
**Iron ores — Determination of total
iron content —**

**Part 4:
Potentiometric titration method**

Minerais de fer — Dosage du fer total —

Partie 4: Méthode potentiométrique de 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).

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This document was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

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 4: Potentiometric titration method

WARNING — This document can 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 and determine the applicability of regulatory limitations prior to use.

1 Scope

This document specifies a potentiometric titration method for the determination of total iron content of 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 potassium dichromate solution.

This method is applicable to total iron contents between a mass fraction of 29,04 % and a mass fraction of 72,02 % in natural iron ores and 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 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 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 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

For samples containing not more than a mass fraction of 0,1 % of vanadium, copper or manganese, the test portion is treated with hydrochloric acid in the presence of tin chloride and 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 neutralized with ammonia solution. The precipitate is filtered, washed with water, dissolved with hydrochloric acid and combined with

the main iron solution, which is treated with potassium permanganate and evaporated. Finally, after the combined solution is treated with correlative reagents, the total iron in solution is titrated by a potentiometric titrator.

5 Reagents

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

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

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

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

5.4 Hydrofluoric acid, a mass fraction of 40 % (ρ 1,13 g/ml) or a mass fraction of 48 % (ρ 1,19 g/ml).

5.5 Sulfuric acid, ρ 1,84 g/ml.

5.6 Sulfuric acid, ρ 1,84 g/ml, diluted 1 + 1.

Carefully pour 1 volume of reagent (5.5) into 1 volume of cold water.

5.7 Orthophosphoric acid, ρ 1,7 g/ml.

5.8 Sulfuric acid-orthophosphoric acid mixture.

Pour 150 ml of orthophosphoric acid (5.7) into about 400 ml of water while stirring, add 150 ml of sulfuric acid (5.5), cool in a water bath, dilute with water to 1 l and mix well.

5.9 Ammonia solution, a mass fraction of 28 % (ρ 0,90 g/ml) to a mass fraction of 30 % (ρ 0,96 g/ml).

5.10 Hydrogen peroxide (H₂O₂), a volume fraction of 30 % solution.

5.11 Hydrogen peroxide (H₂O₂), a volume fraction of 30 % solution, diluted 1 + 9.

5.12 Tin(II) hydrochloric acid solution.

Dissolve 130 g of tin metal in about 500 ml of hydrochloric acid (5.1) and dilute with hydrochloric acid to 1 l. This solution should be stored in a brown glass bottle. Use supernatant liquid as needed.

5.13 Tin(II) chloride solution, 100 g/l.

Dissolve 100 g of crystalline tin(II) chloride (SnCl₂·2H₂O) 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.

5.14 Potassium permanganate (KMnO₄) solution, 25 g/l.

5.15 Potassium dichromate (K₂Cr₂O₇) solution, 1 g/l.

5.16 Titanium(III) chloride (TiCl₃) solution, 20 g/l.

Dilute one volume of titanium(III) chloride solution (about a volume fraction of 20 % TiCl₃) with nine volumes of hydrochloric acid (5.2). 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 solutions as needed.

5.17 Potassium disulfate (K₂S₂O₇), fine powder.**5.18 Iron, standard solution, 0,1 mol/l.**

Transfer 5,58 g of pure iron (purity greater than a mass fraction of 99,9 %) 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 (5.10) 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.

1,00 ml of this solution is equivalent to 1,00 ml of the standard potassium dichromate solution (5.19).

5.19 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.

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 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.

5.20 Indigo carmine [indigo-5,5'-disulfonic acid disodium salt (C₁₆H₈O₈N₂S₂Na₂)] solution, 0,1 g/100 ml.

Dissolve 0,1 g of indigo carmine in a cold mixture of 50 ml sulfuric acid (5.6) and 50 ml of water.

6 Apparatus

The pipette and volumetric flask specified shall conform to ISO 648 and ISO 1042, respectively.

Use ordinary laboratory apparatus and the following.

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

6.2 Platinum crucible with a lid, capacity 25 ml to 30 ml and having a lid.

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

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

6.5 Platinum electrodes, either as a pair or as a dual platinum electrode.

6.6 Magnetic stirrers and rotators or propeller rod stirrer, of chemically inert material and variable speed.

6.7 Amperometric titrator, suitable for volumetric analysis, equipped with an ammeter (0,50 μ A) or an equivalent means for the electrometric indication of the end-point, equipped with a X-Y graph plotter.

6.8 Burettes, of suitable capacity (25 ml to 50 ml), conforming to class A specifications (or equivalent), possessing preferably brown glass reservoir bottle and electro-volumeter.

The burette should be vented solely by an anhydrous atmosphere of suitable capacity. Fillers should not be pressurized through the lower inlet of the burette.

6.9 Titration cells, preferably, brown glass vessels of 400 ml to 500 ml capacity. The entries for the platinum electrodes should preferably be near the cell walls, while the burette tip should preferably be centred to ensure rapid distribution of the added reagent.

NOTE A suitable titration cell is shown diagrammatically in [Annex B](#) and suitable platinum electrodes are shown diagrammatically in [Annex C](#).

7 Sampling and samples

7.1 Laboratory sample

For analysis, use a laboratory sample of 160 μ m nominal top 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 $\leq 160 \mu\text{m}$.

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 less than 160 μ m particle 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 particle size of less than 160 μ m.

7.2 Preparation of test samples

7.2.1 General

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

7.2.2 Method specified in ISO 7764

This method is not applicable to the following type of ores:

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

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a way that it is representative of the whole contents of the container.

7.2.3 Method specified in ISO 2596

This method is applicable to all type of ores. Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a way that it is representative of the whole contents of the container. Bring the test sample into air-equilibrium with the laboratory atmosphere in accordance with ISO 2596.

