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Iron ores — Determination of water soluble chloride content — Ion-selective electrode method

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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. 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 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 9517 was prepared by Technical Committee ISO/TC 102, *Iron ores.*

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

Iron ores — Determination of water soluble chloride content — Ion-selective electrode method

1 Scope

This International Standard specifies an ion-selective electrode method for the determination of the water soluble chloride content of iron ores. This method is applicable to a concentration range of 0,005 % (m/m) to 0,1 % (m/m) of water soluble chloride in natural iron ores, and concentrates and agglomerates including sinter products.

NOTE — Water soluble chloride is that part of the chloride content of an iron ore extractable by leaching with aqueous solution under substantially neutral conditions.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard 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

Digestion of the test portion in water containing potassium sulfate, transfer of the suspension to a volumetric flask and dilution to volume. Dry filtration, treatment of an aliquot with potassium persulfate solution and addition of neutral buffer. Addition of ionic strength adjuster solution and potentiometric determination of chloride concentration using a chloride ion electrode and a double junction reference electrode.

4 Reagents

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

The preparation of reagent and calibration solutions and all operations specified in 5, 6 and 7 in this method shall be conducted in an area adequately isolated from any areas in which hydrochloric acid is used.

4.1 Potassium sulfate (K_2SO_4) solution, 2 g/l.

4.2 Potassium sulfate (K_2SO_4) solution, 4 g/l.

4.3 Potassium persulfate ($K_2S_2O_8$) solution, 1,5 g/100 ml.

Prepare freshly for each series of tests.

4.4 Sodium nitrate solution $c(NaNO_3) = 5$ mol/l.

Dissolve 42,5 g of sodium nitrate in about 60 ml of water, transfer to a 100 ml volumetric flask, dilute to volume and mix.

4.5 Phosphate buffer solution.

Dissolve 2,72 g of potassium dihydrogen phosphate (KH_2PO_4) and 2,84 g of disodium hydrogen phosphate (Na_2HPO_4) in 40 ml of water. Transfer to a 100 ml volumetric flask, dilute to volume and mix.

4.6 Stirring bar cleaning solution.

Add carefully to about 700 ml of water, 150 ml of sulfuric acid (ϱ 1,84 g/ml) and 150 ml of phosphoric acid (ϱ 1,7 g/ml) and mix.

4.7 Chloride standard solution A, 1 000 µg Cl/ml.

Dry about 2 g of sodium chloride at 105 °C for 1 h and cool in a desiccator. Weigh 0,824 g of the dried material, dissolve in about 50 ml of water and transfer to a 500 ml volumetric flask. Dilute to volume and mix.

1 ml of chloride standard solution A contains 1 000 µg of chloride.

4.8 Chloride standard solution B, 50 µg Cl/ml.

Measure 25,0 ml of chloride standard solution A into a 500 ml volumetric flask, dilute to volume and mix.

1 ml of chloride standard solution B contains 50 µg of chloride.

4.9 Chloride standard solution C, 20 µg Cl/ml.

Measure 10,0 ml of chloride standard solution A into a 500 ml volumetric flask, dilute to volume and mix.

1 ml of chloride standard solution C contains 20 µg of chloride.

NOTE — Standard solutions B (4.8) and C (4.9) should be freshly prepared.

4.10 Calibration solutions.

Prepare the calibration solutions specified in table 1 for the expected range of chloride content.

If the chloride content is unknown, prepare calibration solutions containing 5,0 µg, 10,0 µg and 50,0 µg Cl/ml. If the chloride content is then found to be less than 0,012 % (m/m), prepare additional calibration solutions containing 2,0 µg and 3,0 µg Cl/ml. For higher chloride contents, prepare any additional solutions required in accordance with table 1.

