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

**Part 2:  
Combustion/titration method**

*Minerais de fer — Dosage du soufre —*

*Partie 2: Méthode par combustion et titration*

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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 (see [www.iso.org/directives](http://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](http://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 the following URL: [Foreword - Supplementary information](#).

The committee responsible for this document is ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This second edition cancels and replaces the first edition (ISO 4689-2:2004), of which [4.4](#), [5.2](#), [8.2.4](#) and [Figure 1](#) have been technically revised.

ISO 4689 consists of the following parts, under the general title *Iron ores — Determination of sulfur content*:

- *Part 1: Barium sulfate gravimetric method*
- *Part 2: Combustion/titration method*
- *Part 3: Combustion/infrared method*

## Introduction

This part of ISO 4689 was originally published as ISO 4690:1986. Under a policy of rationalization of the numbering system used in ISO/TC 102, it has been decided to re-designate this document as ISO 4689-2. It was further decided to introduce a combustion/infrared method, numbered ISO 4689-3.

When next revised, ISO 4689:1986 will be re-designated as ISO 4689-1.

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# Iron ores — Determination of sulfur content —

## Part 2: Combustion/titration method

**WARNING** — This part of ISO 4689 may involve hazardous materials, operations, and equipment. This part of ISO 4689 does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this part of ISO 4689 to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

### 1 Scope

This part of ISO 4689 specifies a combustion/titration method for the determination of the sulfur content of iron ores.

This method is applicable to sulfur contents between 0,002 % (mass fraction) and 0,25 % (mass fraction) in natural iron ores, iron ore concentrates, and agglomerates, including sinter products. The results are not affected by the presence of fluoride.

### 2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385-1, *Laboratory glassware — Burettes — Part 1: General requirements*

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

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

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

ISO Guide 35, *Reference materials — General and statistical principles for certification*

### 3 Principle

The sample is mixed with tungsten(VI) oxide and heated at 1 200 °C in a resistance furnace, using nitrogen as a carrier gas.

The evolved sulfur dioxide is absorbed in dilute hydrochloric acid solution containing starch and potassium iodide, and the solution is titrated continuously during evolution with a standard volumetric solution of potassium iodate.

### 4 Reagents

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

**4.1 Magnesium perchlorate**,  $\text{Mg}(\text{ClO}_4)_2$ , anhydrous, free flowing, particle size 0,5 mm to 2 mm.

4.2 **Tungsten(VI) oxide**, ( $WO_3$ ).

4.3 **Tin(II) chloride**,  $SnCl_2 \cdot 2H_2O$ , particle size 0,5 mm to 2 mm.

4.4 **Sodium hydroxide coated silica**, particle size 0,5 mm to 2 mm.

4.5 **Hydrochloric acid**,  $\rho$ , 1,16 g/ml to 1,19 g/ml, diluted 1 + 66.

4.6 **Potassium iodide**, KI, 3 % (mass fraction) solution.

4.7 **Starch**, 2 % (mass fraction) solution.

Make a suspension of 2,0 g of starch in 10 ml of water, add to 50 ml of boiling water and stir. Cool, dilute to 100 ml and mix.

Prepare this solution immediately prior to use.

4.8 **Potassium iodate**,  $KIO_3$ , standard volumetric solution, 0,001 042 mol/l.

The potassium iodate should be previously dried for 2 h at 130 °C.

Weigh, to the nearest 0,000 2 g, 0,223 g of dried potassium iodate and dissolve in water. Cool, transfer to a 1 l volumetric flask, dilute to volume and mix.

1 ml of this standard volumetric solution is equivalent to 0,10 mg of sulfur.

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## 5 Apparatus

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Ordinary laboratory apparatus, including one-mark pipettes and one-mark volumetric flasks complying with the specifications of ISO 648 and ISO 1042 respectively, as well as the following. See [Figure 1](#).

5.1 **Nitrogen supply**.

5.2 **Drying tower**, containing sodium hydroxide coated silica ([4.4](#)) and magnesium perchlorate ([4.1](#)).

5.3 **Flowmeter**, graduated from 0 to 1 l/min.

5.4 **Resistance furnace**, capable of maintaining a temperature of  $1\ 200\ ^\circ\text{C} \pm 25\ ^\circ\text{C}$ .

5.5 **Refractory combustion tube**, capable of withstanding a temperature of  $1\ 200\ ^\circ\text{C} \pm 25\ ^\circ\text{C}$ .

5.6 **Refractory combustion boat**, with loose-fitting lid, or a suitable refractory combustion boat capable of accommodating a porous cartridge, as shown in [Figure 2](#) a) or b) respectively. The following dimensions can be used as guidelines.

