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

Part 2: Single element calibration procedure

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Foreword

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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 document 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 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.

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

Part 2:
Single element calibration procedure

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 sets out a wavelength dispersive X-ray fluorescence procedure for the determination of various elements in iron ores. The method is applicable to iron ores regardless of mineralogical type.

2 Normative references

The following documents are referred to in the text in such a way that some of all of their content constitutes requirements of this document. For dated reference, 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 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 7764, *Iron ores — Preparation of predried test samples for chemical analysis*

ISO 8655-2, *Piston-operated volumetric apparatus — Part 2: Pipettes*

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

3 Terms and definitions

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

ISO and IEC maintain terminology databases for use in standardization at the following addresses.

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

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

4 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. Sodium nitrate may be added to the flux to ensure complete oxidation of all components, particularly iron and sulfur. Any of four methods for glass disc preparation may be used: three use lithium borate as flux; the other uses sodium borate.

X-ray fluorescence measurements are based on the "line only" principle. If desired, backgrounds can be measured to obtain net line intensities. This method is applicable to data from simultaneous and sequential X-ray fluorescence spectrometers.

This method relies on measuring all components of the sample, other than volatiles. If some components are not measured, errors will result in the measured components (see 8.5.2).

Results are obtained after matrix corrections for inter-element effects.

5 Reagents and materials

During analysis, only reagents of recognized high purity, and only grade 2 water as specified in ISO 3696 shall be used.

Where reagents have been ignited, they shall be stored during cooling in a desiccator and weighed as soon as possible.

5.1 Silicon dioxide, (SiO_2), nominally 99,999 % SiO_2.

The silicon dioxide shall contain less than 3 µg/g of each of the other elements listed in Table 1. It shall be heated to 1 000 °C in a platinum crucible for a minimum of 2 h and cooled in a desiccator.

5.2 Aluminium oxide, (Al_2O_3), analytical reagent grade, α form.

If the α form is used, it shall be heated to 1 000 °C in a platinum crucible for a minimum of 2 h. If the aluminium oxide is not the α form, it shall be converted to the α form by heating to 1 250 °C in a platinum crucible for a minimum of 2 h. It shall be cooled in a desiccator and weighed as soon as it is cooled.

5.3 Iron(III) oxide, (Fe_2O_3), purity of 99,995 % or more Fe_2O_3.

The iron(III) oxide shall contain less than 3 µg/g of each of the other elements listed in Table 1. It shall be heated at 1 000 °C in a platinum crucible for a minimum of 1 h and cooled in a desiccator.

5.4 Titanium dioxide, (TiO_2).

Analytical grade titanium dioxide shall be heated at 1 000 °C in a platinum crucible for a minimum of 1 h and cooled in a desiccator.

Phosphorus is a common impurity in TiO_2 and a reagent low in phosphorus shall be selected. The selected reagent shall be checked, as even nominally high-purity reagents can be significantly contaminated, e.g. a supposed 99,99 % TiO_2 grade reagent has been found to contain about 0,5 % P_2O_5.

5.5 Potassium dihydrogen orthophosphate solution, (KH_2PO_4).

Potassium dihydrogen orthophosphate KH_2PO_4 of purity 99,0 % or more shall be dried at 105 °C for 1 h and cooled in a desiccator. 3,481 g of the dried potassium dihydrogen orthophosphate shall be dissolved in 100 ml water in a volumetric flask. One ml of this solution contains 7,92 mg phosphorous and 10,0 mg potassium.

5.6 Calcium carbonate, ($CaCO_3$).

Analytical grade calcium carbonate shall be dried at 105 °C for 1 h and cooled in a desiccator.

5.7 Manganese (II) sulfate hydrate solution, ($MnSO_4 \cdot 5H_2O$).

8,777 (= 5,497 + 5 × 0,656) g of manganese sulfate hydrate $MnSO_4 \cdot 5H_2O$ of purity 99 % or more shall be dissolved in 100 ml water in a volumetric flask. Manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$) may be used as an alternative reagent of purity 99 % or more and 6,153 (= 5,497 + 0,656) g of the reagent shall be dissolved in 100 ml water in a volumetric flask. One millilitre of the solution contains manganese 20,0 mg and sulfur 11,67 mg.

5.8 Magnesium nitrate hexahydrate, [$Mg(NO_3)_2 \cdot 6H_2O$], purity of 99,0 % or more.

5.9 1 000 mg/l element standards for V, Cr, Co, Ni, Cu, Zn, As, Pb and Ba.

Single element standard water solutions with 1 000 mg/l concentration and 0,5 to 6 % of nitric acid shall be used. It is recommended to use commercially available standards. When standard solutions are prepared in the laboratory, 1,000 g of pure metal (99,99 % or more) shall be dissolved in diluted nitric acid. Water shall be added to this solution such that the prepared standard solution is 1 000 ml.

For the standard water solution for Cr, a solution of potassium dichromate solution ($K_2Cr_2O_7$) with nitric acid may be used.

5.10 Sodium nitrate, ($NaNO_3$).

Analytical grade sodium nitrate shall be dried at 105 °C for 1 h and cooled in a desiccator.

5.11 Ammonium iodide, (NH_4I).

Laboratory reagent grade ammonium iodide does not need to be dried but shall be stored in a desiccator.

5.12 Desiccant.

The desiccant shall be freshly regenerated self-indicating silica gel.

5.13 Flux.

5.13.1 General

One of fluxes from Flux A, Flux B, Flux C or Flux D, as described in 5.13.2, 5.13.3 and 5.13.4, shall be used. The levels of contamination in the flux shall be checked (see 10.1). Because levels of contamination can vary from batch to batch, the same batch of flux shall be used for all discs (iron ore, blank and calibration) involved in the batch of determinations.

5.13.2 Flux A and Flux D

Flux A and Flux D shall be prepared by fusion of a mixture of anhydrous lithium tetraborate ($Li_2B_4O_7$) and anhydrous lithium metaborate ($LiBO_2$) using the procedure specified in Annex A. Flux shall be dried at 500 °C for a minimum of 4 h and stored in a desiccator.

5.13.3 Flux B

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

5.13.4 Flux C

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

NOTE If this flux is used, sulfur will not be reported.

6 Apparatus

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 allowed to cool in the same crucible. Both methods will produce glass discs of the same quality.

A conventional electric furnace, high-frequency furnace, or a gas burner may be used for heating. There are disc-making machines commercially available, and these may be used to fuse and cast the discs.

A platinum lid may be used to cover the crucible if fusing in a furnace, but not if fusing over a flame, as this enhances sulfur loss.

Where a high-frequency furnace or a gas burner is used for heating, a check shall be made to determine if sulfur is lost during disc preparation. A mixture that contains 90 % Fe_2O_3 and 10 % $CaSO_4$ shall be prepared and used to prepare replicate discs using normal fusion times and times of twice and thrice normal. The intensity of SKα from the discs should not vary by more than 2 % relative.

Single-volume pipettes, one-mark volumetric flasks and piston pipettes to be used shall comply with specifications of ISO 648, ISO 1042 and ISO 8655-2, respectively.

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

6.2 Crucible and mould.

The crucible and mould shall be made from a non-wetting platinum alloy. Either platinum/gold or platinum/gold/rhodium alloys are suitable.

If more than one crucible or more than one mould is used for casting, these crucibles or moulds shall all be used in the specimen preparation test in Annex C. It is essential to use all of the crucibles or moulds in the test described in Annex C, as casting vessels can become distorted with use, giving the analytical surface a curvature that will result in error.

Sometimes, even undistorted crucibles or moulds give curvatures unique to the particular crucible or mould.

6.2.1 Crucible

Where the crucible is used for fusion only, it shall have sufficient capacity to hold the flux and sample required for fusion. Where the crucible is used as a mould as well as for fusion, it shall have a flat bottom, to enable production discs with minimum curvature.

6.2.2 Mould

Because the bottom of the disc is the analytical surface, the inside bottom surface of the mould shall be flat and shall 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 shall be greater than 2 mm thick. The mould shall have a flat bottom, to enable production of discs with minimum curvature.

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

The furnace shall be capable of maintaining higher temperatures where it is to be used for converting Al_2O_3 to the α form (1 250 °C), or for preparing Flux A (1 100 °C).

The furnace may be of a conventional type with heating elements, or may be a high-frequency furnace. The furnace shall be cleaned regularly to prevent contamination of the samples.

6.4 Gas-oxygen burner.

Where fusions are made over a gas-oxygen flame, provision shall be made for oxygen enhancement of the flame to minimize sulfur loss and crucible contamination. The temperature of the melt shall be in the range 1 000 °C to 1 050 °C. The temperature shall be checked using an optical pyrometer while the crucible contains several grams of flux. Alternatively, if an optical pyrometer is not available, about 3 g of potassium sulfate (m.p. 1 069 °C) shall be put in an empty crucible and the flame adjusted so that it all just melts in the open crucible. A gas burner may be used for heating the mould, and it shall be adjusted so that the mould is a bright red heat (approximately 950 °C). A Meker burner shall not be used, as loss of sulfur and the uptake of iron from the glass into the platinum ware can result.

6.5 Desiccator.

6.6 Spatulas, non-magnetic, for weighing of the test portion and for mixing.

6.7 X-ray fluorescence spectrometer, of any wavelength dispersive, vacuum (or helium) path, simultaneous or sequential type, X-ray fluorescence spectrometer, provided that the instrument has been checked.

Performance checks shall be carried out in accordance with the precision tests set out in Annex D, accumulating at least 2×10^7 counts for each measurement.

6.8 Ultrasonic bath, optional. It may be used to aid cleaning of the platinum ware.

6.9 Cooling device.

It is recommended that the mould and glass be cooled using an air jet. Commercial disc-making machines use this method. A drawing of a suitable device is given in Annex I.

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.

7 Sampling and samples

7.1 Laboratory sample

For analysis, laboratory samples of −100 µm particle size which has been taken and prepared in accordance with ISO 3082 shall be used. In the case of ores having significant contents of combined water or oxidizable compounds, samples of particle size of −160 µm shall be used.

7.2 Preparation of test samples

7.2.1 General

Depending on the ore type, air-equilibrate test samples shall be prepared in accordance with either ISO 2596 in 7.2.2 or ISO 7764 in 7.2.3.

7.2.2 Method specified in ISO 2596

The method is applicable to all types of ores.

The laboratory samples shall be thoroughly mixed, and in multiple increments, a test sample shall be extracted in such a manner that it is representative of the entire content in the container. The test sample shall be brought into equilibrium with the laboratory atmosphere in accordance with ISO 2596.

7.2.3 Method specified in ISO 7764

The method is not applicable to the following types of ores:

a) processed ores containing metallic iron;

b) natural or processed ores in which the sulfur content is higher than 0,2 %;

c) natural or processed ores in which the content of combined water is higher than 2,5 %.

The laboratory samples shall be thoroughly mixed and, multiple increments shall be taken, a test sample shall be extracted in such a manner that it is representative of the whole contents of the container.

8 Procedure

8.1 General

The concentration range covered for each of the component elements is given in Table 1.

Table 1 — Range of application of the method

Component element	Concentration range for referee purposes %	Concentration range for analysis %
Fe	31 to 72	31 to 72
Si	0,16 to 11,8	0,16 to 11,8
Ca	0,011 to 13,7	0,011 to 13,7
Mn	0,016 to 2,0	0,016 to 2,0
Al	0,036 to 4,2	0,036 to 4,2
Ti	0,013 to 4,5	0,013 to 4,5
Mg	0,012 to 1,7	0,012 to 1,7
P	0,001 3 to 0,6	0,001 3 to 0,6
S	0,011 to 0,76	0,011 to 0,76
K	0,008 to 0,46	0,008 to 0,46
V	0,002 to 0,32	0,002 to 0,32
Cr	—	0,006 to 0,067
Co	—	0,006 to 0,023
Ni	0,008 to 0,038	0,008 to 0,038
Cu	0,007 to 0,17	0,007 to 0,17
Zn	0,005 to 0,36	0,005 to 0,36
As	—	0,003 to 0,11
Pb	—	0,001 to 0,23
Ba	—	0,011 to 0,74

When the influence of absorption or spectral overlap by trace heavy elements to reporting elements is small enough and can be ignored, those trace heavy elements can be omitted from measuring elements.

The applicable ranges for referee and non-referee methods are also to be determined based on results of international trials.

The operator shall have demonstrated the ability to consistently make discs with high precision. This ability shall be verified by carrying out the procedure given in Annex C.

The operator shall periodically test all moulds according to Annex C, because their shape can become distorted with repeated use.

In preparing discs, great care shall be taken to avoid contamination and, in particular, the crucible in which the fusion is carried out shall be thoroughly cleaned prior to use (see 8.4.7).

8.2 Number of determinations

Carry out two analyses independently for duplicate fused discs prepared on different days in accordance with Annex J for each test sample (see 7.2).

8.3 Check analysis and blank test

In each run, 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.

When analysis is carried out on several samples of the same ore type at the same time, the analytical result of one certified reference material may be used.

When a new reagent as for flux from a different bottle is used, it is recommended to measure a blank sample to check the impurities and contamination due to sample preparation, before the analysis is carried out on ore sample(s). The blank disc shall be prepared with 100 % Fe_2O_3.

8.4 Preparation of discs

8.4.1 Weighing

Table 2 shows the components used in making the glass discs. Provided that the proportions are kept approximate to those given in Table 2, the masses can be varied to suit mould diameter. If a disc diameter used differs from those given in Table 2, masses should be adjusted to be approximately proportional to the area of the glass disc.

Table 2 — Masses of specimen components

Component	Typical masses g	Mass g	
		Disc diameter	
		32 mm	40 mm
Flux	6,80	3,52 to 6,40	5,50 to 10,00
$NaNO_3$	0,40 or 0	0,21 to 0,37 or 0	0,33 to 0,58 or 0
Sample	0,66	0,35 to 0,60	0,55 to 0,94

The specified masses may be weighed as “catch” weights, recording the mass weighed to the nearest 0,001 g for the flux and sodium nitrate portions, and to the nearest 0,000 1 g for the test and calibration portions. If masses used are higher than recommended, crystallization and segregation with consequent cracking are likely to occur as the glass cools.

If desired, ammonium iodide (5.11) can be used as a releasing agent. If added at this stage, no more than 0,01 g shall be added. Alternatively, a smaller amount may be added prior to casting (see 8.4.4). Exceeding the recommended amount of releasing agent of ammonium iodide can introduce error in the titanium result due to the overlap. ILβ_2 interferes with Ti$K\alpha$.

Because the components are hygroscopic, they shall be weighed as soon as possible after reaching room temperature following heating and without any undue delay between each weighing. Weighing may be made directly 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 shall be taken to ensure complete transfer of the contents into the fusion crucible.

8.4.2 Mixing

Thoroughly mix the components in the crucible using a spatula or similar implement, taking care that no material is lost. The mixing implement used should be free of sharp or pointed edges, in order to ensure that the interior of the crucible is not damaged by scratching. 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.

It is imperative that the crucible be tapped gently on the bench top, as too severe an impact will result in the loss of some of the finer material and possible deformation of the crucible. Care shall be taken to mix the components thoroughly to aid reproducibility of disc preparation.

8.4.3 Fusion

For samples containing sulfur as sulfide, the fusion mixture is to be preoxidised by heating to 700 °C for 10 min prior to fusion. Place the crucible in the electric furnace (6.3) or on the gas-oxygen burner (6.4) at a temperature of 1 000 °C to 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 can be adhering to the sides of the crucible.

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

8.4.4 Casting

If ammonium iodide was not added as a release agent earlier, it may be added to the melt just prior to casting.

