
**Direct reduced iron and hot briquetted
iron — Determination of metallic iron —
Iron(III) chloride titrimetric method**

*Minerais de fer prééduits et fer briqueté à chaud — Dosage du fer
métallique — Méthode titrimétrique au chlorure de fer(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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of normative document:

- an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;
- an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

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.

ISO/TS 16878 was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This document is issued as a Technical Specification (according to the ISO/IEC Directives, Part 1, 3.1.1.1) as a "prospective standard for provisional application" in the field of direct reduced iron and hot briquetted iron because there is an urgent need for guidance on how standards in this field should be used to meet an identified need.

This document is not to be regarded as an "International Standard". It is proposed for provisional application so that information and experience of its use in practice may be gathered. Comments on the content of this document should be sent to Technical Committee ISO/TC 102, Subcommittee SC 2.

A review of this Technical Specification will be carried out not later than 3 years after its publication with the options of: extension for another 3 years; conversion into an International Standard; or withdrawal.

Introduction

The determination of metallic iron has in the past been carried out by a method using bromine-methanol (ISO 5416). Due to the undesirability of using bromine, a method using iron(III) chloride has been developed. This method is also more likely than ISO 5416 to determine all relevant metallic iron.

As insufficient participants took part in the inter-laboratory test programme conducted to derive precision values for this method, the method cannot be used for referee purposes.

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Direct reduced iron and hot briquetted iron — Determination of metallic iron — Iron(III) chloride titrimetric method

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

1 Scope

This Technical Specification specifies an iron(III) chloride titrimetric method for the determination of the mass fraction of metallic iron in hot briquetted iron (HBI) and direct reduced iron (DRI).

This method cannot be used for referee purposes.

NOTE The term 'metallic iron' means those forms of iron not bonded to oxygen and not present as pyrite; it includes iron present as cementite (Fe_3C).

2 Normative references

The following referenced documents are indispensable for the application 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 385-1, *Laboratory glassware — Burettes — Part 1: General requirements*

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

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

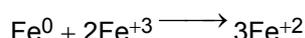
ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 11323, *Iron ore and direct reduced iron — Vocabulary*

ISO 10835, *Direct reduced iron and hot briquetted iron — Sampling and sample preparation*

3 Principle

Iron present in the oxidation state Fe^0 in the sample is oxidized to Fe^{+2} by the action of FeCl_3 according to the reaction:



The Fe^{+2} is titrated with a solution of potassium dichromate using sodium diphenylamine sulfonate as an indicator.

4 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11323 apply.

5 Reagents

All reagents used in this procedure are to be prepared using analytical reagent-grade chemicals, unless otherwise specified. The water used for preparing solutions shall comply with grade 2 of ISO 3696.

5.1 Iron(III) chloride hexahydrate

To a 2 000 ml container holding 600 ml of water, add 250 g of iron(III) chloride hexahydrate and agitate until it is completely dissolved. Dilute with water to a volume of 1 l.

5.2 Sulfuric acid (1,84 g/ml).

5.3 Phosphoric acid (1,7 g/ml).

5.4 Sulfuric acid (15 %)/phosphoric acid (15 %) mixture.

To a 3 000 ml beaker add 1 000 ml of water. Place the beaker in a cool place and add slowly, while stirring, 300 ml of phosphoric acid (5.3). Allow to cool. Add slowly, while stirring, 300 ml of sulfuric acid (5.2) and allow to cool. Dilute this mixture to 2 000 ml while stirring. Store the solution in a 2 000 ml high-density polyethylene bottle or equivalent container.

5.5 Sodium diphenylamine sulfonate

Dissolve 0,2 g of sodium diphenylamine sulfonate in 100 ml of water.

5.6 Standard potassium dichromate solution (0,1 N)

Dry potassium dichromate at 150 °C for 3 h. Remove potassium dichromate from the oven and cool to room temperature in a desiccator or over silica gel. Weigh 9,806 3 g of potassium dichromate [with a minimum purity of 99,9 % (mass fraction)] into a weighing scoop and transfer qualitatively to a 2 000 ml volumetric flask. Add 1 500 ml of water and dissolve potassium dichromate. When dissolution is complete, dilute to volume and mix thoroughly.