Combustion boat		Cartridge	
Length	80 mm	Length	50 mm
Width	13 mm	Internal diameter	15 mm
Depth	9 mm		

5.7 **Tin(II) chloride absorption tube**, of narrow glass tubing containing approximately of solid tin(II) chloride ([4.3](#)), suitably plugged with inert wool to prevent the reagent being blown into the absorption



vessel. A U-tube is suitable. Where necessary, this is inserted in the train at the exit of the combustion tube at point X in [Figure 1](#).

If the sample is known or thought to contain chloride, e.g. in the form of sodium chloride, chlorapatite, or scapolite, the chlorine formed during combustion of the sample should be removed by passing the gas stream through solid tin(II) chloride in a suitable tube or vessel ([5.7](#)) prior to absorption and titration. If numerous samples having chloride contents  $>1$  (mass fraction) are to be analysed, it is advisable to determine the absorption capacity of the tin(II) chloride in order to be able to judge the most suitable interval for reagent replacement. In such cases, a larger absorption vessel may be preferred.

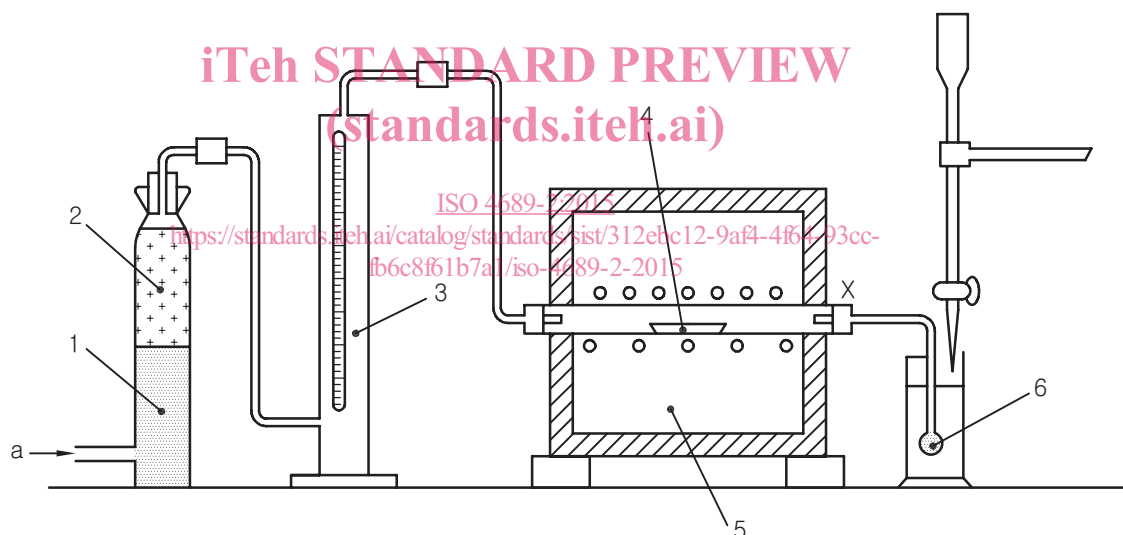
The tin(II) chloride absorption tube should also be fitted if the chloride content of the test sample is unknown.

