INTERNATIONAL STANDARD

ISO 9516-1

First edition
2003-04-01

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

Part 1: Comprehensive procedure

Minerais de fer — Dosage de divers éléments par spectrométrie de fluorescence de rayons X —

Partie 1: Procédure détaillée

Reference number
ISO 9516-1:2003(E)

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Published in Switzerland

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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

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

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 9516-1 was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This first edition, together with ISO 9516-2, cancels and replaces ISO 9516:1992 by the augmentation of the range of elements under analysis and the diversification into two procedures.

ISO 9516 consists of the following parts, under the general title *Iron ores — Determination of various elements by X-ray fluorescence spectrometry*:

— *Part 1: Comprehensive procedure*

— *Part 2: Simplified procedure*

Introduction

In this part of ISO 9516, Table 1 indicates that some determinations may be used for referee purposes and others for routine analysis only.

A simplified procedure for routine use with all determination will be published in ISO 9516-2.

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

Part 1: Comprehensive procedure

WARNING — This part of ISO 9516 may involve hazardous materials, operations and equipment. This part of ISO 9516 does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this part of ISO 9516 to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This part of ISO 9516 sets out a wavelength dispersive X-ray fluorescence procedure for the determination of iron, silicon, calcium, manganese, aluminium, titanium, magnesium, phosphorus, sulfur, potassium, tin, vanadium, chromium, cobalt, nickel, copper, zinc, arsenic, lead and barium in iron ores. The method has been designed to cope with iron ores having high ignition losses.

The method is applicable to iron ores regardless of mineralogical type. The concentration range covered for each of the component elements is given in Table 1. The determination of total iron cannot be used for referee purposes.

Table 1 — Range of application of the method

Component element	Concentration range for referee purposes %	Concentration range for analysis %
Fe		38 to 72
Si	0,2 to 6,5	0,2 to 6,5
Ca	0,019 to 12,7	0,019 to 12,7
Mn	0,02 to 0,82	0,02 to 0,82
Al	0,1 to 3,5	0,1 to 3,5
Ti	0,016 to 4,7	0,016 to 4,7
Mg	0,2 to 2,0	0,2 to 2,0
P	0,006 to 0,6	0,006 to 0,6
S	0,04 to 0,6	0,007 to 0,6
K	0,008 to 0,45	0,012 to 0,45
Sn		0,006 to 0,015
V	0,001 7 to 0,3	0,001 7 to 0,3
Cr		0,006 to 0,024
Co		0,006 to 0,018
Ni		0,011 to 0,013
Cu		0,012 to 0,061
Zn	0,006 9 to 0,166	0,005 to 0,166
As		0,008 to 0,06
Pb	0,018 to 0,32	0,018 to 0,32
Ba		0,036 to 0,4

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3082:1998, *Iron ores — Sampling and sample preparation procedures*

ISO 7764:1985, *Iron ores — Preparation of predried test samples for chemical analysis*

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

X-ray fluorescence measurements are based on the “line only” principle. It is not necessary to measure backgrounds on each glass disc, as background equivalent concentrations (BEC) are determined on several blank glass discs at the line position using concentration-based line overlap corrections. If desired, backgrounds can be measured to obtain net line intensities. The method is applicable to data from simultaneous and sequential X-ray fluorescence spectrometers.

The method relies on measuring all components of the sample, other than volatiles. If some components are not measured, then errors will result in the measured components (see 7.2.2).

Calibration is carried out using pure chemicals. Results are obtained after matrix corrections for inter-element effects.

4 Reagents and materials

During analysis, only reagents of recognized high purity shall be used.

NOTE 1 Where reagents have been ignited, they should be covered during cooling in the desiccator and weighed as soon as possible.

NOTE 2 Reagents 4.2, 4.5, 4.7, 4.8, 4.9, 4.11, 4.13, 4.15, 4.16, 4.18 and 4.20 are used only for the preparation of the synthetic calibration standard, and are not required if the synthetic calibration standard is available commercially.

4.1 **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.

4.2 **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 cool.

4.3 Iron(III) oxide, (Fe_2O_3), nominally 99,999 % 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.

4.4 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.

4.5 Potassium dihydrogen orthophosphate, (KH_2PO_4)

Analytical grade potassium dihydrogen orthophosphate shall be dried at 105 °C for 1 h and cooled in a desiccator.

4.6 Calcium carbonate, ($CaCO_3$)

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

4.7 Calcium sulfate, ($CaSO_4 \cdot 2H_2O$)

Analytical grade calcium sulfate dihydrate shall be dehydrated at 700 °C for 1 h and cooled in a desiccator.

4.8 Manganese oxide, (Mn_3O_4)

Manganese oxide shall be prepared by heating analytical grade manganese oxide (MnO_2, MnO or Mn_3O_4) for 15 h at 1 000 °C in a platinum crucible and then cooling. The lumpy material shall be crushed to a fine powder, heated for 1 h at 200 °C and cooled in a desiccator.

4.9 Magnesium oxide, (MgO)

Analytical grade magnesium oxide shall be dried in a platinum crucible by slowly heating from room temperature to 1 000 °C. After 1 h at 1 000 °C, the crucible containing the magnesium oxide shall be placed in a desiccator and weighed as soon as it is cool, as magnesium oxide readily absorbs carbon dioxide from the atmosphere.

4.10 Sodium nitrate, ($NaNO_3$)

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

4.11 Tin oxide, (SnO_2)

Analytical grade tin oxide shall be heated at 400 °C for a minimum of 1 h and cooled in a desiccator.

4.12 Vanadium(V) oxide, (V_2O_5)

Analytical grade vanadium(V) oxide shall be heated at 400 °C for a minimum of 1 h and cooled in a desiccator.

4.13 Chromium(III) oxide, (Cr_2O_3)

Analytical grade chromium(III) oxide shall be heated at 400 °C for a minimum of 1 h and cooled in a desiccator.

4.14 Cobalt oxide, (Co_3O_4)

Analytical grade cobalt oxide shall be heated at 400 °C for a minimum of 1 h and cooled in a desiccator.

4.15 Nickel oxide, (NiO)

Analytical grade nickel oxide shall be heated at 400 °C for a minimum of 1 h and cooled in a desiccator.

4.16 Copper oxide, (CuO)

Analytical grade copper oxide shall be heated at 400 °C for a minimum of 1 h and cooled in a desiccator.

4.17 Zinc oxide, (ZnO)

Analytical grade zinc oxide shall be heated at 400 °C for a minimum of 1 h and cooled in a desiccator.

4.18 Di-sodium hydrogen arsenate, ($Na_2HAsO_4 \cdot 7H_2O$)

The analytical grade reagent shall be weighed as received.

4.19 Lead oxide, (PbO)

Analytical grade lead oxide shall be heated at 400 °C for a minimum of 1 h and cooled in a desiccator.

4.20 Barium carbonate, ($BaCO_3$)

Analytical grade barium carbonate shall be heated at 105 °C for a minimum of 1 h and cooled in a desiccator.

4.21 Ammonium iodide, (NH_4I)

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

4.22 Desiccant

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

4.23 Flux

4.23.1 General

Flux A, flux B or flux C, as described in 4.23.2, 4.23.3 and 4.23.4, may be used. The levels of contamination in the flux shall be checked (see 9.1). Because levels of contamination may 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.

4.23.2 Flux A

Flux A 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.

4.23.3 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.

4.23.4 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.

4.24 Calibration standard

Two independent (i.e. prepared on different days) batches (labelled Day 1 and Day 2) of calibration standard shall be prepared by the procedure specified in Annex C. The composition of the calibration standard, given in Table 2, approximates that of an iron ore. The contents of some elements are higher than would be expected in an iron ore, but this is advantageous for obtaining a reliable calibration.