5.7 Inert gas, carbon dioxide (CO₂), argon (Ar) or nitrogen (N₂).

6 Apparatus

Use one-mark A-grade volumetric flasks complying with the specifications of ISO 648 and ISO 1042 respectively, and the following.

6.1 Analytical balance, capable of weighing to the nearest 0,1 mg.

6.2 Erlenmeyer flask, wide mouth (500 ml).

6.3 Stopper, to fit the Erlenmeyer flask, modified to allow nitrogen to pass through the beaker.

6.4 Hotplate, with a magnetic stirrer.

6.5 Magnetic stirrer bar.

6.6 Measuring cylinder, of an appropriate volume.

6.7 **A-grade burette**, Mark A, complying with the specifications of ISO 385-1.

6.8 **Non-magnetic spatula**.

6.9 **Graduated measuring cylinder**.

7 Sampling and sample preparation

For analysis, use a laboratory sample of minus 160 μm particle size which has been taken and prepared in accordance with ISO 10835. Metallized fines should be dried in an inert atmosphere and stored where possible in an airtight container flushed with a dry inert gas to prevent re-oxidation of the sample.

Thoroughly mix the laboratory sample using non-magnetic materials. Taking multiple increments with a non-magnetic spatula, extract a test sample of not less than 25 g in such a manner that it is representative of the whole of the contents of the container. When taking the test portion for the purpose of analysis, expose the sample to air for as short a time as practical. After weighing, immediately replace the remaining material in its container, flush with an inert gas and store.

8 Procedure

8.1 General

A schematic representation of the procedure is given in Annex A.

8.2 Number of determinations

All determinations should be carried out in duplicate. If necessary, make further determinations in accordance with the flowsheet given in Annex B.

8.3 Preparation of test portions

Accurately weigh $0,2000 \text{ g} \pm 0,0005 \text{ g}$ of the test sample. Record the sample mass (m).

8.4 Determination

Transfer the sample to a 500 ml Erlenmeyer flask and add sufficient water to the sample to cover the stirring bar (at least 15 ml).

Dispense 35 ml of ferric chloride solution (5.1) into the flask after first eliminating air from the flask by slushing with a controlled flow of inert gas. Control the temperature of the solution to below 80 °C.

Adjust the nitrogen flow to a gentle stream and fit the stopper to the flask.

WARNING — Adjust the nitrogen flow while the stopper is not fitted to the flask. Adjusting the nitrogen flow while the stopper is fitted to the beaker may cause the solution to be forced out of the beaker.

Heat the solution, while stirring, for 20 min.

Remove from the hotplate and cool in an ice bath or cold water, maintaining the nitrogen flow, until the solution is at room temperature.

Remove the stopper and add 30 ml of sulfuric acid/phosphoric acid solution (5.4), 200 ml of water and 1 ml of sodium diphenylamine sulfonate indication (5.5).

Titrate the solution with 0,1 N potassium dichromate (5.6) to the first permanent end-point (purple colour).

Perform a blank by following the procedure without the sample. Record the blank titration volume as V_0 .

NOTE A blank needs to be performed every time a new batch of ferric chloride solution is prepared.

9 Expression of results

Determine the mass fraction of metallic iron, w_{Fe} , expressed as a percentage, in the sample using Equation (1):

$$w_{\text{Fe}} = \frac{(V - V_0) \times N \times 5,585}{m \times 3} \quad (1)$$

where

V is the volume, in millilitres, of potassium dichromate consumed during the titration of the sample;

V_0 is the volume, in millilitres, of potassium dichromate consumed during the titration of the blank;

N is the normality of potassium dichromate solution;

m is the sample mass, in grams.

10 Number of tests and permissible tolerances

The test shall be carried out in duplicate. If the difference between the paired results is within the permissible range (R_d), the mean value of the results shall be reported as the final result to one decimal place. If the difference between the paired results exceeds R_d , further test(s) shall be carried out in accordance with the flowsheet given in Annex B.

The permissible range (R_d) for this method is 0,46.

NOTE The results obtained in a limited inter-laboratory test programme are contained in Annex C.