**5.8 Cylinder**, 100 ml, tall form, to hold the absorbing solution.

**5.9 Bubbler**, multi-hole, to reach to the bottom of the cylinder ([5.8](#)).

**5.10 Burette**, conforming to ISO 385-1, graduated in divisions of 0,05 ml.

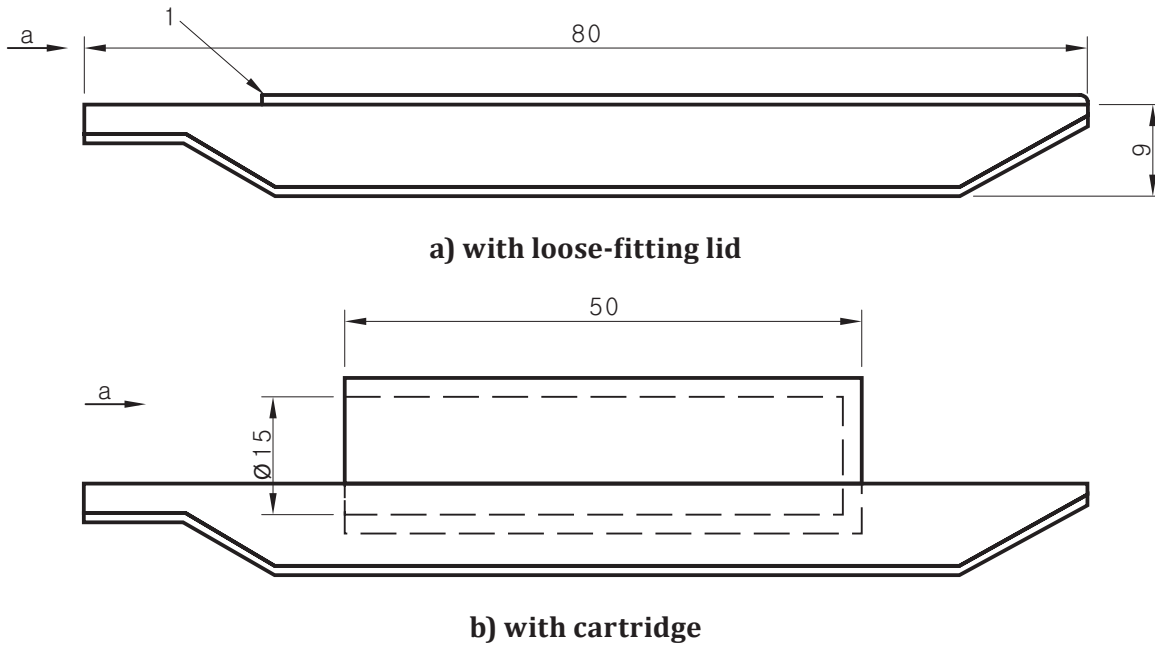
For determination of low sulfur contents [ $<0,005$  % (mass fraction)], alternative titration devices such as a piston burette or a suitable micro-syringe capable of delivering small, precise aliquots of titrant may be used.



#### Key

- 1 sodium hydroxide coated silica
- 2 anhydrous magnesium perchlorate
- 3 flowmeter
- 4 combustion boat
- 5 resistance furnace
- 6 multihole bubbler
- a Nitrogen.

**Figure 1 — Combustion apparatus**



- Key**
- 1 loose-fitting lid
  - a Gas flow.

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Figure 2 — Combustion boat

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**6 Sampling and samples**

**6.1 Laboratory sample**

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

**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 entire contents of the container. Dry the test sample at  $105 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$  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 is carried out either by the same operator at a different time or by a different operator, including in either case, appropriate recalibration.

## 7.2 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, approximately the mass of the predried test sample specified in [Table 1](#).

For 1 g of sample, the combustion boat or cartridge should accommodate the increased bulk of sample plus tungsten(VI) oxide.

The test portion should be taken and weighed quickly to avoid re-absorption of moisture.

**Table 1 — Mass of test portion**

Sulfur content % (mass fraction)	Mass g
0,002 to 0,100	1,0
0,100 to 0,25	0,5

## 7.3 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](#).

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 will become necessary.

Where 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.

Where 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.

## 7.4 Determination

Place the test portion in a small weighing bottle containing 1,0 g of tungsten(VI) oxide ([4.2](#)) and mix thoroughly.

Transfer 80 ml of hydrochloric acid ([4.5](#)), 1 ml of potassium iodide solution ([4.6](#)), and 1 ml of starch solution ([4.7](#)) to the absorption cylinder ([5.8](#)) and place this in position at the end of the combustion train. Adjust the nitrogen flowrate to between 150 ml/min and 200 ml/min and titrate the absorbing solution with potassium iodate solution ([4.8](#)) until the colour of the solution is pale blue. Normally, a few drops of the potassium iodate solution ([4.8](#)) are sufficient.

Transfer the mixture of test portion and tungsten(VI) oxide to a refractory combustion boat fitted with a loose-fitting lid ([5.6](#)) and insert into the hot zone of the furnace ([5.4](#)) at 1 200 °C.

Alternatively, the mixture of test portion and tungsten(VI) oxide can be placed inside a porous cartridge, which is placed in a refractory combustion boat [see [Figure 2 b](#)].

Leave the boat standing in the hot zone for approximately 1 min and then pass nitrogen at a flowrate of 150 ml/min to 200 ml/min through the furnace. With the nitrogen flowing continuously, titrate the absorbing solution with potassium iodate solution ([4.8](#)), keeping the solution just blue in colour.

Titration should be carried out during the evolution of sulfur gases in order to prevent sulfur dioxide being swept out of solution by the flow of carrier gas. It may be necessary to reduce the gas flow to 150 ml/min when titrating samples of high sulfur content. A faster flow rate of 300 ml/min may be necessary when analysing samples of very low sulfur content, to ensure complete transfer of evolved sulfur gases into the absorbing solution.