Table 1 — Calibration solutions required for each range of chloride content

Test sample Cl content % (m/m)	Calibration solution Cl content µg/ml
0,005 to 0,025	2,0; 3,0; 5,0; 10,0
0,012 to 0,025	5,0; 10,0
0,025 to 0,10	10,0; 25,0; 50,0

For the preparation of the required calibration solutions, measure into a series of 100 ml volumetric flasks the aliquots of chloride standard solutions specified in table 2.

Table 2 — Preparation of calibration solutions

Calibration solution Cl content µg/ml	Standard solution Aliquot volume ml	Standard solution
2,0	10,0	C (4.9)
3,0	15,0	C (4.9)
5,0	10,0	B (4.8)
10,0	20,0	B (4.8)
25,0	50,0	B (4.8)
50,0	5,0	A (4.7)

Add to the aliquot of standard solution in the 100 ml volumetric flasks, 6 ml of potassium persulfate solution (4.3), 35 ml of potassium sulfate solution (4.2), 2 ml of phosphate buffer solution (4.5) and 2 ml of sodium nitrate solution (4.4) (ionic strength adjuster). Dilute to volume and mix.

NOTE — Calibration solutions containing from 2,0 µg to 10,0 µg Cl/ml should be prepared on the day of use.

5 Apparatus

Any one-mark pipettes and volumetric flasks required shall comply with the specifications of ISO 648 and ISO 1042 respectively.

Ordinary laboratory equipment and

5.1 Magnetic stirrer (optional, see 7.6.4 note 1).

5.2 Magnetic stirrer-hotplate.

5.3 PTFE or **polyethylene-covered stirring bars,** 25 mm to 30 mm long.

NOTE — Before use, stirring bars shall be cleaned to remove adhering iron ore and chloride contamination by leaching in the cleaning solution (4.6) for 30 min and then in water for 30 min. Only clean tweezers should be used for handling the cleaned stirring bars.

5.4 Filtration apparatus, glass or polycarbonate plastic, with 25 mm to 50 mm diameter cellulose membrane microfilters of less than 1 µm pore size[1].

NOTE — The microfilters should at all times be handled only with clean tweezers.

5.5 Ion-selective electrode meter, or **high-sensitivity pH meter,** or **high-impedance millivolt meter,** capable of reading with a sensitivity of 0,1 mV.

5.6 Chloride ion-selective electrode and separate double junction, free flowing, reference electrode.

NOTES

1 Both of the electrodes shall be maintained and used in accordance with manufacturers' specifications and the outer chamber solution in the reference electrode should be changed as specified and replenished as necessary. The flowrate across the nitrate/test solution junction should be such that the level of the outer chamber solution falls at a rate of approximately 4 mm to 5 mm per day.

2 As some chloride ion-selective electrodes are light sensitive, they should not be used in direct sunlight or in very bright daylight.

3 "Combined" electrodes, which normally are not provided with a reference electrode incorporating a double junction, are not suitable.

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 less than 160 µm.

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1) Millipore (XX10 apparatus with HAWP filters), Sartorius, Gelman are examples of suitable apparatus available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these types of apparatus.

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 °C ± 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

NOTE — For technical reasons, a blank test as usually understood cannot be conducted in methods using ion-selective electrodes. In this method the procedure in 7.4.2 is substituted.

In each run, one analysis of a certified reference material of the same type of ore shall be carried out in parallel with the analyses 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 of the same type of ore at the same time, the analytical value of one certified reference material may be used.

7.3 Temperature setting

7.3.1 Magnetic stirrer-hotplate

Determine the temperature setting required to maintain a temperature of 90 °C to 95 °C in a 35 ml volume of water.

7.3.2 Laboratory hotplate

Preheat the hotplate and determine the temperature setting required to produce, in a 50 ml volume of water, a temperature of at least 90 °C (but without boiling) after heating for 25 min.

7.4 Preliminary tests

7.4.1 Electrode system check test

Before use of the electrodes for each series of tests, carry out the following check test of electrode function.

Add to a 150 ml or 250 ml beaker, 100 ml of water, a stirring bar (5.3) and 2 ml of sodium nitrate solution (4.4). Place the electrodes in the solution, stir for 5 min and record the electrode potential in millivolts (E_1).

