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Iron ores — Determination of lead and/or zinc content — Flame atomic absorption spectrometric method

Minerais de fer — Dosage du plomb et/ou du zinc — Méthode par spectrométrie d'absorption atomique dans la flamme

Reference number
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Foreword

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International Standard ISO 8753 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.

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Iron ores — Determination of lead and/or zinc content — Flame atomic absorption spectrometric method

1 Scope and field of application

This International Standard specifies a flame atomic absorption spectrometric method for the determination of the lead and/or zinc content of iron ores.

This method is applicable to a concentration range of 0,001 to 0,5 % (m/m) of lead and 0,001 to 0,5 % (m/m) of zinc 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 and removal of silica by treatment with hydrochloric acid and hydrofluoric acid. Oxidation with nitric acid.

Evaporation to dryness, followed by dilution and filtration. Ignition of the residue. Fusion with sodium carbonate. Dissolution of the cooled melt with hydrochloric acid. Reservation of the solution.

Extraction of iron in the filtrate with MIBK. Recovery of lead and zinc extracted. Decomposition of MIBK with nitric acid. Evaporation to dryness and dissolution of salts with the reserved solution and hydrochloric acid.

Aspiration of the solution into the flame of an atomic absorption spectrometer using an air-acetylene burner.

Comparison of absorbance values obtained for lead or for zinc with those obtained from the calibration solutions.

4 Reagents

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

4.1 Sodium carbonate, anhydrous.

4.2 Methyl isobutyl ketone (MIBK), high purity.

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 10 + 6.

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

4.6 Hydrochloric acid, ϱ 1,16 to 1,19 g/ml, diluted 2 + 98.

4.7 Nitric acid, ϱ 1,4 g/ml.

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

4.9 Lead standard solutions.

4.9.1 Stock lead standard solution.

Dissolve 1,000 g of high purity lead metal (free from iron) in 40 ml of nitric acid (ϱ 1,4 g/ml, diluted 1 + 1). Cool and dilute to 1 000 ml in a volumetric flask and mix.

1 ml of the stock solution contains 1 000 µg of lead.

4.9.2 Standard solution A.

Transfer 10,0 ml of stock lead standard solution (4.9.1) to a 100 ml volumetric flask. Dilute to the mark and mix.

1 ml of this standard solution contains 100 µg of lead.

4.9.3 Standard solution B.

Transfer 10,0 ml of standard solution A (4.9.2) to a 100 ml volumetric flask. Dilute to the mark and mix.

1 ml of this standard solution contains 10 µg of lead.

4.10 Zinc standard solutions.

4.10.1 Stock zinc standard solution.

Dissolve 1,000 g of high purity zinc metal (free from iron) in 40 ml of hydrochloric acid (4.5). Cool and dilute to 1 000 ml in a volumetric flask and mix.

1 ml of the stock solution contains 1 000 µg of zinc.

4.10.2 Standard solution C.

Transfer 10,0 ml of stock zinc standard solution (4.10.1) to a 1 000 ml volumetric flask. Dilute to the mark and mix.

1 ml of this standard solution contains 10 µg of zinc.

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 Polytetrafluoroethylene (PTFE) beaker, of capacity 250 ml, with a PTFE cover.

5.2 Atomic absorption spectrometer, equipped with an air-acetylene burner. The atomic absorption spectrometer used will be satisfactory if it meets the following criteria :

a) *Minimum sensitivity* — the absorbance of the calibration solution of highest concentration (7.4.4) is at least 0,25.

b) *Curve linearity* — the slope of the calibration graph covering the top 20 % concentration range (expressed as a change in absorbance) is not less than 0,7 of the value of the slope for the bottom 20 % concentration range determined in the same way.

c) *Minimum stability* — the standard deviation of the absorbance of the calibration solution of highest concentration and the standard deviation of the absorbance of the zero calibration solution, each being calculated from a sufficient number of repetitive measurements, are less than 1,5 % and 0,5 % respectively of the mean value of the absorbance of the calibration solution of highest concentration.

NOTES

1 The use of a strip chart recorder and/or digital readout device is recommended to evaluate the criteria and for all subsequent measurements.

2 Instrument parameters may vary with each instrument. The following parameters were successfully used in several laboratories and they can be used as guidelines.

	Pb	Zn
— Hollow cathode lamp, mA	6	8
— Wavelength, nm	283,3	213,9
— Air flow rate, l/min	14	14
— Acetylene flow rate, l/min	3	3

In systems where the values shown above for gas flow rates do not apply, the ratio of the gas flow rates may still be a useful guideline.

