International Standard 4689

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Iron ores — Determination of sulfur content — Barium sulfate gravimetric method

Minerais de fer — Dosage du soufre — Méthode gravimétrique au sulfate de baryum

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Foreword

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International Standard ISO 4689 was prepared by Technical Committee ISO/TC 102, *Iron ores*.

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INTERNATIONAL STANDARD **ISO 4689-1986 (E)**

Iron ores — Determination of sulfur content — Barium sulfate gravimetric method

1 Scope and field of application

This International Standard specifies a barium sulfate gravimetric method for the determination of the sulfur content of iron ores.

This method is applicable to a concentration range of 0,01 to 1,0 % (m/m) of sulfur in natural iron ores, and iron ore concentrates and agglomerates including sinter products.

2 References

ISO 3081, *Iron ores — Increment sampling — Manual method.*

ISO 3082, *Iron ores — Increment sampling and sample preparation — Mechanical method.*[1]

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 treatment with potassium chlorate and hydrochloric and nitric acids followed by evaporation to dryness. Dissolution of the salts in hydrochloric acid and filtration of the insoluble residue. Removal of the major portion of the iron in the filtrate by extraction with methyl isobutyl ketone.

Ignition of the insoluble residue and removal of silicon dioxide by evaporation with hydrofluoric and nitric acids. Fusion of the residue with sodium carbonate followed by leaching and filtration. Acidification of the filtrate and combination with the main solution.

Reduction of any remaining iron to the bivalent state, adjustment of the acidity and addition of barium chloride solution. Filtration of barium sulfate and gravimetric determination.

4 Reagents

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

4.1 Potassium chlorate ($KClO_3$), powder.

4.2 Sodium carbonate (Na_2CO_3), anhydrous.

4.3 Zinc.

Use zinc with the lowest available sulfur content and with a particle size of 1 to 3 mm.

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

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

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

4.7 Hydrochloric acid, ϱ 1,16 to 1,19 g/ml, diluted 2 + 100.

4.8 Nitric acid, ϱ 1,4 g/ml.

4.9 Hydrofluoric acid, 40 % (m/m), ϱ 1,13 g/ml, or 48 % (m/m), ϱ 1,185 g/ml.

4.10 Acid mixture: hydrochloric acid (4.4) + nitric acid (4.8), 4 + 1.

NOTE — Do not store this mixture; prepare immediately before use.

4.11 Barium chloride ($BaCl_2 \cdot 2H_2O$), 100 g/l solution.

Dissolve 100 g of crystalline barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in 1 litre of water, cover and heat to boiling point. Keep warm on a water bath for a minimum of 2 h and allow to cool to room temperature overnight. Store the solution in a plastics bottle and before each use, filter the required volume through a close-texture filter paper.

4.12 Hydrochloric acid wash solution, containing barium chloride.

Filter 10 ml of barium chloride solution (4.11) through a close-texture filter paper, and dilute to 1 000 ml with hydrochloric acid solution (4.7).

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[1] At present at the stage of draft.

4.13 Sodium nitrate ($NaNO_3$), saturated solution.

4.14 Sodium carbonate (Na_2CO_3), 20 g/l solution.

Store in a plastics bottle.

4.15 Ammonium thiocyanate (NH_4SCN), 100 g/l solution.

4.16 Silver nitrate, 20 g/l solution.

4.17 Methyl orange, 0,1 g/100 ml solution.

Dissolve 0,10 g of methyl orange in 100 ml of water.

4.18 Methyl isobutyl ketone [$CH_3COCH_2CH(CH_3)_2$] (4-Methylpentan-2-one).

Pre-treat as follows before use : transfer 200 ml of methyl isobutyl ketone and 100 ml of hydrochloric acid solution (4.6) to a 500 ml separating funnel, and shake thoroughly for about 1 min. Allow the layers to separate and discard the lower aqueous layer.

5 Apparatus

Ordinary laboratory apparatus.

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 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, the amount of the predried test sample (6.2) specified in the table.