Prior to weighing, a sufficient aliquot of the calibration standard shall be heated at 900 °C for 20 min and cooled in a desiccator.

Table 2 — Composition of the calibration standard

Component element	Content %	Oxide content %
Fe	44,764	64,000 Fe_2O_3
Si	4,44	9,500 SiO_2
Ca	3,067	4,2913 CaO
Mn	1,441	2,000 Mn_3O_4
Al	2,65	5,000 Al_2O_3
Ti	0,899	1,500 TiO_2
Mg	3,016	5,000 MgO
P	1,16	2,660 P_2O_5
S	0,921	2,300 SO_3
K	1,46	1,758 9 K_2O
Sn	0,157 5	0,200 SnO_2
V	0,112 0	0,200 V_2O_5
Cr	0,136 8	0,200 Cr_2O_3
Co	0,146 8	0,200 Co_3O_4
Ni	0,157 2	0,200 NiO
Cu	0,159 8	0,200 CuO
Zn	0,160 7	0,200 ZnO
As	0,084 7	0,111 8 As_2O_3
Pb	0,185 7	0,200 PbO
Ba	0,179 1	0,200 BaO
Na	0,052 0	0,070 1 Na_2O

5 Apparatus

5.1 General

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.

5.2 Analytical balance, capable of weighing to four decimal places.

5.3 Crucible and mould

5.3.1 General

The crucible and mould shall be made from a non-wetting platinum alloy.

NOTE 1 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 D.

NOTE 2 It is essential to use all of the crucibles or moulds, as casting vessels may 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.

5.3.2 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 to fit the spectrometer.

5.3.3 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.

5.4 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.

5.5 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 added to the 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 may result.

5.6 Desiccator

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

Vibrating spatulas are not acceptable, because they can lead to segregation of the sample.

5.8 X-ray fluorescence spectrometer, of any wavelength dispersive, vacuum (or helium) path 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 E, accumulating at least 2×10^7 counts for each measurement.

The dead time for FeKα is determined in the method described in Annex F, and this dead time may be used for all elements when using a sequential instrument. However, where separate counting channels are used for the different elements (simultaneous instruments), or where the detector is changed, the dead time of each channel shall be determined independently. The procedure is given in Annex F.

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

5.10 Cooling device

NOTE 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 G.

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.

6 Sampling and samples

Samples shall be taken and prepared in accordance with ISO 3082. The predried test samples shall be prepared according to the procedure specified in ISO 7764. The calibration standards shall be heated to 900 °C for 20 min prior to weighing and then cooled in a desiccator.

7 Procedure

7.1 Preparation of discs

7.1.1 General

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

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

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 7.1.8).

7.1.2 Weighing

Table 3 shows the components used in making the glass discs. Provided that the proportions are kept approximate to those given in Table 3, the masses can be varied to suit mould diameter and shape (see Note 1).

Table 3 — Masses of specimen components

Component	Standard masses [a] g	Mass g	
		Disc diameter	
		32 mm	40 mm
Flux	6,80	4,10 to 4,61	6,40 to 7,20
$NaNO_3$	0,40	0,24 to 0,27	0,38 to 0,42
Sample	0,66	0,41 to 0,44	0,64 to 0,68

[a] Values used to calculate alpha coefficients.

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 desired, ammonium iodide (4.21) 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 7.1.5)

NOTE 1 If a disc diameter used differs from those given in Table 3, masses should be adjusted to be approximately proportional to the area of the glass disc. If masses used are higher than recommended, crystallization and segregation with consequent cracking are likely to occur as the glass cools.

NOTE 2 Bromides are used as releasing agents but, since BrLα interferes with AlKα, they are not used in this part of ISO 9516.

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 weighings. Weighings may be made direct into the crucible to be used in the fusion, or into a clean glass vial. Because of static effects, glass vials are preferable to plastic. If a vial is used, care shall be taken to ensure complete transfer of the contents into the fusion crucible.

7.1.3 Mixing

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

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.

NOTE 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.

7.1.4 Fusion

For samples containing sulfur as sulfide, the fusion mixture is to be preoxidized by heating to 700 °C for 10 min prior to fusion. Place the crucible in the electric furnace (5.4) or on the gas-oxygen burner (5.5) 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 may be adhering to the sides of the crucible.

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

7.1.5 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 (5.10) and allow the glass to solidify.

b) Casting in a separate mould

If the glass is to be cast in a separate mould, the mould 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 (5.10) and allow the glass to solidify.

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

7.1.6 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.

7.1.7 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.

NOTE 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.

7.1.8 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 2M), 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.

7.1.9 Monitor discs

To compensate for drifts in X-ray tube output intensity, all X-ray measurements shall be made relative to a monitor disc. Although different monitor discs could be used for each component, it is most convenient to use a single disc, containing all components to be measured. The requirements of the monitor disc are that it be stable, at least for the time necessary to complete all the measurements associated with a batch of analyses. Also, the monitor shall contain sufficient amounts of each element in order to ensure that each analytical line is much higher than the BEC. Suitable stable monitor discs made for the analysis of iron ore are commercially available.

Although discs prepared in accordance with the normal procedure described in 7.1.1 to 7.1.11 are not stable over prolonged periods, they are stable for a sufficient period to allow such a disc to be used as a monitor. One of the calibration discs would, therefore, be a suitable monitor, and in such a case this particular disc shall be clearly identified. The same monitor shall be used for Day 1 and Day 2 measurements.

7.1.10 Calibration discs

Calibration shall be carried out using discs prepared according to the masses and various proportions set out in Table 4, where w is the standard mass of chemical compound (referred to as “sample” in Table 4) prepared in accordance with Clause 4.

If handled carefully and stored under desiccation, the glass discs can be used for several weeks. The analytical surface shall under no circumstances be touched by hand.

Table 4 — Synthetic standard set

Disc identity	Number	Description	Sample components	
			Weight of compound g	Weight of SiO_2 (4.1) g
Si A, B	2	100 % SiO_2	N/A	1,00 w
Fe A, B	2	100 % Fe_2O_3	1,00 w of Fe_2O_3 (4.3)	N/A
30Fe/Si A, B	2	30 % Fe_2O_3:70 % SiO_2	0,30 w of Fe_2O_3 (4.3)	0,70 w
66Fe/Si A, B	2	66 % Fe_2O_3:33 % SiO_2	0,66 w of Fe_2O_3 (4.3)	0,33 w
Ca/Si	1	10 % CaO:90 % SiO_2	0,179 w of $CaCO_3$ (4.6)	0,90 w
Ti/Si	1	10 % TiO_2:90 % SiO_2	0,10 w of TiO_2 (4.4)	0,90 w
V/Si	1	10 % V_2O_5:90 % SiO_2	0,10 w of V_2O_5 (4.12)	0,90 w
Cr/Si	1	10 % Cr_2O_3:90 % SiO_2	0,10 w of Cr_2O_3 (4.13)	0,90 w
Mn/Si	1	10 % Mn_3O_4:90 % SiO_2	0,10 w of Mn_3O_4 (4.8)	0,90 w
Co/Si	1	10 % Co_3O_4:90 % SiO_2	0,10 w of Co_3O_4 (4.14)	0,90 w
Pb/Si	1	10 % PbO:90 % SiO_2	0,10 w of PbO (4.19)	0,90 w
Zn/Si	1	10 % ZnO:90 % SiO_2	0,10 w of ZnO (4.17)	0,90 w
Ba/Si	1	10 % BaO:90 % SiO_2	0,129 w of $BaCO_3$ (4.20)	0,90 w
SynCal A, B	2	Synthetic calibration standard [a]	1,00 w of calibration standard (4.24)	N/A

[a] Use Day 1 calibration standard for the first set, and Day 2 calibration standard for the second set.