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 should 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 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 2 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

Transfer the test portion (7.3) to a 250 ml PTFE beaker (5.1). Moisten with a few millilitres of water, add 40 ml of hydrochloric acid (4.3) and 10 ml of hydrofluoric acid (4.8), cover with a PTFE cover. Heat on a hotplate at 100 °C, then increase the heat to 200 °C. Evaporate to dryness. Add 5 ml of nitric acid (4.7) and evaporate to nearly 1 ml. Dissolve the salts with 10 ml of hydrochloric acid (4.3) and evaporate to dryness again.

Dissolve the salts with 5 ml of hydrochloric acid (4.3). Add 10 ml of water and filter through a close-texture paper into a 250 ml beaker. Remove all adhering particles from the beaker with a rubber-tipped rod, wash with hydrochloric acid (4.6) until the paper is free from iron stain, and wash the paper three times with hot water. Reserve the residue and combined filtrate and washings.

7.4.2 Treatment of residue

Place the paper and residue into a platinum crucible, dry and char the paper at a low temperature and ignite in a muffle furnace at 550 °C. Add 0,5 g of sodium carbonate (4.1) and fuse over a Bunsen burner (about 900 to 1 000 °C) until a clear melt is obtained. Dissolve the cooled melt with 5 ml of hydrochloric acid (4.5), heat to remove carbon dioxide and reserve the solution.

7.4.3 Treatment of combined filtrate and washings

Evaporate the filtrate and washings (7.4.1) just to dryness. Dissolve the salts with 20 ml of hydrochloric acid (4.4), and transfer to a 200 ml separating funnel. Rinse the beaker with 20 ml of hydrochloric acid (4.4) and combine these washings with the main solution. Add 50 ml of MIBK (4.2) and shake thoroughly for 1 min. Allow the layers to separate, then run the lower aqueous solution into a 250 ml beaker. Wash the organic phase by extracting with 10 ml of hydrochloric acid (4.4), transfer the washings to the beaker.

Heat the solution gently and expel almost all of the MIBK in the solution. Then add 5 ml of nitric acid (4.7) and evaporate to dryness. Dissolve the salts with 15 ml of hydrochloric acid (4.5). Combine this solution with the reserved solution from 7.4.2.

Transfer the solution to a 50 ml volumetric flask, and dilute to volume with water and mix. Depending on the concentration (see table 1) use the solution for atomic absorption measurement either without dilution or as specified. When dilution is required, transfer the appropriate aliquot to a 250 ml beaker. Add the amount of sodium carbonate (4.1) and hydrochloric acid (4.5) indicated in table 1. Heat the solution to remove carbon dioxide. Cool and make up to 100 ml in a volumetric flask with water. (See the note to table 2.) (This solution is the final test solution.)

Transfer corresponding amounts of blank test solution to a 250 ml beaker, add the same volume of sodium carbonate (4.1) and hydrochloric acid (4.5) as used for the test solution. Heat the solution to remove carbon dioxide. Cool and make up to 100 ml in a volumetric flask with water and mix. (This solution is the diluted blank test solution.)

7.4.4 Preparation of the set of lead and zinc calibration solutions

Transfer 1,0 g of sodium carbonate (4.1) to each of six 250 ml beakers. Add 20 ml of hydrochloric acid (4.3) and appropriate aliquots of lead standard solutions A or B and zinc standard solution C as listed in table 2. Heat the solution to remove carbon dioxide. Cool and make up to 100 ml in a volumetric flask.

NOTE — The range of lead and zinc which can be covered may vary from instrument to instrument. Attention should be paid to the minimum criteria given in 5.2. For instruments with high sensitivity smaller aliquots of the standard solutions can be used.

7.4.5 Adjustment of atomic absorption spectrometer

Set the wavelength for lead (283,3 nm) or zinc (213,9 nm) to obtain minimum absorbance. Fit the correct burner and, in accordance with manufacturer's instructions, light the appropriate flame. After 2 min preheating of the burner, adjust fuel and burner to obtain maximum absorbance while aspirating the calibration solution of highest concentration (see 7.4.4), and evaluate the criteria in 5.2.

Aspirate water and the calibration solution to establish that the absorbance reading is not drifting and then set the initial reading for water to zero absorbance.

7.4.6 Atomic absorption measurements

Aspirate the calibration solutions and the final test solution in order of increasing absorption, starting with diluted blank test solution and the zero calibration solution, with the final test solution being aspirated at the proper point in the series. Aspirate water between each solution and record the readings when stable responses are obtained.

