
**Iron ores — Determination of
chlorine content — X-ray fluorescence
spectrometric method**

*Minerais de fer — Dosage du chlore — Méthode par spectrométrie de
fluorescence de rayons X*

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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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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*.

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Introduction

This Technical Report summarizes the results of inter-laboratory testing for the determination of chlorine in iron ores by X-ray fluorescence. The method was developed by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*. As no other methods for determination of chlorine exist in ISO/TC 102, the method was designed to complement method ISO 9516-1. A method for water soluble chloride does exist (ISO 9517) but the range of application of ISO 9517 is significantly less than the XRF method described in this Technical Report. The method described in this Technical Report represents the first attempt of the committee to determine total chloride.

Evaluation of the data from the inter-laboratory test indicated that the method could not be considered for publication as an International Standard as the precision of the method was less good than the precision of the method for water soluble chloride described in ISO 9517. In addition, a test on the trueness of the method was not possible as no potential test samples that were certified for Cl were available. Although the test samples used were characterized using neutron activation, the XRF values were biased with respect to the neutron activation values and the neutron activation method itself was not considered to be a standard method.

Although the method was not considered suitable for publication as an International Standard, it was agreed that the method was otherwise suitable for use in the industry and the committee agreed that it should be published as a Technical Report.

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Iron ores — Determination of chlorine content — X-ray fluorescence spectrometric method

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

1 Scope

This Technical Report sets out a wavelength dispersive X-ray fluorescence procedure for the determination of chlorine in iron ores.

The method is applicable to a concentration range of 0,027 % to 1,15 % of chlorine in iron ores regardless of mineralogical type.

It is not intended that this method be used for the purpose of trade in iron ores due to the precision of the method.

2 Principle

The glass discs for X-ray fluorescence measurement are prepared by incorporating the test portion of the iron ore sample, via fusion, into a borate glass disc using a casting procedure. By using a fused glass disc, particle size effects are eliminated.

The method is applicable to data from simultaneous and sequential X-ray fluorescence spectrometers.

Calibration is carried out using pure chemicals, with chlorine added as a stock solution of sodium chloride. Because the oxygen of the flux is the dominant element in the glass disc, and because oxygen is a heavy absorber to Cl K α , matrix effects are small and calibration is based on a linear relationship between concentration and measured fluorescent intensity. Background measurements are made to determine net line intensities.

3 Reagents and materials

3.1 During analysis, use only reagents of recognized high purity.

Where reagents have been ignited, they should be covered during cooling in the desiccator and weighed as soon as possible.

3.2 Iron (III) oxide (Fe₂O₃), nominally 99,999 % Fe₂O₃.

The iron (III) oxide should contain less than 3 μ g/g of chlorine. It should initially be heated at 1 000 °C in a platinum crucible for a minimum of 12 h to reduce contaminant concentrations and cooled in a desiccator. Subsequently, if required, it should be re-ignited at 1 000 °C for 1 h and cooled in a desiccator.

3.3 Sodium chloride (NaCl), 13,2 g/l solution.

Analytical grade sodium chloride should be dried at 105 °C for 1 h and cooled in a desiccator. Weigh 13,2 g dried sodium chloride into a 1 000 ml one-mark volumetric flask and dilute to volume.

3.4 Desiccant, should be a freshly-regenerated self-indicating silica gel.

3.5 Flux.

3.5.1 General

Flux A or flux B may be used. The levels of contamination in the flux should be checked (see 8.1). Because levels of contamination may vary from batch to batch, the same batch of flux should be used for all discs (iron ore, blank, and calibration) involved in the batch of determinations.

3.5.2 Flux A

Flux A should be prepared by fusion of a mixture of anhydrous lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) and anhydrous lithium metaborate (Li_2BO_2) by the procedure specified in Annex A. Flux should be dried at 500 °C for a minimum of 4 h and stored in a desiccator.

3.5.3 Flux B

Flux B should be prepared using lithium tetraborate by the procedure specified in Annex B. Flux should be dried at 500 °C for a minimum of 4 h and stored in a desiccator.

4 Apparatus

4.1 General

A conventional electric furnace, high-frequency furnace, gas burner or a commercial disc-making machine may be used to fuse and cast the discs.

4.2 Balance, an analytical balance capable of weighing to four decimal places.

4.3 Crucible and mould, made from a non-wetting platinum alloy.

NOTE Either platinum/gold or platinum/gold/rhodium alloys are suitable.