7.1.11 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, should 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.

7.2 Measurements

7.2.1 General

The analytical lines to be used and suggested conditions of measurement are given in Table 5. Other instrument parameters (collimators and detectors) shall be selected according to the particular element.

In the set of discs listed in Table 4, Fe, 30Fe/Si, 66Fe/Si and Si are used to determine alpha(Fe,Fe). Discs Ti/Si, V/Si, Co/Si, Pb/Si, Zn/Si and Ba/Si are used to determine overlap factors. The overlap factors should be constant, but may change with spectrometer alignment. The discs listed in Table 4 need not be included with each set of analyses; the factors determined previously can be used. However, all discs shall be included at least once each four weeks and, if alpha(Fe,Fe) or line overlap factors vary significantly, the cause shall be determined and the problem remedied.

Table 5 — Suggested analytical lines, crystals and operating conditions

Component element	Line (7.2.3)	Voltage, kV [a] (7.2.4)	Crystal [b] (7.2.5)	Specific line overlaps (7.2.7)
Fe	Kα	80 or 40	LiF(200)or LiF(220)	—
	Kβ	80 or 40	LiF(200)or LiF(220)	—
Si	Kα	30 or 50	PE	—
Ca	Kα	30 or 50	LiF(200) or PE or Ge(111)	—
Mn	Kα	80 or 50	LiF(200)	CrKβ
Al	Kα	30 or 50	PE	BaLα(3), CrKβ(4)
Ti	Kα	80 or 40	LiF(200)	BaLα
Mg	Kα	30 or 50	TlAP or multi-layer	—
P	Kα	30 or 50	Ge(111) or PE	—
S	Kα	30 or 50	Ge(111) or PE	CoKα(3), PbMα
K	Kα	30 or 50	LiF(200)	—
Sn	Lα	30 or 50	LiF(200)	CoKα(2)
V	Kα	80 or 50	LiF(200)	TiKβ, BaLβ
Cr	Kα	80 or 50	LiF(200)	VKβ
Co	Kα	80 or 50	LiF(200)	FeKβ
Ni	Kα	80 or 50	LiF(200)	CoKβ
Cu	Kα	80 or 50	LiF(200)	—
Zn	Kα	80 or 50	LiF(200)	—
As	Kα	80 or 50	LiF(200)	PbLα
Pb	Lβ1	80 or 50	LiF(200)	—
	Mα	30 or 50	PE	—
Ba	Lα	80 or 40	LiF(200)	TiKα
	Lβ1	80 or 40	LiF(200)	TiKβ, VKα

[a] The first figure will normally give better performance, but performance will depend on tube used.

[b] The first crystal listed is preferred.

7.2.2 Effect of errors or omissions

There are various circumstances where all twenty elements may not be determined. If a simultaneous instrument is used, there may not be analytical channels for all elements. In plant control, there may be no point in doing 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 absorption coefficient of the glass (the matrix factor) 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 6 shows the error, as a relative percentage, for each analyte where there is a 1 % error in a component. The error may be not estimating a component if it has a significant concentration. The calculations have been made for a typical iron ore.

Table 6 can be used to estimate at what level a minor element may 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 6 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.

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 6, it can be seen that the omission of measuring 250 ppm BaO will give such an error. From Table 6 it can be seen that an error of 1 % in BaO gives a relative error of 4 % 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 follows:

$$0{,}025 \times 4{,}3 \times 90/100 = 0{,}097\ \%.$$

7.2.3 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.

7.2.4 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 may be advantageous to use a low voltage (40 kV) for the lighter elements and a higher voltage for the heavier elements. If tube operating conditions are changed during analysis, this may result in slight instability in the spectrometer output. Since Fe content is required to be determined with very high precision, Fe has to be measured in a separate run with constant tube conditions if conditions vary for the other elements.

Some spectrometers are limited to less than 80 kV. In these cases, use the highest available voltage. The tube current is governed by the maximum power that can be applied to the X-ray tube; consult the manufacturer's specification for this information.

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. Fe Kα or Ca Kα), 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, but they should not be used as a method for reducing the count rate, as they will alter matrix effects. The exception to this will be the determination of Mn and Cr using a Cr target X-ray tube where a filter will be required to achieve low backgrounds.

Table 6 — Error, in relative %, resulting from a 1 % error in a component

	Affected component																			
	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
Plus 1 %																					
SiO_2	0,57		0,54	0,58	0,22	0,70	0,43	0,65	1,33	0,59	2,40	1,02	1,16	0,67	1,40	1,64	1,39	2,35	1,17	1,73	0,54
CaO	2,01	0,55		2,04	0,54	2,32	1,03	0,83	1,71	0,94	4,31	3,44	3,94	2,37	4,96	5,79	4,93	8,33	1,56	5,76	1,28
Mn_3O_4	0,90	0,48	0,56		0,48	0,52	0,94	0,69	1,38	0,59	2,48	0,79	1,61	3,02	4,24	4,97	4,24	7,21	1,24	1,42	1,17
Al_2O_3	0,50	0,40	0,49	0,51		0,62	0,38	0,59	1,19	0,52	2,17	0,90	1,02	0,58	1,24	1,44	1,22	2,07	1,06	1,54	0,48
TiO_2	1,81	0,52	0,61	1,83	0,53		1,04	0,77	1,52	0,66	2,74	1,42	3,53	2,14	4,47	5,23	4,46	7,56	1,36	2,34	1,31
MgO	0,45	0,37	0,44	0,47	0,38	0,56		0,55	1,10	0,49	1,98	0,82	0,92	0,53	1,11	1,30	1,10	1,87	0,98	1,40	0,42
P_2O_5	0,63	0,24	0,59	0,65	0,24	0,77	0,47		1,43	0,63	2,64	1,13	1,28	0,74	1,56	1,83	1,54	2,63	1,28	1,91	0,58
SO_3	0,71	0,27	0,67	0,73	0,27	0,86	0,52	0,40		0,70	2,92	1,26	1,43	0,84	1,76	2,06	1,74	2,97	0,77	2,14	0,65
K_2O	1,97	0,53	1,71	2,00	0,52	2,29	0,99	0,80	1,66		4,26	3,39	3,88	2,32	4,85	5,67	4,82	8,14	1,52	5,68	1,22
SnO_2	3,11	0,95	1,45	3,15	0,94	3,54	1,77	1,44	2,93	1,49		5,25	6,04	3,67	7,59	8,85	7,56	12,68	2,63	8,72	2,15
V_2O_5	1,86	0,55	0,64	1,88	0,56	0,93	1,08	0,80	1,57	0,70	2,84		1,71	2,20	4,60	5,39	4,59	7,80	1,43	2,44	1,37
Cr_2O_3	2,53	0,72	0,84	1,32	0,73	0,95	1,41	1,04	2,04	0,91	3,72	1,85		2,99	6,23	7,28	6,22	10,52	1,86	3,09	1,77
Co_3O_4	1,09	0,62	0,74	0,47	0,62	0,61	1,20	0,91	1,80	0,80	3,26	0,89	1,00		2,88	6,40	5,48	9,33	1,63	1,53	1,50
NiO	1,15	1,25	1,50	1,21	1,25	1,66	2,39	1,83	3,62	1,63	6,61	2,46	2,85	2,57		5,36	10,97	18,39	3,29	4,15	2,96
CuO	1,13	1,33	1,60	1,22	1,34	1,77	2,54	1,97	3,85	1,73	7,11	2,60	2,97	1,36	4,22		4,80	19,56	3,53	4,38	2,81
ZnO	1,21	1,49	1,83	1,32	1,49	1,99	2,81	2,19	4,36	1,97	8,00	2,90	3,29	1,42	2,00	5,45		21,63	3,95	4,88	2,70
As_2O_3	1,39	1,67	2,11	1,56	1,50	2,36	1,26	2,48	4,91	2,25	9,15	3,40	3,80	1,59	2,41	2,67	2,14		4,49	5,70	1,54
PbO	2,91	0,94	2,54	2,97	0,91	3,43	1,67	1,46	3,07	2,56	10,41	5,11	5,89	3,45	6,83	7,97	6,81	13,08		8,48	2,00
BaO	4,30	1,28	1,60	3,99	1,28	2,36	2,34	1,90	3,81	1,73	7,06	3,61	6,35	5,09	10,47	12,21	10,48	17,49	3,45		2,75
Cl	0,39	0,33	0,38	0,40	0,34	0,50	0,66	0,49	1,00	0,42	1,75	0,72	0,80	0,46	0,97	1,13	0,95	1,63	0,87	1,22	

7.2.5 Crystals

The crystals listed in Table 5 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.

