INTERNATIONAL STANDARD

# ISO 2597-2

Third edition
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# Iron ores — Determination of total iron content —

## Part 2: Titrimetric methods after titanium(III) chloride reduction

*Minerais de fer — Dosage du fer total —*

*Partie 2: Méthodes titrimétriques après réduction au chlorure de titane(III)*



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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).

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 of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (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 ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This third edition cancels and replaces the second edition (ISO 2597-2:2015), which has been technically revised with the following changes:

— the Scope has been reworded to describe the second method using perchloric acid;

— a terms and definitions clause has been added as Clause 3 and the subsequent clauses have been renumbered accordingly;

— in 4.2 (previously 3.2) a description of the second method using perchloric acid has been added;

— in the second paragraph of 4.1.1 (previously 3.1.1), “water more hydrochloric acid” has been replaced with “water and hydrochloric acid”;

— in 5.19 (previously 4.19), “5,58” has been replaced with “7,978 1”;

— Clause 5, potassium disulfate ($K_2S_2O_7$) has been added as a reagent (5.23);

— in the sixth paragraph of 8.5.1.1 (previously 7.5.1.1), “4.20” has been replaced with “5.23”;

— in the description for $V_1$ in 9.1 (previously 8.1), “4.13” has been replaced with “5.20”;

— in 9.2.4 (previously 8.2.4), Formula (8) and the relevant descriptions have been modified to harmonize this subclause across all International Standards for which ISO/TC 102/SC 2 is responsible.

A list of all parts in the ISO 2597 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.

 

# Iron ores — Determination of total iron content —

## Part 2:
## Titrimetric methods after titanium(III) chloride reduction

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

## 1 Scope

This document specifies two titrimetric methods, free from mercury pollution, for the determination of total iron content in iron ores, using potassium dichromate as titrant after reduction of the iron(III) by tin(II) chloride and titanium(III) chloride. The excess reductant is then oxidized by either dilute potassium dichromate (Method 1) or perchloric acid (Method 2).

Both methods are applicable to a concentration range of 30 % mass fraction to 72 % mass fraction of iron 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 385, *Laboratory glassware — Burettes*

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

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

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 80000-1:2009, *Quantities and units — Part 1: General*

## 3 Terms and definitions

No terms and definitions are listed in this document.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

# 4 Principle

## 4.1 Decomposition of the test portion

### 4.1.1 Acid decomposition

For samples containing not more than 0,05 % mass fraction of vanadium, the test portion is treated with hydrochloric acid in the presence of tin chloride.

The residue is filtered, ignited and treated with hydrofluoric and sulfuric acids. The mixture is fused with potassium disulfate and the cold melt is dissolved in water and hydrochloric acid and combined with the main iron solution, which is treated with potassium permanganate and evaporated.

### 4.1.2 Fusion-filtration

For samples containing more than 0,05 % mass fraction of vanadium, the test portion is fused with a mixture of fluxes, the cold melt is leached with water and the precipitate is filtered, washed in sodium hydroxide solution, dissolved in hydrochloric acid and evaporated.

## 4.2 Titration of iron

The major portion of the iron(III) is reduced by tin(II) chloride and the remainder of the iron(III) is reduced by titanium(III) chloride. The excess reductant is oxidized with either dilute potassium dichromate solution (Method 1) or dilute perchloric acid (Method 2). The reduced iron is titrated with potassium dichromate solution using the sodium diphenylaminesulfonate indicator.



# 5 Reagents

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

**5.1 Hydrochloric acid**, $\rho$ 1,16 g/ml to 1,19 g/ml. (Methods 1 and 2.)

**5.2 Hydrochloric acid**, $\rho$ 1,16 g/ml to 1,19 g/ml, diluted 1 + 1. (Methods 1 and 2.)

**5.3 Hydrochloric acid**, $\rho$ 1,16 g/ml to 1,19 g/ml, diluted 1 + 12. (Methods 1 and 2.)

**5.4 Hydrochloric acid**, $\rho$ 1,16 g/ml to 1,19 g/ml, diluted 2 + 100. (Methods 1 and 2.)

**5.5 Hydrofluoric acid**, 40 % mass fraction ($\rho$ 1,13 g/ml) or 48 % mass fraction ($\rho$ 1,19 g/ml). (Methods 1 and 2.)

**5.6 Sulfuric acid**, $\rho$ 1,84 g/ml. (Methods 1 and 2.)

**5.7 Sulfuric acid**, $\rho$ 1,84 g/ml, diluted 1 + 1, carefully pour 1 volume of reagent 5.6 into one volume of cold water. (Methods 1 and 2.)