Repeat the measurements at least twice more. If necessary, convert the average of the readings for each solution to absorbance. Obtain the net absorbance of each calibration solution by subtracting the absorbance of the zero calibration solution. Similarly, obtain the net absorbance of the final test solution by subtracting the absorbance of the diluted blank test solution.

Prepare a calibration graph by plotting the net absorbance values of the calibration solutions against the concentrations, in micrograms per millilitre, of lead or zinc.

Convert the net absorbance values of the final test solution to micrograms of lead and/or zinc per millilitre by means of the calibration graph.

Table 1 — Dilution guide for test solution*

Element	Expected content, w, of element in sample % (m/m)	Aliquot ml	Mass of sodium carbonate (4.1) to be added g	Volume of hydrochloric acid (4.5) to be added ml
Lead	$0{,}001 < w_{Pb} \leqslant 0{,}05$	—	—	—
	$0{,}05 < w_{Pb} \leqslant 0{,}2$	20	0,8	32
	$0{,}2 < w_{Pb} \leqslant 0{,}25$	10	0,9	36
	$0{,}25 < w_{Pb} \leqslant 0{,}5$	5	0,95	38
Zinc	$0{,}001 < w_{Zn} \leqslant 0{,}006$	—	—	—
	$0{,}006 < w_{Zn} \leqslant 0{,}02$	25	0,75	30
	$0{,}02 < w_{Zn} \leqslant 0{,}06$	10	0,9	36
	$0{,}06 < w_{Zn} \leqslant 0{,}12$	5	0,95	38
	$0{,}12 < w_{Zn} \leqslant 0{,}3$	2	0,98	39
	$0{,}3 < w_{Zn} \leqslant 0{,}5$	1	0,99	40

* Dilution shown will provide concentrations of lead and zinc falling within the range of the calibration solutions (7.4.4). For instruments with high sensitivity, smaller portions of the test solution may be preferable. For 1 ml or 2 ml of aliquot, make preliminary dilution in order to avoid dilution error. Treat the blank test solution similarly.

Table 2 — Calibration solutions

Solution number	Lead			Zinc	
	Standard solution A (4.9.2) ml	Standard solution B (4.9.3) ml	Concentration µg/ml	Standard solution C (4.10.2) ml	Concentration µg/ml
0	0	0	0	0	0
1	0	20	2	5	0,5
2	5	0	5	10	1
3	10	0	10	15	1,5
4	15	0	15	20	2
5	20	0	20	25	2,5

8 Expression of results

8.1 Calculation of lead or zinc content

The lead or zinc content, w, expressed as a percentage by mass to five decimal places, is calculated from the equation

$$w = \frac{\varrho V}{m_1 \times 10\,000} \qquad \ldots(1)$$

where

ϱ is the concentration, in micrograms per millilitre, of lead or zinc in the final test solution;

V is the volume, in millilitres, of final test solution;

m_1 is the mass of sample, in grams, in the final test solution, taking account of any preliminary dilution which may have been made.

$$m_1 = \frac{m \times V_1}{50}$$

where

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

V_1 is the volume, in millilitres, of the aliquot taken in 7.4.3 (see table 1). When no dilution has been made $V_1 = 50$.

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[1] :

Lead

$$r = 0{,}033\,2\,X + 0{,}000\,4 \qquad \ldots(2)$$
$$P = 0{,}058\,7\,X + 0{,}002\,8 \qquad \ldots(3)$$
$$\sigma_r = 0{,}011\,7\,X + 0{,}000\,1 \qquad \ldots(4)$$
$$\sigma_L = 0{,}019\,0\,X + 0{,}001\,0 \qquad \ldots(5)$$

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

Zinc

$$r = 0{,}041\,5\,X + 0{,}001\,1 \qquad \ldots(6)$$

$$P = 0{,}104\,8\,X + 0{,}003\,0 \qquad \ldots(7)$$

$$\sigma_r = 0{,}014\,7\,X + 0{,}000\,4 \qquad \ldots(8)$$

$$\sigma_L = 0{,}035\,5\,X + 0{,}001\,0 \qquad \ldots(9)$$

where

X is the lead or zinc content, expressed as a percentage by mass, of the predried test sample;

- within-laboratory equations (2, 4, 6, 8) : the arithmetic mean of the duplicate values,
- between-laboratories equations (3, 5, 7, 9) : 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;

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 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 :

$$|A_c - A| \leqslant 2\sqrt{\frac{s_{Lc}^2 + \dfrac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_r^2}{n}} \qquad \ldots(10)$$

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 $n = 1$);

σ_L and σ_r are as defined in 8.2.1.