7.2.6 Counting times

After assembly of measurement conditions for all elements, and prior to analysing samples, the required counting times for each element shall be determined as set out below.

The sensitivity, m, as c/s/%, for each element is given by

$$m = \frac{\text{RS.MS} - \text{RB.MB}}{\text{CS}}$$

where

m is the sensitivity;

RS is the intensity, counts per second, from the calibration standard SynCal A; measured for 10 s;

MS is the approximate matrix correction for SynCal A for the analyte, given in Table 7;

RB is the intensity, counts per second, from the blank sample FeA; measured for 10 s (= 0 where measuring FeKα);

MB is the approximate matrix correction for the blank sample FeA, given in Table 7.

CS is the oxide concentration of SynCal A, given in Table 7.

The required counting time T, in seconds, for each element is then given by

$$T = \frac{\text{MS}(m \times p + \text{RB.MB})}{S^2 \times m^2}$$

where

S is the required standard deviation when determining the concentration p.

p and S for the various elements are given in Table 7.

The count rates shall not exceed the permissible limit determined in Annex F. In any case, the count rate should not exceed 5×10^5 c/s. If count rates exceed this limit, the X-ray tube current can be reduced for these measurements but, because such a change may give rise to some instability in some instruments, it is preferable to reduce the count rate by using a finer collimator, another crystal or a weaker line of the element.

7.2.7 Line overlaps

Relevant specific line overlaps are shown in Table 5. Note that certain well-known overlaps are not shown since the overlapping element is low in the materials under consideration. Note also that overlap corrections are applied for the effect of elements that do not give a specific overlap since they contribute to the BEC.

Table 7 — Constants used in the determination of approximate counting times

Component	CS	MS	MB	p	S
Fe_2O_3	64,0	1,85	0	90	0,02
SiO_2	9.5	1,26	1,26	5	0,02
CaO	4,29	1,37	1,30	0,6	0,005
Mn_3O_4	2,0	1,57	1,48	0,1	0,001
Al_2O_3	5,0	1,24	1,25	2,5	0,015
TiO_2	1,5	1,33	1,17	0,15	0,002
MgO	5,0	1,23	1,24	0,15	0,01
P_2O_5	2,66	1,28	1,26	0,05	0,001
SO_3	2,3	1,29	1,27	0,02	0,001
K_2O	1,76	1,34	1,29	0,05	0,0005
SnO_2	0,2	1,32	1,29	0,02	0,001
V_2O_5	0,2	1,14	1,18	0,004	0,000 5
Cr_2O_3	0,2	1,18	1,23	0,02	0,000 5
Co_3O_4	0,2	1,57	1,63	0,01	0,000 5
NiO	0,2	2,75	3,54	0,05	0,000 5
CuO	0,2	2,79	3,62	0,005	0,000 4
ZnO	0,2	2,91	3,69	0,005	0,000 4
As_2O_3	0,111 8	3,15	3,88	— [a]	— [a]
PbO Mα	0,2	1,30	1,27	0,005	0,001
Lα	0,2	2,23	3,69	0,005	0,001
BaO	0,2	1,16	1,18	0,02	0,002

[a] The count time for As shall be equal to that calculated for Zn.

7.2.8 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 TIAP crystal and Rh tubes.

7.2.9 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.

7.2.10 Simultaneous-type instruments

Where using simultaneous-type instruments, the manufacturer will supply crystals to determine each element. These may or may not correspond to those listed in Table 5.

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

Provided that the crystal/slit combination gives a BEC not exceeding those listed in Table 8, they may be used.

7.2.11 Sample holders

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

7.2.12 Measurement sequence

All X-ray measurements of groups of discs shall be bracketed by monitor disc measurements, i.e. the measuring sequence shall be such that a monitor disc is measured first and last. The period between monitor readings should not exceed 4 h. With some older or less stable spectrometers, it may be desirable to measure the monitor more frequently. Regardless of the type of monitor used (calibration standard or other), the same monitor shall be used for Day 1 and Day 2 measurements.

Monitor drift shall be limited to 0,1 % in Fe between monitor measurements. If this limit is exceeded, all Fe measurements shall be repeated. If the instability persists, then the cause shall be determined and rectified.

7.2.13 Subsequent determinations

The full measurement sequence given above provides all the data for a complete calibration. If subsequent test samples are to be analysed, the number of calibration samples may be reduced.

Fe/Si is used to determine alpha(Fe,Fe), and once this has been determined, it need not be determined again unless there is some major change to the equipment or operating conditions.

If a very stable monitor specimen was used during calibration, then the SynCal samples can be omitted.

Ca/Si, Ti/Si, V/Si, Cr/Si, Mn/Si, Co/Si, Pb/Si, Zn/Si and Ba/Si are used to determine overlap factors, which should not vary over short periods, but are sensitive to slight long-term angular drifts of the spectrometer. Therefore, these discs shall be measured at intervals of two weeks. If stored carefully in a desiccator, discs can be used for one month.

The FeA, B discs shall be remade each week.

An entire set of blank and calibration discs shall be prepared after four weeks or when a new batch of flux is used.

8 Calculation of results

8.1 General

NOTE Results are calculated using the program given in Annex H. If required, a disc containing an executable file may be obtained from CSIRO Land and Water.

The program used to convert intensities to concentrations uses line-only intensities; if backgrounds are measured, they shall be subtracted from the line intensities prior to further calculations. Alpha corrections are made using “loss eliminated” alphas. Intensity-based line overlap corrections are used. Catch weights are used for all components (flux, $NaNO_3$ and sample) for both calibration samples and test samples.

If desired, the program may be rewritten or a commercial package may be used, provided that the program makes the same calculations and meets the specifications given in 8.3.

8.2 Input data for program

NOTE Three files of input data are required. A set of sample input data is given in Annex I.

8.2.1 Alpha coefficient file, ALPHAS.MAT

To eliminate errors due to mass changes in the glass due to sample loss during fusion, loss eliminated alpha coefficients are used. Coefficients shall be calculated according to measurement conditions, i.e. operating voltage and geometry, etc.

The file should have the structure of ALPHAS.Mat in Annex I. The first sixteen lines give information on the conditions for which the alphas have been calculated. Line 3 gives the number of component oxides for which alphas have been calculated. Line 4 gives the number of lines for which alphas have been calculated. Nine spaces are used for the component oxide formulae, and the individual alpha factors in the body of the table shall be separated by a space or a comma.

