
**Iron ores — Determination of sulfur
content —**

**Part 1:
Barium sulfate gravimetric method**

Minerais de fer — Dosage du soufre —

Partie 1: Méthode gravimétrique au sulfate de baryum



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Published in Switzerland

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 102, *Iron Ores*, Subcommittee SC 02, *Chemical analysis*.

This first edition of ISO/TS 4689-1 cancels and replaces the first edition of ISO 4689:1986, which has been technically revised.

The main changes are as follows:

- the decomposition method of samples has been changed from the original acid dissolution and alkali melting method to soda-zinc oxide semi melting method.

A list of all parts in the ISO 4689 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

In this document, a new way of melting the samples for determination of sulfur content by barium sulfate gravimetric method is specified as follows.

- Samples are semi-molten with sodium carbonate and zinc oxide.
- The sulfate ions are leached by electromagnetic stirring and separated from the iron and other interference elements such as lead, antimony, bismuth, tin, silicon, titanium, etc.

This method is also suitable for complex natural and artificial sample analysis.

This document consists of Part 1 of the ISO 4689 series, *Iron ores — Determination of sulfur content*.

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Iron ores — Determination of sulfur content —

Part 1:

Barium sulfate gravimetric method

1 Scope

This document 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 a mass fraction of sulfur from 0,01 % to 3,9 % in natural iron ores, iron ore concentrates and agglomerates including sinter products.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 2596, *Iron ores — Determination of hygroscopic moisture in analytical samples — Gravimetric, Karl Fischer and mass-loss methods*

ISO 3082, *Iron ores — Sampling and sample preparation procedures*

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

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

4 Principle

The analysis principle is as follows:

- a) decomposition of a test portion by treatment with a soda-zinc oxide flux mixture to a semi-molten state;
- b) water leaching of sulfate ion with electro-magnetic stirring and filtration of the insoluble residue;
- c) transformation of sulfate ion to barium sulfate through adjustment of the acidity and addition of barium chloride solution;
- d) filtration of barium sulfate and gravimetric determination;
- e) removal of the interference of Cr, Sn, P through hydrogen peroxide, citric acid and calcium carbonate.

5 Reagents

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

5.1 Sodium carbonate-zinc oxide mixed flux, grind Na_2CO_3 to -100 mesh, blend Na_2CO_3 and ZnO by 3:2 (mass ratio).

5.2 Calcium carbonate.

5.3 Hydrofluoric acid, ρ 1,15 g/ml.

5.4 Hydrochloric acid solution, mix $\rho = 1,15$ g/ml hydrochloric acid and distilled water by 1:1 (volume ratio).

5.5 Sulfuric acid solution, mix $\rho = 1,84$ g/ml sulfuric acid and distilled water by 1:1 (volume ratio).

5.6 Hydrogen peroxide, 30 % (mass fraction).

5.7 Ethanol (ethyl).

5.8 Citric acid solution, 50 % (mass fraction).

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

5.10 Silver nitrate, 10 g/l solution.

5.11 Methyl orange, 1 g/l solution.

5.12 Barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), 100 g/l solution.

Dissolve 100 g of crystalline barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in 1 l of water, cover and heat to boiling point. Keep warm on a water bath for a minimum of 2 h and allow cooling to room temperature overnight. Store the solution in a plastic bottle and, before each use, filter the required volume through a close-texture filter paper.

5.13 Hydrochloric acid wash solution, containing barium chloride. Filter 10 ml of barium chloride solution ([5.12](#)) through a close-texture filter paper, add 40 ml hydrochloric acid ([5.4](#)), dilute to about 1 000 ml.

6 Apparatus

The usual laboratory apparatus and, in particular, the following shall be used.

6.1 Glass plate suction funnel, 150 ml.

An example is given in [Annex D, Figure D.1](#).

6.2 Water filtration membrane, 0,2 μm .

6.3 Sand core filter, 300 ml.

An example is given in [Annex D, Figure D.2](#).

7 Sampling and samples

7.1 Laboratory sample

For analysis, use a laboratory sample of -100 µm particle size which has been taken and prepared in accordance with ISO 3082. In the case of ores with significant contents of combined water or oxidizable compounds, use a particle size of -160 µm.

