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

Minerais de fer — Dosage de l'arsenic — Méthode spectrophotométrique au bleu de molybdène

Reference number
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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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 7834 was prepared by Technical Committee ISO/TC 102, *Iron ores*.

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

WARNING — Attention is drawn to the toxic nature of arsenic and its solutions and of other reagents used in this method and to the need to take particular care in the handling and disposal of solutions.

1 Scope and field of application

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

This method is applicable to a concentration range of 0,000 1 to 0,1 % (*m/m*) (1 to 1 000 µg/g) of arsenic in natural iron ores, and iron ore concentrates and agglomerates including sinter products.

2 References

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

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.*

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

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

3 Principle

Decomposition of a test portion by sintering with sodium peroxide and leaching with water and hydrochloric acid.

Transfer of the solution to a distillation flask, evaporation of part of the solution, treatment with potassium bromide and hydrazine sulfate, followed by adjustment of the acidity. Distillation of arsenic trichloride and collection of the distillate in nitric acid.

Evaporation to dryness and baking at controlled temperature, followed by treatment with ammonium molybdate-hydrazine reagent to form an arseno-molybdenum blue complex.

Spectrophotometric measurement of the absorbance at approximately 840 nm.

4 Reagents

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

NOTE — In order to obtain reliable values at the lowest levels of arsenic content in test samples (< 20 µg/g), reagents should be selected or purified so that the value for the absorbance of the blank test measured in a cell of 20 mm optical path length is not greater than 0,025, equivalent to 1 µg of arsenic. In particular, nitric acid may need to be redistilled, or the apparatus cleaning procedures (5.2) may need to be applied more rigorously.

4.1 Sodium peroxide (Na_2O_2), fine powder.

4.2 Potassium bromide (KBr).

4.3 Hydrazine sulfate ($N_2H_4 \cdot H_2SO_4$).

4.4 Hydrochloric acid (ϱ 1,16 to 1,19 g/ml).

4.5 Nitric acid (ϱ 1,4 g/ml), diluted 1 + 1.

4.6 Sulfuric acid (ϱ 1,84 g/ml), free from phosphorus.

4.7 Ammonium molybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$], solution, 10 g/l.

To 400 ml of water in a 1 litre beaker, add carefully, with stirring, 133 ml of sulfuric acid (4.6). Cool, add 10 ± 0,1 g of ammonium molybdate and dissolve with stirring. Transfer to a 1 litre volumetric flask or stoppered measuring cylinder, dilute to the mark with water and mix.

4.8 Hydrazine sulfate ($N_2H_4 \cdot H_2SO_4$) solution, 0,15 g/l.

4.9 Molybdate-hydrazine reagent.

To 70 ml of water in a 100 ml volumetric flask, add 10 ± 0,1 ml of ammonium molybdate solution (4.7) and 10 ml of hydrazine sulfate solution (4.8). Dilute to the mark with water and mix. Prepare freshly for each series of tests.

4.10 Arsenic, standard solution A, 200 µg/ml.

Dry several hundred milligrams of arsenic trioxide (As_2O_3) at 105 °C for 1 h. Dissolve 0,132 g of the dried product in 2 ml of 40 g/l sodium hydroxide solution, add 30 ml of water, neutralize with sulfuric acid (4.6) diluted 1 + 9, using methyl orange indicator, and add 4 g of sodium hydrogen carbonate. Dilute in a volumetric flask to 500 ml with water and mix.

1 ml of standard arsenic solution A contains 200 µg of arsenic.

4.11 Arsenic, standard solution B, 5 µg/ml.

Transfer by pipette 25 ml of standard arsenic solution A (4.10) to a 1 litre volumetric flask, dilute to the mark with water and mix.

1 ml of standard arsenic solution B contains 5 µg of arsenic.

5 Apparatus

NOTE — Unless otherwise indicated, any pipettes and volumetric flasks shall be one-mark pipettes and volumetric flasks complying with the specifications of ISO 648 and ISO 1042.

Ordinary laboratory apparatus and

5.1 Zirconium or vitreous carbon crucibles, approximately 30 ml capacity.

5.2 Distillation apparatus, comprising a 250 ml distillation flask fitted with a side neck and delivery funnel, twin-head adapter, a splash head and water-cooled condenser (figure 1). Mark the flask at the 45 ml and 50 ml capacity points.