The alphas are for use with mass fractions for oxide components. The factor 0,01 in various equations throughout the calculation program (line numbers 801 to 805) is to allow concentrations R(N,I) to be used as percent. If the software used calculates alphas based on percents, alphas shall be multiplied by a factor of 100, or the 0,01 factor shall be omitted from the calculation program.

NOTE There are a number of programs that can be used to calculate alpha coefficients. The program that generated the alphas in Annex I was created by CSIRO Land and Water. In selecting a program, compliance with the specifications of 8.3 should be ensured.

8.2.2 Name and weight data file, DATASET.WT

The data file shall be set out in accordance with the example given in Annex I. Line 1 gives the number of glass discs, the number of measured lines, and the nominal flux and sample masses. The figures for the sample and flux masses are based on the masses for flux and sample used to calculate alphas. For each glass disc this ratio will vary if catch weights are used, but a correction is made to compensate for this change in the glass composition.

The first 20 discs are as follows:

Monitor

Syncal A

Syncal B

Si A

Si B

Fe A

Fe B

30Fe/Si A

30Fe/Si B

66Fe/Si A

66Fe/Si B

Ca/Si

Ti/Si

V/Si

Cr/Si

Mn/Si

Co/Si

Pb/Si

Zn/Si

Ba/Si

In each case the disc name is followed by the masses of flux, sodium nitrate, sample and SiO_2 used to make the glass. Where SiO_2 has not been added, the mass shall be given as zero. The test samples follow immediately. The last disc shall be a monitor. Monitor readings may be taken at any stage apart from the compulsory readings at the beginning and end. Where monitor readings are made, the disc name shall be "MONITOR".

8.2.3 Intensity data file, DATASET.INT

Apart from the extension, the file name shall be the same as that for the **.WT** file and the sample order shall be the same in the two files. The first line of the **.INT** file is for comments. The second line contains headings for the intensities. Intensities shall be separated by a space or a comma. Twelve spaces have been assigned for the disc name.

8.3 Use of commercial packages

Most modern X-ray spectrometers come with software to process XRF results. Such packages may be used, provided that the following qualifications are met:

a) Some XRF spectrometers have hardware correction of dead time. The user shall carry out the dead time determination in accordance with Annex F and have an adjustment made if required.

b) Most software is not designed to make drift corrections using before and after monitor readings taken prior to the sample readings. In such a case, the monitor shall be measured as described in 7.2.12, and then, for each element, successive readings of the monitor shall be used to check that the drift is less than 0,1 % for Fe and less than 1,0 % for other elements.

c) Any calculation program shall use a calculation algorithm similar to that of the program given in Annex H. It should be based on concentrations rather than intensities; this applies to both the alpha and the overlap corrections. The program shall be capable of using loss-corrected alphas, and in particular it shall accept and use the alpha(i,i) factor for each element. If catch weights are used in weighing, it shall be able to correct for the differing flux/sample ratios. Loss eliminated alphas are used and the correction for catch weights involves multiplying all results for a sample by a constant factor after all other corrections have been made. If the nominal flux and sample masses are F and S and the actual masses are f and s, then the factor is $S.f/F.s$

d) Most spectrometer software includes a program for calculating alphas. Alternatively, there are separate commercial packages to perform the same function. In selecting a program, care shall be taken to check that the program uses a full tube spectrum for the primary radiation and that full secondary fluorescence corrections are made.

9 General treatment of results

9.1 Acceptability of background equivalent concentration (BEC)

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

BECs shall not exceed those shown in Table 8. If the BECs are too high, they indicate contamination of the flux or an instrument operating well below optimum. In such cases, the cause shall be determined and rectified.

Table 8 — 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
P	0,02
S	0,05
K	0,07
Sn	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.	

9.2 Repeatability and permissible tolerances

For each of the elements analysed, the precision of this analytical method is expressed by the regression equations given in Table 9.

Table 9 — Regression equations

Element	σ_d	σ_L	R_d	P
Fe	0,029 1 + 0,001 4 X	0,115 1	0,082 4 + 0,003 9 X	0,398 1
Si	0,005 5 X + 0,004 4	0,022 5	0,012 5 + 0,015 5 X	0,018 9 + 0,012 6 X
Ca	0,003 8 X + 0,001 1	0,004 5 X + 0,000 8	0,010 7 X + 0,003 2	0,016 6 X + 0,003 3
Mn	0,013 8 X + 0,000 4	0,004 3 X – 0,000 2	0,038 9 X + 0,001 1	0,030 7 X + 0,001 2
Al	0,005 8 X + 0,004 5	0,007 7	0,016 5 X + 0,012 8	0,017 3 X + 0,010 0
Ti	0,003 9 X + 0,000 9	0,008 1 X – 0,000 6	0,011 0 X + 0,002 7	0,023 5 X + 0,002 9
Mg	0,005 6 X + 0,005 4	0,010 1 X + 0,004 7	0,015 9 X + 0,015 2	0,029 7 X + 0,019 2
P	0,005 7 X + 0,000 5	0,004 5 X + 0,000 4	0,016 3 X + 0,001 3	0,017 1 X + 0,001 4
S	0,013 3 X + 0,000 7	0,008 3 X + 0,000 5	0,037 6 X + 0,002 0	0,033 9 X + 0,002 8
K	0,006 4 X + 0,000 8	0,002 3	0,018 2 X + 0,002 2	0,007 3
Sn	0,000 9	0,000 6	0,002 6	0,002 8
V	0,005 9 X + 0,000 3	0,010 4 X + 0,000 3	0,016 6 X + 0,000 9	0,031 9 X + 0,001 2
Cr	0,024 4 X + 0,000 4	0,069 3 X + 0,000 2	0,069 0 X + 0,001 2	0,196 7 X + 0,001 1
Co	0,000 6	0,001 1	0,001 7	0,003 3
Ni	0,000 8	0,001 8	0,002 2	0,005 3
Cu	0,021 8 X + 0,000 7	0,001 7	0,061 7 X + 0,002 0	0,005 4
Zn	0,004 9 X + 0,000 6	0,001 2	0,013 9 X + 0,001 8	0,004 1
As	0,014 6 X + 0,000 4	0,061 2 X + 0,000 3	0,041 2 X + 0,001 2	0,163 8 X + 0,001 5
Pb	0,001 8	0,004 6	0,005 0	0,013 8
Ba	0,015 3 X + 0,002 1	0,005 4	0,043 4 X + 0,006 0	0,017 3

Key

X is the content of element in the sample;
σ_d is the independent duplicate standard deviation;
σ_L is the between-laboratories standard deviation;
R_d is the independent duplicate limit;
P is the permissible tolerance between laboratories.

9.3 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 7.

Compute the following quantity:

$$\mu_{1,2} = \frac{\mu_1 + \mu_2}{2}$$

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

$\mu_{1,2}$ is the mean of the final results.

Substitute $\mu_{1,2}$ for X and calculate P.

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

9.4 Check for trueness

The trueness of the analytical method shall be checked by applying it to a certified reference material (CRM) or a reference material (RM) (see 7.1.11). Calculate the analytical result (μ) for the CRM/RM using the procedures in 8.1 and 8.2, and compare it with the reference or certified value A_c. There are two possibilities:

a) $|\mu_c - A_c| \leqslant C$ in which case the difference between the reported result and the certified/reference value is statistically insignificant;

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

where

μ_c is the final result for the certified reference material;

A_c is the certified/reference value for the CRM/RM;

C is a value dependent on the type of CRM/RM used.

NOTE Certified reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35:1989, *Certification of reference materials — General and statistical principles*.

For a CRM certified by an interlaboratory test programme:

$$C = \sqrt{\sigma_L^2 + \frac{\sigma_d^2}{n} + V(A_c)}$$

where

V (A_c) is the variance of the certified value A_c (= 0 for a CRM certified by only one laboratory);

n is the number of replicate determinations carried out on the CRM/RM.

