sigma_L = 0,031 0 X + 0,000 3 \quad \dots (5)$$

where

$X$  is the sulfur 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;

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

$r$  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.

### 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 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:

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

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 certified 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 of the condition 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), one or more additional tests shall be carried out in accordance with the flowsheet presented in annex A, simultaneously with an analysis of a certified reference material of the same type of ore.

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

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

- 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;
- if the certification has been made by only one laboratory or if the interlaboratory results are missing, use the following condition:

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

### 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 five decimal places for contents of sulfur higher than 0,01 % and to six decimal places for contents lower than 0,01 %. For contents higher than 0,01 % the value is rounded off to the third decimal place as specified in a), b) and c). In a similar manner, with the ordinal numbers increased by one, the value for sulfur contents lower than 0,01 % is rounded off to the fourth decimal place.

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.

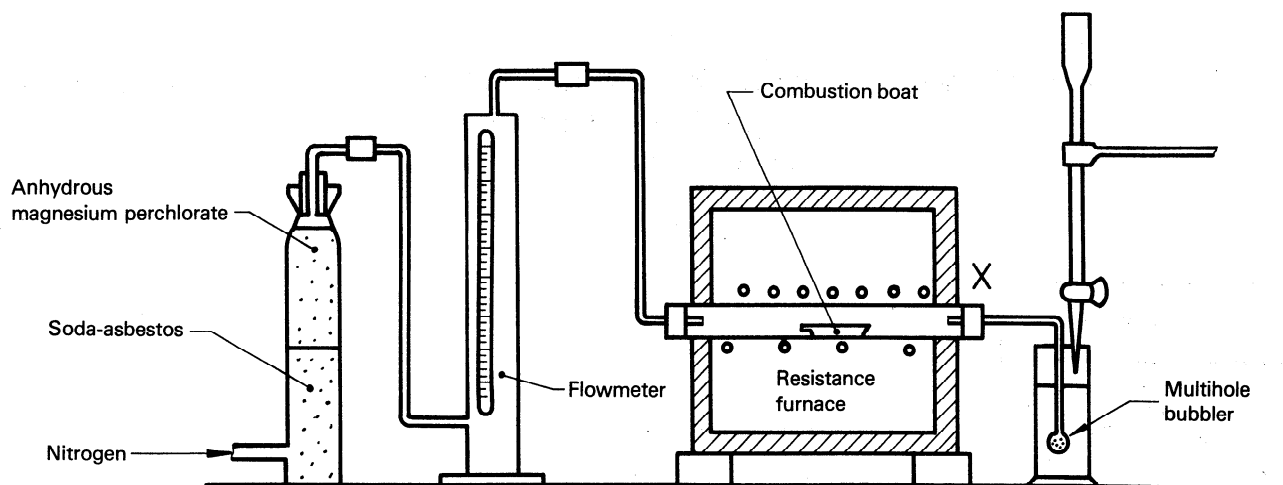
b) When the figure in the fourth decimal place is 5 and there is a figure other than 0 in the fifth decimal place, or when the figure in the fourth decimal place is greater than 5, the figure in the third decimal place is increased by one.

c) When the figure in the fourth decimal place is 5 and there is no figure 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.

## 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 in influence on the result, either for the test sample or the certified reference material(s).



NOTE — This figure is not drawn to scale.