Apparatus fitted with hemispherical ground joints may also be used.

NOTES

1 Prior to first use, the distillation apparatus and distillate collection beaker should be cleaned with chromic acid cleaning mixture (or equivalent) and rinsed well, to ensure that all internal surfaces are film-wettable. This condition should be maintained as necessary. The ground glass joints should be cleaned free from organic lubricants and then lubricated with the minimum quantity of sulfuric acid (4.6). Alternatively, PTFE sleeves may be used.

2 Apparatus used after the distillation stage (the collection beaker and, where applicable, the pipette and 100 ml volumetric flask) should be given the following special cleaning treatment :

Prior to first use, apply a chromic acid or equivalent treatment followed by rinsing with water then treatment with nitric acid (ϱ 1,4 g/ml) diluted 1 + 10, allowing the solution to stand in the vessel for several hours. Such vessels should be reserved only for arsenic determinations and labelled accordingly. In routine use, the standing time in diluted nitric acid can be reduced to 30 min. Detergents, which may contribute phosphate interference, should never be used in this procedure.

3 The heater should be capable of achieving a distillation rate of at least 2 ml/min. If difficulty is experienced, use a suitable insulating tape to insulate the splash head (SH in figure 1).

5.3 Spectrophotometer, capable of measurement of absorbance at wavelengths up to 840 nm.

6 Sampling and samples

6.1 Laboratory sample

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.

6.2 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 ± 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 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 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 0,001 g, approximately 1 g of the predried test sample obtained in accordance with 6.2.

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

7.4 Determination

7.4.1 Decomposition of the test portion

Weigh into a zirconium or vitreous carbon crucible (5.1) 3 g of sodium peroxide (4.1). Immediately add the weighed test portion (7.3), mix with a thin metal spatula or glass rod and place in a muffle furnace at 420 ± 10 °C for 1 h.

Cool completely to room temperature (the crucible may be placed on a metal block if desired), cover with a watch glass and, momentarily lifting the cover, add 0,5 ml of water around the outside of the sinter. Allow the reaction to subside (several minutes) then add a further 1 ml of water in the same way. After several minutes add 15 ml of water and when the reaction has again subsided, heat to complete the disintegration. Fit the twin-head adapter, and the transfer adapter (TA in figure 1) to the distillation flask on the distillation stand and transfer the crucible contents to the flask. Add 15 ml of water and 10 ml of hydrochloric acid (4.4) to the crucible, boil to dissolve any residual material and transfer to the flask, rinsing with 20 to 25 ml of water. Boil gently to remove chlorine and evaporate to a volume of 45 to 50 ml. Allow the solution to cool to about 50 °C.

7.4.2 Distillation of arsenic trichloride

Complete the assembly of the apparatus (figure 1) and add 55 ml of hydrochloric acid (4.4) to the delivery funnel. Fit the receiver adapter, immersing the tip in 10 ml of nitric acid (4.5) in a 250 ml tall-form beaker marked at the 75 ml point. Using a dry transfer adapter (TA in figure 1), add 2 g of potassium bromide (4.2) and 1 g of hydrazine sulfate (4.3). Substitute a thermometer fitting for the transfer adapter and add the hydrochloric acid (4.4) to the flask.

Distil (at a rate of about 2 ml/min), maintaining the temperature of the vapour in the head at about 108 °C, to obtain a total volume in the receiver of 75 ml.

NOTE — An antibumping agent may be used if necessary.

Depending on the expected arsenic content, either use the entire distillate or measure aliquots of this solution in accordance with table 1. With test samples of arsenic content of less than 60 µg/g, use the entire distillate. With arsenic contents above 60 µg/g, transfer the distillate to a 100 ml volumetric flask, dilute to the mark with water and mix.

Table 1 — Aliquot portions of distillate

Range of arsenic content µg/g	Aliquot portion from 100 ml ml
1 to 60	No aliquot; entire distillate
50 to 200	25
150 to 500	10
300 to 1 000	5

Transfer the distillate and blank test respectively or any aliquot portion of the test and blank test to 250 ml tall-form beakers.

7.4.3 Spectrophotometric measurement

Evaporate the distillate, or aliquot portion, to dryness at a temperature not greater than 130 °C.