NOTE — Stir at a rate that will displace any air bubbles from the electrode surface but without causing a vortex.

Add 1 ml of chloride standard solution A (4.7), stir for 5 min to allow a stable reading to be obtained and record the electrode potential, (E_2). Add 10 ml of chloride standard solution A (4.7), stir for 5 min and again record the electrode potential, (E_3). The electrodes can be regarded as operating satisfactorily when the difference between E_2 and E_3 is 57 mV ± 2 mV for a temperature of the test solutions within the range 20 °C to 25 °C.

7.4.2 Contamination check test

To ensure that the apparatus and reagents are free from chloride contamination, carry out the complete procedure specified in 7.6 without the addition of a test portion. The electrode potential reading obtained should be within 20 mV of the reading E_1 obtained in 7.4.1. If not, the cleaning procedures should be repeated. If the potential reading is again not within 20 mV of E_1, use a different source of potassium sulfate and then, if necessary, potassium persulfate or buffer reagents.

7.5 Test portion

Weigh, to the nearest 0,001 g, approximately 2 g of the predried test sample, (6.2).

7.6 Determination

7.6.1 Leaching of water soluble chloride

Transfer the test portion (7.5) to a 150 ml beaker and, using tweezers, add a cleaned plastics-covered stirring bar (5.3). Add 35 ml of potassium sulfate solution (4.1), place on a preheated magnetic stirrer-hotplate (7.3.1) set at the required temperature, cover and stir for 1 h. Remove from the hotplate and cool in a water bath, transfer the solution and suspended solids to a 50 ml volumetric flask and dilute to volume. Allow to settle for 10 min.

7.6.2 Filtration

Assemble the microfilter filtration apparatus (5.4) on a dry 250 ml filter flask and, using tweezers, fit the specified microfilter membrane (5.4). Without washing, transfer as much as possible of the solution and suspended solids to the filter, and complete the filtration without washing.

7.6.3 Treatment of the test solution

Measure an aliquot of 45,0 ml (20,0 ml + 25,0 ml) of the filtrate into a 100 ml tall form beaker, add 3 ml of potassium persulfate solution (4.3) and 1,0 ml of phosphate buffer solution (4.5). Place the solution on a preheated hotplate (7.3.2) and heat for 30 min. Cool in a water bath and transfer to a 50 ml volumetric flask that has not been used in 7.6.1 in the current series of tests. Add to the beaker 1 ml of sodium nitrate solution (4.4) and transfer to the volumetric flask with rinsing. Dilute to volume and mix, retaining the beaker.

7.6.4 Measurement of electrode potential

Prepare the appropriate calibration solutions (4.10) and stand these solutions together with the test solution in an ambient temperature water bath. When equilibrium has been obtained, remove all solutions from the bath.

Transfer the test solution back to the retained 100 ml beaker and, using tweezers, add a clean plastics-coated stirring bar (5.3). Allow to stand for 15 min to allow the temperature to reach equilibrium with ambient temperature.

Place the electrode system in the beaker and, after stirring magnetically on a non-hotplate stirrer (5.1) at ambient temperature for 5 min to allow a stable reading to be obtained, record the electrode potential.

NOTES

1 If a separate non-hotplate stirrer is not available, ensure that the stirrer-hotplate is at ambient temperature. In either case, place a piece of cardboard between the stirrer and the beaker to avoid heating effects from the stirrer.

2 Stir at a rate that will displace air bubbles from the electrode surface, but without causing a vortex.

7.6.5 Preparation of calibration graph

Select the calibration solutions (4.10) appropriate to the chloride concentration, using the guideline values for potential against chloride concentration given in table 3.

Table 3 — Electrode potentials related to chloride concentration

Chloride concentration μg Cl/ml	Electrode potential mV
1 to 10	260 to 190
10 to 50	195 to 155

7.6.6 Measurement of chloride concentration

Process the calibration solutions as specified in 7.6.4 and measure the electrode potentials in ascending order of concentration, in the same manner as for the test solutions.