NOTE A guideline on significant contents of combined water and oxidizable compounds is incorporated in ISO 7764.

7.2 Preparation of test samples

7.2.1 General

Depending on the ore type, proceed in accordance with either [7.2.2](#) or [7.2.3](#).

7.2.2 Ores having significant contents of combined water or oxidizable compounds

Prepare an air-equilibrated test sample in accordance with ISO 2596 with the following types of ore.

- a) Processed ores containing metallic iron.
- b) Natural or processed ores in which the sulfur content is higher than 0, 2 % mass fraction.
- c) Natural or processed ores in which the content of combined water is higher than 2, 5 % mass fraction.

7.2.3 Ores outside the scope of [7.2.2](#)

Prepare a predried test sample as follows.

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 in accordance with ISO 7764.

8 Procedure

8.1 Number of determinations

Carry out the analysis at least in duplicate in accordance with [Annex A](#), independently, on one 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 is carried out either by the same operator at a different time or by a different operator, including, in either case, appropriate recalibration.

8.2 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 [7.2.3](#).

NOTE The certified reference material is 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.

8.3 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, the amount of the test sample (7.2) specified in Table 1.

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

Table 1 — Mass of test portion and flux mixture

Sulfur content, w_s % (mass fraction)	Mass of test portion g	Mass of flux mixture g
0,01 to 0,100	5,000 0	10,0
> 0,100 to 2,00	1,000 0	8,0
> 2,00 to 4,00	0,500 0	5,0

8.4 Determination

8.4.1 Decomposition of the test portion

The procedure of decomposition is as follows:

- weigh the mixed flux (5.1) into a porcelain crucible (30 ml) and add the test portion according to the masses specified in Table 1;
- if the phosphorous content of the sample is not less than 1 mg, add in 0,4 g calcium carbonate (5.2), then blend and cover with another 2 g mixed flux (5.1);
- semi-fuse the mixture at $780\text{ }^{\circ}\text{C} \pm 20\text{ }^{\circ}\text{C}$ for 60 min;
- cool the crucible in a desiccator to room temperature, then remove the mixture from the crucible by transferring to a 200 ml beaker;
- add 25 ml of water to the crucible and heat it on a low temperature furnace to boil for 5 min;
- pour the solution in the crucible into the original beaker after cooling a little, then rinse the crucible wall with hot water 4 to 5 times;
- add water to the volume of about 100 ml, then stir the solution with a magnetic stirrer for 60 min or extract it by ultrasonic method for 30 min;
- if the solution is green or purple, add a little ethanol (5.7) and heat for a few minutes in the low temperature furnace (to prevent the splashing or loss of the solution) till the colour (green or purple) disappears.

8.4.2 Separation

Filter the solution through medium speed filter paper in a long-necked glass funnel or a glass plate suction funnel (5.1), retaining the residue as far as possible in the original beaker while collecting filtrate in a 500 ml beaker. Wash the beaker 4 to 5 times and the precipitate 7 to 8 times with warm sodium carbonate solution (5.9).

8.4.3 Precipitation of barium sulfate

- a) Add 2 drops of methyl orange solution (5.11) to the filtrate and, if sample has tin, add 4 ml citric acid solution (5.8).
- b) Cover the beaker with a watch glass and add hydrochloric acid (5.4) through the mouth of the beaker till the solution turns red.
- c) Add 5 ml hydrochloric acid (5.4), dilute to about 300 ml and, if sample has chromium, add a few drops of hydrogen peroxide (5.6).
- d) Boil the solution until no bubbles are evident.
- e) While stirring, wash the beaker wall slowly and add 5 ml of barium chloride solution (5.12) from a burette.
- f) Continue stirring for a further 5 min, then cover the beaker with a watch glass and heat the solution on a water bath at 60 °C to 70 °C for about 2 h.
- g) Allow the solution to cool to room temperature overnight.
- h) Filter the barium sulfate precipitate through a close-texture filter paper in a long-necked glass funnel or through water filtration membrane (6.2) in a sand core filter (6.3).