11 Test report

The test report shall include the following information:

- a) a reference to this International Standard, i.e. ISO/TS 16878:2010;
- b) the name and address of the testing laboratory;
- c) the date of the test report;
- d) details necessary for the identification of the sample;
- e) the results of the test, to one decimal place;
- f) any characteristics noticed during the test and any operations which may have had an influence on the results, e.g. drying time, titration end-point;
- g) all operations not specified by this International Standard or regarded as optional;

- h) a reference to verification activities;
- i) the names of the supervisor and person who performed the test.

12 Verification

Checks shall be carried out at regular intervals. The frequency of checking is a matter for each laboratory to determine. The following items shall be checked.

- a) Solutions should be standardized on a weekly basis.
- b) Regularly check nitrogen-pressure measurement devices.
- c) Regularly calibrate weighing devices.
- d) Appropriate records of all verification activities must be maintained.

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Annex A (informative)

Schematic representation of the procedure

Weigh 0,2 g and record exact mass m
Add to flask and stirring rod
Make sure balance is level and clean, use dry, clean flask and rod



Add 15 ml of water
Add 35 ml of FeCl₃



Place on hotplate under nitrogen
Solution temperature 80 °C, check nitrogen-pressure gauge



Cool in ice bath under nitrogen to room temperature



Add 30 ml of sulfuric/phosphoric acid
200 ml of demineralized water
1 ml of indicator



Titrate with 0,1 N
potassium dichromate
with a correctly standardized solution

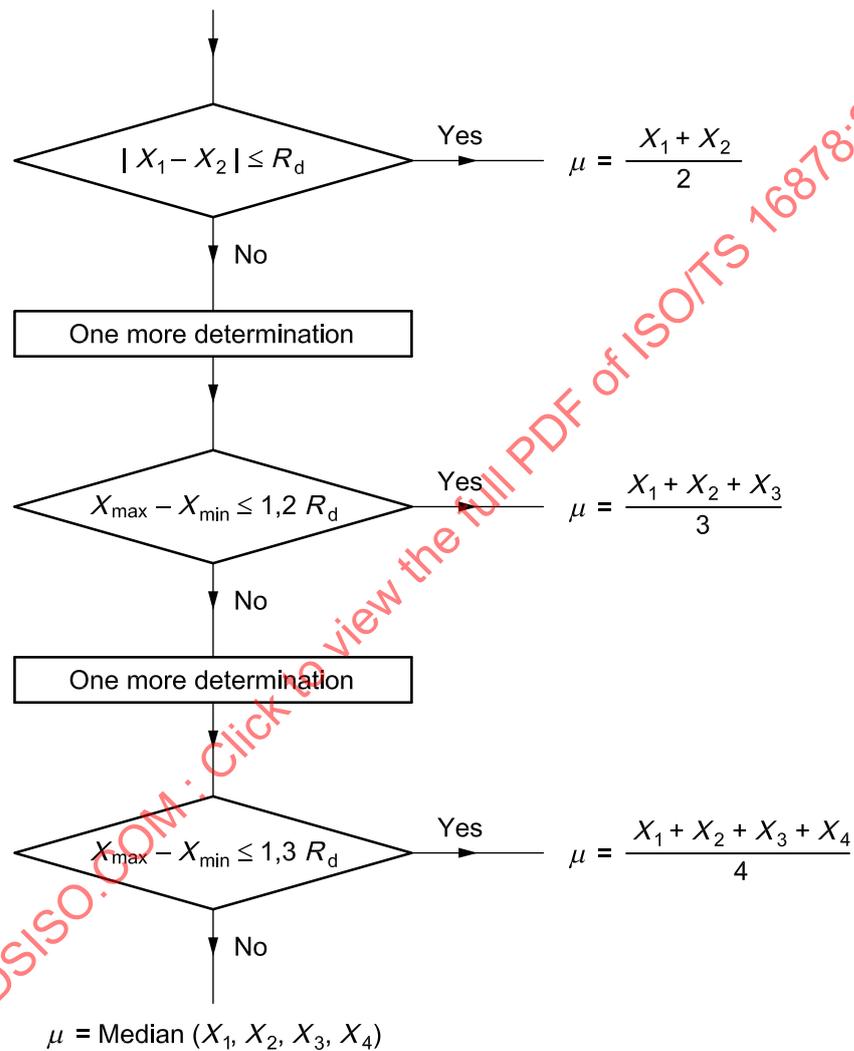


Calculate the test results to one decimal place, according to Clause 8

Annex B (normative)