In this case, no more than 0,002 g shall be added. 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 (6.9) 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 shall 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 (6.9) 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.

8.4.5 Visual inspection

Prior to storage, discs shall be inspected visually, paying particular attention to the analytical surface. The discs shall not contain undissolved material, and shall be whole and free from crystallization, cracks and bubbles. Defective discs shall be re-fused in the crucible, or discarded and substitute discs prepared.

8.4.6 Disc storage

As soon as possible (while the glass is still warm), transfer the discs to a desiccator so that absorption of moisture and the possibility of contamination are minimized. When not being measured, discs shall be stored in a clean desiccator.

To avoid contamination of the analytical surface, the specimen shall be handled by its edges and the surface shall not be touched by hand or treated in any way. Specifically, it shall not be washed with water or other solvents, ground or polished.

If paper labels are used on the backs of discs, great care should be taken to ensure that the labels do not contact the analytical surfaces of other discs. Paper labels are clay coated and readily cause contamination by silicon and aluminium. For the same reason, paper envelopes should not be used to store the discs.

8.4.7 Cleaning of platinum ware

Although the crucible and mould are fabricated from an alloy that is not wetted by the glass, in order to ensure absolute precision, they shall be cleaned between each fusion. Immersion in hot hydrochloric, citric or acetic acid (approximately 2 M), for about 1 h is usually sufficient, but they should be inspected to ensure that all residual glass has been removed.

A rapid method of cleaning is to put the crucible or mould into a beaker containing the acid. Place the beaker in a small ultrasonic bath for about 1 min or until all residual glass is removed, then rinse the mould in distilled water and dry before using.

An alternative method of cleaning is to fuse several grams of flux in the crucible, moving the melt around to clean the entire inner surface. The molten flux is then poured from the crucible. If a droplet adheres to the crucible, this can easily be flaked off when the crucible is cold.

If new platinum ware is used without pre-conditioning by the cleaning described above, then the Fe results will be unreliable until conditioning occurs. New platinum ware can also release contaminants without conditioning.

8.4.8 Test discs

One disc from each test sample shall be prepared. At least one certified reference material, of the same type as the ore used in the test discs, shall be prepared. Prior to fusing test discs, crucibles should be thoroughly clean, particularly if the same crucibles were used to prepare the calibration discs, some of which are high in trace elements.

8.5 Measurement

8.5.1 General

The analytical lines to be used and suggested operating conditions are given in Table 3. Other instrument parameters (collimators and detectors) shall be selected according to the particular element.

Table 3 — Suggested analytical lines, crystals and operating conditions

Component element	Line (see 8.5.3)	Voltage (see 8.5.4) kV	Crystal [a] (see 8.5.5)	Specific line overlaps (see 8.5.6)
Fe	Kα Kβ	40 to 80 40 to 80	LiF(200) or LiF(220) LiF(200) or LiF(220)	— —
Si	Kα	25 to 50	PE	—
Ca	Kα	25 to 50	LiF(200) or PE or Ge(111)	—
Mn	Kα	50 to 80	LiF(200)	CrKβ
Al	Kα	25 to 50	PE	BaLα(3), CrKβ(4)
Ti	Kα	40 to 80	LiF(200)	BaLα
Mg	Kα	25 to 50	TlAP or multi-layer	—
P	Kα	25 to 50	Ge(111) or PE	—
S	Kα	25 to 50	Ge(111) or PE	CoKα(3), PbMα
K	Kα	25 to 50	LiF(200)	—
V	Kα	50 to 80	LiF(200)	TiKβ, BaLβ

[a] The first crystal listed is preferred.

Table 3 *(continued)*

Component element	Line (see 8.5.3)	Voltage (see 8.5.4) kV	Crystal [a] (see 8.5.5)	Specific line overlaps (see 8.5.6)
Cr	Kα	50 to 80	LiF(200)	VKβ
Co	Kα	50 to 80	LiF(200)	FeKβ
Ni	Kα	50 to 80	LiF(200)	CoKβ
Cu	Kα	50 to 80	LiF(200)	—
Zn	Kα	50 to 80	LiF(200)	—
As	Kα Kβ	50 to 80 50 to 80	LiF(200) LiF(200)	PbLα —
Pb	Lβ1 Mα	50 to 80 25 to 50	LiF(200) Ge(111) or PE	— FeKα(3)
Ba	Lα Lβ1	40 to 80 40 to 80	LiF(200) LiF(200)	TiKα TiKβ, VKα

[a] The first crystal listed is preferred.

8.5.2 Effect of errors or omissions

There are various circumstances where all 19 elements will possibly not be determined. If a simultaneous instrument is used, there will possibly not be analytical channels for all elements. In plant control, it is probably not necessary to do all the minor elements. Where the source material is constant and known, it is probably unnecessary to do the minor elements on all samples.

When converting intensities to concentrations, the intensities are multiplied by the term (the matrix factor) of absorption and enhancement effects and this factor receives contributions from all components of the sample, so if one or more components are not determined then all other components will be in error. The method then relies on the measurement of all components of the sample.

Table 4 shows the error, as a relative percentage, for each analyte where there is a 1 % error in a component.

The error can be not estimating a component if it has a significant concentration. The calculations have been made for a typical iron ore.

Table 4 can be used to estimate at what level a minor element can be omitted from the analysis without exceeding a predetermined error.

Where small errors are involved in a component, the resulting errors to other components are proportional to the initial error, and if more than one component is in error, or omitted, the errors are additive.

The errors shown in Table 4 have been calculated on the basis of matrix errors only. Overlap errors can give rise to additional errors. In such cases, the error to a component is an absolute concentration, i.e. the error is not proportional to the concentration of the analyte. Overlap errors are more important for minor elements. No attempt has been made to quantify these errors as they are dependent on instrument parameters. See Table 3 for possible line overlaps.

Iron is the element required with high precision, and if 0,1 % Fe_2O_3 is regarded as the maximum error that can be tolerated then, using Table 4, it can be seen that the omission of measuring 250 ppm BaO will give such an error. From Table 4, it can be seen that an error of 1 % in BaO gives a relative error of 2,97 % in Fe_2O_3, so that if the Fe_2O_3 content of the ore is 90 % the resulting error due to 0,025 % BaO is calculated as Formula (1):

$$0{,}025 \times 2{,}97 \times 90/100 = 0{,}067\ \% \tag{1}$$

8.5.3 Analytical lines

Line-only positions are measured. It is not necessary to measure background intensities, but if desired they can be measured and net intensities recorded.

8.5.4 XRF generator settings

The voltage, in kilovolts, is not critical and normally with a simultaneous instrument will be set in the range 40 kV to 60 kV. Where using a sequential instrument, it can be advantageous to use a low voltage (40 kV) for the lighter elements and a higher voltage for the heavier elements. It should be noted that certain spectrometers cannot be run at the highest voltage specified in Table 3, and it is not necessary to do so. If tube operating conditions are changed during analysis, this can result in slight instability in the spectrometer output. Since Fe content is required to be determined with very high precision, Fe shall be measured in a separate run with constant tube conditions if conditions vary for the other elements.

When XRF generators are powered up, it is common for the instrument to drift for some time, typically 30 min to 60 min. Therefore, prior to measurement, the generator should be powered up and left to stabilize.

All measurements shall be made under vacuum, using a detector (proportional or scintillation counter) appropriate to the wavelength being measured, and using specimen rotation if available. A Cr, Cr/Au, Sc, Sc/Mo, Sc/W or Rh target X-ray tube shall be used. It is recommended that pulse height selection be used, particularly in the case where low concentrations are being determined. Where count rates are very high (e.g. FeKα or CaKα), either wide pulse height settings or no upper level shall be used.

In special circumstances (e.g. determining Cr or Mn using a Cr type tube), primary beam filters may be used. A filter will be required to achieve low backgrounds for the determination of Mn and Cr using a Cr target X-ray tube.

Table 4 — Error, in relative %, resulting from a 1 % error in a component for flux

Case	Compound																				
a)	Interfered	Affected																			
		Fe_2O_3	SiO_2	CaO	Mn_3O_4	Al_2O_3	TiO_2	MgO	P_2O_5	SO_3	K_2O	SnO_2	V_2O_5	Cr_2O_3	Co_3O_4	NiO	CuO	ZnO	As_2O_3	PbO	BaO	Cl
	SiO_2	0,37	---	0,31	0,28	0,10	0,31	0,09	0,27	0,27	0,30	0,30	0,32	0,32	0,26	0,14	0,14	0,14	0,13	0,13	0,31	0,28
	CaO	1,25	0,12	---	0,91	0,12	0,98	0,12	0,12	0,12	0,18	0,27	1,01	1,03	0,87	0,49	0,49	0,49	0,48	0,47	0,98	0,13
	Mn_3O_4	0,56	0,19	0,18	---	0,19	0,19	0,18	0,19	0,19	0,17	0,17	0,19	0,38	1,36	0,78	0,79	0,79	0,79	0,78	0,18	0,19
	Al_2O_3	0,33	0,24	0,27	0,24	---	0,28	0,08	0,24	0,25	0,27	0,27	0,28	0,28	0,22	0,13	0,12	0,12	0,12	0,11	0,28	0,25
	TiO_2	1,24	0,14	0,19	0,90	0,14	---	0,13	0,14	0,14	0,17	0,17	0,37	1,01	0,86	0,49	0,49	0,49	0,49	0,49	0,34	0,14
	MgO	0,30	0,24	0,26	0,22	0,23	0,26	---	0,24	0,24	0,25	0,25	0,26	0,26	0,20	0,11	0,11	0,11	0,10	0,10	0,26	0,24
	P_2O_5	0,41	0,11	0,34	0,30	0,10	0,34	0,09	---	0,29	0,33	0,33	0,34	0,34	0,28	0,16	0,16	0,15	0,15	0,14	0,34	0,30
	SO_3	0,45	0,12	0,37	0,33	0,11	0,37	0,10	0,13	---	0,35	0,36	0,37	0,37	0,31	0,17	0,17	0,17	0,16	0,16	0,37	0,32
	K_2O	1,24	0,11	0,99	0,90	0,11	0,96	0,11	0,11	0,11	---	0,27	0,99	1,01	0,86	0,49	0,49	0,49	0,48	0,47	0,95	0,12
	SnO_2	1,96	0,23	0,54	1,42	0,22	1,50	0,21	0,24	0,26	0,44	---	1,56	1,59	1,37	0,78	0,78	0,78	0,78	0,75	1,50	0,28
	V_2O_5	1,29	0,15	0,18	0,94	0,14	0,31	0,14	0,15	0,15	0,17	0,17	---	0,40	0,89	0,51	0,51	0,51	0,50	0,50	0,32	0,15
	Cr_2O_3	1,74	0,17	0,20	0,39	0,17	0,25	0,17	0,17	0,17	0,19	0,20	0,42	---	1,21	0,69	0,69	0,69	0,69	0,69	0,25	0,17
	Co_3O_4	0,59	0,23	0,21	0,12	0,22	0,21	0,22	0,23	0,23	0,22	0,21	0,21	0,21	---	0,30	0,99	1,00	1,01	1,02	0,21	0,23
	NiO	0,34	0,27	0,28	0,24	0,26	0,28	0,26	0,27	0,28	0,28	0,29	0,31	0,32	0,49	---	0,36	1,17	1,21	1,23	0,30	0,28
	CuO	0,33	0,29	0,31	0,25	0,28	0,30	0,27	0,29	0,30	0,30	0,31	0,32	0,33	0,23	0,29	---	0,38	1,28	1,30	0,32	0,30
	ZnO	0,35	0,32	0,34	0,27	0,31	0,33	0,30	0,32	0,33	0,34	0,35	0,35	0,36	0,23	0,05	0,33	---	1,43	1,46	0,35	0,34
	As_2O_3	0,43	0,38	0,44	0,35	0,33	0,43	0,10	0,39	0,40	0,43	0,43	0,45	0,44	0,28	0,08	0,05	0,03	---	1,58	0,44	0,41
	PbO	1,98	0,29	1,37	1,45	0,24	1,57	0,20	0,34	0,42	1,23	1,26	1,63	1,66	1,38	0,74	0,73	0,73	0,97	---	1,57	0,92
	BaO	2,97	0,35	0,62	1,92	0,32	0,84	0,28	0,37	0,39	0,56	0,58	0,97	1,74	2,07	1,19	1,19	1,20	1,21	1,22	---	0,42
	Cl	1,09	0,10	0,84	0,80	0,08	0,86	0,08	0,11	0,13	0,80	0,81	0,88	0,90	0,75	0,43	0,43	0,42	0,41	0,40	0,86	---
	Na_2O	0,26	0,21	0,22	0,20	0,21	0,23	0,20	0,21	0,21	0,22	0,22	0,23	0,23	0,18	0,10	0,10	0,10	0,09	0,09	0,23	0,21

NOTE 1 Case a) is the estimated errors calculated for Flux C and 10,0 of flux/sample mass ratio. The estimated errors of Flux A and D are almost identical to them.

NOTE 2 Case b) is the estimated errors calculated for Flux B and 10,0 of flux/sample mass ratio.