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

- i) Wash the beaker once with hydrochloric acid wash solution (5.13), 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 (5.13).
- j) 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 (5.10).

8.4.4 Weighing

Place the paper and precipitate from 8.4.3 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.

9 Expression of results

9.1 Calculation of sulfur content

The sulfur content, w_s , is calculated as a percentage by mass, to five decimal places, using Formula (1):

$$w_s = \frac{(m_1 - m_2) - (m_3 - m_4)}{m} \times 0,137\,4 \times 100 \quad (1)$$

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 is the mass, in grams, of the test portion (8.3);
- 0,137 4 is the mass ratio of sulfur in barium sulfate.

9.2 General treatment of results

9.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed by the following regression [Formulae \(2\)](#) to [\(5\)](#):

$$R_d = 0,035 X - 0,001 \quad (2)$$

$$P = 0,036 X + 0,007 \quad (3)$$

$$\sigma_d = 0,0125 X - 0,0005 \quad (4)$$

$$\sigma_L = 0,0128 X + 0,0027 \quad (5)$$

where

- X is the sulfur content, expressed as a percentage by mass, of the test sample, calculated as follows:
- within-laboratory [Formulae \(2\)](#) and [\(4\)](#); the arithmetic mean of the duplicate values;
 - between-laboratories [Formulae \(3\)](#) and [\(5\)](#); the arithmetic mean of the final results [\(9.2.3\)](#) of the two laboratories;
- R_d is the permissible tolerance within a laboratory (repeatability);
- P is the permissible tolerance between laboratories;
- σ_d is the within-laboratory standard deviation;
- σ_L is the between-laboratories standard deviation.

Additional information is given in [Annexes B](#) and [C](#).

9.2.2 Check for trueness

The trueness of the analytical method shall be checked by applying it to a certified reference material (CRM) or a reference material (RM). Calculate the analytical result, μ , for the CRM/RM using the procedures in [9.1](#) and [9.2](#), and compare it with the reference or certified value A_c .

There are two possibilities:

- a) $|\mu_c - A_c| \leq C$, in which case the difference between the reported result and the certified/reference value is statistically insignificant;
- b) $|\mu_c - A_c| > C$, in which case the difference between the reported result and the certified/reference value is statistically significant;

where

- μ_c is the final result for the certified reference material;

A_c is the certified/reference value for the CRM/RM;

C is a value dependent on the type of CRM/RM used, see [Formula \(6\)](#).

Certified reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35.

C shall be calculated using [Formula \(6\)](#):

$$C = 2 \sqrt{\frac{s_{Lc}^2 + \frac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_d^2}{n}} \quad (6)$$

where

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 carried out on the CRM/RM;

σ_L and σ_d are as defined in [9.2.1](#).

The following procedure should be used when the information on the RM certificate is incomplete:

- 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;
- if the certification has been made by only one laboratory or if the interlaboratory results are missing, use [Formula \(7\)](#):

$$C = 2 \sqrt{2 \sigma_L^2 + \frac{\sigma_d^2}{n}} \quad (7)$$

A CRM certified by only one laboratory should be avoided, unless it is known to have an unbiased certified value.

9.2.3 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.