NOTE — A hotplate or a water bath may be used for the evaporation provided that the surface temperature of the hotplate, as determined by a contact thermometer (or a conventional thermometer immersed in a small volume of sulfuric acid), has been shown to be not higher than 130 °C at any point.

Place the beaker containing the dry residue in an oven at 130 ± 5 °C, for 30 min.

NOTE — Alternatively, a hotplate as specified in the above note may be used provided that a minimum temperature of 125 °C is obtained.

Cool, add 20 ml of freshly prepared molybdate-hydrazine reagent (4.9) and place on a hotplate set to produce 95 ± 5 °C in the solution, for 25 to 30 min.

NOTE — A water bath may be used but it is not strictly necessary. A hotplate which has been set to produce, in a test beaker containing water, a temperature of 95 ± 5 °C at various positions on the plate, has been found satisfactory.

Cool to room temperature and transfer to a 25 ml volumetric flask using molybdate-hydrazine reagent (4.9) to rinse the beaker and to complete the dilution to the mark. Measure in a 10 mm cell the absorbance at the peak absorbance wavelength at about 840 nm against a zero reference of molybdate-hydrazine reagent (4.9). Correct the absorbance value with the absorbance of the blank test or diluted blank test.

NOTE — If absorbance values of less than 0,025 are obtained in a cell of 10 mm optical path length, then a cell of 20 mm optical path length should be used. In this case the blank test and calibration series should also be read in a 20 mm cell.

7.5 Preparation of the calibration graph

Measure aliquots of standard arsenic solution B (4.11) of 0, 1, 2, 5 and 12 ml and transfer successively to the distillation apparatus. Dilute to 50 ml with water, add 2,5 ml of hydrochloric acid (4.4) and continue as in 7.4.2 and 7.4.3.

Plot the relationship between the quantity of arsenic and the absorbance corrected for zero arsenic addition, and calculate the slope factor (Z) as defined in 8.1. The value of Z should be approximately 76 for a 10 mm cell.

8 Expression of results

8.1 Calculation of arsenic content

Calculate the arsenic content, W_{As}, expressed in micrograms per gram, to three decimal places for contents lower than 100 µg/g and to two decimal places for contents higher than 100 µg/g, using the equation

$$W_{As} = \frac{E \times Z \times D}{m} \quad \ldots (1)$$

where

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

E is the absorbance of the test solution or aliquot of the test solution measured against the reagent reference solution (4.9) corrected by the value for the blank test or diluted blank test;

Z is the slope factor of the calibration curve expressed as

$$\frac{\text{µg As in 25 ml}}{\text{absorbance}}$$

D is the dilution factor (when no aliquot is taken $D = 1$, otherwise D = 100/volume of aliquot).

8.2 General treatment of results

8.2.1 Repeatability and permissible tolerance

The precision of this analytical method, in micrograms per gram, is expressed by the following regression equations[1]:

$$r = 0{,}046\,0\,X + 0{,}90 \quad \ldots (2)$$

$$P = 0{,}105\,8\,X + 0{,}83 \quad \ldots (3)$$

$$\sigma_r = 0{,}016\,3\,X + 0{,}32 \quad \ldots (4)$$

$$\sigma_L = 0{,}035\,6\,X + 0{,}21 \quad \ldots (5)$$

where

X is the arsenic content, expressed in micrograms per gram, of the test sample :

— 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 laboratory (repeatability);

P is the permissible tolerance between laboratories;

σ_r is the within-laboratory standard deviation;

σ_L is the between-laboratories standard deviation.

8.2.2 Acceptance of analytical values

The result obtained for the certified reference material 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 both in accuracy and precision with this method, the following formula may be used to test the significance of the difference:

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

where

A_c is the certified value;

A is the result or the mean of results obtained for the reference material;

s_{Lc} is the between-laboratories standard deviation of the certifying laboratories;

s_{Wc} is the within-laboratory standard deviation of the certifying laboratories;

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

N_c is the number of certifying laboratories;

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

σ_L and σ_r are as defined in 8.2.1.

If condition (6) is satisfied, i.e. 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 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 a corresponding blank test and 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, it is advisable not to use this

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

material for this purpose. In case its use is unavoidable, use the formula

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

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 three decimal places for contents of arsenic lower than 100 µg/g or to two decimal places for contents higher than 100 µg/g.

For contents of arsenic lower than 100 µg/g the value calculated to three decimal places is rounded off to the first decimal place as specified in a), b) and c) below.