Table 4 *(continued)*

Case	Compound																				
b)	Inter-fered	Affected																			
		Fe_2O_3	SiO_2	CaO	Mn_3O_4	Al_2O_3	TiO_2	MgO	P_2O_5	SO_3	K_2O	SnO_2	V_2O_5	Cr_2O_3	Co_3O_4	NiO	CuO	ZnO	As_2O_3	PbO	BaO	Cl
	SiO_2	0,23	---	0,21	0,19	0,07	0,21	0,06	0,19	0,19	0,20	0,20	0,21	0,21	0,18	0,12	0,12	0,11	0,11	0,10	0,21	0,19
	CaO	0,77	0,08	---	0,63	0,08	0,65	0,08	0,08	0,08	0,12	0,18	0,67	0,68	0,60	0,40	0,39	0,39	0,38	0,35	0,65	0,09
	Mn_3O_4	0,35	0,13	0,12	---	0,13	0,12	0,13	0,13	0,13	0,12	0,11	0,12	0,25	0,95	0,63	0,63	0,63	0,62	0,59	0,11	0,13
	Al_2O_3	0,20	0,17	0,19	0,17	---	0,19	0,06	0,17	0,17	0,18	0,18	0,19	0,19	0,16	0,10	0,10	0,10	0,10	0,09	0,19	0,18
	TiO_2	0,77	0,10	0,12	0,62	0,10	---	0,10	0,09	0,10	0,11	0,11	0,23	0,67	0,60	0,40	0,40	0,40	0,39	0,37	0,21	0,10
	MgO	0,19	0,17	0,18	0,15	0,16	0,17	---	0,17	0,17	0,17	0,17	0,17	0,17	0,14	0,09	0,09	0,09	0,09	0,09	0,17	0,17
	P_2O_5	0,25	0,08	0,23	0,21	0,07	0,22	0,07	---	0,21	0,22	0,22	0,23	0,23	0,20	0,13	0,13	0,12	0,12	0,11	0,22	0,21
	SO_3	0,28	0,08	0,25	0,23	0,08	0,25	0,07	0,09	---	0,24	0,24	0,25	0,25	0,21	0,14	0,14	0,14	0,13	0,12	0,25	0,23
	K_2O	0,77	0,08	0,67	0,62	0,08	0,64	0,08	0,08	0,08	---	0,18	0,66	0,67	0,60	0,40	0,39	0,39	0,38	0,36	0,64	0,08
	SnO_2	1,22	0,16	0,36	0,98	0,15	1,00	0,15	0,17	0,18	0,29	---	1,03	1,06	0,96	0,63	0,63	0,63	0,62	0,58	1,00	0,19
	V_2O_5	0,80	0,10	0,12	0,64	0,10	0,20	0,10	0,10	0,10	0,11	0,11	---	0,25	0,62	0,41	0,41	0,41	0,39	0,37	0,21	0,10
	Cr_2O_3	1,07	0,12	0,13	0,27	0,12	0,15	0,12	0,12	0,12	0,12	0,12	0,27	---	0,84	0,56	0,56	0,55	0,54	0,51	0,15	0,12
	Co_3O_4	0,37	0,16	0,14	0,09	0,16	0,13	0,16	0,16	0,16	0,14	0,14	0,13	0,13	---	0,24	0,80	0,80	0,79	0,75	0,13	0,16
	NiO	0,19	0,19	0,19	0,16	0,19	0,18	0,18	0,19	0,19	0,19	0,19	0,19	0,19	0,34	---	0,29	0,94	0,94	0,91	0,19	0,20
	CuO	0,19	0,20	0,20	0,16	0,20	0,19	0,20	0,21	0,21	0,20	0,21	0,20	0,20	0,14	0,24	---	0,30	1,00	0,96	0,20	0,21
	ZnO	0,20	0,23	0,23	0,17	0,22	0,21	0,21	0,23	0,23	0,23	0,23	0,22	0,22	0,15	0,04	0,27	---	1,11	1,08	0,22	0,24
	As_2O_3	0,26	0,27	0,29	0,23	0,23	0,28	0,07	0,27	0,28	0,29	0,29	0,29	0,28	0,19	0,07	0,05	0,03	---	1,17	0,29	0,29
	PbO	1,22	0,20	0,93	0,99	0,17	1,04	0,14	0,24	0,29	0,84	0,85	1,07	1,09	0,96	0,60	0,59	0,59	0,77	---	1,04	0,64
	BaO	1,84	0,24	0,41	1,32	0,23	0,54	0,20	0,26	0,27	0,37	0,38	0,63	1,14	1,44	0,96	0,96	0,96	0,95	0,91	---	0,29
	Cl	0,68	0,07	0,57	0,55	0,06	0,57	0,05	0,08	0,09	0,55	0,55	0,59	0,60	0,53	0,35	0,34	0,34	0,32	0,30	0,57	---
	Na_2O	0,17	0,15	0,15	0,14	0,15	0,15	0,15	0,15	0,15	0,15	0,15	0,15	0,15	0,13	0,08	0,08	0,80	0,08	0,08	0,15	0,15
	Na_2O	0,17	0,15	0,15	0,14	0,15	0,15	0,15	0,15	0,15	0,15	0,15	0,15	0,15	0,13	0,08	0,08	0,80	0,08	0,08	0,15	0,15

NOTE 1 Case a) is the estimated errors calculated for Flux C and 10,0 of flux/sample mass ratio. The estimated errors of Flux A and D are almost identical to them.

NOTE 2 Case b) is the estimated errors calculated for Flux B and 10,0 of flux/sample mass ratio.

8.5.5 Crystals

The crystals listed in Table 3 are those preferred for the measurements, particularly for sequential-type instruments. Other crystals could, however, be used if these are not available. In the case of PKα, the Ge(111) crystal is recommended because it does not give second-order wavelengths. If, however, this crystal is unavailable, and a PE crystal is used, pulse height selection shall be used and the settings very carefully selected, so that the possibility of interference from the second-order wavelength of CaKβ is minimized.

8.5.6 Line overlaps

Relevant specific line overlaps are shown in Table 3. Note that certain well-known overlaps are not shown since the overlapping element is low in the materials under consideration.

8.5.7 Collimators

Coarse or fine collimators can be used, but where there is the likelihood of line interference, a fine collimator should be used (e.g. in the determination of manganese using a chromium target X-ray tube, and the determination of phosphorus using a PE crystal). In general, the fine collimator will give lower overlap interferences and BECs.

Where crystal fluorescence contributes significantly to BEC, it is also advisable to use a fine collimator, e.g. magnesium determinations using TlAP (thallium acid phthalate) crystal and Rh tube.

8.5.8 Pulse height settings

Where there is interference from a second order line, narrow pulse height settings should be used to minimize interference. Also, where crystal fluorescence contributes to background, it may be possible to reduce the BEC by using a narrower than normal pulse height analyser window setting.

8.5.9 Counting time

The standard deviation of X-ray intensity can be estimated by determining the square root of total counts. This generally applies to relatively low count rates (about 300 kc/s or lower). At higher count rates the counting statistical error is worse than calculated. Follow the recommendation of the instrument manufacturer. The calculation procedure to obtain the counting time for an element to measure with a required precision by counting statistics is described below.

The dedicated calibration curve for the determination of counting time shall be obtained for each element. The calibration is obtained from the concentrations and X-ray intensities of two calibration samples for each element.

Iron	Fe_2O_3 100 %
Other than Iron	Calibration standard sample of the element and blank (Fe_2O_3 100 %)

For iron, background intensity is ignored to estimate counting time.

The counting time of iron can be calculated by Formula (2):

$$T = \{100 \times [1 + \alpha_{\mathrm{FeFe}} (s_i + 100)]\}^2 / \left(s_i^2 \times I_{\mathrm{Fe}}\right) \qquad (2)$$

where

T is the measuring time (s);

s_i is the specified precision of analyte i (%);

I_{Fe} is the intensity of Fe of Fe_2O_3 100 % disc;

α_{FeFe} is the alpha coefficient of Fe_2O_3 for Fe_2O_3 analysis calculated using fundamental parameter method.

The number of 100 in Formula (2) is 100 % of Fe_2O_3 concentration in Fe_2O_3 100 % disc.

For the elements other than iron, the calibration curve without correction is defined as Formula (3).

$$C_i = A_i I_i - B_i \tag{3}$$

where

C_i is the concentration of analyte i (%);

I_i is the X-ray intensity of analysing element i (c/s);

A_i, B_i are the calibration coefficients of analyte i.

The counting time to get the specified precision is obtained by Formula (4).

$$T = A_i (C_i + B_i) / s_i^2 \tag{4}$$

where

T is the measuring time (s);

C_i is the concentration of analyte i (%);

s_i is the specified precision of analyte i (%).

Formula (4) represents the calculation of counting time without background subtraction. It is necessary to consider the statistical variation of background intensity when background subtraction is performed for an element. At high count rates, the time T required shall be lengthened. Follow the manufacturer's recommendations of the instrument.

Annex H describes examples of counting time calculation.

8.5.10 Simultaneous instruments

Where using simultaneous-type instruments, the manufacturer will supply crystals to determine each element.

These possibly will or will not correspond to those listed in Table 3.

Likewise, there is no selection of collimators for simultaneous instruments. The slit size will be predetermined by the manufacturer.

8.5.11 Sample holders

Sample holders for disc presentation shall be matched in accordance with the reproducibility test specified in Annex D.

8.5.12 Measurement sequence

To have a measurement sequence, it is important to pay attention to X-ray intensities measured by X-ray fluorescence spectrometers that fluctuate over time. Drift correction (see 8.6) is required to eliminate the influence of this effect on the analyses results.

8.6 Drift correction

Drift correction is performed by correcting X-ray intensities of ore samples with the drift correction coefficients which are obtained by measuring monitor discs beforehand. Care shall be taken for the drift correction of Fe, because high precision is especially required for the analysis of Fe.

8.6.1 Preparation of drift correction monitor discs

Monitor discs should be prepared by adjusting the amount of reagents such that the fluorescent X-ray intensity of iron is greater than the intensity corresponding to 60 % of iron (T. Fe) concentration in iron calibration, and such that the intensities of other components are greater than the intensities corresponding to 80 % relative to the upper laboratory limits. The total concentration of all components as oxides may exceed 100 %.

These concentration conditions don't necessarily need to be met by a single disc. As long as all conditions are met, it is acceptable to prepare multiple discs.

It is not necessary that the monitor disc (or set of discs) be prepared using flux specified in this standard. Other flux or matrices of the monitor disc (or set of discs) are acceptable as long as the intensities of the individual elements and their homogeneity is guaranteed.

The reagents to add for elements including iron may be other than those specified in Clause 5. As an example of preparation, a mixture of produced iron ore with the amount of "*w*" of laboratory specified mass and reagents for the components, for which concentrations specified above are not satisfied, can be used for the preparation.

It is desired that the monitor disc (or set of discs) does not deteriorate over time due to X-ray radiation or humidity. Soda glass and metal discs are examples of stable monitors and commercially available monitor discs may be used.

If deterioration of the monitor disc (or set of discs) cannot be avoided, determine the duration over which deterioration is negligible and prepare a new monitor disc (or set of discs) during this time for replacement.

If the duration of negligible change for discs prepared with a flux specified in this standard is already known, it is allowed to use this duration. If it is not known, determine the duration.

There are two methods of drift correction. The α method uses one monitor disc, whereas the αβ method uses two. The αβ method using high intensity and low intensity monitors can correct the background intensity drift as well as sensitivity. The monitor disc described above shall be used in the α method and for the high disc for the αβ method. A blank disc (SiO_2 100 %, Fe_2O_3 100 %) shall be used for the low disc in the αβ method. This blank monitor disc should be different from the one used for setting up the calibration. Either the α or αβ method may be used for the drift correction.

If the monitor disc (or set of discs) is known to change over time, prepare at least two discs (or set of discs) and always keep one disc (or set of discs) for backup. The backup disc (or set of discs) should always be stored in a desiccator. The monitor disc (or the set of discs) in use should also be stored in a desiccator except for when being measured.

8.6.2 Drift correction using monitor disc

8.6.2.1 Counting time of monitor disc

When the drift correction coefficients are updated, the X-ray intensity statistical variation of the monitor disc measurement introduces error in the analysis result. To reduce statistical error due to drift correction, the counting time of the monitor disc (or set of discs) shall be more than twice that of the samples.

8.6.2.2 Calculation of drift correction coefficient

Monitor discs shall be measured when calibration discs are measured for drift correction. The monitor disc intensity is used as the reference intensity. Backup monitor discs should also be measured at the same time. Monitor discs are measured just prior to sample analysis or after the spectrometer is started up.

The drift correction coefficient for α method is determined as Formula (5).

$$\alpha_i = M_{0i} / M_{1i} \tag{5}$$

where

M_{0i} is the intensity of the monitor disc measured in calibration disc measurement (reference intensity);

M_{1i} is the intensity of monitor disc measured just prior to sample analysis;

α_i is the drift correction coefficient.

When the monitor disc needs to be replaced, measure the new monitor disc immediately after the drift correction coefficient has been updated with the original monitor disc. The drift corrected intensity with the new monitor disc using the new drift correction coefficient is used as the new reference intensity.

$$M_{0\mathrm{N}i} = \alpha_i \times M_{\mathrm{N}i} \tag{6}$$

where

$M_{0\mathrm{N}i}$ is the reference intensity of the new monitor disc;

$M_{\mathrm{N}i}$ is the measured intensity of the new monitor disc immediately after replacement.

Subsequently, replace M_{0i} with $M_{0\mathrm{N}i}$ and use the new monitor disc to determine the drift correction coefficient.

The drift correction coefficients for the αβ method are determined as Formula (7) and Formula (8);

$$\alpha_i = (M_{0i\mathrm{H}} - M_{0i\mathrm{L}}) / (M_{1i\mathrm{H}} - M_{1i\mathrm{L}}) \tag{7}$$

$$\beta_i = (M_{1i\mathrm{H}} \times M_{0i\mathrm{L}} - M_{0i\mathrm{H}} \times M_{1i\mathrm{L}}) / (M_{1i\mathrm{H}} - M_{1i\mathrm{L}}) = M_{0i\mathrm{H}} - (\alpha_i \times M_{1i\mathrm{H}}) \tag{8}$$

where

$M_{0i\mathrm{H}}$ is the initial intensity of the high monitor disc obtained at the time of calibration disc measurement (reference intensity);

$M_{0i\mathrm{L}}$ is the initial intensity of the low monitor disc obtained at the time of calibration disc measurement (reference intensity);

$M_{1i\mathrm{H}}$ is the intensity of the high monitor disc just prior to sample analysis;

M_{1iL} is the intensity of the low monitor disc just prior to sample analysis;

α_i , β_i are the drift correction coefficients.

When a monitor disc needs to be replaced, measure the new monitor disc immediately after the drift correction coefficients have been updated with the original monitor discs. The drift corrected intensity with the new monitor disc is used as the new reference intensity.

$$M_{0Ni} = \alpha_i \times M_{Ni} + \beta_i \tag{9}$$

where

M_{0Ni} is the reference intensity of the new monitor disc;

M_{Ni} is the measured intensity of the new monitor disc immediately after replacement.

Subsequently, replace M_{0iH} or M_{0iL} with M_{0Ni} and use the new monitor disc to determine drift correction coefficients.

The software provided by the instrument manufacturer usually provides the functionality above to perform drift correction.

8.6.2.3 Calculation of drift corrected intensity

To calculate the corrected intensity I_{ic} for each sample, use the new correction coefficient(s) determined in the drift correction update as shown below.

The drift correction of α method is determined by Formula (10).

$$I_{ic} = \alpha_i \times I_i \tag{10}$$

where

I_i is the intensity of the analysing sample before drift correction;

I_{ic} is the intensity of the analysing sample after drift correction.

The drift correction of αβ method is determined by Formula (11).

$$I_{ic} = \alpha_i \times I_i + \beta_i \tag{11}$$

where

I_i is the intensity of the analysing sample before drift correction;

I_{ic} is the intensity of the analysing sample after drift correction.

The software provided by the instrument manufacturer usually provides the functionality above to perform drift correction.

8.6.2.4 Time interval for updating drift correction coefficients

Measured X-ray intensities fluctuate over time. The X-ray intensity of iron should be measured with a high precision. Therefore, it is necessary to analyse a given set of ore samples consecutively within a time period over which the drift rate of X-ray intensity does not exceed the limit (0,1 % for iron, 1 % for other elements). The time period over which the X-ray intensity drift rate does not exceed the limit shall be determined in advance. For example, in the case in which the time period is 4 h, the drift correction coefficients should be updated by measuring the monitor disc (or set of discs) again 4 h later in order to continue to analyse ore samples without error due to drift. The usable period of drift correction shall be determined based on the period when the drift rates of X-ray intensities do not exceed the limit by measuring the monitor disc (or set of discs) once every 30 min over a certain period of time. The high intensity monitor disc is used to determine the time interval in case of the αβ method.

8.6.2.5 Determination of the usable duration for monitor discs

It is often the case that monitor discs deteriorate over time. Therefore, it is necessary to determine the usable duration of monitor discs in advance. The backup discs shall also be used as reference discs in the procedure below.

The procedures to determine the usable duration of monitor discs are as follows, and these procedures shall be performed periodically (for example once per month) until the duration is determined.

a) Measure monitor disc(s) to update the drift correction coefficient(s).

b) Measure backup disc(s) to obtain the drift corrected intensity(s).

c) Calculate the change rate of the drift corrected intensity over the original intensity of the backup monitor disc obtained in 8.6.2.2 and determine if the calculated rate is less than the limit (0,1 % for iron, 1 % for other elements). The high monitor disc is measured in case of αβ method.

d) When the calculated rate does not exceed the limit, the original disc is regarded as not deteriorated.

e) When the calculated rate exceeds the limit, repeat steps from a) to d) above.

f) When the calculated rate for the second time does not exceed the limit, the monitor disc is considered not deteriorated.

g) When the second calculated rate exceeds the limit, the monitor disc shall be discarded because it is considered deteriorated. Then the backup monitor disc shall be used as the regular monitor disc and its original intensity shall be registered as the reference intensity.

