International Standard 6831

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Iron ores — Determination of sodium and/or potassium contents — Flame atomic absorption spectrometric method

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

First edition — 1986-09-15

UDC 553.31 : 543.422 : 546.32/.33 **Ref. No. ISO 6831-1986 (E)**

Descriptors : minerals and ores, iron ores, chemical analysis, determination of content, sodium, potassium, atomic absorption method.

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 6831 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.

Printed in Switzerland

Iron ores — Determination of sodium and/or potassium contents — 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 sodium and/or potassium content of iron ores.

This method is applicable to a concentration range of 0,002 to 1,0 % (m/m) [1] of sodium or potassium 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.* [2]

ISO 3083, *Iron ores — Preparation of samples — Manual method.* [3]

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

3 Principle

Decomposition of a test portion by treatment with hydrochloric acid and hydrofluoric acid. Evaporation to dryness. Repetition of the evaporation with a new portion of hydrochloric acid. Dissolution with hydrochloric acid and appropriate dilution. Aspiration into the air-acetylene flame of the atomic absorption apparatus.

Measurement of the absorbance value obtained for sodium or potassium in comparison with those obtained from calibration solutions for sodium or potassium.

4 Reagents

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

NOTE — Reagents are to be selected or purified for the lowest possible blank value.

4.1 Hydrochloric acid, ϱ 1,16 to 1,19 g/ml.

4.2 Hydrofluoric acid, 40 % (m/m) (ϱ 1,13 g/ml) or 48 % (m/m) (ϱ 1,19 g/ml).

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

4.4 Background solution.

Dissolve 43 g of high purity iron oxide powder [4] in 500 ml of hydrochloric acid (4.1). Allow to cool and dilute with water to 1 000 ml.

4.5 Sodium, standard solution corresponding to 0,01 g of Na per litre.

Pulverize about 4 g of high purity sodium chloride in an agate mortar, dry in an oven at 105 to 110 °C for 2 h and allow to cool to room temperature in a desiccator. Dissolve 2,542 g in water, dilute with water to 1 000 ml in a volumetric flask and mix.

Transfer [5] 10,0 ml of this solution to a 1 000 ml volumetric flask, dilute with water to the mark and mix.

Store this standard solution in a plastic bottle.

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

4.6 Potassium, standard solution corresponding to 0,02 g of K per litre.

1) The method has not been tested on ores containing more than 0,50 % (m/m) of sodium and 0,51 % (m/m) of potassium. (See annex B.)

2) At present at the stage of draft.

3) At present at the stage of draft. (Revision of ISO 3083-1973.)

4) Instead of iron oxide, the use of metallic iron with a suitable oxidant is permitted. (The alkali content of the oxidant shall be low.)

5) Glass equipment may be used.

Pulverize about 3 g of high purity potassium chloride in an agate mortar, dry in an oven at 105 to 110 °C for 2 h and allow to cool to ambient temperature in a desiccator. Dissolve 1,907 g in water, dilute with water to 1 000 ml in a volumetric flask and mix.

Transfer[1] 10,0 ml of this solution to a 500 ml volumetric flask, dilute with water to the mark and mix.

Store this standard solution in a plastic bottle.

1 ml of this standard solution contains 20 µg of potassium.

5 Apparatus

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

5.1 Polytetrafluoroethylene (PTFE) beakers, of capacity 100 ml, provided with PTFE covers.

5.2 PTFE-coated magnetic stirring bars.

5.3 PTFE digestion bomb.

5.4 Plastic pipettes.

5.5 Plastic volumetric flasks and storage bottles.

5.6 Magnetic stirring hotplates.

NOTES

1 Platinum vessels may be used instead of PTFE beakers.

2 Except where stated, glass equipment shall be avoided, as it could contaminate the solutions.

3 The caps of the plastic bottles should be of a type which does **not** contain a separate wad insert. Such inserts usually contain a sodium compound which will contaminate the solution.

4 In order to obtain reliable values, the equipment should be cleaned and checked as follows:

a) Rinse all volumetric ware, including the pipettes used for preparing the calibration solutions, with hydrochloric acid solution (4.3) before use. Check calibration regularly or as needed.

b) Clean PTFE vessels and stirring bars by stirring with 50 ml of hydrochloric acid solution (4.3) and heating for 15 min. Reject the rinsings and conduct a blank test in each vessel in turn exactly as specified in 7.3. If any absorbance value is above the limit specified in 7.3, the cleaning procedure should be repeated or acid reagents of a higher purity should be used. At no stage should the stirring bars be handled with the fingers.

c) Platinum vessels, exclusively used for alkali analyses according to this International Standard, can be cleaned by the same method as the PTFE vessels [see b)]. Otherwise, they must be pre-cleaned by fusion with lithium tetraborate or lithium borate, until the absorbance readings fall to those for the lithium salt alone.

d) Rinse storage bottles with hydrochloric acid solution (4.3) before use.