**5.8 Orthophosphoric acid**, $\rho$ 1,7 g/ml. (Methods 1 and 2.)

**5.9 Perchloric acid**, 72 % mass fraction ($\rho$ 1,7 g/ml), diluted 1 + 1. (Method 2.)

**5.10 Sulfuric acid–orthophosphoric acid mixture**, pour 150 ml of orthophosphoric acid (5.8) into about 400 ml of water while stirring, add 150 ml of sulfuric acid (5.6), cool in a water bath, dilute with water to 1 l and mix well. (Methods 1 and 2.)

**5.11 Sodium hydroxide (NaOH)**, solution, 20 g/l. (Methods 1 and 2.)

**5.12 Hydrogen peroxide ($H_2O_2$)**, 30 % by volume solution. (Methods 1 and 2.)

**5.13 Hydrogen peroxide ($H_2O_2$)**, 30 % by volume solution, diluted 1 + 9. (Method 1.)

**5.14 Tin(II) chloride solution**, 100 g/l, dissolve 100 g of crystalline tin(II) chloride ($SnCl_2 \cdot 2H_2O$) in 200 ml of hydrochloric acid (5.1) by heating the solution in a water bath. Cool the solution and dilute with water to 1 l. This solution should be stored in a brown glass bottle with a small quantity of granular tin metal. (Methods 1 and 2.)

**5.15 Potassium permanganate ($KMnO_4$) solution**, 25 g/l. (Methods 1 and 2.)

**5.16 Potassium dichromate ($K_2Cr_2O_7$) solution**, 1 g/l. (Method 1.)

**5.17 Titanium(III) chloride ($TiCl_3$) solution**, 20 g/l, dilute one volume of titanium(III) chloride solution (about 20 % $TiCl_3$) with nine volumes of hydrochloric acid (5.2). (Methods 1 and 2.)

Alternatively, dissolve 1,3 g of titanium sponge in about 40 ml of hydrochloric acid (5.1) in a covered beaker by heating in a water bath. Cool the solution and dilute with water to 200 ml. Prepare fresh solution as needed.

**5.18 Flux mixture**, mix one portion of anhydrous sodium carbonate ($Na_2CO_3$) and two portions of sodium peroxide ($Na_2O_2$). (Methods 1 and 2.)

**5.19 Iron standard solution**, 0,1 mol/l. Transfer 7,978 1 g of iron(III) oxide (purity greater than 99,9 % mass fraction) to a 500 ml beaker flask and place a small filter funnel in the neck. Add 75 ml of hydrochloric acid (5.2) in small increments and heat until dissolved. (Methods 1 and 2.)

Cool, transfer to a 1 000 ml volumetric flask and mix well.

Instead of iron oxide, the use of pure metallic iron with a suitable oxidant is permitted.

To prepare the solution 0,1 mol/l, transfer 5,58 g of pure iron (purity greater than 99,9 % mass fraction) to a 500 ml Erlenmeyer flask and place a small filter funnel in the neck. Add 75 ml of hydrochloric acid (5.2) in small increments and heat until dissolved. Cool and oxidize with 5 ml of hydrogen peroxide (5.13) added in small portions. Heat to boiling and boil to decompose the excess hydrogen peroxide and to expel chlorine. Cool, transfer to a 1 000 ml volumetric flask and mix well. (Methods 1 and 2.)

1,00 ml of this solution is equivalent to 1,00 ml of the standard potassium dichromate solution (5.20).

**5.20 Potassium dichromate (99,9 % minimum purity), standard solution**, 0,016 67 mol/l, pulverize about 6 g of potassium dichromate reagent in an agate mortar, dry at 140 °C to 150 °C for 2 h, and cool to room temperature in a desiccator. (Methods 1 and 2.)

Transfer 4,903 g of this material to a 300 ml beaker, dissolve in about 100 ml of water, transfer quantitatively to a 1 000 ml volumetric flask, make up to volume with water after cooling to 20 °C and mix well. Record the temperature at which this dilution was made (20 °C) on the stock bottle. Measure the temperature at each use to correct the volume of titrant used.

The volumetric flask should previously be calibrated by weighing the mass of water contained at 20 °C and converting to volume.

Water used for preparation should previously be equilibrated at room temperature.

A calibrated mercury thermometer, graduated in 0,1 °C divisions and having a marked dipping line, should be used. Take a sufficient volume of standard solution for dipping the thermometer and transfer to a suitable beaker. Measure the temperature of the solution to the nearest 0,1 °C, after dipping for more than 60 s.

**5.21 Indigo carmine [5,5'-disulfonic acid disodium salt ($Cl_6H_8O_8N_2S_2Na_2$)] solution**, 0,1 g/100 ml, dissolve 0,1 g of indigo carmine in a cold mixture of 50 ml sulfuric acid (5.7) and 50 ml of water. (Method 1.)

**5.22 Sodium diphenylaminesulfonate indicator solution**, 0,2 g/100 ml, dissolve 0,2 g of sodium diphenylaminesulfonate ($C_6H_5NHC_6H_4SO_3Na$) in a small volume of water and dilute to 100 ml. (Method 1 and Method 2.)