When the monitor disc is replaced with the backup monitor disc in step g), a new backup monitor disc shall be prepared, and its X-ray intensity is measured and the drift corrected intensity shall be recorded.

When a monitor disc is determined to be deteriorated, the period from the initial use of the monitor disc to the last test with the result being within the limit for the procedure above shall be the usable duration.

The usable duration for monitor disc(s) used for drift correction α or αβ method shall be determined according to the procedures above. The low monitor disc for αβ method is sensitive to contamination, and the drift corrected intensity of the low monitor disc shall be examined. In case this monitor disc becomes contaminated, the intensity increases and the drift corrected X-ray intensity of the backup monitor disc will be lower than the original intensity. If the intensity change due to contamination is significant, replace the low monitor disc with the backup monitor disc.

9 Calculation of results

9.1 General

Calculation of concentrations based on measured intensities is carried out using the calibration equation with correction terms described below.

a) Correction for absorption and enhancement of X-rays by co-existing elements.

   The alpha coefficient obtained by using either the fundamental parameter (FP) method or empirical regression calculation for each element is used for the correction.

b) Correction for the influence of loss and gain on ignition.

For samples containing combined water or carbonate iron compounds, preparation of fused discs can cause evaporation of H_2O and CO_2 leading to loss on ignition. On the other hand, when iron is present as Fe_3O_4 in iron ore, iron is oxidized resulting in the development of gain on ignition and remains as Fe_2O_3 in the fused disc. Accordingly, the total concentration of the sum of all components from the sample does not add up to 100 %. The difference between 100 % and total concentration can be expressed as loss or gain on ignition. The gain on ignition can be considered as negative loss of ignition. The influence of loss on ignition and gain on ignition can be corrected using correction alphas obtained by using a calculation model of alpha coefficients calculation in which the ignition loss is removed from correcting components.

c) Correction for sample, flux and oxidizer (remaining oxidizer) masses.

Mass variations of sample, flux and remaining oxidizer in each fused disc affect the concentration of elements in fused disc. The influence of mass variation is corrected using the actual masses obtained for each fused disc.

d) Correction for overlap.

The influences of line overlaps by coexisting elements are corrected in the equation using a correction model with concentrations of interfering elements.

e) Oxides for quantification.

All elements in samples exist as oxides in fusion discs. Actual forms of oxides shall be defined with composition formulae of the oxide compounds in the software. When any oxides such as Mn_3O_4 and Co_3O_4 are not defined, the compounds shall be registered in advance. The composition formulae of the oxides for iron ore analysis are shown in Table 8. In addition, composition formula of flux to be used shall be registered in the software. When the flux is mixed flux such as Flux A and D, enter number of atoms for each element of Li, B and O calculated considering mixing ratio and composition formulae of $Li_2B_4O_7$ and $LiBO_2$. Preset the oxides and flux in the analytical parameters of the software and the oxides are utilized in quantification and matrix correction alpha calculation using the fundamental parameter method.

9.2 Calibration equation

Since each element is contained as an oxide in the fused disc, the concentrations as oxide compounds shown in Table 8 are used for quantification.

Correction for sample, flux and oxidizer (sodium nitrate) mass variations can be carried out by three different correction equations. One of these equations shall be used depending on the software provided with the X-ray fluorescence spectrometer, since they yield practically equivalent quantitative results for iron ore samples with the fusion method. The calibration Equation 2 [see Formula (15)] and Equation 3 [see Formula (20)] can be derived from the basic equation of calibration Equation 1 [see Formula (12)].

Note that the values of correction alphas of components are the same for the three calibration methods.

Select a calibration method from Equation 1 to 3 according to the availability by the instrument software.

a) Calibration Equation 1

The general equation [see Formula (12)] is used for the calibration equation including correction for sample, flux and oxidizer (sodium nitrate) mass and matrix correction except for the analysis of Fe_2O_3.

$$C_i = A_i I_i \left(1+\alpha_{ii}C_i + \sum\alpha_{ij}C_j + K_{i\mathrm{XF}} + \alpha_{i\mathrm{F}}R_\mathrm{F} + \alpha_{i\mathrm{X}}R_X\right) - B_i - \sum L_{ij}C_j \quad (12)$$

where

C_i is the concentration of analysing component i;

A_i is the calibration slope;

I_i is the drift corrected intensity of analysing element;

α_{ii} is the self-absorption alpha coefficient;

α_{ij} is the alpha coefficient of correcting component j;

C_j is the concentration of correcting component;

B_i is the background equivalent coefficient (BEC);

L_{ij} is the overlapping coefficient;

$\alpha_{i\mathrm{F}}$ is the alpha coefficient of flux/sample mass ratio;

R_F is the flux/sample mass ratio;

$\alpha_{i\mathrm{X}}$ is the alpha coefficient of oxidizer/sample mass ratio;

R_X is the remaining oxidizer/sample mass ratio;

$K_{i\mathrm{XF}}$ is the mass ratio correction constant.

The alpha coefficients obtained by the FP method are used for the mass ratio alpha coefficients of $K_{i\mathrm{XF}}$, $\alpha_{i\mathrm{F}}$ and $\alpha_{i\mathrm{X}}$. When mass ratio corrections of oxidizer/sample and remaining oxidizer/sample are not required, the terms from $K_{i\mathrm{XF}}$ in the parentheses are not used. The alpha coefficients α_{ij} for coexisting elements are calculated by the FP method or empirical regression. The calibration slope, BEC and overlapping coefficients are determined based on measured X-ray intensities of calibration discs and concentrations of the discs by regression calculation using the equation above. The absorption corrections using alpha coefficients α_{ij} are applied to all coexisting elements in the samples. Overlapping correction is applied only to the elements for which correction is required.

Formula (13) is used for the analysis of iron,

$$C_\mathrm{Fe} = A_\mathrm{Fe} I_\mathrm{Fe} \left(1 + \alpha_\mathrm{FeFe} C_\mathrm{Fe} + \sum \alpha_{\mathrm{Fe}j} C_j + K_\mathrm{Fe,XF} + \alpha_\mathrm{Fe,F} R_\mathrm{F} + \alpha_\mathrm{Fe,X} R_\mathrm{X}\right) - B_\mathrm{Fe} \tag{13}$$

where

C_Fe is the iron (Fe_2O_3) concentration of analysing component;

A_Fe is the calibration slope of iron;

I_Fe is the drift corrected X-ray intensity of iron;

α_FeFe is the self-absorption alpha coefficient;

$\alpha_{\mathrm{Fe}j}$ is the alpha coefficient of the other component j;

C_j is the concentration of the other component j;

B_Fe is the background equivalent coefficient (BEC) of iron;

$\alpha_\mathrm{Fe,F}$ is the alpha coefficient of flux/sample mass ratio of iron;

R_F is the flux/sample mass ratio;

$\alpha_\mathrm{Fe,X}$ is the alpha coefficient of oxidizer/sample mass ratio of iron;

R_X is the remaining oxidizer/sample mass ratio;

$K_{Fe,XF}$ is the mass ratio correction constant of iron.

If there is larger difference of flux/sample mass ratio of a disc with nominal mass ratio, some quantified error can appear when gross intensity is used and the value of B_i (BEC) is large. The next calibration equation [see Formula (14)] with the term of B_i corrected by mass ratios may be used.

$$C_i = A_i I_i \left(1 + \alpha_{ii} C_i + \sum \alpha_{ij} C_j + K_{iXF} + \alpha_{iF} R_F + \alpha_{iX} R_X\right) - B_i \left(1 + R_F + R_X\right) - \sum L_{ij} C_j \tag{14}$$

where

R_F is the flux/sample mass ratio;

R_X is the product of (remaining oxidizer/sample mass ratio) and 100.

b) Calibration Equation 2

Remaining oxidizer Na_2O is regarded as a component in sample for the correction of remaining oxidizer to sample mass ratio in Formula (15).

$$C_i = A_i I_i \left(1 + \alpha_{ii} C_i + \sum \alpha_{ij} C_j + K_{iF} + \alpha_{iF} R_F + \alpha_{Na2O} C_{Na2O}\right) - B_i - \sum L_{ij} C_j \tag{15}$$

where C_{Na2O} is the remaining oxidizer/sample mass ratio.

K_{iF} and α_{iF} can be given as follows;

$$K_{iF} = -1{,}0 \tag{16}$$

$$\alpha_{iF} = 1 / R_{F0} \tag{17}$$

where R_{F0} is the nominal flux/sample mass ratio.

By substituting these terms into Formula (15), the term K_{iF} is cleared and Formula (18) is derived.

$$C_i = A_i I_i \left(1 + \alpha_{ii} C_i + \sum \alpha_{ij} C_j + \alpha_{iF} \Delta R_F + \alpha_{Na2O} C_{Na2O}\right) - B_i - \sum L_{ij} C_j \tag{18}$$

where ΔR_F is the difference of mass ratios between nominal to actual ($\Delta R_F = R_F - R_{F0}$).

The alpha coefficient α_{Na2O} of remaining oxidizer to sample mass ratio is obtained assuming that Na_2O is contained in the sample. C_{Na2O} is the concentration of remaining oxidizer mass regarding the sample mass as 100 % as described above. When oxidizer in fusion is not used, the term of $\alpha_{Na2O} C_{Na2O}$ is not used in Formula (18).

In the case of Equation 2, if there is larger difference of flux/sample mass ratio of a disc with nominal mass ratio, some quantified error can appear when gross intensity is used and the value of B_i (BEC) is large. Formula (19) with the term of B_i corrected with mass ratios may be used.

$$C_i = A_i I_i \left(1 + \alpha_{ii} C_i + \sum \alpha_{ij} C_j + \alpha_{iF} \Delta R_F + \alpha_{Na2O} C_{Na2O}\right) - B_i \left(1 + R_F + C_{Na2O} / 100\right) - \sum L_{ij} C_j \tag{19}$$

c) Calibration Equation 3

The correction of remaining oxidizer is treated in the same manner as in calibration Equation 2.

Flux/sample mass ratio is not included in the correction equation. All of the concentrations of components including remaining oxidizer are the values recalculated with nominal flux/sample mass ratio.

$$C_i{}' = A_i I_i \left(1 + \alpha_{ii} C_i{}' + \sum \alpha_{ij} C_j{}' + \alpha_{\mathrm{Na_2O}} C_{\mathrm{Na_2O}}{}'\right) - B_i - \sum L_{ij} C_j{}' \quad (20)$$

The converted concentration shall be obtained.

$$C_i{}' = (R_{\mathrm{F0}} / R_{\mathrm{F}}) C_i \quad (21)$$

where

$C_i{}'$ is the converted concentration of each component with nominal flux/sample mass ratio;

C_i is the concentration of each component.

This conversion is also adapted to Na_2O concentration for the correction of remaining oxidizer/sample mass ratio. The quantitative calculation results shall be converted to concentration in sample by using standard and mass ratio inversely in the equation above.

Theoretical background of the calibration equation with corrections above is interpreted in Annex E.

9.3 Calculation of alpha coefficient

The alpha coefficients in the correction term of the calibration equation shall be calculated by the FP method or empirical method.

The alpha coefficients for coexisting elements α_{ij}, alpha coefficient of flux/sample mass ratio $\alpha_{i\mathrm{F}}$, alpha coefficient of oxidizer/sample mass ratio $\alpha_{i\mathrm{X}}$ can be calculated using theoretically computed intensities of fluorescent X-rays of each measuring line by the FP method.

In the alpha coefficient calculation by the FP method, theoretical intensities of assumed typical composition and compositions in which a certain amount of concentration of each component is changed from the typical composition are calculated using the FP method and each coefficient is obtained based on the calibration equation using the computed theoretical intensities.

In order to obtain accurate alpha coefficients, it is essential to calculate the coefficients using the parameters of X-ray tube and optical conditions that match the actual conditions of the spectrometer being used.

The parameters used in the theoretical intensity calculation of fluorescent X-rays are geometric structure, target material, beryllium window thickness and voltage of the X-ray tube, which determine primary X-ray distribution. In addition, primary beam filter material, thickness, and incident angle between incident X-ray direction and sample surface and take-off angle between detecting angle and sample surface are necessary.

The calculation of alpha coefficient α is carried out according to the calibration equation described above and the method should include the following:

a) The algorithm for calculating alpha coefficients should give optimized coefficients to the typical composition specified.

b) The alpha coefficients are calculated with a model that ignition loss is removed from the correction components and considered as balance. This method effectively corrects for the influence of ignition loss by itself even for iron ore samples with high ignition loss.

c) The alpha coefficients of flux/sample and remaining oxidizer/sample mass ratios should be calculated according to one of the three equations described in 9.2.

A detailed calculation method is described in Annex F.

9.4 Correction for sample, flux and oxidizer mass

9.4.1 General

In order to save time on precisely weighing samples, the actual flux, oxidizer and sample masses in preparing each fused disc can be used to correct for the variations.

Mass correction consists of flux/sample and remaining oxidizer/sample mass ratio corrections.

9.4.2 Correction of flux/sample mass ratio

The flux/sample mass ratio correction is done using mass ratio of flux to sample R_F.

$$R_F = F / S \tag{22}$$

where

F is the mass of flux;

S is the mass of sample.

The constant term of mass ratio of flux to sample K_{iF} is determined by the product of correction coefficient of mass ratio of flux to sample and nominal mass ratio of flux to sample.

$$K_{iF} = -\alpha_{iF} / R_{FS} \tag{23}$$

where R_{FS} is the nominal mass ratio of flux to sample.

Nominal mass ratio of flux to sample is standard mass ratio.

Formula (24) shows the mass ratio correction terms only in the calibration equation.

$$K_{iF} + \alpha_{iF} R_F = \alpha_{iF} (R_F - R_{FS}) \tag{24}$$

where R_F is the mass ratio of flux to sample of the fused disc.

Formula (24) means that this flux ratio term corrects with the difference between the actual mass ratio of the fused disc and the mass ratio of nominal mass ratio. Therefore, this correction term can be removed when the mass correction is not required.

In the calibration Equation 3, this flux/sample mass ratio correction is not used, but all concentrations are converted to nominal flux/sample mass ratio as described in 9.2 c).

9.4.3 Correction of remaining oxidizer/sample mass ratio

Sodium nitrate ($NaNO_3$) is used as an oxidizer and it remains as Na_2O in the disc after fusion. Accordingly, the correction for oxidizer mass is done with mass ratio of remaining oxidizer and sample.

The remaining oxidizer mass is the mass of Na_2O and is obtained by the product of $NaNO_3$ mass and 0,364 6. The converted mass to remaining oxidizer is used for the correction.

(mass of Na_2O) = 0,364 6 × (mass of $NaNO_3$)

The mass ratio correction equation for oxidizer/sample has the same form as that of the mass ratio correction for flux/sample in calibration Equation 1[see 9.2 a)].

The oxidizer to sample mass ratio constant of K_{iX} is shown as Formula (25).

$$K_{iX} = -\alpha_{iX} R_{XS} \tag{25}$$

where R_{XS} is the nominal mass ratio of remaining oxidizer to sample in the fused disc (mass of Na_2O/mass of sample).

Nominal mass ratio of remaining oxidizer to sample is the standard mass ratio.

Formula (26) shows the correction terms of remaining oxidizer to sample mass ratio for the calibration equation.

$$K_{iX} + \alpha_{iX} R_{XS} = \alpha_{iX} \left(R_X - R_{XS} \right) \tag{26}$$

where R_X is the remaining oxidizer to sample mass ratio (mass of Na_2O/mass of sample).

Formula (26) means that the remaining oxidizer to sample mass ratio term corrects with the difference between actual mass ratio of the fused disc and the mass ratio of nominal mass ratio. Therefore, this correction term can be removed when mass ratio correction is not required.

