INTERNATIONAL STANDARD

ISO
4694
First edition
1987-04-15

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

Iron ores — Determination of fluorine content — Ion-selective electrode method

Minerais de fer — Dosage du fluor — Méthode par électrode sélective

Reference number
ISO 4694 : 1987 (E)

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 4694 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

INTERNATIONAL STANDARD ISO 4694 : 1987 (E)

Iron ores — Determination of fluorine content — Ion-selective electrode method

1 Scope and field of application

This International Standard specifies an ion-selective electrode method for the determination of the fluorine content of iron ores.

This method is applicable to a concentration range of 0,005 to 1 % (m/m)[1] of fluorine 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

Fusion of a test portion in sodium hydroxide and dissolution in water and hydrochloric acid. Dry filtration followed by direct potentiometric determination, using a fluoride ion electrode in the presence of sodium citrate buffer.

4 Reagents

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

4.1 Sodium hydroxide, pellets, dry.

4.2 Sodium hydroxide, 300 g/l solution.

Dissolve 75 g of sodium hydroxide pellets in 250 ml of water.

4.3 Hydrochloric acid, ϱ 1,16 to 1,19 g/ml, free from fluorine.

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

4.5 Sodium citrate, buffer solution, $c(Na_3C_6H_5O_7 \cdot 2H_2O) = 1$ mol/l.

In a 1 litre beaker dissolve 294,1 g of tri-sodium citrate dihydrate in about 800 ml of water. Adjust to pH 5,0 ± 0,1 with hydrochloric acid (4.4).

Transfer to a 1 litre volumetric flask and dilute to the mark with water.

NOTE — Alternatively, in the case of tri-sodium citrate 5,5-hydrate, use 357,2 g.

4.6 Fluorine, standard solutions.

All of the following solutions (4.6.1 to 4.6.5) shall be stored in plastics bottles.

4.6.1 Standard solution A.

Dry a suitable quantity of sodium fluoride at 105 °C.

Dissolve 1,108 g of the dried sodium fluoride in water, transfer to a 1 litre volumetric flask and dilute to the mark with water.

1 ml of this standard solution contains 500 µg of fluorine.

4.6.2 Standard solution B.

Pipette 100,0 ml of solution A into a 500 ml volumetric flask, and dilute to the mark with water.

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

4.6.3 Standard solution C.

Pipette 50,0 ml of solution B into a 500 ml volumetric flask, and dilute to the mark with water.

---

[1] This method has been tested internationally on samples with fluorine contents ranging from 0,005 to 0,214 % (m/m). (See annex B.)

Prepare this solution just before use.

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

4.6.4 Standard solution D.

Pipette 50,0 ml of solution C into a 500 ml flask, and dilute to the mark with water.

Prepare this solution just before use.

1 ml of this standard solution contains 1 µg of fluorine.

4.6.5 Standard solution E.

Pipette 50,0 ml of solution D into a 500 ml flask, and dilute to the mark with water.

Prepare this solution just before use.

1 ml of this standard solution contains 0,1 µg of fluorine.

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 Silver crucibles, of capacity 100 ml.

NOTE — Nickel crucibles can be used, possibly providing for overhead stirring.

5.2 Plastics beakers, of capacity 100 ml, or **plastics vials,** of capacity 50 ml.

5.3 Plastics volumetric flasks, of capacity 100 ml, calibrated at 20 °C and marked appropriately.

5.4 Magnetic stirrers, with polyethylene-covered stirring bars, 2,5 cm × 0,4 cm.

5.5 Plastics funnels.

5.6 pH meter - high impedance millivoltmeter, providing digital readout to 0,1 mV.

5.7 Fluoride ion-selective electrode.

5.8 Calomel reference electrode.

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 Check test

In each run, 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 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 the amount of the predried test sample (6.2) specified in table 1.

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

Table 1 — Mass of test portion

Expected fluorine content, w_F	Mass of test portion
%(m/m)	mg
$0{,}005 < w_F \leqslant 0{,}02$	500 ± 0,2
$0{,}02 < w_F \leqslant 0{,}05$	200 ± 0,1
$0{,}05 < w_F \leqslant 1$	100 ± 0,1

7.4 Determination

NOTES

1 Clean the silver crucibles before each use by carrying out a blank fusion with several grams of sodium hydroxide.

2 Rinse all other items of equipment copiously with water.

7.4.1 Decomposition of the test portion

WARNING — The use of molten sodium hydroxide requires the wearing of safety glasses. The use of gloves is advised. Dissolution of the fused melt must be done carefully.

Place the test portion (7.3) in a silver crucible (5.1) and add 3 g of sodium hydroxide pellets (4.1), covering the test portion as far as possible. Place the crucible and contents in a muffle furnace at 525 ± 20 °C for about 10 min, swirl for several seconds and return to the muffle furnace for a further 5 min.