Figure 1 — Apparatus for the combustion method

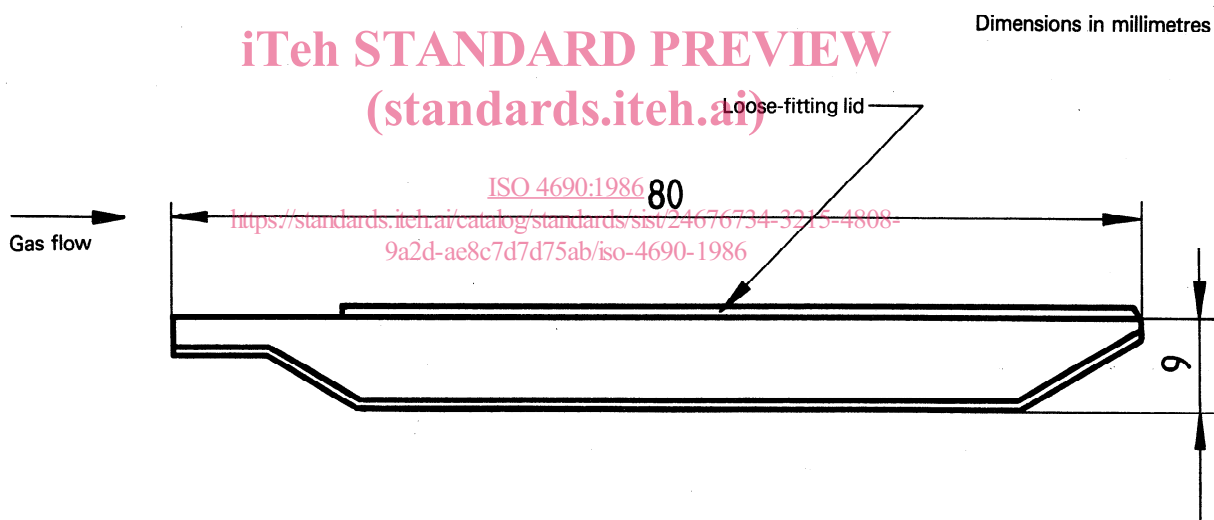


Figure 2 a) — Combustion boat with loose-fitting lid

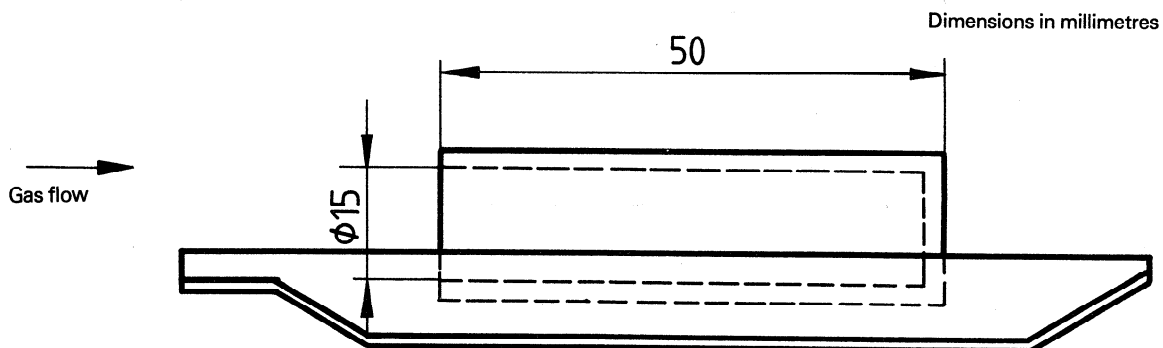


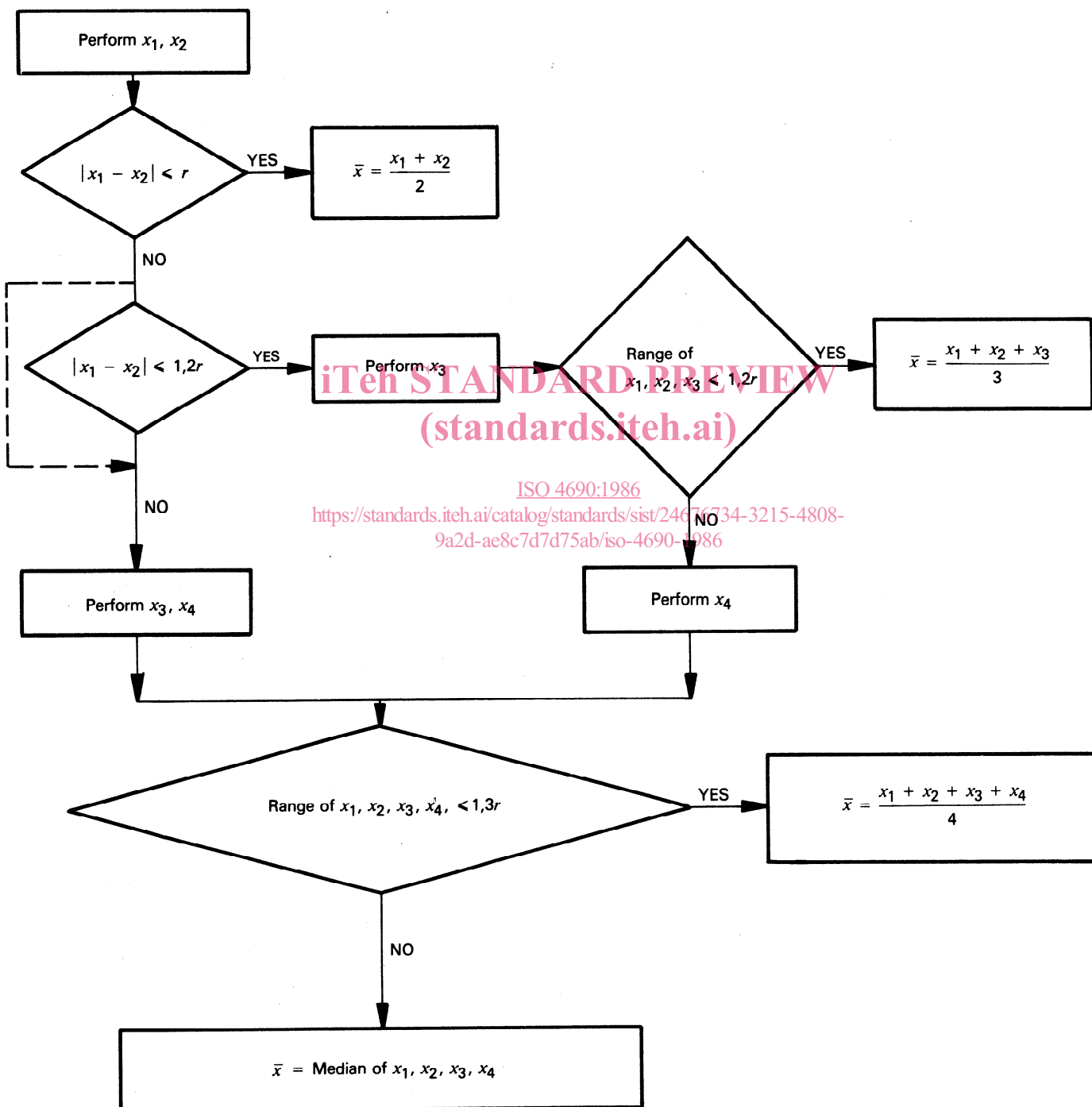
Figure 2 b) — Combustion boat with cartridge

NOTE — The dimensions are shown as guidelines only.

## Annex A

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

(An integral part of this International 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 this International Standard.)

The regression equations in 8.2.1 have been derived from the results of international analytical trials carried out in 1974/1975 on five iron ore samples, involving 37 laboratories in 10 countries.

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

The test samples used were:

Sample	Sulfur content [% (m/m)]
Hamersley pellets	0,002
Nimba	0,007
Kiruna D	0,020
Rompin	0,073
Texada	0,250

#### NOTES

- 1 A report of the international trial and a statistical analysis of the results (Document ISO/TC 102/SC 2 N 427E, March 1976) is available from either the Secretariat of ISO/TC 102/SC 2 or the Secretariat of ISO/TC 102.
- 2 The statistical analysis has been performed in accordance with the principles embodied in ISO 5725.

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