The correction of remaining oxidizer/sample mass ratio is performed assuming that remaining oxidizer Na_2O is contained in sample in calibration Equation 2 and 3 as described in 9.2 b) and c).

9.4.4 Mass ratio correction constant in calibration Equation 1

The constant term K_{iXF} in the calibration Equation 1 [see 9.1 a)] for mass ratio correction is the sum of constants flux to sample mass ratio and remaining oxidizer to sample mass ratio.

$$K_{iXF} = K_{iF} + K_{iX} \tag{27}$$

9.5 Calculation of calibration

9.5.1 Preparation of calibration discs

See 8.4 for general preparation procedure of calibration discs.

9.5.1.1 Calibration discs for iron

Weigh 1,00*w*, 0,95*w*, 0,90*w*, 0,85*w*, 0,80*w*, 0,75*w*, 0,70*w*, 0,50*w*, and 0,30*w* of Fe_2O_3 (5.3), where *w* is a unit of mass specified by the laboratory. In addition, weigh Flux and $NaNO_3$ as specified by the laboratory and record the weights of those reagents rounded to the nearest tenth mg. Put those weighed reagents in a crucible and make fused discs according to 8.4.2 to 8.4.4.

Two fused discs shall be made for every iron concentration specified. Additionally, prepare two fused discs in which 1,0*w* of SiO_2 (5.1) and laboratory specified masses of Flux and $NaNO_3$ are added.

9.5.1.2 Calibration discs for silicon

Weigh 0,1*w* of SiO_2 (5.1), 0,90*w* of Fe_2O_3 (5.3) and laboratory specified masses of Flux and $NaNO_3$ and record the masses of those reagents rounded to the nearest tenth mg. Put those weighed reagents in a crucible and make fused discs according to 8.4.2 to 8.4.4. Two fused discs shall be made.

9.5.1.3 Calibration discs for calcium

Weigh 0,2*w* of $CaCO_3$ (5.6), 0,90*w* of Fe_2O_3 (5.3) and laboratory specified masses of Flux and $NaNO_3$ and record the masses of those reagents rounded to the nearest tenth mg. Put those weighed reagents in a crucible and make fused discs according to 8.4.2 to 8.4.4. Two fused discs shall be made.

9.5.1.4 Calibration discs for aluminium

Weigh 0,065w of Al_2O_3 (5.2), 0,90w of Fe_2O_3 (5.3) and laboratory specified masses of Flux and $NaNO_3$ and record the masses of those reagents rounded to the nearest tenth mg. Put those weighed reagents in a crucible and make fused discs according to 8.4.2 to 8.4.4. Two fused discs shall be made.

9.5.1.5 Calibration discs for titanium

Weigh 0,075w of TiO_2 (5.4), 0,90w of Fe_2O_3 (5.3) and laboratory specified masses of Flux and $NaNO_3$ and record the masses of those reagents rounded to the nearest tenth mg. Put those weighed reagents in a crucible and make fused discs according to 8.4.2 to 8.4.4. Two fused discs shall be made.

9.5.1.6 Calibration discs for magnesium

Weigh 0,21w of magnesium nitrate hexahydrate (5.8), 0,90w of Fe_2O_3 (5.3) and laboratory specified masses of Flux and $NaNO_3$ and record the masses of those reagents rounded to the nearest tenth mg. Put those weighed reagents in a crucible and make fused discs according to 8.4.2 to 8.4.4. Two fused discs shall be made.

9.5.1.7 Calibration discs for manganese and sulfur

Weigh Flux (5.13) and $NaNO_3$ to laboratory specified masses and weigh 0,90w of Fe_2O_3(5.3) and place weighed reagents in a crucible. Record the masses of those reagents rounded to the nearest one tenth of one mg. Then, pipette approximately (400 × w) µl of manganese sulfate solution (5.7) using a piston pipette and a tip (type A), and heat at the appropriate temperature to dry. Record the volume of the solution. 1 000 µl of the manganese sulfate solution contains manganese 20,0 mg and sulfur 11,67 mg (5.7) so that adding 200 µl of the solution containing manganese 4,0 mg results in manganese 0,8 % in fused disc when w is 0,5 g. Adjust the volume of solution settable by a piston pipette. Produce two fused discs in accordance with procedures described from 8.4.2 to 8.4.5.

9.5.1.8 Calibration discs for potassium and phosphorus

Weigh Flux (5.13) and $NaNO_3$ to laboratory specified masses and weigh 0,90w of Fe_2O_3 (5.3) and place weighed reagents in a crucible. Record the masses of those reagents rounded to the nearest one tenth of one mg. Then, pipette approximately (400 × w) µl of dihydrogen phosphate solution (5.5) using a piston pipette and a tip (type A), and heat at the appropriate temperature to dry. Record the volume of the solution. 1 000 µl of the dihydrogen phosphate solution contains 7,92 mg phosphorous and 10,0 mg potassium (5.5) so that adding 200 µl of the solution containing phosphorous 1,584 mg results in phosphorous 0,316 8 % in fused disc when w is 0,5 g. Adjust the volume of solution settable by a piston pipette. Produce two fused discs in accordance with procedures described from 8.4.2 to 8.4.5.

9.5.1.9 Calibration discs for V, Cr, Co, Ni, Cu, Zn, As, Pb, Ba

Weigh Flux (5.13) and $NaNO_3$ to laboratory specified masses and weigh 0,90w of Fe_2O_3 (5.3) and place weighed reagents in a crucible. Record the masses of those reagents rounded to the nearest one tenth of one mg. Add 2 to 5 ml of 1 000 mg/l standard solutions (5.9) for each element which make the concentration of each element 0,5 % to 1,0 % in sample except for Cu, using a single-volume pipette. It is difficult to release a cooled fused disc from a mould with Cu concentration in range from 0,5 % to 1,0 %. Accordingly, prepare fusion discs with lower Cu concentration such as 0,1 % which are easier to release from the mould. Record the volume of the solution. For example, in case of w = 0,5 g, by adding 2,5 ml of standard solution (5.9, except for Cu) with a 2,5 ml single-volume pipette, the concentration of each element is 0,5 %.

Heat them at the appropriate temperature to dry. Produce two fused discs in accordance with procedures described from 8.4.2 to 8.4.5.

It is not always possible to prepare fused discs normally due to foaming and volume expansion during fusing in a crucible when a mixture of Flux and nitric acid solution is dried before fusion especially in Flux B

($Na_2B_4O_7$). In this case, heat and dry the mixture of the reagent Fe_2O_3 and standard solution without Flux in a crucible. Then add Flux and $NaNO_3$ to the crucible for fusion.

NOTE When a solution of potassium dichromate ($K_2Cr_2O_7$) is used for Cr, the solution contains 752 mg/l of potassium and the potassium remains in fused discs.

9.5.1.10 Calibration disc summary

Tables 5 and 6 show reagent masses and calibration disc concentrations described from 9.5.1.1 to 9.5.1.9.

The calibration discs should be handled carefully, and the analytical surface shall under no circumstances be touched by hand.

Table 5 — Calibration discs for iron calibration

Disc no.	Reagents		Concentration	
	Fe_2O_3	SiO_2	Fe_2O_3	SiO_2
	mass	mass	%	%
1	1,0w	-	100	0
2	0,95w	-	95	0
3	0,90w	-	90	0
4	0,85w	-	85	0
5	0,80w	-	80	0
6	0,75w	-	75	0
7	0,70w	-	70	0
8	0,50w	-	50	0
9	0,30w	-	30	0
10	-	1,0w	0	100

Table 6 — Calibration discs for elements other than iron

Disc no.	Comp.	Reagent Mass			Concentration	
		Fe_2O_3	Elements other than Fe		Fe_2O_3	Comp.
		mass	Reagents	mass	%	%
11	SiO_2	0,90w	SiO_2	0,10w	90,0	10,00
12	CaO	0,90w	$CaCO_3$	0,20w	90,0	11,21
13	Al_2O_3	0,90w	Al_2O_3	0,065w	90,0	6,50
14	TiO_2	0,90w	TiO_2	0,075w	90,0	7,50
15	MgO	0,90w	$Mg(NO_3)_2 \cdot 6H_2O$	0,21w	90,0	3,30
16	Mn_3O_4	0,90w	m$MnSO_4 \cdot 5H_2O$ (Mn 20 g/l, S 11,67 g/l)	(400w µl)	90,0	(1,11)
	SO_3					(1,17)
17	K_2O	0,90w	KH_2PO_4 (K 10,0 g/l, P 7,92 g/l)	(400w µl)	90,0	(0,48)
	P_2O_5					(0,73)
18	V_2O_5	0,90w	V 1 000 mg/l	(6w ml)	90,0	(1,07)
19	Cr_2O_3	0,90w	Cr 1 000 mg/l (K 752 mg/l)	(6w ml)	90,0	(0,88) (K_2O 0,33)
20	Co_3O_4	0,90w	Co 1 000 mg/l	(6w ml)	90,0	(0,82)
21	NiO	0,90w	Ni 1 000 mg/l	(6w ml)	90,0	(0,77)
22	CuO	0,90w	Cu 1 000 mg/l	(1,0w ml)	90,0	(0,125)
23	ZnO	0,90w	Zn 1 000 mg/l	(6w ml)	90,0	(0,75)

Table 6 *(continued)*

Disc no.	Comp.	Reagent Mass			Concentration	
		Fe_2O_3 mass	Elements other than Fe		Fe_2O_3	Comp.
			Reagents	mass	%	%
24	As_2O_3	0,90*w*	As 1 000 mg/l	(6*w* ml)	90,0	(0,79)
25	PbO	0,90*w*	Pb 1 000 mg/l	(6*w* ml)	90,0	(0,65)
26	BaO	0,90*w*	Ba 1 000 mg/l	(6*w* ml)	90,0	(0,67)

Prepare duplicate fused discs for the discs in Table 5 and Table 6.

The values in parentheses slightly vary depending on sample masses.

9.5.2 Calculation of concentrations of calibration discs

The concentrations of components of calibration discs depend on nominal and actual flux/sample mass ratio and calibration equation to be used. Concentrations for elements of calibration discs prepared in 9.5.1 shall be obtained following the calibration Equation (9.2).

Note the next two points in concentration calculation.

1) Define nominal masses of flux, oxidizer and sample (*w*).

2) Calculate concentrations from the ratio of mass of target element as oxide to nominal sample mass (*w*). When adding elements with liquids, obtain oxide masses converting from element masses using Table 8.

Individual calculations are summarized below.

a) Mass ratio of flux to sample [R_F, Formula (22)]

$$R_F = \text{flux mass} / \text{sample mass}$$

b) Concentration of elements in calibration discs (C_i)

$$C_i = (S / S_0) \times 100$$

where

S_0 is the nominal sample mass (*w*);

S is the oxide mass of target element.
In the case of Fe_2O_3 calibration discs, S is the mass of Fe_2O_3 or SiO_2.
In the case of calibration discs prepared by adding powder reagents, S is the mass as oxide (the compound such as $CaCO_3$, convert it to oxide form such as CaO).
In the case of calibration discs prepared by adding liquid reagents, S is the mass as oxide (multiply liquid weight by concentration of adding elements and convert it to oxide mass).

When calibration Equation 3 [see 9.2 c)] is used, all concentrations shall be corrected with mass ratio of flux to sample [see Formula (21)].

$$C_i' = (R_{F0} / R_F) \times C_i$$

where

R_{F0} is the nominal mass ratio of flux to sample;

R_F is the mass ratio of flux to sample for each calibration disc.

c) Remaining oxidizer/sample mass ratio and concentration of Na_2O

The calculations for oxidizer are different by calibration equation.

Obtain remaining oxidizer mass first

$$\text{remaining oxidizer mass} = \text{oxidizer mass}\,(NaNO_3) \times 0{,}364\,6$$

Calibration Equation 1 [see 9.2 a)]

$$R_X = \text{remaining oxidizer mass} / \text{sample mass}$$

Calibration Equation 2 [see 9.2 b)]

$$C_{Na2O} = (\text{remaining oxidizer mass} / \text{sample mass}) \times 100$$

Calibration Equation 3 [see 9.2 c)]

$$C_{Na2O}' = (\text{remaining oxidizer mass} / \text{sample mass}) \times 100 \times (R_{F0} / R_F)$$

The concentrations above are used for the calculations of calibration coefficients.

9.5.3 Measurement of calibration discs

Measure the fluorescent X-rays of each component using the calibration discs prepared in 9.5.1 following 7.2.

Measure drift correction discs (or set of discs) during calibration as frequently as required by 8.6.2.4 for iron ore analysis.

9.5.4 Calculation of calibration coefficients

9.5.4.1 Calculation of alpha coefficients for iron ore

Since the calculation of alpha coefficients using the FP method (see 9.3) depends on unique parameters for each instrument such as X-ray tube type, tube voltage, and incident and take-off angles, it is recommended to use the software of the computer connected to the instrument for alpha coefficient calculation.

The following are important points for actual operation.

a) Coefficient calculation method assuming the difference between total concentrations and 100 % is loss on ignition (or gain on ignition). The component of loss on ignition is not included in the correction terms.

b) Set nominal mass ratio of flux to sample for the calculation.

c) Calculate correction coefficient for flux to sample mass ratio in calibration Equation 1 [see 9.2 a)] and Equation 2 [see 9.2 b)].

d) Set nominal mass ratio of remaining oxidizer to sample to calculate correction coefficient for mass ratio of remaining oxidizer to sample in calibration Equation 1 when oxidizer is used for disc preparation.

e) Calculate correction coefficient of Na_2O in calibration Equation 2 and Equation 3 [see 9.2 c)] assuming Na_2O exists in the sample when oxidizer is used for disc preparation.

9.5.4.2 Calculation of calibration coefficients for iron

By using the fluorescent X-ray intensities of iron $[I_{Fe}(i)]$ obtained in 9.5.3 for the 20 discs prepared in 9.5.1.1 for iron calibration, $C_{Fe}(i)$, $R_X(i)$, and $R_F(i)$, obtained from added amounts of individual reagents, and $K_{Fe,XF}$, $\alpha_{Fe,F}$ and $\alpha_{Fe,X}$ obtained in 9.5.4.1, the coefficients A_{Fe}, B_{Fe} and α_{FeFe} in the next equation are obtained. The equation below is for calibration Equation 1. The differences from calibration Equation 2 and Equation 3 are the correction terms of mass ratios for flux/sample and remaining oxidizer/sample (see 9.2).

$$C_{\mathrm{Fe}} = A_{\mathrm{Fe}} I_{\mathrm{Fe}} \left(1 + \alpha_{\mathrm{FeFe}} C_{\mathrm{Fe}} + \alpha_{\mathrm{Fe,Si}} C_{\mathrm{Fe,Si}} + K_{\mathrm{Fe,XF}} + \alpha_{\mathrm{Fe,F}} R_{\mathrm{F}} + \alpha_{\mathrm{Fe,X}} R_{X}\right) - B_{\mathrm{Fe}} \tag{28}$$

The term of $\alpha_{\mathrm{Fe,Si}} C_{\mathrm{Fe,Si}}$ is only for the discs for SiO_2 100 % and the coefficient of $\alpha_{\mathrm{Fe,Si}}$ obtained by the fundamental parameter method is used. When an oxidizer is not added in fusion preparation, the terms related to oxidizer are not used.

The calculation of the coefficients using the least square method is described in Annex G.

The software provided by the instrument manufacturer usually provides the calculation above.