NOTE This type of CRM should be avoided unless it is known to have an unbiased certified value.

9.5 Calculation of 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, Mg

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

9.6 Oxide factors

Element concentrations may be obtained by multiplying by the factors shown in Table 10 and in the calculation program (see Annex I).

Table 10 — 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
SnO_2	**Sn**	0,787 7
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

10 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 part of ISO 9516, i.e. ISO 9516-1;

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 part of ISO 9516 which may have had an influence on the result, for either the test sample or the certified reference material(s).

Annex A
(normative)

Preparation of flux A

A.1 Scope

This annex describes a procedure for the preparation of flux A 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 1 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.

NOTE 2 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.

NOTE 1 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.

NOTE 2 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 may occur, but this should be minor with the 5 mm thickness stipulated.

NOTE 3 If a graphite crucible is used, the glass may 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.

NOTE 4 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 5 The powdered glass is slightly hygroscopic and will slowly absorb moisture.

Table A.1 — Reagent masses for flux A

Reagent	Mass g
$Li_2B_4O_7$	24,00
$LiBO_2$	44,00

Annex B
(normative)

Preparation of flux B or flux C

B.1 Scope

This annex describes a procedure for the preparation of flux B from sodium tetraborate or 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)

Preparation of synthetic calibration standard

C.1 Scope

This annex describes the procedure for the preparation of the synthetic calibration standard.

C.2 Reagents

The reagents used in the preparation of the synthetic calibration standard are listed in Table C.1. Reagents shall be prepared according to the instructions in Clause 4.

Table C.1 — Reagent masses for the preparation of calibration standard

Reagent	Mass g
Fe_2O_3 (4.3)	64,00
SiO_2 (4.1)	9,50
$CaCO_3$ (4.6)	4,783 7
$CaSO_4$ (4.7)	3,911
Mn_3O_4 (4.8)	2,000
Al_2O_3 (4.2)	5,00
TiO_2 (4.4)	1,500
MgO (4.9)	5,00
KH_2PO_4 (4.5)	5,082
SnO_2 (4.11)	0,20
V_2O_5 (4.12)	0,20
Cr_2O_3 (4.13)	0,20
Co_3O_4 (4.14)	0,20
NiO (4.15)	0,20
CuO (4.16)	0,20
ZnO (4.17)	0,20
$Na_2HAsO_4 \cdot 7H_2O$[a] (4.18)	0,352 7
PbO (4.19)	0,20
$BaCO_3$ (4.20)	0,257 4

[a] When the calibration standard is heated to 900 °C, the mass of this reagent will be reduced to 1,00 g.

C.3 Procedure

a) Mix the reagents listed in Table C.1 by shaking in a large plastic container, crushing any large lumps.

b) Transfer the powder to a 100 ml tungsten carbide barrel of a ring mill; grind for 2 min to 3 min.

c) Remove the powder from the grinder.

d) Mix the powder by passing it through a riffle splitter several times.

e) Transfer the powder to a platinum dish and place in the electric furnace (5.4) at ambient temperature. Slowly increase the furnace temperature to 950 °C over a period of not less than 1 h. Maintain this temperature for 20 min and then remove and cool the mix in a desiccator with self-indicating silica gel desiccant.

NOTE If any powder adheres to the crucible, make sure this is removed and incorporated with the rest of the powder. A plastic rod may be used to remove the powder. Do not use a glass rod.

f) Repeat the grinding and mixing, and then store in an airtight container.

Two independent batches (prepared on different days) shall be prepared. However, it is not necessary to prepare this material fresh for each set of analyses, since the material may be used over a long period of time.

When extracting a sample from this standard, a method that gives a representative sample shall be used, e.g. riffle splitter, rotary sample divider.

The weights specified in Table C.1 are not obligatory. Use of lesser or greater amounts of reagent is allowed, *but the ratio of each component shall not change*.

Prior to weighing, this standard shall be heated at 900 °C for 20 min (see 4.24)

Annex D
(normative)

Standard deviation of specimen preparation

D.1 Scope

This annex describes a procedure for the determination of the precision of specimen preparation.

NOTE This procedure for determining the standard deviation of specimen preparation should be undertaken by each operator prior to commencing work on actual test specimens. New operators should repeat this procedure at regular intervals of not more than 2 months, until they can consistently obtain Fe_2O_3 precision of less than 0,1 % in Fe.

D.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 7.1.4 to 7.1.7.

b) If more than one crucible or more than one mould is used for casting in sample preparation, these crucibles or moulds shall all be used in the preparation of 10 replicates.

c) Measure the intensity of the FeKα radiation for each of the 10 replicate specimens, accumulating at least 2×10^7 counts for each specimen. Re-measure specimen 1 at the end.

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

D.3 Assessment of results

D.3.1 General

The standard deviation of specimen preparation is calculated in the BASIC program DISCERR given in D.4. If desired, the program may be rewritten or a commercial package may be used, provided that the programs carry out the same calculations. The program calculates the errors of disc preparation and disc measurement.

D.3.2 Input standard weights

Refer to Table 3 (7.1.2) for input standard masses for flux, $NaNO_3$ and sample.

D.3.3 Input dead time and set background

Dead time, as determined using the method given in Annex F, is input with microseconds as the units. The program converts microseconds to seconds. Approximate background is 0,1.

D.3.4 Input data

The data file shall be set out in accordance with the example given in D.5. W1 is the mass of flux, W2 is the mass of $NaNO_3$, and W3 the sample mass. Catch weights are used for all components. R(1,N) and R(2,N) are the count rates (expressed as counts per second) for FeKα for independent sets Run 1 and Run 2. Line 11 contains R(1,1) and R(2,1) remeasured to correct for drift.