The sample may be fused with the flux in a crucible and then poured into a separate mould or, if an appropriately shaped crucible is used, the fusion may be carried out and the glass is allowed to cool in the same crucible. Both methods will produce glass discs of the same quality.

The crucible should have sufficient capacity to hold the flux and sample required for fusion. Where the crucible is to be used as a mould as well as for fusion, it should have a flat bottom of a diameter appropriate to the spectrometer. The inside of the crucible should be polished regularly with approximately 3 µm diamond paste to ensure that the glass disc releases easily. To prevent deformation through repeated heating and cooling, the base should be thicker than 2 mm.

Because the bottom of the disc is the analytical surface, the inside bottom surface of the mould should be flat and should be polished regularly with approximately 3 µm diamond paste to ensure that the glass disc releases easily from the mould. To prevent deformation through repeated heating and cooling, the base should be greater than 2 mm thick.

4.4 Electric furnace, capable of maintaining a temperature in the range of 1 000 °C to 1 050 °C.

The furnace may be of a conventional type with heating elements or may be a high-frequency furnace. The temperature of the melt should be in the range 1 000 °C to 1 050 °C and is not to exceed 1 050 °C to minimize loss of chlorine by volatilization. The temperature should be checked using an optical pyrometer while the crucible contains several grams of flux. Alternatively, if an optical pyrometer is not available, heat about 10 g of potassium sulphate (mp 1 069 °C) in a crucible for 10 min. There should be no evidence that the salt has melted during heating, but it may be sintered. If the potassium sulphate has melted, then repeat at a lower fusion temperature.

The furnace should be regularly cleaned to prevent contamination of the samples.

4.5 Gas-oxygen burner.

Where fusions are made over a gas-oxygen flame, the flame should not be excessively oxygen-rich to minimize chlorine loss. As for the electric furnace, temperature is not to exceed 1 050 °C to minimize loss of chlorine by volatilization. The temperature is to be checked using an optical pyrometer or by heating potassium sulphate as described in 4.4. A gas burner may be used for heating the mould and it is to be adjusted so that the mould is a bright red (approximately 950 °C). A Meker burner should not be used, as uptake of iron from the glass into the platinum ware may occur.

4.6 Desiccator.

4.7 **Spatulas**, non-magnetic, for weighing of the test portion and for mixing. Vibrating spatulas are not acceptable because they can lead to segregation of the sample.

4.8 **X-ray fluorescence spectrometer**, any wavelength dispersive, vacuum (or helium) path, X-ray fluorescence spectrometer, provided that the instrument has been checked.

Performance checks should be carried out in accordance with the precision tests set out in AS 2563, accumulating at least 10^5 counts for each measurement.

4.9 Ultrasonic bath.

This item is optional. It may be used to aid cleaning of the platinum ware.

4.10 Cooling device.

It is recommended that the mould and glass be cooled using an air jet. Commercial disc-making machines use this method.

Whatever the method of cooling, it is vital that samples be treated identically, as the curvature of the analytical surface of the disc depends on the rate of cooling.

4.11 **Laboratory glass ware**, one-mark pipettes (0,5 ml and 1,0 ml) and a one-mark 1 000 ml volumetric flask complying with the specifications of ISO 648 or ISO 1042, respectively.

4.12 **Cotton gloves**, recommended to be worn by operators when handling fused beads to minimize chlorine contamination.

5 Sampling and samples

5.1 Laboratory sample

For analysis, use a laboratory sample of minus 100 µm 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 minus 160 µm.

5.2 Preparation of test sample

5.2.1 Preparation of pre-dried test samples

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. Dry the test sample at (105 ± 2) °C, as specified in ISO 7764.

5.2.2 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 ores:

- processed ores containing metallic iron;
- natural or processed ores in which the sulphur content is higher than 0,2 % (m/m);
- natural or processed ores in which the content of combined water is higher than 2,5 % (m/m).

6 Procedure

6.1 Preparation of discs

6.1.1 General

Independent duplicate sets (day 1 and day 2) of test samples, blanks and calibration samples should be prepared. The expression "independent" implies that the repetition of the procedure be carried out at a different time or by a different operator.

The operator should have demonstrated the ability to make discs consistently with high precision. This ability should be verified each month.