1) Glass equipment may be used.

5.7 Atomic absorption spectrometer.

The atomic absorption spectrometer used will be satisfactory if it meets the following criteria:

a) *Minimum sensitivity* — the absorbance of the highest calibration solution (see 7.5.3) is at least 0,25.

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

c) *Minimum stability* — the standard deviation of the absorbance of the most concentrated calibration solution and that 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 most concentrated calibration solution.

NOTES

1 The use of a strip-chart recorder and/or digital read-out device is recommended to evaluate these criteria and for all subsequent measurements.

2 Instrument parameters will vary with each instrument. The following parameters were successfully used in several laboratories and they can be used as guidelines. Solutions were aspirated into an air-acetylene flame of a premix burner:

	Na	K
Hollow cathode lamp, mA	10	10
Wavelength, nm	589,0	766,5
Air flow-rate, l/min	10	10
Acetylene flow-rate, l/min	2	2

In systems where the values shown 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 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 Safety precautions

Follow the manufacturer's instructions for igniting and extinguishing the air-acetylene flame to avoid possible explosion hazards. Wear tinted safety glasses whenever the burner is in operation.

7.3 Blank test and check test

Before proceeding to the treatment of test portions, ensure that the cleaning procedures conducted in note 4 to clause 5 together with the quality of the reagents being used have produced a blank test value for the sodium and potassium determinations in each case not greater than the equivalent of 0,002 % (m/m) alkali content in the ore.

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. (See the note.)

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.

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.

7.4 Test portion

Taking several increments, weigh, to nearest 0,000 2 g, approximately 0,5 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.

7.5 Determination

In order to prevent contamination during analysis, the following precautions shall be taken:

a) finger contact with sample, solutions and stirring bars shall be avoided;

b) mouth suction of pipettes shall not be permitted;

c) smoking shall be prohibited in the immediate environment.

7.5.1 Decomposition of the test portion

Transfer the test portion (7.4) to a 100 ml PTFE beaker (5.1) [1]. Moisten it with a few drops of water, then add 10 ml of hydrochloric acid (4.1) and 10 ml of hydrofluoric acid (4.2). Add a PTFE-coated magnetic stirring bar (5.2) and cover with a PTFE cover. Adjust the temperature of the stirring hotplate (5.6) so that a temperature of about 98 °C will be maintained in water in a covered PTFE beaker. Heat, with stirring, for 45 min or until no further dissolution of the test portion occurs. Remove the cover, stop the stirrer, leaving the bar in the solution, and evaporate to dryness. Add 5 ml of hydrochloric acid (4.1) and evaporate again to dryness. Dissolve the salts in 5 ml of hydrochloric acid (4.1) and 40 ml of water and transfer to a 100 ml one-mark plastic volumetric flask (5.5). Dilute to the mark with water and mix.

NOTE — If any significant amount of residue remains, conduct the digestion process in a stirred PTFE digestion bomb (5.3) for 45 min at 160 °C.

7.5.2 Treatment of the solution

If the concentration of the alkali elements is too high, it is necessary to dilute the test solution. Transfer by plastic pipette (5.4) y ml of the test solution to a 100 ml one-mark plastic volumetric flask, add 0,1 × (100 − y) ml of the background solution (4.4), dilute with water to the mark and mix (see the table).

A diluted test solution shall be measured together with a diluted blank test solution, containing the same amount of background solution as the test solution. Prepare the diluted blank test solution as follows: Pipette y ml of the blank test solution into a 100 ml one-mark plastic volumetric flask, add 0,1 × (100 − y) ml of the background solution, dilute to the mark with water and mix.

Table — Dilution guide for test solution

Sodium		Potassium	
Concentration range %	Aliquot from 100 ml y	Concentration range %	Aliquot from 100 ml y
0,002 to 0,030	—	0,002 to 0,060	—
0,030 to 0,10	30,0	0,060 to 0,20	30,0
0,10 to 0,30	10,0	0,20 to 0,60	10,0
0,30 to 0,60	5,0	0,60 to 1,00	5,0
0,60 to 1,00	3,0*		

* Take 30 ml and dilute to 100 ml, aliquot 10 ml.

1) See note 1 under 5.6.