NOTES

1 Between measurements, rinse the electrodes and blot dry with tissue.

2 If electrode response becomes slow (> 5 min), follow the manufacturer's recommendations for removing possible deposits from the electrode sensing membrane.

3 The electrode assembly should not be subjected to large variations in temperature. If this occurs, sufficient time should be allowed for temperature equilibration between the test and calibration solutions to be achieved.

Regard the first series of readings as guidelines, so that readings of calibration and test solutions may then be grouped in ascending order with completion of sets of readings within the same decade of chloride concentration, before proceeding to the next. Accept the readings from this second set as definitive.

Using single-cycle semilogarithmic graph paper, prepare separate calibration graphs for each decade of chloride concentration as necessary, plotting chloride concentration on the logarithmic axis and decreasing electrode potential on the linear axis.

NOTE — At concentrations below 3 μg Cl/ml, a certain amount of curvature will be observed.

Read the chloride concentration of the test solution from the calibration graph.

8 Expression of results

8.1 Calculation of water soluble chloride content

The water soluble chloride content of the test sample as a percentage by mass is calculated to five decimal places using the equation

$$w_{Cl}(\%) = \frac{1,11\,\varrho_{Cl}}{200\,m} \qquad \ldots (1)$$

where

ϱ_{Cl} is the concentration, in micrograms per millilitre, of chloride in the test solution obtained from the calibration graph;

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

1,11 is the ratio 50,0/45,0.

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]:

$$r = 0,074\,4\,X + 0,001\,7 \qquad \ldots (2)$$

$$P = 0,165\,6\,X + 0,003\,2 \qquad \ldots (3)$$

$$\sigma_r = 0,026\,3\,X + 0,000\,6 \qquad \ldots (4)$$

$$\sigma_L = 0,055\,4\,X + 0,001\,0 \qquad \ldots (5)$$

where

X is the water-soluble chloride 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-laboratory 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.

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

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:

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

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 $n = 1$);

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 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 certified reference material 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 that this material not be used in the application of the standard. In case its use is unavoidable, use the formula