Cool and add about 60 ml of water to the crucible. Add a stirring bar (5.4) and place on a magnetic stirrer for 5 min to facilitate dissolution. Cool. Transfer the solution to a 100 ml plastics volumetric flask (5.3). Rinse the crucible with 10 ml of hydrochloric acid (4.4) and rub down the walls.

Transfer the rinsings to the volumetric flask and dilute to the mark. Filter through a dry close-textured filter paper, collecting the filtrate in a plastics beaker or vial (5.2). Reject the first runnings and continue the filtration to collect about 40 ml of solution for aliquotting.

NOTE — Dissolution of the fusion melt can be carried out with hot water.

7.4.2 Preparation of the set of calibration solutions

Pipette into a series of 100 ml plastics volumetric flasks, the volumes of standard solutions shown in table 2.

Table 2 — Preparation of calibration solutions

Flask	Fluoride ion concentration	Volume of standard solution (4.6)
	µg/ml	
1	0,02	20 ml Solution E
2	0,05	50 ml Solution E
3	0,1	10 ml Solution D
4	0,3	30 ml Solution D
5	1,0	10 ml Solution C
6	3,0	30 ml Solution C
7	10,0	10 ml Solution B

Add 5 ml of sodium hydroxide solution (4.2) to each flask, and dilute to the mark with water.

7.4.3 Measurement

Pipette 20 ml of test solution into a 50 ml plastics beaker or vial and add 20 ml of buffer solution (4.5). Mix carefully.

For the calibration, pipette 20 ml of each of the calibration solutions (see table 2) into a series of plastics vials. Add 20 ml of buffer solution (4.5) by pipette and mix carefully.

Measure the fluoride ion concentration as specified in 7.4.3.1 to 7.4.3.6.

7.4.3.1 With the pH meter-millivoltmeter (5.6) in the "mV" mode, connect the fluoride ion electrode (5.7) to the metal electrode socket and the reference electrode (5.8) to the socket for measuring potentials.

7.4.3.2 Place the electrodes in the solution to be measured, check that there are no air bubbles on the surface of the lanthanum fluoride crystal, and stir the solution at a constant speed.

NOTE — Before use, the ion-selective electrode should be conditioned in the solution of lowest fluoride concentration until the potential stabilizes. The time required for stabilization is a function of the response of the electrode, and can take from 15 min to 1 h.

7.4.3.3 In a preliminary run, quickly work through the readings on the calibration solutions and the test solutions to be able to arrange them in order of increasing concentration. In these tests, wait about 2 min after introducing the electrodes before taking the readings.

7.4.3.4 Follow with a second run, commencing with the least concentrated solution, interposing standards and samples in increasing order. Allow 5 min to be able to record stable values of the potentials.

NOTES

1 After each reading, carefully rinse the electrodes with water and dry with tissue.

2 When taking readings, all anomalies must be eliminated and the reading must be as precise as possible. A difference in potential of 1 mV causes a relative error of 4 %.

7.4.3.5 Plot the calibration graph on semi-log paper, with the potentials on the linear axis and the fluoride ion concentration on the logarithmic axis.

NOTE — A certain amount of curvature will be observed at concentrations below 0,3 µg of fluoride per millilitre [equivalent to 0,15 µg of fluoride per millilitre because of the dilution (2 ×) with buffer]. The factor 2 does not enter the calculations as the dilution applies equally to standards and test samples.

7.4.3.6 Read the fluorine content of the test solution from the calibration graph.

8 Expression of results

8.1 Calculation of fluorine content

The fluorine content, w_F, expressed as a percentage by mass, is calculated to five decimal places using the equation

$$w_F\,(\%) = \frac{\varrho_F \times 10}{m} \qquad \ldots (1)$$

where

ϱ_F is the concentration, in micrograms per millilitre, of fluorine in the test solution;

m is the mass, in milligrams, of the test portion.

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]

$$r = 0{,}063\,0\,X + 0{,}002\,3 \qquad \ldots (2)$$

$$P = 0{,}148\,1\,X + 0{,}003\,2 \qquad \ldots (3)$$

$$\sigma_r = 0{,}022\,7\,X + 0{,}000\,8 \qquad \ldots (4)$$

$$\sigma_L = 0{,}051\,2\,X + 0{,}001\,0 \qquad \ldots (5)$$

where

X is the fluorine content, expressed as a percentage by mass, of the predried test sample, calculated as follows:

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

— between-laboratories equations (3, 5); 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 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:

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

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 condition is less than or equal to the right-hand side, then the difference $|A_c - A|$ is statistically insignificant; otherwise, it is statistically significant.

When the difference is significant, the analysis shall be repeated, simultaneously with an analysis of the test sample. If the difference is again significant, the procedure shall be repeated using a different certified reference material of the same type of ore.