Store the solution in a brown glass bottle.

**5.23 Potassium disulfate ($K_2S_2O_7$)**, fine powder. (Methods 1 and 2.)

# 6 Apparatus

The pipette and volumetric flask specified shall be in accordance with ISO 648 and ISO 1042, respectively.

Ordinary laboratory apparatus and the following.

**6.1 Alumina, zirconium or vitreous carbon crucible**, capacity 25 ml to 30 ml, crucibles should be cleaned before use to avoid contamination with iron.



**6.2 Burette**, class A, in accordance with ISO 385.



**6.3 Weighing bottle**, of approximate volume 10 ml and approximate mass 6 g.

**6.4 Platinum crucible**, capacity 25 ml to 30 ml and having a lid.

**6.5 Weighing spatula**, of a non-magnetic material or demagnetized stainless steel.

**6.6 Muffle furnace**, suitable for operation in the range 500 °C to 800 °C.

# 7 Sampling and samples

## 7.1 Laboratory sample

For analysis, use a laboratory sample of 100 µm nominal top size that 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 160 µm nominal top size.

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

If the determination of total iron relates to a reducibility test, prepare the laboratory sample by crushing and pulverizing, to 100 µm nominal top size, the whole of one of the reducibility test portions which has been reserved for chemical analysis. In the case of ores having significant contents of combined water or oxidizable compounds, use a 160 µm nominal top size.

 

## 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. Prepare test portions in accordance with the Japanese weighing method given in Annex B.

# 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 (see 7.2).



NOTE The expression “independently” means that the second and any subsequent result(s) is (are) not affected by the previous result(s). For this particular analytical method, this condition implies that the repetition of the procedure is to be carried out either by the same operator at a different time, or by a different operator, including appropriate recalibration in either case.

## 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 test sample of the certified reference material shall be prepared in the manner appropriate to the type of ore involved (see 7.2 and NOTE 1 below).

NOTE 1 The certified reference material is of the same type as the sample to be analysed and the properties of the two materials are sufficiently similar to ensure that in either case no significant changes in the analytical procedure will be 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 used 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.

NOTE 2 The certified reference material is used only to validate the performance of the analytical procedure and expressly not to standardize the potassium dichromate solution.

## 8.3 Determination of hygroscopic moisture content

Where the ore type conforms to the specifications of 7.2.2, determine the hygroscopic moisture content in accordance with ISO 2596, simultaneously with the taking of the test portion (see 8.4) for the determination of the iron content.

## 8.4 Test portion

Taking several increments, weigh to the nearest 0,000 2 g, approximately 0,4 g of the test sample (see 7.2), using a non-magnetic spatula (6.5).

For samples having an iron content higher than 68 % mass fraction, weigh approximately 0,38 g.

Where the ore type is outside the scope of 7.2.2, transfer the portion to a weighing bottle and determine the mass of the test portion to the nearest 0,000 2 g in accordance with the Japanese weighing method given in Annex B.

## 8.5 Determination

### 8.5.1 Decomposition of the test portion

#### 8.5.1.1 Acid decomposition (for samples containing ≤ 0,05 % mass fraction vanadium)

Place the test portion (see 8.4) in a dried 300 ml or 400 ml beaker, project some water on the inside wall of the beaker and suspend the test portion in water while swirling.



Add 20 ml of hydrochloric acid (5.1) and 10 to 20 drops tin(II) chloride solution (5.14), cover the beaker with a watch glass, heat the solution gently at about 80 °C for 1 h and continue heating without boiling at a higher temperature for about 10 min to decompose the portion.



Normally, the test portion is completely decomposed after 50 min. In case of difficulty in decomposing the test portion, add some new drops of tin(II) chloride solution (5.14) and keep the test portion in a hotplate. The total decomposition time cannot exceed 90 min.

NOTE Boiling is avoided to prevent volatilization loss of iron(Ill) chloride.

Remove the beaker from the source of heat, wash the watch glass in a jet of water, and dilute to 50 ml with warm water. Filter the insoluble residue on a filter paper. Scrub the remainder of the residue on the beaker wall using a policeman and transfer the remainder on to the filter paper with a small volume of warm hydrochloric acid (5.4). Wash the residue with warm hydrochloric acid (5.4) until the yellow colour of iron(Ill) chloride is no longer observed, and then wash in warm water six to eight times. Collect the filtrate and washings in a 500 ml or 600 ml beaker. Evaporate this main solution without boiling to about 70 ml (see NOTE above).

Place the filter paper and residue in a platinum crucible (6.4), dry then char the paper and finally ignite at 750 °C to 800 °C for 1 h. Allow the crucible to cool, moisten the residue with several drops of sulfuric acid (5.7), add about 5 ml of hydrofluoric acid (5.5), and heat gently to remove silica and sulfuric acid (until white fumes are no longer observed).