In preparing discs, great care is to be taken to avoid contamination and, in particular, the crucible in which the fusion is carried out should be thoroughly cleaned prior to use (see 6.1.10). To minimize contamination sources, it is recommended that chlorine- and sodium-based cleaners are avoided in the laboratory area. It is recommended that operators wear clean cotton gloves when handling fused beads.

6.1.2 Weighing

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 Table 1 shows the components used in making the glass discs. Provided that the proportions are kept approximately as given in Table 1, the masses can be varied to suit mould diameter and shape (see Note after Table 1).

Table 1 — Masses of specimen components

Component	Standard masses, g	Mass, g	
		Disc diameter	
		32 mm	40 mm
Flux	6,80	4,10 to 4,61	6,40 to 7,20
Sample	0,66	0,41 to 0,44	0,64 to 0,68

The specified masses may be weighed as "catch" weights, recording the mass weighed to the nearest 0,001 g for the flux and to the nearest 0,000 1 g for the test and calibration portions.

NOTE If a disc diameter used differs from those given in Table 1, masses are to be adjusted to be approximately proportional to the area of the glass disc. If masses used are higher than recommended, crystallization and segregation with consequent cracking are likely to occur as the glass cools.

Because the components are hygroscopic, they should be weighed as soon as possible after reaching room temperature following heating and without any undue delay between weighings. Weighings may be made direct into the crucible to be used in the fusion or into a clean glass vial. Because of static effects, glass vials are preferable to plastic. If a vial is used, care should be taken to ensure complete transfer of the contents into the fusion crucible.

6.1.3 Mixing

Thoroughly mix the components in the crucible using a microspatula or similar implement, taking care that no material is lost. Brush any fine material adhering to the mixing implement back into the crucible. Gently tap the bottom of the crucible on the bench top to ensure that any material adhering to the crucible wall, above the general level of the mixed components, is reincorporated into the bulk of the mix.

The mixing implement used should be free of sharp or pointed edges to ensure that the interior of the crucible is not damaged by scratching.

NOTE It is imperative that the crucible be tapped *gently* on the bench top, as a too severe impact will result in the loss of some of the finer material and possible deformation of the crucible.

6.1.4 Fusion

Place the crucible in the electric furnace (4.4) or on the gas-oxygen burner (4.5) at a temperature of 1 000 °C to 1 050 °C (and not greater than 1 050 °C) and maintain this temperature for 10 min. At least once during this period, after the sample is dissolved, briefly swirl the mixture. While swirling, incorporate into the melt any material that may be adhering to the sides of the crucible.

If a furnace is used for heating, it may be necessary to remove the crucible from the furnace for the purpose of swirling. When the furnace is opened, the temperature may drop. The specified temperature should be regained before the time period starts.

6.1.5 Casting

Casting is then carried out by one of the following methods:

a) Casting in the crucible

If the glass is to be cast in the crucible, remove the crucible from the furnace, place on a suitable cooling device (4.10) and allow the glass to solidify.

b) Casting in a separate mould

If the glass is to be cast in a separate mould, the mould should be pre-heated over a gas flame to red heat (900 °C to 1 050 °C). While the mould is still hot, pour the melt into the mould from the crucible. Remove the mould from the heat source and place it on the cooling device (4.10) and allow the glass to solidify.

NOTE Failure to ensure that the mould is scrupulously clean prior to casting will result in discs sticking to the mould and possibly cracking.

6.1.6 Calibration discs

The synthetic set for calibration comprises six fused discs: two discs containing 100 % Fe₂O₃ only and four discs containing 100 % Fe₂O₃ “spiked” with a known amount of chlorine added using the NaCl stock solution (3.3). The mass of Fe₂O₃ and volume of stock solution is set out in Table 2, where *w* is the standard mass of chemical compound (referred to as “sample” in Table 2) prepared as described in Clause 3.

Addition of the stock solution is best achieved by adding the prescribed aliquot of solution to the crucible containing thoroughly mixed flux and the ignited spectroscopically pure Fe₂O₃. Once the solution is added, to minimize mechanical losses due to the spitting of wet reagents for the spiked discs, bulk moisture should be removed by drying for 2 h at 100 °C. Remaining hydrated moisture (present in the flux sample mixture) can be removed by drying at 300 °C for 10 min. Prior to fusions, samples should be mixed to ensure homogeneity.