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

Table — Mass of test portion and volume of acid mixture (4.10) required for decomposition

Sulfur content, w_S % (m/m)	Mass of test portion g	Volume of acid mixture ml
$0,01 < w_S \leq 0,1$	5,0	70
$0,1 < w_S \leq 0,5$	2,0	40
$0,5 < w_S \leq 1,0$	1,0	25

7.4 Determination

7.4.1 Decomposition of the test portion

Place the test portion (7.3) in a 500 ml beaker, add 1 g of potassium chlorate (4.1) and 3 to 4 ml of water, and mix thoroughly.

Add, in accordance with the table, the required volume of acid mixture (4.10) and heat gently to decompose the test portion. Evaporate the solution to dryness on a hot-plate heated to about 150 °C, cool and add 10 ml of hydrochloric acid (4.4).

Again evaporate to dryness, continuing the heating at about 110 °C for 30 min. Cool, add 30 ml of hydrochloric acid (4.6) and warm to dissolve soluble salts.

NOTE — Samples that are not decomposed in 1 to 2 h by this procedure should be digested by keeping the solution warm for an extended period.

Add 25 ml of water and boil for about 5 min. Filter the solution through a close-texture paper, collecting the filtrate in a 500 ml beaker. Wash the paper and residue with the warm hydrochloric acid (4.7) until iron(III) ion can no longer be detected in the washings by testing a small portion with the ammonium thiocyanate solution (4.15). Reserve the filtrate and washings. Transfer the filter paper containing the residue to a platinum crucible.

7.4.2 Extraction of the bulk of the iron

Evaporate the filtrate and washings (7.4.1) to about 10 ml. Cool and transfer the solution to a 200 ml separating funnel, using a total of 50 ml of hydrochloric acid (4.5), taken in several portions, to rinse the beaker. Add 50 ml of the methyl isobutyl ketone (4.18) and shake thoroughly for about 1 min. Allow the layers to separate, then drain the lower aqueous layer into a second 200 ml separating funnel. Wash the organic layer by adding 10 ml of hydrochloric acid (4.5) and shaking for about 30 s. Allow the layers to separate, then combine the aqueous layer with the first. Repeat the washing of the organic phase with another 10 ml of hydrochloric acid (4.5), combine the aqueous solutions and reject the organic phase.

Add 50 ml of methyl isobutyl ketone (4.18) to the funnel containing the aqueous solution and shake thoroughly for about 1 min. Allow the layers to separate, then run the lower aqueous solution into a 500 ml beaker. Wash the organic phase by extracting twice with 10 ml of hydrochloric acid (4.5), transferring the washings to the beaker. Evaporate the combined aqueous solutions almost to dryness.

Add 10 ml of acid mixture (4.10) to the salts and evaporate to dryness to decompose the organic matter. Add 10 ml of hydrochloric acid (4.4) and evaporate to dryness on a hot-plate heated to about 150 °C. Add a further 10 ml of hydrochloric acid (4.4) and evaporate to dryness, continuing the heating at 110 °C for about 30 min. Cool, add 5 ml of hydrochloric acid (4.4) and 30 ml of water to dissolve the salts, and reserve as the main solution.

7.4.3 Treatment of the residue

Moisten the filter paper containing the residue obtained in 7.4.1 with 1 or 2 drops of sodium nitrate solution (4.13), carefully heat the crucible to char the paper, then ignite at a temperature of 800 to 850 °C. Allow the crucible to cool and moisten the ignited residue with a few drops of nitric acid (4.8). Add about 5 ml of hydrofluoric acid (4.9), and heat gently to dryness to remove silicon dioxide and nitric acid.

NOTE — With high silicon contents, the treatment to remove silicon dioxide may be repeated with another 5 ml of hydrofluoric acid (4.9).

Allow the crucible to cool, add 3 g of sodium carbonate (4.2) and fuse the residue at about 1 000 °C for 15 min. Place the cold crucible in a 300 ml beaker, add about 100 ml of warm water and heat to dissolve the melt. Remove the crucible and rinse with water.

Filter the solution through a close-texture filter paper, collecting the filtrate in a 300 ml beaker. Wash the filter paper several times with sodium carbonate solution (4.14), and discard the residue. Add 0,5 ml of methyl orange indicator solution (4.17) to the filtrate and washings and neutralize the solution by adding hydrochloric acid (4.6) in small portions, while stirring. Add 5 ml of hydrochloric acid (4.6) in excess and combine this solution with the main solution from 7.4.2.

