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**Iron ores — Determination of various  
elements by X-ray fluorescence  
spectrometry —**

**Part 4:  
Performance-based method using  
fusion preparation method**

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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 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](http://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*.

A list of all parts in the ISO 9516 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](http://www.iso.org/members.html).

## Introduction

X-ray fluorescence (XRF) spectrometry is a multi-elemental non-destructive analytical methodology used for quantitative and qualitative determinations. It is element specific covering an elemental range from boron (B) to uranium (U).

Once the sample has been dissolved into a borate glass it may be introduced to the spectrometer for analysis. The sample is then irradiated by intense radiation from an X-ray tube. Analysis of fused glass beads offers advantages over pressed powder techniques as it eliminates particle size effects, and it produces a homogeneous specimen for each element.

In some instances, the relationship between intensity (or intensity ratios) and concentration can be linear. For most analytes there is no direct straightforward relationship between intensity and concentration. With samples of differing compositions, the X-rays are absorbed differently in the different samples giving rise to what are generally referred to as matrix effects. These inter-element effects can be corrected using mathematical models derived from the known physics of X-rays.

Calibration can be based on binary standards (prepared from pure oxides or liquid solutions), reference materials, secondary standards, or combinations therewith.

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# Iron ores — Determination of various elements by X-ray fluorescence spectrometry —

## Part 4: Performance-based method using fusion preparation 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 performance-based method for the chemical analysis of natural and processed iron ores by fused bead wavelength and energy dispersive X-ray fluorescence (XRF).

It is applicable to all elements of interest when adequate calibrations have been established.

### 2 Normative references (standards.iteh.ai)

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 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*

ISO Guide 31, *Reference materials — Contents of certificates, labels and accompanying documentation*

ISO Guide 35, *Reference materials — Guidance for characterization and assessment of homogeneity and stability*

### 3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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/>

#### 3.1

##### primary standard

standard that is designated or widely acknowledged as having the highest metrological qualities and whose value is accepted without reference to other standards of the same quantity

Note 1 to entry: The concept of a primary standard is equally valid for base quantities and derived quantities.

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Note 2 to entry: A primary standard is never used directly for measurement other than for comparison with other primary standards or reference standards.

### 3.2 reference material

**RM**  
standard, generally having the highest metrological quality available at a given location or in a given organization, from which measurements made there are derived

### 3.3 certified reference material

**CRM**  
material, e.g. iron ores, supplied by an organization conforming to the requirements for the competence of *reference material* (3.2) producers

Note 1 to entry: The requirements for the competence of reference material producers are given in ISO 17034.

Note 2 to entry: CRMs shall be supplied with a certificate of analysis giving information on the average value and standard deviation (with and between laboratory precision statistics) and measurement of uncertainty in accordance with ISO Guide 31.

### 3.4 accepted reference value

**ARV**  
value that serves as an agreed upon reference for comparison, and which is derived as:

- a theoretical or established value, based on scientific principles;
- an assigned or certified value, based on experimental work of some national or international organization;
- a consensus or certified value, based on collaborative experimental work under the auspices of a scientific or engineering group.

Note 1 to entry: When none of the above are available, the ARV is the expectation of the (measurable) quantity, i.e. the mean of a specified population of measurements.

### 3.5 referee method

<analytes of commercial significance> method that is independent of other methods (i.e. calibrated with primary standards or able to arrive at the final results using direct measurements or calculations from known physical/chemical laws) and is in the initial stages of the traceability chain

Note 1 to entry: Primary methods include gravimetry, titrimetry, coulometry and isotope dilution mass spectrometry.

## 4 Reagents and materials

### 4.1 Pure reagents

Reagents shall be of analytical quality and, wherever possible, be pure oxides or carbonates, except for the calibration of such elements as sulfur, chlorine, bromine, or phosphorus, which do not form stable oxides or carbonates, where some guarantee of stoichiometry is required.

Reagents shall be free of (or corrected for) the presence of moisture (and, in the case of oxides, carbon dioxide) when weighed out for fusion.