In a similar manner, with the ordinal numbers decreased by one, the value for contents of arsenic higher than 100 µg/g calculated to two decimal places is rounded off to the units place.

a) When the figure in the second decimal place is less than 5, it is discarded and the figure in the first decimal place is kept unchanged.

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

c) When the figure in the second decimal place is 5 and there is no figure other than 0 in the third decimal place, the 5 is discarded and the figure in the first 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 :

a) name and address of the testing laboratory;

b) date of issue of the test report;

c) reference to this International Standard;

d) details necessary for the identification of the sample;

e) result of the analysis;

f) reference number of the result;

g) any characteristics noticed during the determination, and any operations not specified in this International Standard which may have had an influence on the result, either for the test sample or for the certified reference material(s).

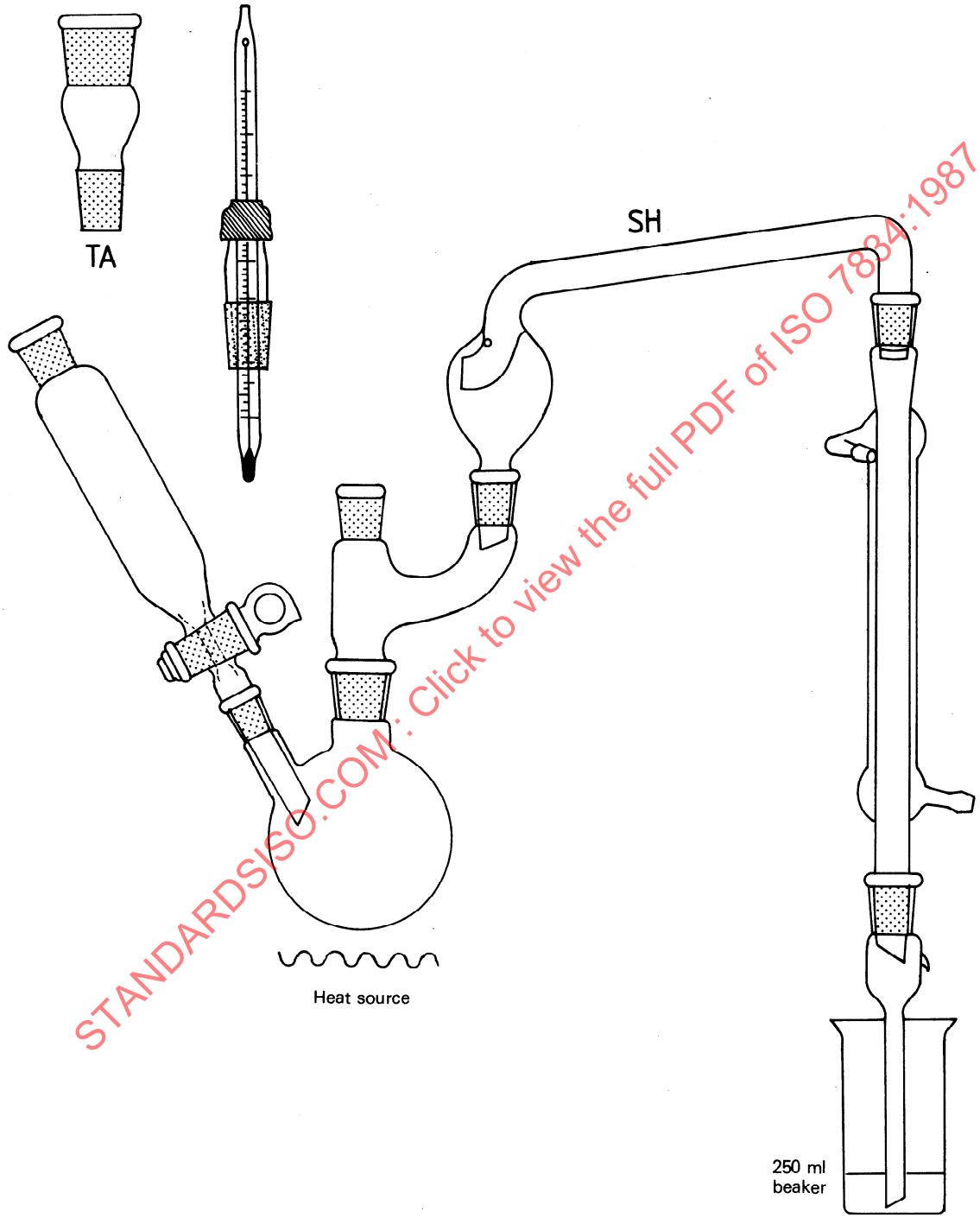
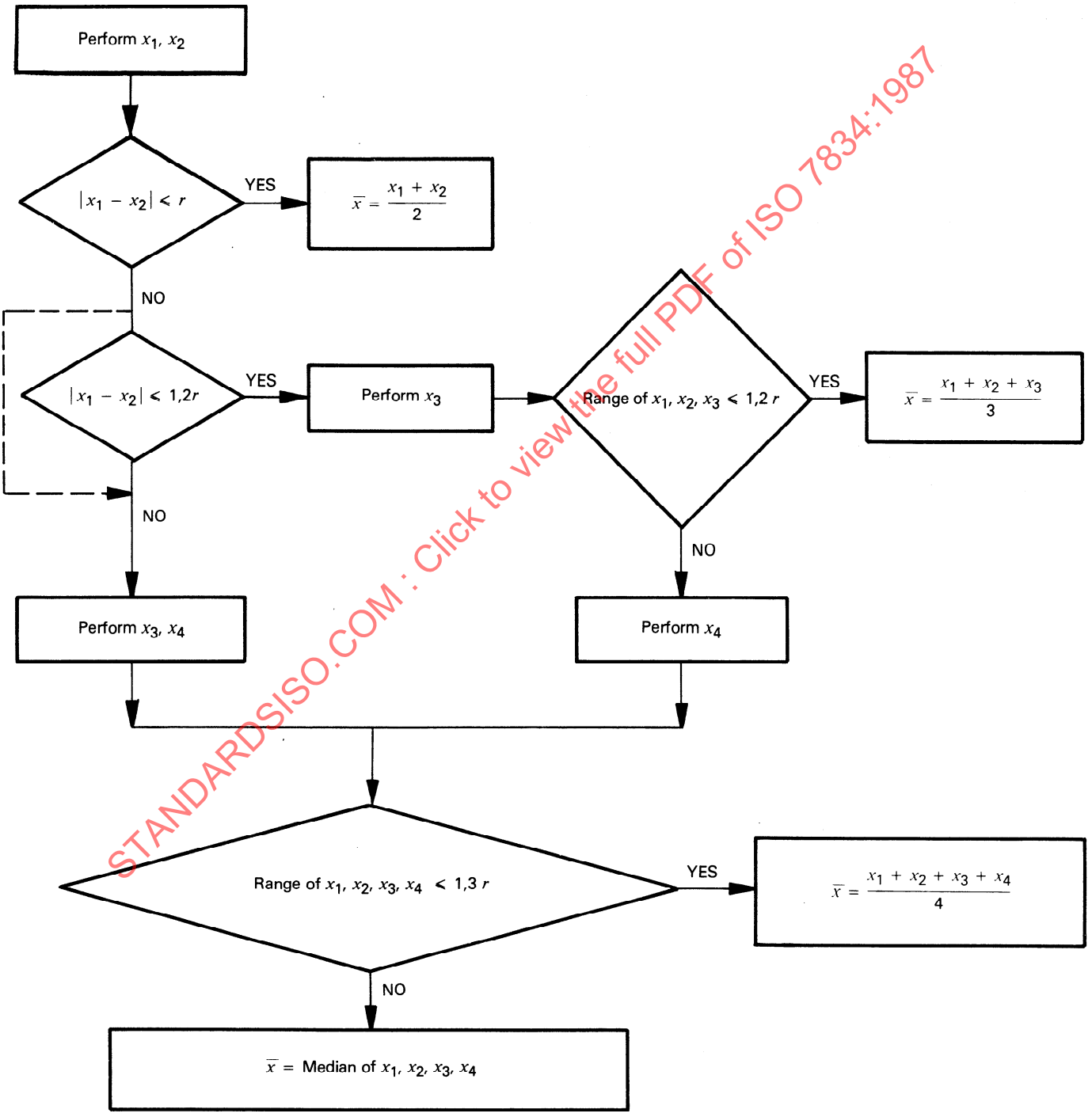


Figure 1 — Arsenic distillation apparatus

Annex A

Flowsheet on 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.