7.4.4 Precipitation of barium sulfate

Cover the beaker containing the combined solution with a watch glass, and heat to evaporate the solution to 25 ml. Allow to cool, add 3 ml of hydrochloric acid (4.6) and 50 ml of water, and heat to dissolve soluble salts. Heat on a water bath at 60 to 70 °C and add 1,0 g of zinc (4.3) to reduce the remaining iron(III) to iron(II). Immediately after complete dissolution of the zinc, filter the solution through a close-texture filter paper, collecting the filtrate in a 300 ml tall-form beaker. Wash the paper and residue with hydrochloric acid (4.7) until the volume of the filtrate is approximately 120 ml, then discard the residue.

Heat the solution to 60 to 70 °C, then, while stirring, slowly add 5 ml of barium chloride solution (4.11) from a burette. Continue to stir for a further 5 min, then cover the beaker with a watch glass and heat the solution on a water bath at 60 to 70 °C for about 2 h. Allow the solution to cool to room temperature overnight.

Filter the barium sulfate precipitate through a close-texture filter paper.

NOTE — If necessary, a small amount of filter pulp may be used to prevent the fine precipitate from passing through the filter.

Wash the beaker once with hydrochloric acid wash solution containing barium chloride (4.12) and with the aid of a rubber-tipped glass rod, remove the precipitate still adhering to the walls of the beaker, transferring it to the filter paper using hydrochloric acid wash solution containing barium chloride (4.12). Wash out the beaker several times with the same solution and wash the precipitate on the filter paper with warm water until chloride ion is no longer detected in the washings by testing with silver nitrate solution (4.16).

7.4.5 Weighing

Place the paper and precipitate from 7.4.4 in a tared platinum crucible. Dry and char the paper at a low temperature then carefully ignite, first at about 500 °C for 20 min and then at about 800 °C for the same period. Cool the crucible in a desiccator to room temperature and weigh as barium sulfate. Repeat the ignition at 800 °C until constant mass, to the nearest 0,000 1 g, is obtained.

8 Expression of results

8.1 Calculation of sulfur content

The sulfur content, w_S, is calculated as a percentage by mass, to five decimal places, using the equation

$$w_S\,(\%) = \frac{[(m_1 - m_2) - (m_3 - m_4)] \times 0{,}137\,4 \times 100}{m_5}$$

$$= \frac{[(m_1 - m_2) - (m_3 - m_4)] \times 13{,}74}{m_5} \qquad \ldots \ (1)$$

where

m_1 is the mass, in grams, of the platinum crucible containing barium sulfate from the test portion;

m_2 is the tare, in grams, of the platinum crucible used for the determination;

m_3 is the mass, in grams, of the platinum crucible for the blank test;

m_4 is the tare, in grams, of the platinum crucible for the blank test;

m_5 is the mass, in grams, of the test portion (7.3);

0,137 4 is the mass ratio of sulfur in barium sulfate.

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]

$$r = 0{,}026\,X + 0{,}004 \qquad \ldots \ (2)$$

$$P = 0{,}027\,X + 0{,}006 \qquad \ldots \ (3)$$

$$\sigma_r = 0{,}009\,X + 0{,}002 \qquad \ldots \ (4)$$

$$\sigma_L = 0{,}007\,X + 0{,}002 \qquad \ldots \ (5)$$

where

X is the sulfur 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 sample (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.