If condition (10) 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 either equation (2) or (6) as appropriate in 8.2.1, 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 :

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

$$|A_c - A| \leqslant 2\sqrt{2\sigma_L^2 + \frac{\sigma_r^2}{n}} \qquad \ldots(11)$$

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 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 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 the figure 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 factors

$$w_{PbO}\,(\%) = 1{,}077\,2\, w_{Pb}\,(\%)$$

$$w_{ZnO}\,(\%) = 1{,}244\,7\, w_{Zn}\,(\%)$$

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;

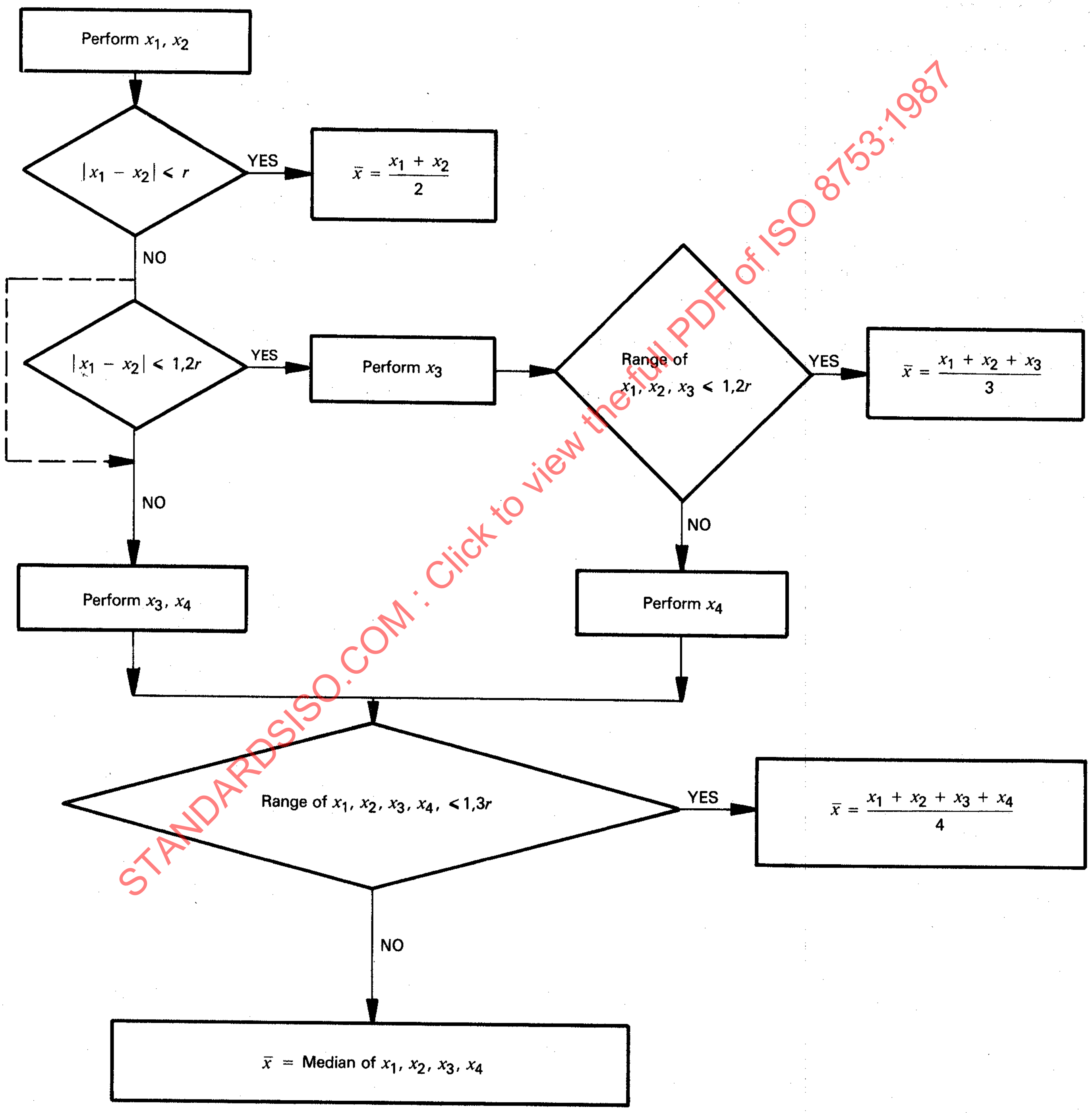
d) reference number of the result;

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

(an integral part of this International Standard)



r : as defined in 8.2.1.