Flowsheet for the procedure for the acceptance of test results

Start with independent duplicate results



Annex C (informative)

Results of inter-laboratory test programme

Four samples of DRI and one certified reference material, covering the range 11 % to 85 % mass fraction of metallic iron, were circulated to 19 laboratories for an international round robin test. Samples were ground to $-150 \mu\text{m}$ and sealed in vials before distribution, to remove any variation due to different sample preparation techniques at the various laboratories.

Results were provided from five laboratories and communication was received from another three.

The results were plotted in Figures C.1 to C.5. In general, the laboratories agree closely, with results falling within a range of mass fractions of metallic iron of less than 1 %.

The results were statistically analysed using ISO 5725-2. The independent duplicate limit, R_d , which is the maximum difference expected between two independent duplicate measurements at a 95 % probability level, was found to be 0,46 for metallic iron (average result as there is no reliable trend in R_d with increasing metallic iron level).

The permissible tolerance between laboratories, P , which is the maximum difference expected between mean results from two different laboratories at a 95 % probability level, was found to be 0,47 for metallic iron.

These results compare favourably with the numbers published in ISO 5416 (metallic iron determination by bromine-methanol titrimetric method) of $R_d = 0,52$ and $P = 1,7$ (for a mass fraction of metallic iron of 85 %).

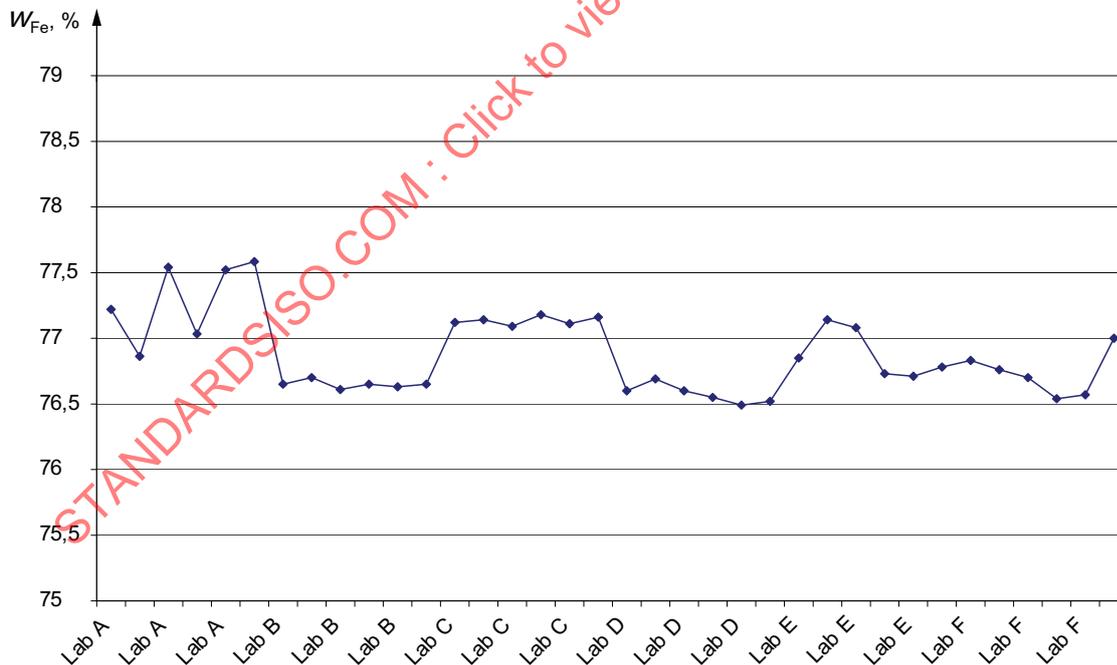


Figure C.1 — Metallic iron analyses for sample No. HB 1831 (DRI sample with 0,6 % carbon)