Reagents shall be used in a known stoichiometry in terms of content. In order to achieve this, they can be treated before use. Generally, the oxides of iron, silicon, manganese, aluminium, titanium and magnesium shall be heated to 1 000 °C. More information can be found in ISO 9516-1. The procedures specified in ISO 9516-1 ensure that the correct oxidation state is obtained.



All laboratory reagents used for referee methods shall be traceable.

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

## 4.2 Flux

High purity lithium borate or sodium borate fluxes should be used. Prior to using, the levels of contamination shall be checked. Good results have been obtained with a mixture that contains 6 parts of  $\text{Li}_2\text{B}_4\text{O}_7$  and 11 parts of  $\text{LiBO}_2$  by mass. This composition is a eutectic and can be used at relatively low temperatures.

NOTE 1 This mixture is commercially available under the designation 12:22.

NOTE 2 A typical sample to flux ratio is 1 unit of sample for 10 units of flux.

## 4.3 Releasing agent

To facilitate the casting of the sample-flux mixture and the releasing of the resultant bead after cooling, a releasing agent such as ammonium iodide ( $\text{NH}_4\text{I}$ ) or lithium iodide ( $\text{LiI}$ ) is recommended. Alternatively, lithium bromide ( $\text{LiBr}$ ) can be used.

If a bromide-containing releasing agent is used, the line overlap of the Br L-lines with Al  $\text{K}\alpha$  shall be taken into account.

NOTE Fluxes with an integrated releasing agent are commercially available.

## 4.4 Oxidizing agents

Generally, no oxidizing agents are required if the iron is present as hematite ( $\text{Fe}_2\text{O}_3$ ). However, if the samples to be analysed contain, for example, magnetite ( $\text{Fe}_3\text{O}_4$ ) or if a gas burner is used without oxygen supplement, then the addition of an oxidizing agent to the flux can be required. In those cases, the use of lithium nitrate ( $\text{LiNO}_3$ ) is recommended.

NOTE 1 Sodium nitrate can also be used as an oxidizing agent. This will render the analysis of sodium impossible.

NOTE 2 Typical mass of the oxidizing agent added is 0,5 units to 1 unit by mass for every unit of sample.

## 4.5 Certified reference materials

CRMs prepared in accordance with 5.2 may be used to establish calibration and to validate calibration.

## 4.6 Reference materials

RMs can be materials, e.g. iron ores, homogenized and prepared by a laboratory. The reference analysis of a RM shall be the average result from interlaboratory co-operative testing involving at least four laboratories able to meet the performance criteria.

# 5 Sampling and samples

## 5.1 Laboratory sample

For analysis, use a laboratory sample of less than 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 easily oxidizable compounds, use a particle size of less than 160  $\mu\text{m}$ .

## 5.2 Preparation of test samples, CRMs and RMs

### 5.2.1 General

Depending on the ore type, proceed in accordance with either [5.2.2](#) or [5.2.3](#).

### 5.2.2 Ores having significant contents of combined water or easily 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 non-oxidized 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.

NOTE Loss on ignition can be used as an estimate of combined water.

### 5.2.3 Ores outside the scope of [5.2.2](#)

Prepare a pre-dried test sample by thoroughly mixing the laboratory sample and, taking multiple increments, extracting a test sample in such a manner that it is representative of the whole contents of the container. The pre-dried test portion shall be prepared in accordance with ISO 7764.

## 5.3 Test portion

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. One disc from each test sample shall be prepared.

At least one CRM, of the same type (mineralogy and chemistry) as the ore used in the test discs, should be prepared and analysed.

## 6 Apparatus

The usual laboratory apparatus and, in particular, the following shall be used.

**6.1 Analytical balance**, capable of weighing to four decimal places.

**6.2 Crucibles and moulds.** Articles made of platinum alloy with certified purity. The recommended alloys for making the pieces are platinum, platinum/gold, rhodium or platinum/rhodium.