If the iron quantification range of interest is smaller than as specified here, it is not necessary to use all 20 discs for regression to determine the coefficients in iron calibration. In such cases, discs with concentrations that are not in the concentration of interest can be removed and determining the coefficients with the remaining discs is acceptable.

9.5.4.3 Evaluation of iron calibration coefficients

The calibration coefficients for iron are evaluated by calibration accuracy obtained from the difference between the quantified result of Fe_2O_3 using fluorescent X-ray intensity of iron and theoretical concentration calculated from added amounts of reagents for each calibration disc for iron. The value of accuracy shall be less or equal to 0,1 %, see Formula (29).

$$A_C = \sqrt{\frac{\sum (x_i - c_i)^2}{(n-3)}} \tag{29}$$

where

A_C is the accuracy;

x_i is the quantified result [mass fraction %] of Fe_2O_3 for iron calibration disc i;

c_i is the mass fraction % of Fe_2O_3 obtained from added amounts for iron calibration disc i;

n is the total number of iron calibration standard discs.

The quantification of Fe_2O_3 content is carried out by using the right side of the equation in 9.5.4.2 and Fe_2O_3 content obtained from masses of reagents for the content in the correction term for this evaluation.

If there is a calibration disc in which the absolute value of $(x_i - c_i)$ exceeds 0,14 % in mass fraction, prepare two more discs at the same standard level. If the difference of results with an original disc exceeds 0,14 %, the disc can be rejected, the calibration can be remade and the calibration accuracy can be reassessed.

If the accuracy exceeds 0,1 %, the quantitative result of iron cannot be adopted for report. However, the result of iron should be used for the correction for the analysis of other components.

Maximum count rate in modern spectrometers is generally about 5 × 10^5 c/s depending on spectrometer and detector type. Since counting linearity can deteriorate at high count rates, the maximum count rate should be considered when the calibration accuracy above does not clear the criteria.

9.5.4.4 Check of matrix correction alpha of each component for Fe_2O_3 determination

Quantify Fe_2O_3 concentration using iron fluorescent X-ray intensity measured in 9.5.3, the calibration coefficients obtained in 9.5.4.2 and alpha coefficient for coexisting component obtained by the FP method described in 9.5.4.1 for each calibration disc from 9.5.1.2 to 9.5.1.10. Then, compare the result with the concentration obtained from added amounts of reagents and make sure that the difference of Fe_2O_3 mass fraction is less or equal to 0,1 %.

When the influence of a coexisting component to iron intensity is small, reliable coefficients cannot be determined using empirical data. Alpha coefficients obtained by the FP method shall be used in such a case that estimated relative influence to Fe_2O_3 quantification obtained by the product of a value in Table 4 for Fe_2O_3 and the concentration of coexisting component is small (relatively less than 1,0 %). For example of relative influence of CaO to Fe_2O_3 analysis, the influence of CaO 1 % to Fe_2O_3 is 1,25 for Flux C of lithium flux and concentration of CaO calibration disc is 11,21 % and total relative influence of CaO is 14,01 %. On the other hand, the case of P_2O_5, the total relative influence is 0,30 %.

Typical elements which give significant influence to Fe_2O_3 quantification are CaO and TiO_2.

If the difference is larger than 0,1 % and the influence of a coexisting element is larger than 1,0 %, the correction alpha shall be determined using the quantified result of iron as described below.

Obtain Fe_2O_3 concentration using the calibration coefficients obtained in 9.5.4.2 without correction term *j* component. However, the concentration of iron obtained from the added amounts of reagents $C_{\mathrm{Fe,T}}$ is used to the C_{Fe} in the correction term.

Calculate the correction coefficient for *j* component using Formula (30).

$$\alpha_{\mathrm{Fe}j} = \left(C_{\mathrm{Fe,T}} - C_{\mathrm{Fe,cal}}\right) / \left(A_{\mathrm{Fe}} I_{\mathrm{Fe}} C_j\right) \qquad (30)$$

where $C_{\mathrm{Fe,cal}}$ is the quantified value obtained by iron calibration equation without correction of *j* component.

Adopt the average of the coefficients obtained for individual discs.

The correction coefficients may be obtained by the least square method as described in Annex G.

The calculation described above is a method to determine a correction coefficient $\alpha_{\mathrm{Fe}j}$ with fixed values of calibration coefficients of iron (A_{Fe}, B_{Fe}) and correction coefficient α_{FeFe}. The data used in the calculation are those for duplicated discs of target element (*j*).

Instead of the calculation method above, all of the calibration coefficients of iron (A_{Fe}, B_{Fe}) and correction coefficient $\alpha_{\mathrm{Fe}j}$ may be determined simultaneously using the data of duplicated discs of target element (*j*) and 20 iron calibration discs as an alternative calculation method.

Calibration discs for K/P and Mn/S contain two elements other than Fe. Since coefficients for two elements cannot be obtained simultaneously, calculate the coefficient of K_2O or Mn_3O_4 and use the alpha obtained by the FP method for P_2O_5 or SO_3 when required to calculate alphas by the empirical regression calculation.

9.5.4.5 Calculation of calibration coefficients for components other than iron

By using the fluorescent X-ray intensities (I_i) of component i obtained in 9.5.3 for duplicated calibration discs of an individual component prepared from 9.5.1.2 to 9.5.1.10, fluorescent X-ray intensities ($I_{i,\mathrm{Fe}}$) of component i obtained by measuring the duplicated discs of Fe = 1,00*w* used for iron calibration (Fe_2O_3 100 %), C_i, R_{X}, R_{F} and C_j (*j* = Fe) obtained from added amounts of individual reagents and α_{ij}, $K_{i\mathrm{XF}}$, $\alpha_{i\mathrm{F}}$, $\alpha_{i\mathrm{X}}$ obtained in 9.5.4.1, the coefficients of A_i, B_i in the next equation for calibration Equation 1 are obtained. The differences from calibration Equation 2 and 3 are the correction terms of mass ratios for flux/sample and remaining oxidizer/sample (see 9.2).

$$C_i = A_i I_i \left(1 + \alpha_{ii} C_i + \sum \alpha_{ij} C_j + K_{i\mathrm{XF}} + \alpha_{i\mathrm{F}} R_{\mathrm{F}} + \alpha_{i\mathrm{X}} R_{\mathrm{X}}\right) - B_i \qquad (31)$$

The calculation of the coefficients using the least square method is described in Annex G.

The software provided by the instrument manufacturer usually includes the least square method in Annex G.

For the calibration of Co, calibration discs contain iron and FeKβ line overlaps with CoKα line. Accordingly, the calibration constants and the coefficient for the overlap correction by Fe_2O_3 shall be determined simultaneously for Co as described in 9.5.4.6.

When calibration Equation 1 is used, the influence of mass ratio variation of flux to sample on B_i (BEC) can be corrected using Formula (32).

$$C_i = A_i I_i \left(1 + \alpha_{ii} C_i + \sum \alpha_{ij} C_j + K_{i\mathrm{XF}} + \alpha_{i\mathrm{F}} R_\mathrm{F} + \alpha_{i\mathrm{X}} R_\mathrm{X}\right) - B_i \left(1 + R_\mathrm{F} + R_\mathrm{X}\right) \tag{32}$$

The influence can be large when B_i is large for trace element analysis and can be checked by preparing additional discs for Fe_2O_3 100 % with different flux/sample mass ratio with nominal mass ratio (e.g. 5 % larger) and comparing the quantified result of the discs of nominal and different mass ratios. The calibration constants can be determined using the data of discs of i element and Fe_2O_3 100 % as done in other elements.

9.5.4.6 Calculation of overlap correction coefficients

An overlap correction coefficient shall be determined by using concentrations of the overlap element and X-ray intensities of an analyte for the duplicated discs of the overlap element.

The equation with overlap correction is shown in Formula (33)

$$C_i = A_i I_i \left(1 + \alpha_{ii} C_i + \sum \alpha_{ij} C_j + K_{i\mathrm{XF}} + \alpha_{i\mathrm{F}} R_\mathrm{F} + \alpha_{i\mathrm{X}} R_\mathrm{X}\right) - B_i - \sum L_{ij} C_j \tag{33}$$

Before overlap coefficient calculation of overlap element (j component) for analyte (i component), calibration coefficients of A_i and B_i shall be calculated by adapting the X-ray intensities of the relevant element in the discs prepared in 9.5.1.2 to 9.5.1.9 to the calibration curve in 9.5.4 except for Co.

Calculate the apparent concentration of analytes X_{ij} using Formula (34).

Formula (34) is for calibration Equation 1. The differences from calibration Equation 2 and 3 are the correction terms of mass ratios for flux/sample and remaining oxidizer/sample (9.2).

$$X_{ij} = A_i I_i \left(1 + \alpha_{i\mathrm{Fe}} C_\mathrm{Fe} + \sum \alpha_{ij} C_j + K_{i\mathrm{XF}} + \alpha_{i\mathrm{F}} R_\mathrm{F} + \alpha_{i\mathrm{X}} R_\mathrm{X}\right) - B_i \tag{34}$$

Overlap correction coefficient L_{ij} shall be calculated by Formula (35), because the analyte is not contained in the discs for calibration curves of overlap components.

$$L_{ij} = X_{ij} \times C_j \tag{35}$$

where C_j is the concentration of j component of the disc for calibration.

The average of calculated L_{ij} obtained by measuring each disc shall be used as the correction coefficient.

On the other hand, the overlap correction coefficients may be obtained by the least square method, which is described in Annex G. In this calculation, the values of calibration coefficients (A_i, B_i) and all alpha coefficients are fixed and only L_{ij} are determined by the least square method.

As an alternative calculation method, instead of determining only overlap correction coefficient with fixed calibration coefficients, the overlap correction coefficients L_{ij} may be determined simultaneously with calibration coefficients A_i and B_i using the data (concentrations of analyte C_i, overlap component C_j and intensities of analyte I_i) of the duplicated calibration discs of the analyte, correcting the component and Fe_2O_3 100 %.

For the overlap correction from FeKβ to Co analysis, calibration coefficients of Co (A_Co, B_Co) and overlap correction coefficient for Fe should be calculated simultaneously using the data of the duplicated discs of overlap element, Fe_2O_3 100 % and SiO_2 100 %.

Overlapping lines on analyte measurement lines are shown in Table 3. Some overlaps listed in Table 3 will possibly not appear since the amount of overlap varies with spectral resolution of the instrument. Line overlap correction coefficient obtained in this case is not reliable and should not be used. Unreliable correction coefficients can be identified by negative overlap correction coefficient L_{ij} and too small $L_{ij}C_j$.

NOTE When the value of L_{ij} is smaller than three times of standard deviation of the result in the blank sample (lower limit of detection), the overlap correction can be ignored.

When influence of background intensity variation due to sample matrix difference for trace heavy element analysis appears, overlap correction may be used. For example, there can be cases where influence of background variation can be reduced by correction using an overlap correction term with Fe_2O_3 concentration. The influence of Fe_2O_3 concentration can be checked by comparing quantified results of Fe_2O_3 100 % and Fe_2O_3 0 % (SiO_2 100 %) disc obtained by the calibration of the analyte. The calibration constants and line overlap correction coefficient may be determined simultaneously as done for Co_3O_4 calibration using data of the duplicated discs of element i, Fe_2O_3 100 % and Fe_2O_3 0 %.

9.6 Calculation of concentrations

In case correction for flux/sample or remaining oxidizer/sample mass ratio is required, mass ratio(s) should be calculated in advance before concentration calculation according to the calibration equation used.

9.6.1 Calculation of flux/sample and remaining oxidizer/sample mass ratios

When the correction for flux/sample mass ratio or remaining oxidizer/sample mass ratio is required, the following mass ratios shall be prepared according to the calibration equation used.

a) Flux/sample mass ratio

Calibration Equation 1 [see 9.2 a)]:

Flux/sample mass ratio R_F [see Formula (22)]

$$R_F = \text{flux mass} / \text{sample mass}$$

Calibration Equation 2 [see 9.2 b)]:

Difference of flux/sample mass ratios between sample and nominal ΔR_F [see Formula (18)]

$$\Delta R_F = R_F - R_{F0}$$

where

R_{F0} is the nominal flux/sample mass ratio;

R_F is the flux/sample mass ratio of sample.

Calculate ΔR_F when this term is used.

b) Remaining oxidizer/sample mass ratio

Calibration Equation 1:

Remaining oxidizer/sample mass ratio R_X [see 9.2 a)]

$$R_X = \text{remaining oxidizer mass} / \text{sample mass}$$

Calibration Equation 2:

Converted concentration C_{Na2O} of remaining oxidizer assuming component in sample [see 9.2 b)]

$$C_{Na2O} = (\text{remaining oxidizer mass} / \text{sample mass}) \times 100$$

Calibration Equation 3:

Converted concentration $C_{Na2O}{'}$ of remaining oxidizer assuming component in sample with the correction to nominal flux/sample mass ratio [see 9.2 c), Formula (21)]

$$C_{Na2O}{'} = (\text{remaining oxidizer mass} / \text{sample mass}) \times 100 \times (R_{F0} / R_F)$$

9.6.2 Calculation of initial concentration

Obtain initial concentration $C_i(0)$ for each component using Formula (36).

$$C_i(0) = A_i I_i - B_i \tag{36}$$

where

A_i is the calibration slope of component i;

B_i is the background equivalent concentration (BEC);

I_i is the drift corrected X-ray intensity of analyte i.

The software provided by the instrument manufacturer usually provides this initial calculation and final concentration described in 9.6.3.

9.6.3 Calculation of concentrations

Calibration Equation 1 [see 9.2 a)] is used for the following explanation. The calculation itself is used to obtain the concentration $C_i(1)$ for each component using Formulae (37) and (38).

For iron,

$$C_i(1) = A_i I_i \left[1 + \alpha_{ii} C_i(0) + \Sigma \alpha_{ij} C_j(0) + K_{iXF} + \alpha_{iF} R_F + \alpha_{iX} R_X\right] - B_i \tag{37}$$

For the other components,

$$C_i(1) = A_i I_i \left[1 + \alpha_{ii} C_i(0) + \Sigma \alpha_{ij} C_j(0) + K_{iXF} + \alpha_{iF} R_F + \alpha_{iX} R_X\right] - B_i - \Sigma L_{ij} C_j(0) \tag{38}$$

Repeat the calculation and obtain the n-th concentration $C_i(n)$ using Formulae (39) and (40).

For iron,

$$C_i(n) = A_i I_i \left[1 + \alpha_{ii} C_i(n-1) + \Sigma \alpha_{ij} C_j(n-1) + K_{iXF} + \alpha_{iF} R_F + \alpha_{iX} R_X\right] - B_i \tag{39}$$

For the other components,

$$C_i(n) = A_i I_i \left[1 + \alpha_{ii} C_i(n-1) + \Sigma \alpha_{ij} C_j(n-1) + K_{iXF} + \alpha_{iF} R_F + \alpha_{iX} R_X\right] - B_i - \Sigma L_{ij} C_j(n-1) \tag{40}$$

Stop the iteration when the change in iron ratio $\Delta_{iron} = [C_i(n) - C_i(n-1)] / C_i(n)$ is less than 0,000 1 and $C_i(n)$ for each component is the concentration of the sample. The iteration for Fe_2O_3 should be 15 times to obtain the error within 0,001 %.

Since the final analysed results are the concentrations as oxides, convert the concentrations to those of elements using the factors in Table 8.

In the case of calibration Equation 3 [see 9.2 c)], the concentration is obtained as nominal flux/sample mass ratio, convert the value to concentration in the sample using Formula (41) to obtain the final result.

$$C_i = (R_F / R_{F0}) C_i' \tag{41}$$

where

C_i is the converted concentration of each component for flux/sample mass ratio of sample;

C_i' is the concentration of each component with nominal flux/sample mass ratio.