D.4 Calculation program for standard deviation of specimen preparation

```
REM PROGRAM "DISCERR" WRITTEN BY K.NORRISH, CSIRO DIVISION OF SOILS, 29.3.93

REM THIS BASIC PROGRAM IS FOR CALCULATING DISC ERRORS IN FE2O3 DISCS PREPARED USING CATCH WEIGHTS

REM THE STANDARD DEVIATION FOR ALL DISCS PREPARED IS ALSO CALCULATED

REM CORRECTS FOR DRIFT IN MONITOR

PRG$ = "DISCERR"

DEFDBL S

DIM RESULT(2, 11), CS(10, 4), R(2, 11), SWG(10), MAT(10)

REM *****************************************************

REM INPUT ASSAY IDENTIFICATION

INPUT "ASSAY IDENTIFICATION (TO 8 CHARACTERS) "; NAM$

NAM$ = NAM$ + ".DAT"

OPEN NAM$ FOR INPUT AS #1

REM *****************************************************

REM INPUT STANDARD WEIGHTS

INPUT "STD WEIGHTS OF FLUX, NANO3, SAMPLE "; WS1, WS2, WS3

REM *****************************************************

REM INPUT DEADTIME AND SET BACKGROUND

INPUT "INPUT DEADTIME IN MICROSECS "; DTIM

DTIM = DTIM * .000001

B = -.1                    'SET APPROXIMATE BACKGROUND %

REM *****************************************************

REM INPUT DATA

RM(1) = 0: RM(2) = 0: SWG = 0: CS2 = 0: MAT = 0

FOR N = 1 TO 10

INPUT #1, W1, W2, W3, R(1, N), R(2, N)

REM W1=WT FLUX ; W2=WT NANO3 ; W3=WT SAMPLE ; R(1,N)=COUNTS,RUN 1 ; R(2,N)=COUNTS,RUN2

REM *****************************************************

REM CALCULATE CONCENTRATIONS IN DISCS

SWG(N) = WS1 * W3 / W1 / WS3                    'SAMPLE WT RELATIVE TO STANDARD WT

CS(N, 2) = (W2 * WS1 / W1 - WS2) * 36.46 / WS3      'NA2O EXCESS OR DEFICIT RELATIVE TO STANDARD SAMPLE WT
```

```
REM ******************************************************
REM CALCULATE AVERAGE CONCENTRATION OF 10 DISCS
SWG = SWG + SWG(N)
CS2 = CS2 + CS(N, 2)
NEXT N
CS2 = CS2 / 10                  'AVERAGE EXCESS NA2O
SWG = SWG / 10                  'AVERAGE SAMPLE MASS RELATIVE TO STANDARD SAMPLE MASS
CS1 = 100 * SWG
REM ******************************************************
REM CORRECT FOR DRIFT
INPUT #1, R(1, 11), R(2, 11)        'DISC#1 RERUN TO CHECK DRIFT
FOR L = 1 TO 2
K(L) = (R(L, 11) - R(L, 1)) / 10
FOR N = 2 TO 10
R(L, N) = R(L, N) * R(L, 1) / (R(L, 1) + (N - 1) * K(L))
NEXT N
NEXT L
REM ******************************************************
REM APPLY DEADTIME CORRECTION TO COUNTRATES
FOR L = 1 TO 2
FOR N = 1 TO 10
R(L, N) = R(L, N) / (1 - R(L, N) * DTIM)
RM(L) = RM(L) + R(L, N)
NEXT N
RM(L) = RM(L) / 10    'CALCULATE AVERAGE COUNTRATE FOR EACH RUN
NEXT L
REM ******************************************************
REM CALCULATE AVERAGE MATRIX CORRECTION
ALPHA1 = .68: ALPHA2 = .29        'TYPICAL ALPHA COEFFICIENTS FOR FE AND NA
MAT = 1 + .01 * ((CS1 * ALPHA1) + (CS2 * ALPHA2))
```

```
REM ****************************************************
REM CALIBRATION
S = 0: SQ = 0
FOR L = 1 TO 2
E = (100 - B) * SWG / (RM(L) * MAT)
REM ****************************************************
REM CALCULATION OF RESULTS AND STATISTICS
FOR N = 1 TO 10
RESULT(L, N) = (E * R(L, N) * (1 + .01 * CS(N, 2) * ALPHA2) + B) / (1 - E * .01 * R(L, N) * ALPHA1) / SWG(N)  'MATRIX CORRECTION
SC(N) = SC(N) + RESULT(L, N)
S = S + RESULT(L, N)            'SUM
SQ = SQ + (RESULT(L, N)) ^ 2     'SUM OF SQUARES
NEXT N
NEXT L
REM CALCULATE READING ERROR AND DISC ERROR
FOR N = 1 TO 10
SCQ = SCQ + SC(N) ^ 2
NEXT N
DISCSS = SCQ / 2 - S ^ 2 / 20
TOTALSS = SQ - S ^ 2 / 20
READSS = TOTALSS - DISCSS
READERR = SQR(READSS / 10)
DISCERR = SQR(ABS((DISCSS / 9 - READSS / 10) / 2))
REM DIFFERENCE BETWEEN RUNS
FOR N = 1 TO 10
DIFF(N) = RESULT(1, N) - RESULT(2, N)
NEXT N
```

```
REM ******************************************************
REM PRINT RESULTS
LPRINT LAB$; "   "; PRG$; "  "; DATE$; "  "; " DEADTIME = "; USING "#.###^^^^"; DTIM
LPRINT "B="; B; "      E="; E
LPRINT
LPRINT "           RUN 1         RUN 2        DIFF"
FOR N = 1 TO 10
LPRINT "SAMPLE "; N; USING "  ###.###       "; RESULT(1, N); RESULT(2, N);
LPRINT USING "#.###"; DIFF(N)
NEXT N
LPRINT
LPRINT "    READING ERROR =    "; USING "  #.###       "; READERR
LPRINT "    DISC ERROR    =    "; USING "  #.###       "; DISCERR
LPRINT
END
```

D.5 Sample data set

6.7963,.4074,.6751,434765.6,434662.6

6.8311,.4052,.6846,436992.7,437183.5

6.8107,.3988,.6744,434310.6,434326.0

6.8005,.4019,.6859,438967.4,438988.6

6.8196,.3999,.6792,435889.1,435764.0

6.8045,.4041,.6727,433502.4,433722.6

6.8050,.3956,.6747,434684.4,434740.5

6.8063,.4128,.6992,443148.6,442727.6

6.8021,.4083,.6738,433670.5,433640.5

6.8215,.3939,.6786,435520.3,435414.8

434593.3,434438.5

Annex E
(normative)

Spectrometer precision tests

E.1 Scope

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, but some spectrometers give their output as a voltage reading. Either type may be used.

E.2 Precision

E.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 may 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 $100/\sqrt{N}$ %. In the tests outlined in this part of ISO 9516, 20 measurements are usually made. Where 20 such measurements are made, the observed coefficient of variation shall not exceed 1,5 times that expected. If the observed coefficients of variation are larger than this, corrective measures shall be taken.

E.2.2 Voltage output

Where integrated output intensity is read as a voltage, it is not possible to predict the theoretical error of a voltage reading, so it needs to be determined empirically.

When carrying out tests E.5.1 a) and b), the integration time is adjusted so that the required precision is obtained. Any observed error is due to both counting error and X-ray output variations.

E.3 Test disc

E.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.

E.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.

E.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 may not be possible, as high a count rate as achievable shall be used.

E.4 Instrumental conditions

E.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.

E.4.2 Sequential spectrometers

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

Set the spectrometer to measure FeKα. A broad P.H.A. window shall be used, e.g. a window width of three times the lower level setting selected.

E.4.3 Simultaneous spectrometers

A broad P.H.A. window shall be used with each channel under test, e.g. a window width of three times the lower level setting selected.

E.5 Spectrometer tests

E.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 expected error. If the calculated value exceeds this, it may 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 expected 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.

E.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 E.2.

E.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 E.2.

E.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 E.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 may 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.

E.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 E.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.

NOTE 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 may even vary with crystal and angle.

E.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 E.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.

E.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.

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

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

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

The test disc shall remain in the spectrometer while alternate measurements are made for each detector. Twenty such pairs of measurements are required.

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

As for angular reproducibility (see E.5.6), errors associated with changing of the detector may, or may not, affect the analyses, depending on the measurement sequence used.

E.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 E.2.

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

E.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 E.2. Examples of such devices are:

a) primary beam filters;

b) collimator apertures;

c) attenuators.

Annex F
(normative)

Determination of the dead time and maximum count rate of the equipment

F.1 Introduction

In all counting equipment there is a dead time, i.e. after a count has been registered there is a small time during which the equipment will not register another count; it is effectively "dead". If accurate intensity measurements are required, then observed intensities shall be corrected for dead time losses. Dead time corrections become inaccurate above certain count rates. This procedure is to determine the effect of dead time for the equipment and the maximum count rate to which correction can be accurately applied.

The dead time for a particular spectrometer is not necessarily fixed. Commonly it is different for proportional and scintillation counters and it can vary with electronic instrumental settings, e.g. PHA settings, integration and differentiation time constants. It may even vary with wavelength. For any particular equipment, the factors that affect dead time can only be determined empirically, and if precise analyses are to be made for a particular element then the dead time should be determined at the wavelength and with the electronic instrumental settings to be used during the analysis.