The amount of sample and flux used should respect the volume of the crucible and mould available. It is important to take into account possible projections caused by the movement of the fusion machines during the fusion process.

The surface of the moulds should be perfectly flat throughout the life of the article. Regular polishing and checking the bottom alignment are recommended.

**6.3 Fusion equipment.**

Any gas heating, electric heating or induction heating equipment may be used. Equipment shall be capable of maintaining a temperature of at least 1 050 °C with capacity to vary temperature, time and agitation intensity.

The temperature shall be checked regularly with an optical pyrometer. It is important that during these measurements, the crucible contains a mass of flux similar to the mass that is used in the analysis.

In machines with more than one independent melting position, it is necessary to check their temperature homogeneity. Burners on gas machines and chambers in electrical machines shall maintain temperature stability during the melting process.

For gas burners, to minimize the loss of sulfur during the fusion, provisions shall be made to add oxygen to the flame. Alternatively, oxidizing aids can be added to the flux, see [4.4](#).

**6.4 Electric furnace**, capable of maintaining a temperature of at least 1 050 °C.

**6.5 Gas burner.**

When gas burners are used the temperature of the melt shall be in the range of 1 000 °C to 1 050 °C. To minimize the loss of sulfur during the fusion, provisions shall be made to add oxygen to the flame. Alternatively, oxidising aids can be added to the flux, see [4.4](#).

The temperature shall be checked regularly with an optical pyrometer. It is important that during these measurements, the crucible contains a mass of flux similar to the mass that is used in the analysis.

**6.6 Fusion machine**, with gas heating station(s) or induction furnaces, normally with agitation capacity and which allows the creation of fusion programmes with variation of time, agitation intensity and temperature. In machines with more than one independent melting position, it is necessary to check their temperature homogeneity. Burners, on gas machines and chamber in resistances on electrical machines, shall maintain temperature stability during the melting process.

**6.7 XRF spectrometer.**

Any wavelength dispersive XRF spectrometer equipped with a vacuum path, provided that the instrument has been checked. Performance checks can be carried out in accordance with ISO 9516-1, accumulating at least  $4 \times 10^7$  counts for each measurement. At this number of counts, the counting statistical error will be limited to about 0,016 %. This can depend on the count rate. In case of doubt, check with the instrument manufacturer. See also [7.1.3](#).

Although this method is written for WDXRF equipment, its principles may also be applied to the use of EDXRF instrumentation.

Modern instruments generally have some form of dead time correction, and although the correction is not always perfect, it should be acceptable for this method, which is tolerant of small errors in dead time correction.

## 7 Measurements

### 7.1 General

#### 7.1.1 Analytical line

For the analyte elements Fe, Si, Ca, Mn, Al, Ti, Mg, P, S and K, the  $K\alpha_{1,2}$  (K-L<sub>2,3</sub>) is recommended. For iron, the  $K\alpha_{1,2}$  is the preferred line, provided the count rate is well within the dynamic range of the detector system used. If the count rate is too high, then the  $K\beta_{1,3}$  (K-M<sub>2,3</sub>) can be used. If analytes with an atomic number higher than 52 are analysed, the preferred line is the  $L\alpha_1$  (L<sub>3</sub>-M<sub>5</sub>). For the determination of lead (if included), the  $L\beta_1$  (L<sub>2</sub>-M<sub>4</sub>) should be used. Furthermore, if both As and Pb are analysed, then the interference of the Pb  $L\alpha_1$  (L<sub>3</sub>-M<sub>5</sub>) on As  $K\alpha_{1,2}$  (K-L<sub>2,3</sub>) shall be taken into account or arsenic shall be determined using the As  $K\beta_{1,3}$  (K-M<sub>2,3</sub>) line. If barium is analysed, then either the  $K\alpha_{1,2}$  (or K-L<sub>2,3</sub>), the  $L\alpha_1$  (L<sub>3</sub>-M<sub>5</sub>) or the  $L\beta_1$  (L<sub>2</sub>-M<sub>4</sub>) can be used, depending upon which gives the best results.