7.5.3 Preparation of the set of calibration solutions

From the sodium standard solution (4.5) and the potassium standard solution (4.6), prepare calibration solutions as follows:

Using plastic pipettes, transfer

0; 2,0; 5,0; 10,0; 15,0 ml of solution 4.5 and

0; 15,0; 10,0; 5,0; 2,0 ml of solution 4.6

respectively to 100 ml one-mark plastic volumetric flasks. Add by plastic pipette 10 ml of the background solution (4.4) to each, dilute with water to the mark and mix. These calibration solutions cover the concentration ranges 0 to 3 µg K/ml and 0 to 1,5 µg Na/ml and contain 3 000 µg Fe/ml.

Store the calibration solutions in plastic bottles.

7.5.4 Adjustment of atomic absorption spectrometer

Optimize the response of the instrument as specified in 5.7. Set the wavelength of sodium (589,0 nm) or potassium (766,5 nm) to obtain minimum absorbance. After 10 min preheating of the burner, adjust fuel flow and burner position to obtain maximum absorbance while aspirating the highest calibration solution (see 7.5.3). Aspirate water and the calibration solution to establish that the absorbance reading is not drifting, and then set the reading for water to zero absorbance.

7.5.5 Atomic absorption measurements

Aspirate the calibration and test solutions or diluted test solutions in order of increasing absorption, starting with the blank test solution, or diluted blank test solution, and the zero calibration solution. When a stable response is obtained for each solution, record the readings. Aspirate the test solutions or diluted test solutions at the proper points in the calibration series and record their readings. Aspirate water between each calibration and test solution. Repeat the measurements at least twice.

Obtain the net absorbance of each calibration solution by subtracting the average absorbance of the zero calibration solution. In a similar manner, obtain the net absorbance of the test solution or diluted test solution by subtracting the absorbance of the corresponding blank test solution.

Prepare calibration graphs by plotting the net absorbance values of the calibration solutions against the concentration, in micrograms of sodium and/or potassium per millilitre (the test solution or, if diluted, the diluted test solution is the final test solution).

Convert the net absorbance of the final test solution to micrograms of sodium and/or potassium per millilitre by means of the calibration graphs.

NOTE — With concentration readings the calculation shall be made from absorbances in order to permit checking of the graph's linearity and the blank test value.

8 Expression of results

8.1 Calculation of sodium or potassium content

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

$$\frac{\varrho_M}{m_1 \times 100} \quad \ldots (1)$$

where

ϱ_M is the concentration, in micrograms per millilitre, of sodium or potassium in the final test solution;

m_1 is the mass, in grams, of test sample represented in 100 ml of the final test solution (7.5.5), calculated from the equation

$$m_1 = \frac{m \times V}{100}$$

m being the mass, in grams, of the test portion (7.4);

V being the volume, in millilitres, of the aliquot taken in 7.5.2. When no dilution has been made, $V = 100$.

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)]

Sodium

$$r = 0{,}053\,7\,X + 0{,}000\,7 \quad \ldots (2)$$
$$P = 0{,}070\,2\,X + 0{,}002\,9 \quad \ldots (3)$$
$$\sigma_r = 0{,}019\,4\,X + 0{,}000\,2 \quad \ldots (4)$$
$$\sigma_L = 0{,}021\,2\,X + 0{,}001\,0 \quad \ldots (5)$$

Potassium

$$r = 0{,}029\,7\,X + 0{,}002\,5 \quad \ldots (6)$$
$$P = 0{,}051\,8\,X + 0{,}004\,0 \quad \ldots (7)$$
$$\sigma_r = 0{,}010\,6\,X + 0{,}000\,9 \quad \ldots (8)$$
$$\sigma_L = 0{,}017\,1\,X + 0{,}001\,3 \quad \ldots (9)$$

where

X is the sodium or potassium content, as a percentage by mass, of the test sample, calculated as follows:

— for the within-laboratory equations (2, 4, 6, 8), the arithmetic mean of the duplicate values;

— for the between-laboratories equations (3, 5, 7, 9), 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;

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 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:

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

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;

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 equation (2) or (6) as appropriate, 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, use the following condition:

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

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 for contents of sodium or potassium 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 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 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

$$W_{Na_2O}\,(\%) = 1{,}348\,0 \times W_{Na}\,(\%)$$

$$W_{K_2O}\,(\%) = 1{,}204\,6 \times W_{K}\,(\%)$$

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;