$$|A_c - A| \leqslant 2 \sqrt{2\sigma_L^2 + \dfrac{\sigma_r^2}{n}}$$

8.2.3 Calculation of final result

The final result is the arithmetic mean of the acceptable analytical values for the test sample 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.
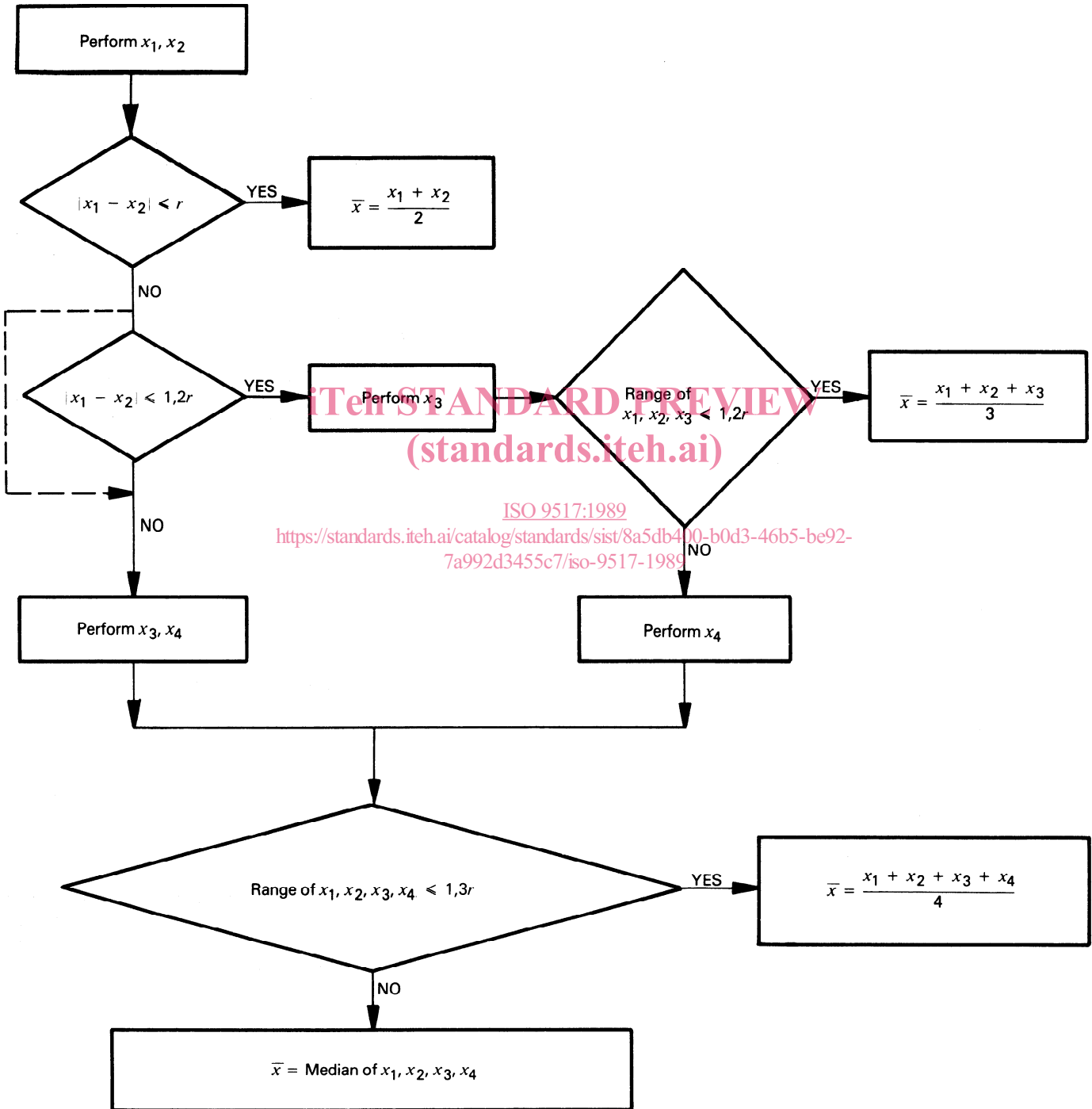
9   Test report

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 noted 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
(normative)

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

Perform x_1, x_2

$|x_1 - x_2| < r$ — YES → $\overline{x} = \dfrac{x_1 + x_2}{2}$

NO

$|x_1 - x_2| \leqslant 1,2r$ — YES → Perform x_3 → Range of $x_1, x_2, x_3 < 1,2r$ — YES → $\overline{x} = \dfrac{x_1 + x_2 + x_3}{3}$

NO

NO

Perform x_3, x_4

Perform x_4

Range of $x_1, x_2, x_3, x_4 \leqslant 1,3r$ — YES → $\overline{x} = \dfrac{x_1 + x_2 + x_3 + x_4}{4}$

NO

$\overline{x} = $ Median of x_1, x_2, x_3, x_4

r is as defined in 8.2.1.

Annex B

(informative)

Derivation of repeatability and permissible tolerance equations

The regression equations in 8.2.1 were obtained by statistical evaluation of the results of international analytical trials carried out in 1983 and 1984 on three iron samples (see table B.1), involving 18 laboratories in 6 countries.

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

Table B.1 — Water-soluble chloride contents of test samples

Sample	Chloride % (m/m)
Mt Newman, fines	0,007
Usinor KDF	0,017
Malmberget (synthetic)	0,097

NOTES

1   A report of the international trials and a statistical analysis of the results (document ISO/TC 102/SC 2 N756 E, July 1984) 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 established in ISO 5725: *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*