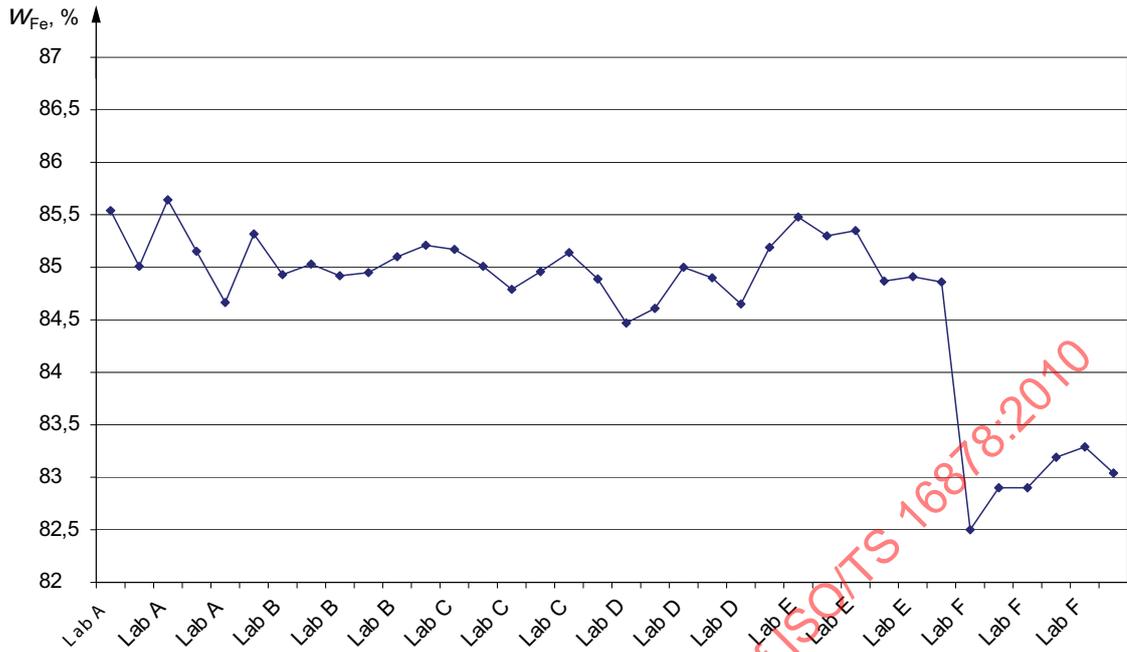


Figure C.2 — Metallic iron analyses for sample No. HB1854 (DRI sample with 3,9 % carbon)