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 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 appropriate recalibration in either case.

8.2 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 ([6.3](#)).

8.3 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 parallel with the analysis of the ore sample(s) under the same conditions. A test sample of the certified reference material shall be prepared as specified in [7.2](#).

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.

The certified reference material should be same type of ore 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.

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

8.4 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 [8.2](#)) for the determination of the iron content.

8.5 Determination

8.5.1 Decomposition of the test portion

Place the test portion (see [8.2](#)) in a dried 300 ml or 400 ml beaker, project about 10 ml of 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 drops of tin(II) hydrochloric acid solution ([5.12](#)), 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.

Boiling should be avoided to prevent volatilization loss of iron(III) chloride.

Remove the beaker from the source of heat, wash the watch glass with a jet of water, and dilute to 50 ml with warm water. Filter the insoluble residue on a close-textured filter paper. Scrub the remainder of the residue on the beaker wall, and transfer the remainder onto the filter paper with a small volume of warm hydrochloric acid (5.3). Wash the residue with warm hydrochloric acid (5.3) until the yellow colour of iron(III) chloride is no longer observed, and then wash with 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).

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

Place the filter paper and residue in a platinum crucible (6.2), dry, char the paper and finally ignite at 750 °C to 800 °C for 1 h by use of a muffle furnace (6.4). Allow the crucible to cool, moisten the residue with several drops of sulfuric acid (5.6), add about 5 ml of hydrofluoric acid (5.4), and heat gently to remove silica and sulfuric acid (until white fumes are no longer observed).

After cooling, add about 3 g of potassium disulfate (5.17) 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 100 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, and add the washings to the solution. Adjust this solution to slight alkalinity by the incremental addition of ammonia solution (5.9). Heat the solution to boil, continue the boiling for a few minutes and remove from the source of heat.

When the precipitate has settled, filter the precipitate of iron hydroxide on a rapid filter paper, and wash with warm water six to eight times. Discard the filtrate and washings.

Place the beaker (without the remaining filtrate and washings) under the funnel and dissolve the precipitate on the filter by pouring over it about 10 ml of hot hydrochloric acid (5.2). Wash the filter first several times with warm hydrochloric acid (5.3), then with warm water until the washings are no longer acid. Collect the filtrate and washings in the beaker and dissolve the remainder of the precipitate on the beaker wall. Combine this solution with the main solution.

Add 5 drops of potassium permanganate solution (5.14), 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 8.5.2.

8.5.2 Reduction

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 (5.13) 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. Follow the procedure specified in 8.5.3.

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 (5.11) dropwise until the solution changes to a faint yellow tint. 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 (5.19) to 100 ml with water.

Wash the inside wall of the beaker with a small amount of hot water. Add 3 to 4 drops of indigo carmine solution (5.20) as indicator, then titanium(III) chloride solution (5.16) 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 (5.15) drop by drop, to oxidize the excess of titanium(III) chloride, until the solution changes to a persistent blue colour that lasts for 5 s.

The temperature of the solution at this time should be greater than 70 °C. If the temperature is 60 °C to 70 °C, permanence of the blue colour should be extended to 15 s.

Place in a cooling bath for several minutes, then dilute the solution to about 300 ml with cold water. Follow the procedure specified in [8.5.3](#).

For samples containing not more than a mass fraction of 0,02 % of copper, a cooling bath may not be used.

8.5.3 Titration

Add 30 ml of sulfuric acid-orthophosphoric acid mixture ([5.8](#)) in the cold solution obtained from [8.5.2](#). Then titrate with the potassium dichromate standard solution ([5.19](#)) using the potentiometric titrator, while stirring. During the titration, the graph plotter can plot a titration curve corresponding to the volume of potassium dichromate standard solution and the value of electric potential.

Titrate and make the titration curve produce a jump. Then continue to titrate with the potassium dichromate standard solution ([5.19](#)) until the titration curve becomes flat. The end point is reached.

NOTE 1 The titration curve can produce only one jump.

NOTE 2 The titration curve can transform into a first derivative curve; the peak value of the first derivative curve is the end point of titration. The first derivative curve can transform into a second derivative curve; the cross point between line of two peaks and abscissa is the end point of titration also (see [Figure 1](#)). For a sample of software for derivative transform, see [Annex E](#).

The ambient temperature of the potassium dichromate solution should be noted. If this differs by more than 1 °C from the temperature at which it was prepared (20 °C), make the appropriate volumetric correction: 0,02 % relative for each 1 °C of difference. (For example, the titre should be decreased when the ambient temperature during the titration is higher than the temperature during preparation of the standard volumetric solution.) A correction for the temperature difference, if any, is essential.

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8.5.4 Blank test <https://standards.iteh.ai/catalog/standards/sist/3ef9741a-86c8-403e-9a5e-0d082d433132/iso-ts-2597-4-2019>

Determine the blank test value (see [8.3](#)) using the same amounts of all reagents and following all the steps of the procedure. Immediately before reduction (see [8.5.2](#)) with tin(II) chloride solution ([5.13](#)), add by means of a one-mark pipette, 10,00 ml of iron standard solution ([5.18](#)) and titrate the solution as described in [8.5.3](#). Record the volume of this titration as (V_0). The blank test value of this titration (V_2) is calculated as $V_2 = V_0 - 10,00$.

NOTE In the absence of iron or existence of a little, the titration curve does not sense the jump, and the end point is not reached. The addition of the iron solution is therefore necessary to promote titration curve response in the blank solution and thus allow a suitable correction for the blank in terms of its equivalent in millilitres of the potassium dichromate standard solution.

The 10 ml one-mark pipette should previously be calibrated by weighing the mass of water delivered and converting to volume.