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

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 $s_{\mathrm{Wc}}^2/n_{\mathrm{Wc}}$ 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:

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

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;

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) reference to this International Standard;

b) details necessary for the identification of the sample;

c) result of the analysis;

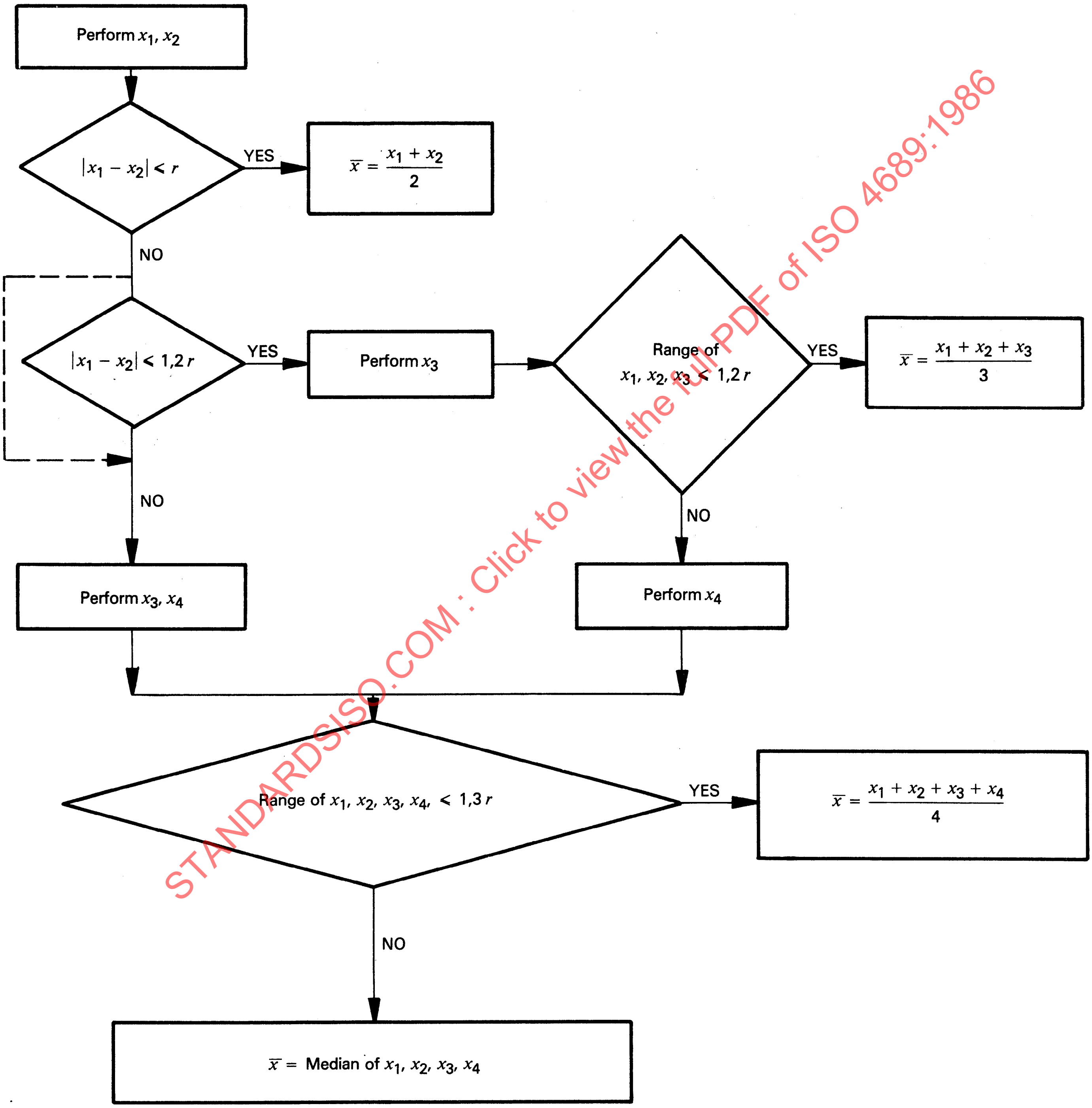
d) reference number of the result;

e) any characteristics noticed during the determination and any operations not specified in this International Standard, or in the International Standards to which reference is made, which may have influenced 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 1974/1975 on five iron ore samples involving 23 laboratories in six countries.

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

The test samples used were:

Sample	**Sulfur content** [% (*m*/*m*)]
Nimba	0,006
Kiruna D	0,019
Rompin	0,078
Texada	0,255
Roasting residue (Purpurerz)	0,534

NOTES

1 A report of the international trial and a statistical analysis of the results (Document ISO/TC 102/SC 2 N 440 E, April 1976) 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.