After cooling, add 3 g of potassium disulfate (5.23) to the crucible, cover the crucible with a lid, heat gently at first then strongly (dull red) until a clear melt is obtained. Cool, place the crucible and lid in a 250 ml or 300 ml beaker, add about 30 ml of warm water and 5 ml of hydrochloric acid (5.1) and warm to dissolve the melt. Remove the crucible and lid, wash with a small volume of warm water. Combine this solution with the main solution.

Add 5 drops of potassium permanganate solution (5.15), heat the solution to just below the boiling point and maintain at this temperature for 5 min to oxidize any arsenic and organic matter. Evaporate without boiling to about 70 ml, and follow the procedure specified in 8.5.2 (see NOTE above).

 

#### 8.5.1.2 Fusion — Filtration (for samples containing more than 0,05 % mass fraction of vanadium and/or samples not being decomposed by the acid-decomposition)

Place the test portion in an alumina, zirconium or vitreous carbon crucible (6.1), add about 4 g of flux mixture (5.18) and mix thoroughly. Place in a muffle furnace (6.6) at 500 °C ± 10 °C for 30 min (see NOTE 1). Remove from the furnace, heat over a burner to melt the sinter within 30 s and, swirling gently, continue heating allowing a total heating time of 2 min.

NOTE 1 Alternatively, a burner can be used instead of the furnace. In this case, fusion of the test portion is carried out as follows: heat the crucible over a burner, first at low temperature until the contents in the crucible begin to melt, then at high temperature (dull red) while swirling until a clear melt is obtained.

Cool, place the crucible in a 300 ml or 400 ml beaker, add about 100 ml of warm water and heat for a few minutes to dissolve the melt. Remove the crucible, wash and add the washings to the solution. Reserve the crucible. Cool the solution and filter through a close-textured filter paper. Wash the filter twice in sodium hydroxide solution (5.11) and discard the filtrate and washings.

NOTE 2 A filter paper, which is used for a fine precipitate such as barium sulfate, is more suitable than a close-textured filter paper.

Transfer the precipitate on the filter to the original beaker by washing in a jet of water, add 10 ml of hydrochloric acid (5.1), and warm to dissolve the precipitate. Place a 500 ml or 600 ml beaker under the funnel, pour the solution through the original filter paper to dissolve the remaining precipitate. Wash the filter three times in warm hydrochloric acid (5.3), and several times in warm hydrochloric acid (5.4). Finally wash with warm water until the washings are no longer acid. Combine the solution and washings in the 500 ml or 600 ml beaker. Place the reserved crucible in the beaker to dissolve any retained iron, remove the crucible, wash and add the washings to the solution. Evaporate this solution without boiling (see NOTE in 8.5.1.1) to about 70 ml and follow the procedure specified in 8.5.2.



### 8.5.2 Reduction

#### 8.5.2.1 Method 1: Oxidation of excess titanium(III) chloride with dilute dichromate solution using indigo carmine indicator solution

Maintain the solution obtained in 8.5.1 at 90 °C to 95 °C and wash the cover and inside wall of the beaker in a small amount of hot water. Immediately add tin(II) chloride solution (5.14) dropwise to reduce iron(III), while swirling the solution in the beaker until only a faint yellow tint of the iron(III) chloride solution remains.

It is essential that some iron(III) remain unreduced. If the solution is made colourless by the excessive addition of tin(II) chloride solution, add hydrogen peroxide (5.13) or potassium permanganate solution (5.15) dropwise until the solution changes to a faint yellow tint.

NOTE It is convenient to use dilute potassium dichromate solution as a reference solution for establishing the desired slight yellow tint of the iron solution. The solution is prepared by diluting 5 ml of potassium dichromate standard solution (5.20) to 100 ml with water.

Wash the inside wall of the beaker using a small amount of hot water. Add 3 to 4 drops of indigo carmine solution (5.21) as indicator, then titanium(III) chloride solution (5.17) drop by drop, while swirling the solution, until it turns blue then colourless. Add 2 to 3 drops in excess. Immediately add dilute potassium dichromate solution (5.16) drop by drop, to oxidize the excess of titanium(III) chloride, until the solution changes to a persistent blue colour which lasts for 5 s.

Place in a cooling bath for several minutes, then dilute the solution to about 300 ml using cold water. Follow the procedure specified in 8.5.2.3.

#### 8.5.2.2 Method 2: Oxidation of excess titanium(III) chloride solution with perchloric acid

Maintain the solution obtained in 8.5.1 at 90 °C to 95 °C and wash the cover and inside wall of the beaker with a small amount of hot water. Immediately add tin(II) chloride solution (5.14) dropwise to

 