10 Test report

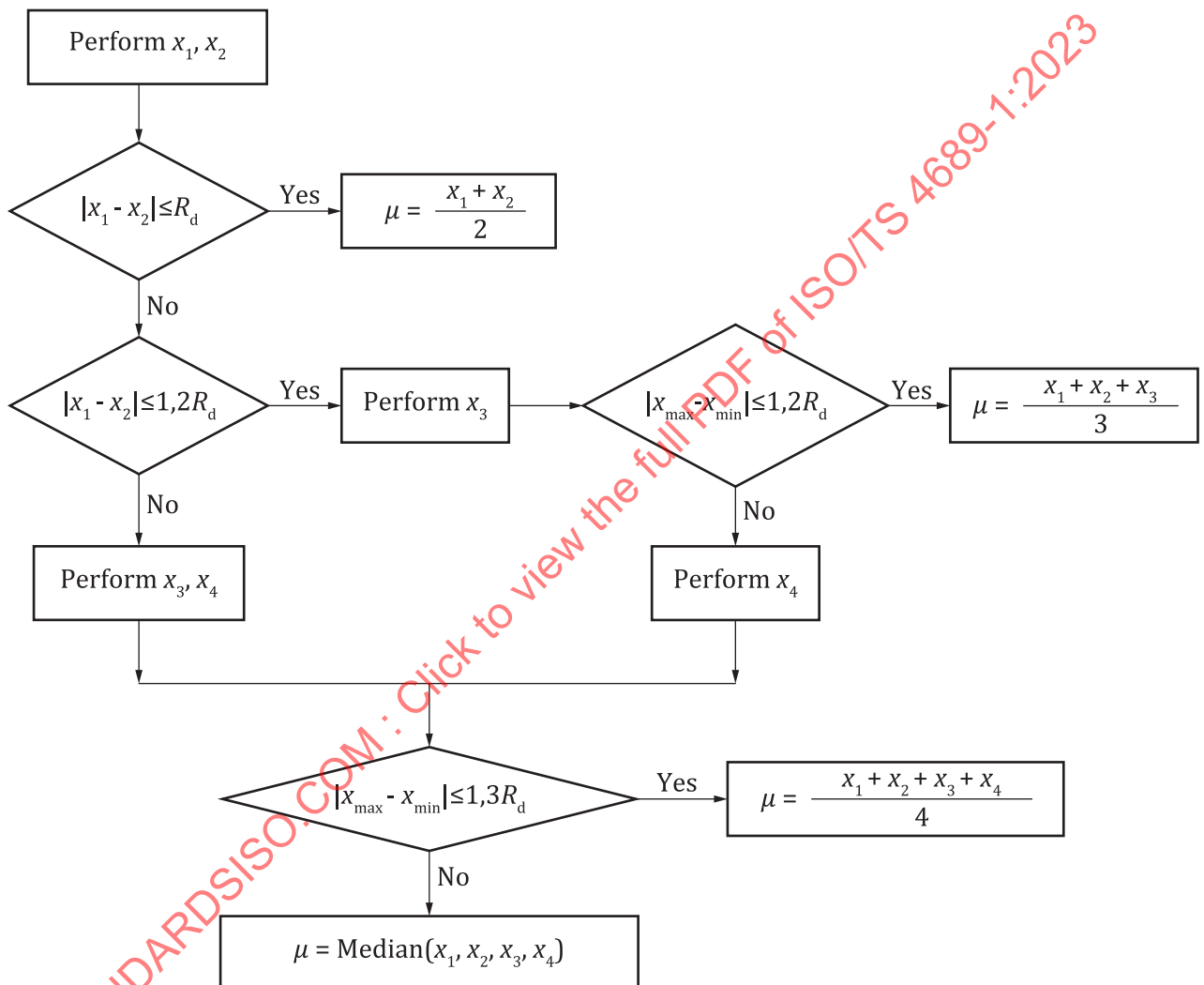
The test report shall include the following information:

- a) a reference to this document, i.e. ISO 4689-1:2023;
- 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 document, or in the International Standards to which reference is made, which can have influenced the result, either for the test sample or the CRM(s).

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Annex A (normative)

Flow sheet of the procedure for the acceptance of analytical values for test samples



Key
 R_d is as defined in [9.2.1](#).

Figure A.1 — Flow sheet of the procedure for the acceptance of analytical values for test samples

Annex B (informative)

Derivation of repeatability and permissible tolerance equations

The regression formulae in [9.2.1](#) were derived from the results of interlaboratory analytical trials carried out in 2014/2015 on four iron ore samples, involving eight laboratories in China.

Graphical treatment of the precision data is given in [Annex C](#).

The test samples used are listed in [Table B.1](#).

NOTE The statistical analysis was performed in accordance with the principles embodied in ISO 5725-2.

Table B.1 — Sulfur contents of test samples

Sample	Sulfur content % (mass fraction)
02-34A	0,010
018-3	0,084
93-40	2,61
7402	3,92