9.6.4 Conversion from oxide to element concentrations

The concentrations obtained above are those of oxide forms.

Covert from oxide to element concentration for all components using Formula (42).

$$C_{ie} = F_i C_i \tag{42}$$

where

C_i is the concentration as oxide of each component;

C_{ie} is the concentration as element of each component;

F_i is the conversion factor from oxide to element concentration.

The conversion factors F_i are listed in Table 8.

10 General treatment of results

10.1 Background equivalent concentration (BEC)

The values for BECs can be found by measuring the blank discs as unknowns using the calibration equations derived earlier.

While BEC will vary with the type and model of the spectrometer, it is highly dependent on both the instrumental settings and possible contamination during either flux or disc preparation. The background shall, therefore, be checked.

High BECs indicates contamination of the flux or an instrument operating at suboptimal conditions. When the BECs exceed the values in Table 7, measures to remove the effect should be taken when possible, because error introduced in the analysed results can exceed the acceptable range.

Table 7 — Expected background equivalent concentrations (BECs) for blank discs

Element	BEC %
Fe	0,13
Si	0,10
Ca	0,10
Mn	0,10
Al	0,10
Ti	0,10
Mg	0,30
NOTE High BECs for Ca are often attributable to impurities in the reagents used in the preparation of the flux.	

Table 7 *(continued)*

Element	BEC %
P	0,02
S	0,05
K	0,07
V	0,08
Cr	0,10
Co	0,10
Ni	0,09
Cu	0,11
Zn	0,10
As	0,08
Pb	0,35
Ba	0,19
NOTE High BECs for Ca are often attributable to impurities in the reagents used in the preparation of the flux.	

10.2 Determination of analytical result

Having computed the independent duplicate results, compare these with the independent duplicate limit (R_d), using the procedure given in Annex J.

Between-laboratories precision is used to determine agreement between the final results reported by two laboratories. The assumption is that both laboratories followed the same procedure as described in Clause 8.

Compute the following quantity using Formula (43):

$$\mu_{12} = (\mu_1 - \mu_2)/2 \tag{43}$$

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

μ_{12} is the mean of final results.

Substitute μ_{12} for *X* of the regression equations of *P*.

If $|\mu_1 - \mu_2| \leq P$, the final results are in agreement.

10.3 Check for trueness

The trueness of the analytical method shall be checked by applying it to a certified reference material (CRM). Calculate the analytical result (μ_C) for the CRM using the procedures in 9.6, and compare it with the certified value A_C. There are two possibilities:

a) $|\mu_C - A_C| \leq C$, in which case the difference between the reported result and the reference/certified value is statistically insignificant.

b) $|\mu_C - A_C| > C$, in which case the difference between the reported result and the reference/certified value is statistically significant.

where

μ_C is the analytical result for the certified reference material;

A_C is the certified value of the CRM;

C is the value dependent on the type of CRM used.

Certified reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35.[1]

C shall be calculated by Formula (44).

$$C = 2\sqrt{\frac{S_{\mathrm{Lc}}^2 + \frac{s_{\mathrm{Wc}}^2}{n_{\mathrm{Wc}}}}{N_{\mathrm{c}}} + \sigma_{\mathrm{L}}^2 + \frac{\sigma_{\mathrm{d}}^2}{n}} \tag{44}$$

where

S_{Lc} is the between-laboratories standard deviation of the certifying laboratories;

s_{Wc} is the within-laboratory standard deviation of the certifying laboratories;

n_{Wc} is the average number of replicate determinations in the certifying laboratories;

N_{c} is the number of certifying laboratories;

n is the number of replicate determinations carried out on the CRM;

$\sigma_{\mathrm{L}} \sigma_{\mathrm{d}}$ are defined in 10.2.

The following procedure should be used when the information on the reference material certificate is incomplete:

— if there are sufficient data to enable the between-laboratories standard deviation to be estimated, delete the expression $s_{\mathrm{Wc}}^2 / n_{\mathrm{Wc}}$ and regard S_{Lc} as the standard deviation of the laboratory means;

— if the certification has been made by only one laboratory or if the inter-laboratory results are missing, C shall be calculated by Formula (45).

$$C = 2\sqrt{2\sigma_{\mathrm{L}}^2 + \frac{\sigma_{\mathrm{d}}^2}{n}} \tag{45}$$

A CRM certified by only one laboratory should be avoided, unless it is known to have an unbiased certified value.

10.4 Calculation of the final result

The following element shall be reported to two decimal places: Fe

The following elements shall be reported to three decimal places: Si, Ca, Mn, Al, Ti and Mg

The following elements shall be reported to four decimal places: P, S, K, V, Cr, Co, Ni, Cu, Zn, As, Pb and Ba.

The final result is the arithmetic mean of the acceptable analytical values for the test sample. The result is calculated to four decimal places and rounded off to the second decimal place as follows:

a) where the figure in the third decimal place is less than 5, it is discarded and the figure in the second decimal place is kept unchanged;

b) where the figure in the third decimal place is 5 and there is a figure other than 0 in the fourth decimal place, or where the figure in the third decimal place is greater than 5, the figure in the second decimal place is increased by one;

c) where the figure in the third decimal place is 5 and there is no figure other than 0 in the fourth decimal place, the 5 is discarded and the figure in the second decimal place is kept unchanged if it is 0, 2, 4, 6 or 8 and is increased by one if it is 1, 3, 5, 7 or 9.

10.5 Oxide factors

Element concentrations may be obtained by multiplying by the factors shown in Table 8 and in the calculation program.

Table 8 — Factors for conversion of oxide contents to element contents

Oxide	Element	Conversion Factor
Fe_2O_3	Fe	0,699 4
SiO_2	Si	0,467 4
CaO	Ca	0,714 7
Mn_3O_4	Mn	0,720 3
Al_2O_3	Al	0,529 3
TiO_2	Ti	0,599 5
MgO	Mg	0,603 1
P_2O_5	P	0,436 4
SO_3	S	0,400 5
K_2O	K	0,830 2
V_2O_5	V	0,560 2
Cr_2O_3	Cr	0,684 2
Co_3O_4	Co	0,734 2
NiO	Ni	0,785 8
CuO	Cu	0,798 9
ZnO	Zn	0,803 4
As_2O_3	As	0,757 4
PbO	Pb	0,928 3
BaO	Ba	0,895 7

11 Test report

The test report shall include the following information:

a) name and address of the testing laboratory;

b) date of issue of the test report;

c) reference to this document, i.e. ISO 9516-2:2024;

d) details necessary for the identification of the sample;

e) result of the analysis;

f) reference number of the result;

g) any characteristics noticed during the determination, and any operations not specified in this document which can have an influence on the result, for either the test sample or the certified reference material(s).

Annex A
(normative)

Preparation of Flux A and Flux D

A.1 General

This annex describes a procedure for the preparation of Flux A and Flux D from lithium tetraborate and lithium metaborate.

A.2 Reagents

A.2.1 Anhydrous lithium tetraborate, ($Li_2B_4O_7$)

A.2.2 Anhydrous lithium metaborate, ($LiBO_2$)

A.3 Apparatus

A.3.1 Crucible, platinum, non-wetting platinum alloy, or graphite crucible having a minimum capacity of 400 ml.

NOTE A platinum or platinum-lined crucible of adequate size can be used, but a crucible or liner fabricated from the commercially available alloys of platinum/gold or platinum/gold/rhodium has the advantage that the melt does not wet the metal surface.

If a graphite crucible is used, it should be made from high quality graphite (ash < 0,2 %); otherwise the flux will be contaminated during preparation. It is also important that any loose surface material be removed by rubbing the surface of the graphite crucible with a cloth.

A.3.2 Electric furnace, capable of maintaining a temperature of 1 100 °C.

A.3.3 Aluminium sheet, commercially available sheet of size 600 mm × 600 mm × 5 mm.

A.4 Preparation of flux

Flux shall be prepared as follows:

a) Weigh suitable quantities of both reagents; mix, then transfer to a platinum or graphite crucible.

   The reagent masses in Table A.1 produce about 68 g of flux. Provided that the same reagent ratios are used, larger or smaller quantities can be made. When making larger quantities however, the reagents should be weighed in separate crucible “charges”, to ensure uniformity throughout the entire batch.

b) Fuse at 1 100 °C; swirl when molten.

c) Maintain the flux in the molten state for 10 min, then pour the melt on to the aluminium sheet.

d) When the melt is cool, grind to a coarse powder and store in an airtight container.

The flux shall be heated at 500 °C for 4 h before use. If it is stored in a desiccator containing silica gel, it can be used for several days without reheating.

To prevent the melt from sticking to the aluminium, the sheet should have a polished surface and, in pouring, the melt should be spread over the sheet rather than be concentrated on one spot. Some buckling of the sheet can occur but this should be minor with the 5 mm thickness stipulated.

If a graphite crucible is used, the glass can be contaminated with graphite powder. The contamination should be slight and need not affect X-ray fluorescence measurements made on discs prepared using this flux. However, if desired, the graphite can be largely eliminated by heating the glass lumps in a platinum dish at 550 °C until the black graphite coating is no longer obvious. Usually overnight is sufficient.

The grinding vessel used should not contaminate the flux with any of the elements being determined. Suitable materials are tungsten-carbide or nickel-chromium alloy.

NOTE The powdered glass is slightly hygroscopic and will slowly absorb moisture.

Table A.1 — Reagent masses for Flux A and Flux D

Flux	Reagent	Mass g
Flux A	$Li_2B_4O_7$ $LiBO_2$	24,00 44,00
Flux D	$Li_2B_4O_7$ $LiBO_2$	34,00 34,00

Annex B
(normative)

Preparation of Flux B and Flux C

B.1 General

This annex describes a procedure for the preparation of Flux B from sodium tetraborate and Flux C from lithium tetraborate.

B.2 Reagents

B.2.1 Anhydrous sodium tetraborate, ($Na_2B_4O_7$) for Flux B.

B.2.2 Anhydrous lithium tetraborate, ($Li_2B_4O_7$) for Flux C.

B.3 Apparatus

B.3.1 Crucible, platinum or non-wetting platinum alloy crucible with a minimum capacity of 400 ml.

B.3.2 Electric furnace.

B.4 Preparation of flux

Dry the sodium tetraborate or lithium tetraborate at 500 °C for 4 h. Cool and store in a desiccator over silica gel desiccant.

Annex C
(normative)

Standard deviation of specimen preparation

C.1 General

This annex describes a procedure to confirm that the precision of 0,1 % for Fe_2O_3 is constantly obtained and the procedure to determine the precision of specimen preparation.

This test procedure shall be carried out at least two times at regular intervals to confirm that the required sample preparation precision is obtained. The interval for testing the mould shall be determined based on its usable duration or the number of discs prepared with it. This interval is determined by the period until the error of a check sample for Fe in a CRM or RM exceeds the tolerance of analysed error whose cause is determined to be used mould.

In the case more than 10 moulds are used in a laboratory, this test procedure below shall be repeated by changing the moulds.

C.2 Procedure

The procedure shall be as follows.

a) Select a high-grade iron ore (> 68 % Fe for Fe_2O_3) and prepare 10 replicate specimens by the procedure specified in 8.4.3 to 8.4.6.

b) If more than one crucible or more than one mould is used for casting in sample preparation, all of these crucibles or moulds shall be used in the preparation.

c) Measure 10 replicate specimens and quantify using calibrations obtained in 9.5.4.2.

d) Remount the specimens in the sample holders and repeat the measurement to obtain two sets of count rates for each specimen.

C.3 Evaluation of the result

The precision of sample preparation is obtained using the quantitative analysis results of Fe_2O_3 from the quantitative analysis results of two sets of 10 fused discs. The precision of sample preparation and the precision of the measurements are estimated using the following calculation. Additionally, the procedure described will estimate the precision of the determination of the concentration of Fe_2O_3.

Fill the quantitative values of Fe in X_{ij} in Table C.1 and calculate disc preparation precision (E_D) and measurement precision (E_R).

Table C.1 — Calculation of precision of sample preparation

Disc (i)	Measurement (j)		
	1	2	Average
1	X_{11}	X_{12}	$\overline{X}_1$
2	X_{21}	X_{22}	$\overline{X}_2$
3	X_{31}	X_{32}	$\overline{X}_3$
4	X_{41}	X_{42}	$\overline{X}_4$
5	X_{51}	X_{52}	$\overline{X}_5$
6	X_{61}	X_{62}	$\overline{X}_6$
7	X_{71}	X_{72}	$\overline{X}_7$
8	X_{81}	X_{82}	$\overline{X}_8$
9	X_{91}	X_{92}	$\overline{X}_9$
10	X_{101}	X_{102}	$\overline{X}_{10}$
	Total average		$\overline{\overline{X}}$

The precision calculation equations are shown as Formulae (C.1) and (C.2).

$$E_D = \sqrt{\frac{\sum_i \sum_j \left(X_{ij} - \overline{\overline{X}}_i\right)^2}{(10 \times 2) - 1} - \frac{\sum_i \sum_j \left(X_{ij} - \overline{X}_i\right)^2}{(2-1) \times 10}} \qquad (C.1)$$

$$E_R = \sqrt{\frac{\sum_i \sum_j \left(X_{ij} - \overline{X}_i\right)^2}{(2-1) \times 10}} \qquad (C.2)$$

E_D in the equation above is the precision of fused disc preparation and E_R is measurement precision. If the measurement precision is comparable to or larger than E_D, the probability of a negative value of the term in the square root of E_D becomes larger. Accordingly, adequate measurement precision should be confirmed in the test of Annex D. If the E_D obtained with the equation above is negative, measure all fused discs again. If the value is negative again, the precision of fused disc preparation can be regarded as similar or less than the measurement precision.

For the criterion of disc making repeatability for sample preparation, E_D shall be equal or less than 0,1 % as standard deviation of the quantitative result of Fe_2O_3 concentration.

Annex D
(normative)

Spectrometer precision tests

D.1 General

This annex sets out procedures for the carrying out of tests to ensure that the spectrometer is operating correctly before it is used.

Output intensities of the spectrometer are usually measured as the number of counts accumulated in a given time.

D.2 Precision

D.2.1 Scaler output

For the following tests, most spectrometers should give a precision of 0,03 % and 10^7 counts is adequate for detecting imprecisions of this order. Instruments can be capable of higher precision and if they are to be tested more rigorously, a greater number of counts shall be accumulated. The number of counts accumulated shall be appropriate to the analytical requirement.

If N counts are repeatedly accumulated and the time recorded in each case, the expected coefficient of variation of the observed counting times is $100/\sqrt{N}$ % according to counting statistical error. In the tests outlined in this document, 20 measurements are usually made. Where 20 such measurements are made, the observed coefficient of variation shall not exceed 1,5 times the counting statistical error. If the observed coefficients of variation are larger than this, corrective measures shall be taken.

At high count rates, the effect of the dead time on the counting statistical error can lead to significant deviations from the usual calculation involving the square root of the number of counts collected. Follow the recommendations of the manufacturer of the spectrometer in this case.

D.3 Test disc

D.3.1 General

The test disc shall be both robust and stable and have a flat analytical surface. A compacted powder (briquette) may be used, but a glass disc into which the analyte(s) has (have) been incorporated by fusion with a borate flux is preferred.

D.3.2 Sequential spectrometers

FeKα is a convenient radiation to use and the amount of iron in the test disc shall be such that, under normal conditions of X-ray tube power, a count rate of approximately 3×10^5 c/s is obtained.