When the range of the two values for the test sample is outside the limit for r calculated according to equation (2) 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 case its use is unavoidable, use the formula:

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

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 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;

---

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

c) when the figure in the fourth decimal place is 5 and there is no figure other than 0 in the fifth decimal place, the 5 is discarded and the figure in the third decimal place is kept unchanged if it is 0, 2, 4, 6 or 8, and is increased by one if it is 1, 3, 5, 7 or 9.

9 Test report

The test report shall include the following information:

a) reference to this International Standard;

b) details necessary for the identification of the sample;

c) result of the analysis;

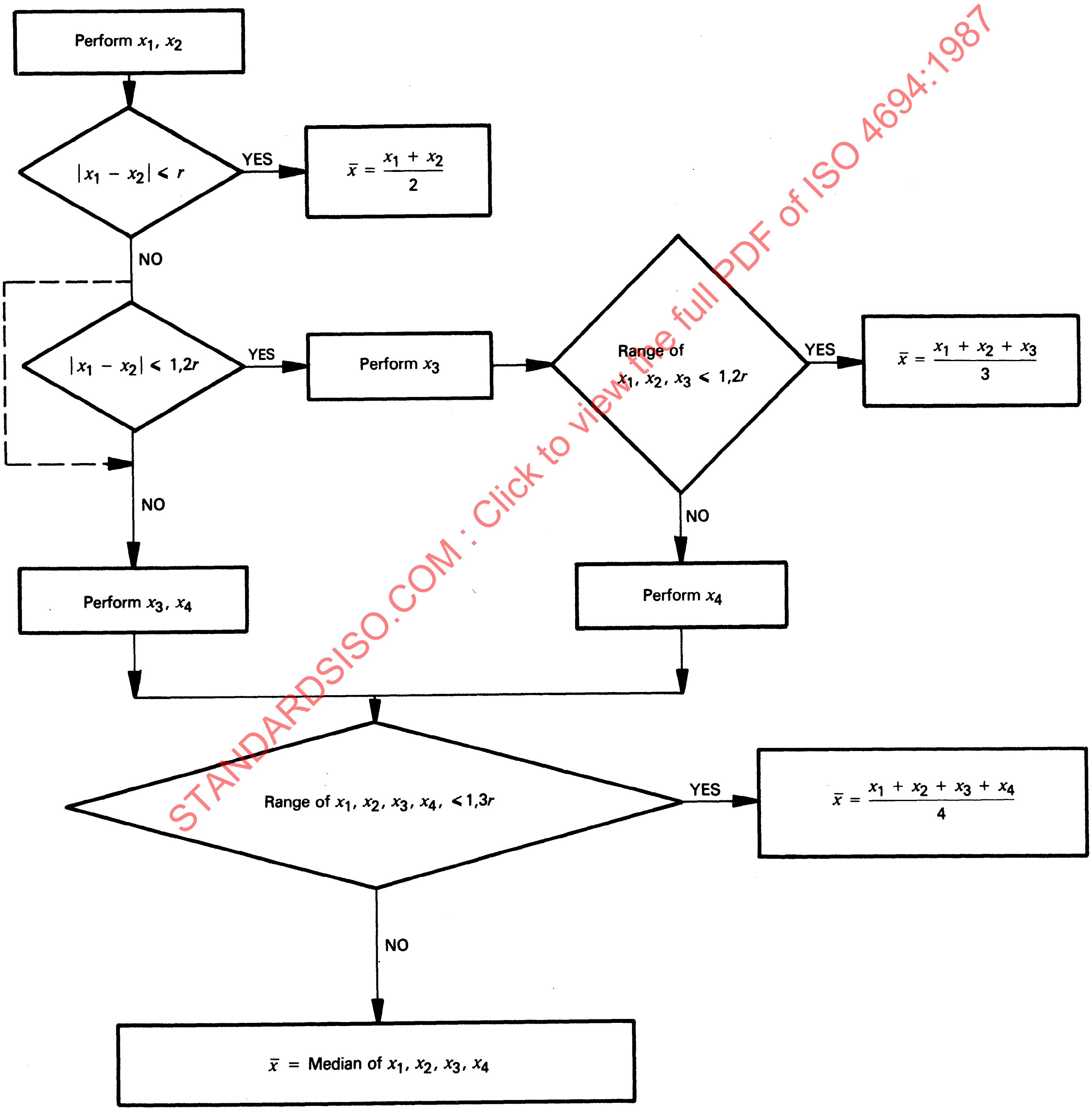
d) reference number of the result;

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.

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 1979/80 on four iron ore samples involving 21 laboratories in 10 countries.

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

The test samples used were:

Sample	Fluorine content [% (m/m)]
Mano River (79-7)	0,005
Kiruna B (79-8)	0,052
Lorraine (79-9)	0,080
Kiruna D (79-10)	0,214

NOTES

1 A report of the international trial and a statistical analysis of the results (Document ISO/TC 102/SC 2 N 590E, November 1979) is available from either the Secretariat of ISO/TC 102/SC 2 or the Secretariat of ISO/TC 102.

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