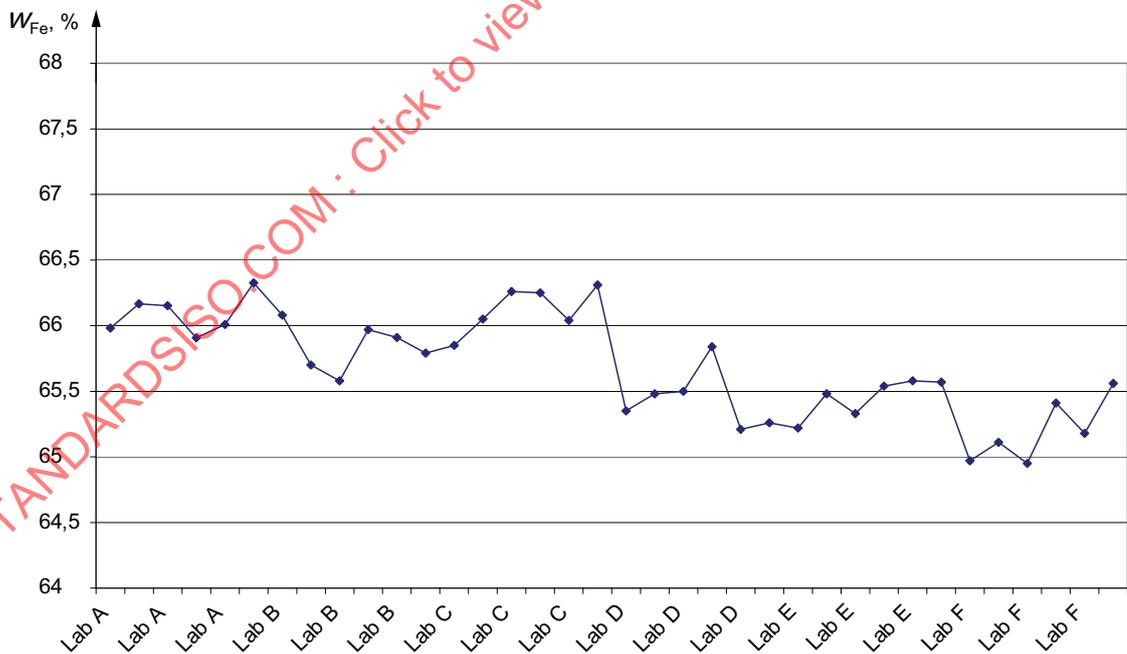


Figure C.3 — Metallic iron analyses for sample No. HB1904 (DRI sample with 0,3 % carbon)

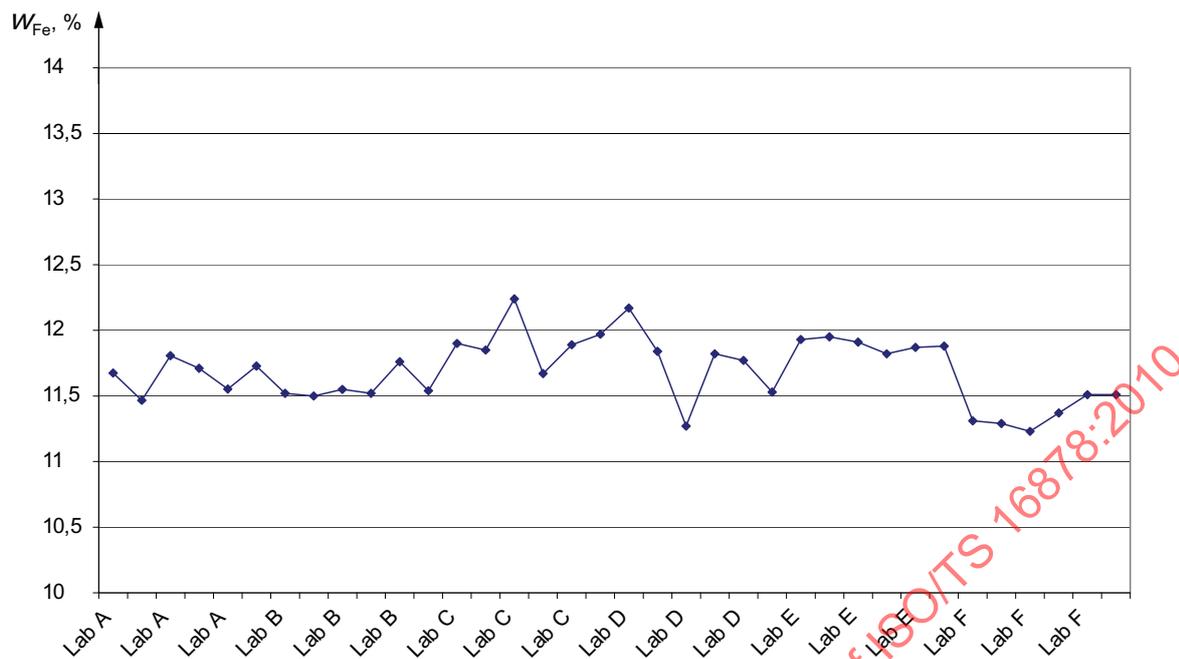


Figure C.4 — Metallic iron analyses for sample No. HB1938 (DRI sample with 0,3 % carbon)



Figure C.5 — Metallic iron analyses for sample No. HB2840 (CRM NBS691, certified at 84,6 % ± 0,6 % metallic iron using the bromine-methanol method, 0,1 % carbon)