D.3.3 Simultaneous spectrometers

A test disc that allows testing of several channels simultaneously is desirable. The test disc shall be such that under normal operating conditions of X-ray tube power, a count rate of approximately 3×10^5 c/s is obtained in each of the channels under test. For channels measuring very light elements where such an intensity will probably not be possible, as high a count rate as achievable shall be used.

D.4 Instrumental conditions

D.4.1 General

The X-ray tube shall be operated at the normal working power. Sample rotation shall be used if possible. All measurements shall be made using the preset count mode. The time required to accumulate the counts shall be recorded to at least two, and preferably three, decimal places of seconds. If a preset count facility is not available, or if the timer does not read to the required level, use the preset time mode and adjust the time so that approximately the same number of counts is accumulated and then record the actual counts for each measurement.

D.4.2 Sequential spectrometers

Use the coarse collimator if there is more than one available (except for the test described in D.5.7). Make all measurements, except for tests specified in D.5.1 and D.5.8, using the gas flow proportional counter as detector.

Set the spectrometer to measure FeKα. A broad pulse-height analyser (P.H.A.) window shall be used.

D.4.3 Simultaneous spectrometers

A broad P.H.A. (pulse height analyser) window shall be used with each channel under test.

D.5 Spectrometer tests

D.5.1 Stability test

a) Make 50 consecutive measurements on the test disc. The test disc shall remain fixed in the spectrometer while all measurements are made.

b) Calculate the coefficient of variation of the results.

c) The test shall be performed using each of the detectors fitted to the spectrometer.

The calculated coefficient of variation shall not exceed 1,3 times the counting statistical error. If the calculated value exceeds this, it can indicate a lack of stability in the equipment since there is only a 1 % probability that a value in excess of 1,3 times the counting statistical error will arise by chance.

If the error is greater than that tolerable, repeat the test. If the error remains high, determine the reason for the excessive error and correct the fault.

D.5.2 Carousel reproducibility test

Make 20 measurements on the test disc, but between each measurement rotate the carousel through one complete revolution.

Assess the results as set out in D.2.

D.5.3 Mounting and loading reproducibility test

This test is designed to check whether there are excessive errors associated with the remounting of a disc in a sample holder and in reloading the sample holder into the carousel.

Make 20 measurements on the test disc, but between each measurement remove the test disc from the sample holder and then remount and reload the test disc using the same sample holder and carousel position. Assess the results as set out in D.2.

D.5.4 Comparison of sample holders

The number of sample holders tested depends on the type and model of the spectrometer used and the measurement procedure adopted.

Make a measurement on the test disc, when mounted, in each of the sample holders being tested. Use the same carousel position.

If the coefficient of variation of the results is excessive (see D.2), the measurement shall be repeated several times if necessary, to determine which sample holders are giving excessively high or low results.

Sample holders that pass the test shall be identified and used when precise analyses are being undertaken.

Sample holders that fail the test do so because they locate the sample at a different distance from the X-ray tube. It can be possible to correct this misplacement by appropriate machining of the sample holder.

NOTE It is common to have large errors associated with variations in the sample holders.

D.5.5 Comparison of carousel positions

With the test disc in the same sample holder, make at least four measurements with the sample holder loaded in each of the carousel positions.

If the coefficient of variation of all the results is excessive (see D.2), the measurements for the individual carousel positions shall be inspected to determine which positions are giving excessively high or low results.

Where possible, errors arising from differences in carousel positions shall be eliminated by adjustment of the carousel positions. This adjustment is normally done by the spectrometer manufacturer.

Where such errors cannot be eliminated mechanically, the intensity ratios for the various carousel positions shall be established relative to one position. Thereafter, where precise analyses are being undertaken, these ratios shall be used to correct the measurements from each carousel position.

If empirical corrections are to be applied for each carousel position, the ratios should be determined for each wavelength where high precision is required. This is necessary as the ratios can vary with collimator and can even vary with crystal and angle.

D.5.6 Angular reproducibility (for sequential spectrometers only)

For this test, the test disc remains in the spectrometer but between each measurement the 2θ angle is altered by 10 degrees and then returned to its original value. Twenty such measurements are required.

Assess the results as set out in D.2.

An error in angular reproducibility will not affect the analyses adversely if measurements on samples are bracketed with those of a monitor without changing the angle between measurements. However, if the measuring sequence involves angular changes between sample and monitor measurements, then high angular reproducibility is essential.

D.5.7 Collimator reproducibility (for sequential spectrometers fitted with an interchangeable collimator facility)

The test disc shall remain in the spectrometer while alternate measurements are made for the coarse and fine collimators. Twenty such pairs of measurements are required.

Note that the counting times for the measurements on the fine and the coarse collimator will be different due to the difference in intensity.

Assess the results for the coarse and fine collimator separately as set out in D.2.

As for angular reproducibility (see D.5.6), errors associated with changing of the collimator can, or will possibly not affect the analyses, depending on the measurement sequence used.

D.5.8 Detector changing reproducibility (for sequential spectrometers fitted with more than one detector)

For this test, the disc shall remain in the spectrometer. The detector used between measurements is changed and then the original detector is selected again for the next measurement.

In some spectrometers, they are designed such that selecting another detector involves a change in the goniometer angle as well and the reproducibility of only detector cannot be obtained. The measuring conditions of other components remain same during the test.

However, result on the alternate detector has less meaning since the measuring conditions for the alternate detector is not suitable for the element. Therefore, it is desirable to perform separate test with suitable analyte for testing other detector(s).

Twenty such pairs of measurements are required.

Assess the results for each detector separately as set out in D.2.

As for angular reproducibility (see D.5.6), errors associated with changing the detector can, or will possibly not affect the analyses, depending on the measurement sequence used.

D.5.9 Crystal changing reproducibility (for sequential spectrometers only)

The test disc shall remain in the spectrometer, but between each measurement the crystal is changed and then returned to its original position. Twenty such measurements are required.

Assess the results as set out in D.2.

As for angular reproducibility (see D.5.6), errors associated with changing of the crystal can, or will possibly not affect the analyses, depending on the measurement sequence used.

D.5.10 Other tests

Some spectrometers have a variety of other devices and where these are operated between the measurements of the monitor and those of the disc, they can give rise to errors. If this is the case, they shall be tested according to the criteria set out in D.2. Examples of such devices are:

a) primary beam filters;

b) collimator apertures;

c) attenuators.

Annex E
(informative)

Theoretical derivation of correction term in calibration

The theoretical background of the calibration equation with absorption correction of coexisting components and mass correction of the sample, flux and sodium nitrate as oxidizer for fused discs derived from fluorescent X-ray intensity equations is described in this annex.

The approximation formula of fluorescent X-rays of elements in fused discs can be expressed as Formula (E.1).

The mass fraction in the fused disc is expressed in the equation.

$$I_i = \frac{k_i W_i}{\mu_{i1} W_1 + \cdots + \mu_{in} W_n + \mu_{i\mathrm{F}} W_\mathrm{F} + \mu_{i\mathrm{X}} W_\mathrm{X}} \tag{E.1}$$

where

- I_i is the fluorescent X-ray intensity of analysing element i;
- μ_{ij} is the mass absorption coefficient of j component for fluorescent X-rays of analysing element i;
- W_i is the mass fraction of elements in fused disc;
- k_i is the constant;
- W_F is the mass fraction of flux in fused disc;
- W_X is the mass fraction of remaining oxidizer (Na_2O) in fused disc.

The mass fractions above are not concentrations in the sample but concentrations in the fused disc and they are expressed as oxides. Loss on ignition is not included since it does not exist in the fused disc.

Formula (E.1) can be rewritten below to express as mass fractions in the sample. The following symbols are used for masses in preparing fused discs.

- S is the mass of sample;
- F is the mass of flux;
- X is the remaining mass of oxidizer (Na_2O remaining in fused disc);
- L is the mass of loss on ignition (LOI);
- G is the mass of gain on ignition (GOI);
- B is the mass of fused disc.

Mass of remaining Na_2O in fused disc is used for sodium nitrate as oxidizer.

Regarding loss on ignition (LOI), the amount of loss as in iron hydroxide is used in the equation. CO_2 from iron carbonate also does not remain in the fused disc so that it is included in ignition loss.

On the other hand, when iron is present as Fe_3O_4, it is oxidized to Fe_2O_3 and the amount of gain can be classified in mass of gain on ignition (GOI) as shown above.

The masses above have the relationship of Formula (E.2).

$$B = S - L + G + F + X \tag{E.2}$$

As shown above, GOI can be regarded as negative LOI.

The relationships between mass fraction in fused disc W_j and mass fraction in sample C_j for each component can be described below using the definitions of masses above.

$W_j = S \times C_j / B$	component in the sample
$W_F = F / B$	flux
$W_X = X / B$	oxidizer (Na_2O)

The intensity equation expressed with mass fractions [see Formula (E.3)] can be obtained by the mass equations [see Formula (E.1)] that substitute the intensity equation.

$$I_i = \frac{k_i C_i \frac{S}{B}}{\frac{S}{B}\mu_{i1}C_1 + \cdots + \frac{S}{B}\mu_{in}C_n + \mu_{iF}\frac{F}{B} + \mu_{iX}\frac{X}{B}} \tag{E.3}$$

Formula (E.3) can be rewritten as Formula (E.4).

$$I_i = \frac{k_i C_i}{\mu_{i1}C_1 + \cdots + \mu_{in}C_n + \mu_{iF}\frac{F}{S} + \mu_{iX}\frac{X}{S}} \tag{E.4}$$

Mass fractions of LOI (C_L) and GOI (C_G) are expressed as follows.

$$C_L = L / S$$

$$C_G = G / S$$

The total mass fraction of components in the sample, including mass fractions of LOI and GOI is 1,0 as shown Formula (E.5).

$$C_1 + C_2 + \cdots + C_n + C_L + C_G = 1{,}0 \tag{E.5}$$

Since LOI and GOI do not exist in fused discs, they are not included in Formula (E.1). Therefore, the total mass faction of sample components is not 1,0 and the difference from 1,0 is LOI or GOI.

Formula (E.4) can be rewritten to the equation of C_i

$$C_i = k_i' I_i \left(\mu_{i1}C_i + \cdots + \mu_{in}C_n + \mu_{iF}\frac{F}{S} + \mu_{iX}\frac{X}{S} \right) \tag{E.6}$$

The mass ratios of flux to sample and remaining oxidizer to sample are defined as R_F and R_X respectively.

$$R_F = F / S$$

$$R_X = X / S$$

The mass ratios are expressed with nominal mass ratio R_{F0}, R_{X0} and the difference.

$$R_F = R_{F0} + \Delta R_F$$

$$R_X = R_{X0} + \Delta R_X$$

These mass ratios were substituted in Formula (E.6).

$$C_i = k_i' I_i (\mu_{i1} C_i + \cdots + \mu_{in} C_n + \mu_{iF} R_F + \mu_{iX} R_X)$$

$$= k_i' I_i [\mu_{i1} C_i + \cdots + \mu_{in} C_n + \mu_{iF} (R_{F0} + \Delta R_F) + \mu_{iX} (R_{X0} + \Delta R_X)] \tag{E.7}$$

$$C_i = k_i' I_i (\mu_{iF} R_{F0} + \mu_{iX} R_{X0})(1 + \alpha_{i1} C_i + \cdots + \alpha_{in} C_n + \alpha_{iF} \Delta R_F + \alpha_{iX} \Delta R_X)$$

$$= k_i'' I_i (1 + \alpha_{i1} C_i + \cdots + \alpha_{in} C_n + \alpha_{iF} \Delta R_F + \alpha_{iX} \Delta R_X) \tag{E.8}$$

where

$$\alpha_{ij} = \frac{\mu_{ij}}{\mu_{iF} R_{F0} + \mu_{iX} R_{X0}}$$

$$\alpha_{iF} = \frac{\mu_{iF}}{\mu_{iF} R_{F0} + \mu_{iX} R_{X0}}$$

$$\alpha_{iX} = \frac{\mu_{iX}}{\mu_{iF} R_{F0} + \mu_{iX} R_{X0}}$$

$$\Delta R_F = R_F - R_{F0}$$

$$\Delta R_X = R_X - R_{X0}$$

Substituting the following relationship with Formula (E.8), Formula (E.9) of calibration Equation 1 [see 9.2 a)] can be obtained.

$$C_i = k_i'' I_i (1 + \alpha_{i1} C_i + \cdots + \alpha_{in} C_n + K_{iFX} + \alpha_{iF} R_F + \alpha_{iX} R_X) \tag{E.9}$$

where $K_{iFX} = -(\alpha_{iF} R_{F0} + \alpha_{iX} R_{X0})$

The constant of K_{iFX} is determined by alpha coefficients of mass ratios and nominal mass ratios.

Formula (E.9) is derived from the approximated intensity equation and is the same as the actual calibration equation to use. When mass ratio correction is not required, the terms from K_{iFX} can be ignored. Additionally, the approximated correction coefficients can be estimated simply by using mass absorption coefficients.

The actual correction coefficients to use shall be calculated using the FP method according to the equation above.

Regarding α_{iF} and K_{iF}, the value α_{iF} is simply the reciprocal number of nominal mass ratio of flux to sample and the value of K_{iF} is 1,0 when an oxidizer is not used.

$$\alpha_{iF} = \frac{\mu_{iF}}{\mu_{iF} R_{F0}} = \frac{1}{R_{F0}} \tag{E.10}$$

$$K_{iF} = \alpha_{iF} R_{F0} = -1,0$$

As described above, the alpha coefficient for mass ratio correction of flux to sample varies by adding oxidizer.

In calibration Equation 2 [see 9.2 b)] and Equation 3 [see 9.2 c)], the remaining oxidizer/sample mass ratio is treated as a component in the sample and Formula (E.11) is derived.

$$C_i = k_i'' I_i \left(1 + \alpha_{i1} C_i + \cdots + \alpha_{in} C_n + K_{iF} + \alpha_{iF} R_F + \alpha_{iX}' C_X\right) \tag{E.11}$$

where

$$\alpha_{iX}' = \frac{\alpha_{iX}}{100}$$

$$C_{iX} = 100 R_{iX}$$

The alpha coefficient for remaining oxidizer α_{iX}' is obtained by the FP method assuming that Na_2O is contained in the sample.

The calibration Equation 3, in which flux/sample mass ratio is corrected by converting the concentration of each component with the nominal flux/sample mass ratio, can be derived by substituting the equations of α_{iF} and K_{iF}.

$$C_i = k_i'' I_i \left(1 + \alpha_{i1} C_i + \cdots + \alpha_{in} C_n - 1 + R_F / R_{F0} + \alpha_{iX}' C_X\right) \tag{E.12}$$

Dividing Formula (E.12) by R_F / R_{F0}, the following calibration Equation 3 is obtained.

$$C_i' = k_i'' I_i \left(1 + \alpha_{i1} C_i' + \cdots + \alpha_{in} C_n' + \alpha_{iX}' C_X'\right) \tag{E.13}$$

where $C_i' = \frac{R_{F0}}{R_F} C_i$

The calibration equation derivation, Formula (E.13), considers only fluorescent X-rays of an analyte. If the intensity used is gross intensity for a component, the intensity includes background intensity in addition to fluorescent X-ray intensity. The approximation formula of gross intensity can be described as Formula (14) assuming the influence of sample matrix is the same for both fluorescent X-ray and background intensities. This hypothesis is approximately true in the short wavelength X-ray range.

$$I_{iG} = I_i + I_B = \frac{k_i W_i}{\sum \mu_j W_j} + \frac{k_B}{\sum \mu_j W_j} \tag{E.14}$$

where

I_{iG} is the gross intensity of analyte i;

I_i is the fluorescent X-ray intensity of analyte i;

I_B is the background intensity.