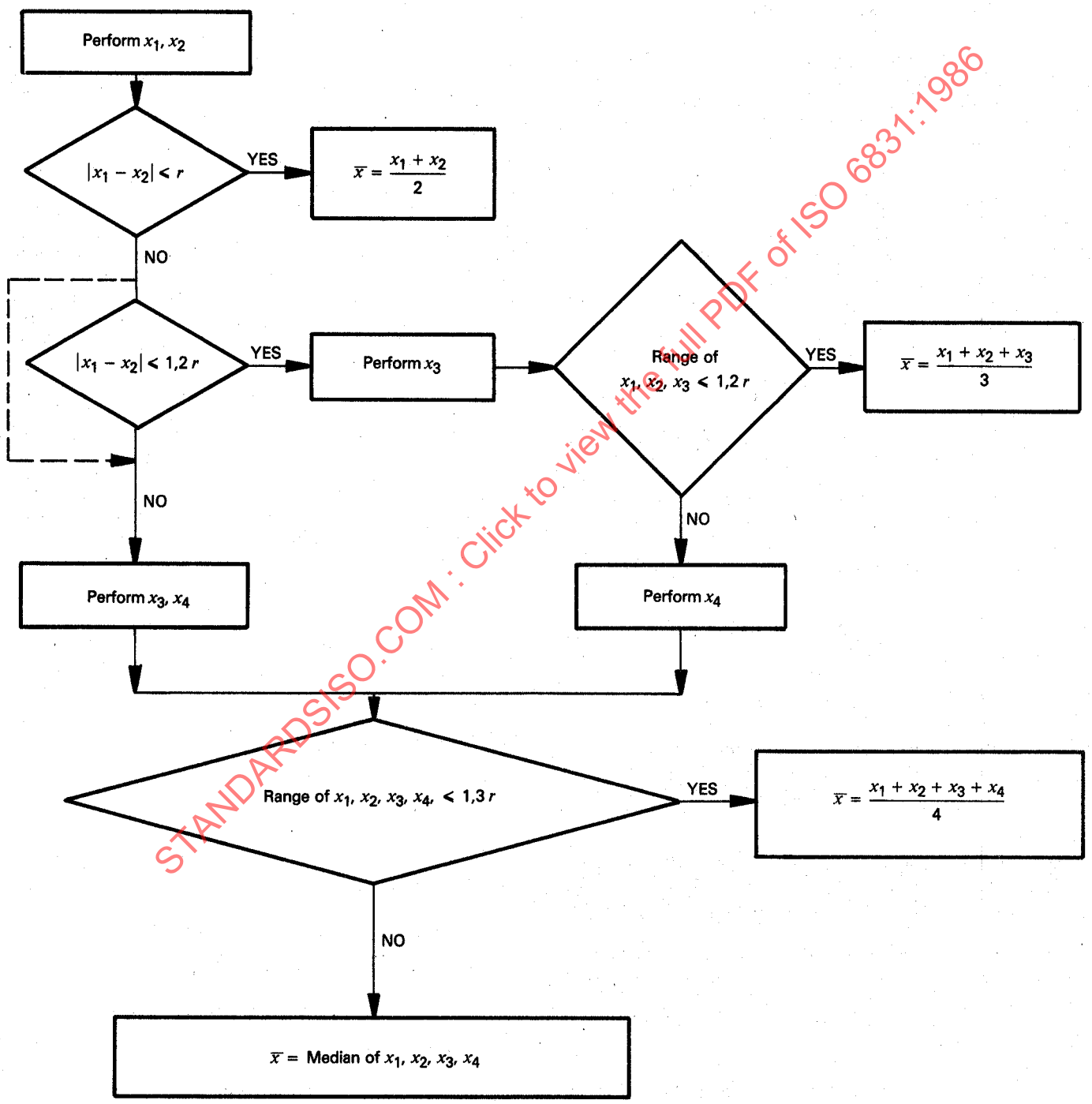
d) reference number of the result;

e) any characteristics noticed during the determination and any operations not specified in this International Standard which may have had an influence on the results, 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 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 1976/1978 on five iron ore samples, involving 39 laboratories in nine countries.

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

The test samples used were:

Sample	Sodium content [% (m/m)]	Potassium content [% (m/m)]
Dampier	0,002 7	0,002 5
Schefferville	0,018 7	0,026 4
Håksberg, concentrate	0,029 7	0,074 1
Malmberget	0,499	0,216
Grängesberg	0,398	0,511

NOTES

1 A report of the international trial and a statistical analysis of the results (Document ISO/TC 102/SC 2 N 509E, June 1978) is available either from the Secretariat of ISO/TC 102/SC 2 or from the Secretariat of ISO/TC 102.

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