The dead time of the equipment results in counting losses that get relatively greater as the count rate increases. Observed count rates are corrected for such losses according to the following equation:

$$R = \frac{R_o}{1 - R_o t} \tag{F.1}$$

where

R is the count rate corrected for dead time losses, in counts per second (c/s);

R_o is the observed count rate, in counts per second (c/s);

t is the dead time, in seconds.

NOTE 1 This equation is valid only if the dead time is non-self-prolonging.

Equation F.1 may also be written as $R = \frac{N_o}{T_o - N_o t}$

where N_o is the number of counts accumulated in T_o seconds.

Where a preset number of counts is used, the counting time is corrected according to

$$T = T_o - N_p t \tag{F.2}$$

where

T_o is the observed time to accumulate the preset number of counts N_p, in seconds;

T is the corrected time, in seconds.

If the preset count of 10^6 is used and t is expressed in microseconds, then:

$$T = T_0 - t \qquad \text{(F.3)}$$

NOTE 2 For instruments having automatic dead time correction facilities, this test should still be carried out to verify that the device is adjusted correctly. Significant deviations from zero, either positive or negative, indicate the need for adjustment of the device.

F.2 Methods of determination of dead time

F.2.1 General

A number of methods are used for determining dead time, but the most satisfactory ones involve changing the X-ray intensity by a fixed, but not necessarily known, ratio. The two intensities are recorded for a range of count rates and the dead time is calculated from these data.

The methods that have been used to obtain a fixed ratio between two count rates are described in a) to e) below.

a) The insertion of a foil into the fluorescent beam, usually in front of the counter.

This method is most easily used by inserting the foil in front of the scintillation counter where this is not in the vacuum system. It requires mechanical additions to the spectrometer so that the foil can be repositioned accurately.

This method has the advantage that once the ratio has been determined for a particular wavelength it will remain constant, and subsequent dead time determinations at this wavelength can be simply and quickly made. Also, once the ratio is known accurately the foil can be used for different spectrometers and by other laboratories.

The method has the disadvantage of requiring additions to the spectrometer and is not suited to modern completely enclosed spectrometers where it is impossible to access the counters.

b) Changing from coarse to fine primary collimator.

This method can be used where alternative collimators are available within the spectrometer, but the collimator changing has to be highly reproducible. This method cannot be used with some modern spectrometers that have single fixed collimators.

c) Using two samples that give different count rates.

This method has the advantage that it can be used with all types of spectrometers but it requires that sample changing is very reproducible. It is the method recommended here.

d) Using the Kα and Kβ lines for one element.

This method requires instruments to measure the Kα and Kβ lines for one element. Since simultaneous instruments are not equipped to do this, it is not recommended.

e) Using mA control to give different count rates.

This method assumes that the X-ray output is directly proportional to the mA setting. If this assumption is true, the method has the great advantage of giving known intensity ratios as the current is varied. The dead time can then be rapidly and simply determined.

The problem is with the assumption that X-ray intensity is directly proportional to the mA setting. A certain mA setting may not give precisely the current selected by the setting. In addition, even where the mA control is good, as with some modern spectrometers, the wave form will vary with current and this will destroy a precisely linear relationship between current and X-ray output. For the above reasons, this method is not recommended.

F.2.2 Recommended method for the determination of dead time

F.2.2.1 Specimens

Two specimens shall be prepared, having analyte contents that differ by a factor of about three. Although pressed powder specimens can be used, there are advantages in using more robust and stable specimens and so the analyte incorporated, via fusion with a borate flux, into glass discs is recommended. The analyte content of the higher specimen shall be sufficiently high that at a little below full X-ray power this sample gives a count rate in excess of that normally encountered; about 10^5 c/s for older spectrometers and 5×10^5 c/s for modern spectrometers that can cope with higher count rates.

F.2.2.2 Setting the X-ray tube high voltage

The two specimens shall be mounted in sample holders so that they can be measured alternately. With the higher analyte specimen in position, set the tube current to the maximum and then adjust the voltage to obtain the maximum count rate desired.

NOTE Most manufacturers stipulate a maximum current-to-voltage loading for their tubes and this should not be exceeded, as tube damage may result.

F.2.2.3 Measurements

Reduce the current to a minimum or to a value that is no greater than 10 % of the maximum, and using the resulting count rate carefully select and set the pulse height analyser settings to be used.

With these settings obtain in order:

a) the time to accumulate 2×10^7 counts for the higher analyte sample, T_1;

b) the time to accumulate 2×10^7 counts for the lower analyte sample, T_2;

c) the time to accumulate 2×10^7 counts for the lower analyte sample, T_2;

d) the time to accumulate 2×10^7 counts for the higher analyte sample, T_1.

The above readings are obtained by using the preset count mode and recording the time to at least three decimal places of seconds. If the timer does not read to the required number of decimal places, or if the equipment does not have a preset count facility, then use a preset time, adjusting the time so that approximately 10^7 counts are accumulated.

Increase the count rate by increasing the current and repeat the measurement, with the voltage fixed. Continue this process of increasing the current and making the required measurements each time until the maximum count rate (maximum current) is reached. If the preset count mode is not used, then the counting time can be reduced as the current is increased, so that for each reading the total counts are about 10^7.

The current settings shall be spaced to approximate a geometric progression. The number of settings used is not critical, but between 5 and 10 shall be used. Typical settings are 5, 8, 10, 14, 18, 24, 36 and 50 mA.

NOTE In some cases, it may be desired to determine the dead time more precisely than can be obtained by accumulating 10^7 counts. The number of counts may be increased but equation (F.2 or F.3) is still valid as long as the time, T_o, is expressed as that required to accumulate 10^6 counts.

F.2.2.4 Calculation of result

Convert the measured data to the time required to accumulate 10^6 counts using the following equation:

$$T = \frac{10^6 T^1}{N} \tag{F.4}$$

where T^1 is the time to accumulate N counts.

Check the reliability of the data by calculating the overall coefficient of variation between the duplicate readings. The expected error ($N = 10^7$) is 0,03 % and the actual error should not exceed 0,05 %, since poor readings affect the reliability of the dead time determination. Average the pairs of readings.

The basis of the calculations is that, when the count rates of the two specimens are corrected for dead time, the ratio of their corrected count rates will be constant and independent of the basic count rate (current setting). If T_1 and T_2 are the times to accumulate 10^7 counts for the higher and lower samples respectively, the ratio Q of the two count rates after dead time correction is, from Equation (F.2), given by:

$$Q = \frac{T_2 - t}{T_1 - t} \tag{F.5}$$

where t is the dead time, in microseconds.

The value of t is adjusted by trial and error to give the minimum coefficient of variation of Q and the error should be near that expected. Often it is not possible to find a value for t that will give a constant value for Q, but if the values of Q are inspected for each dead time, it will be found that for a certain dead time Q may be constant at the lower count rates but have reduced values at the higher count rates. In such cases, the highest count rate data should be deleted from the calculations to see if a value for t can be found that gives close to the expected error for Q. If this is unsuccessful, the next highest count rate data should be deleted and so on.

When the value of t is found for which the coefficient of variation of Q is a minimum and, provided that this is not greater than 1,5 times the expected coefficient of variation, t is the dead time of the counting equipment. However, this dead time can only be applied to count rates that give a constant value of Q, i.e. if it is necessary to drop high count rates from the calculations, then these rates shall not be used for analytical work.

Note that Equation (F.5) is in the form of a linear equation and a value for both Q and t may be found from a linear regression of T_1 against T_2. A normal linear regression, however, assumes errors in only one variable and further, that the errors are constant for the range of the variable. These assumptions lead to small but significant errors in the dead time calculated from a simple linear regression.

F.2.2.5 Example of measurement data and calculation of result

A typical set of measurement data obtained, with iron as analyte, as outlined is given in Table F.1 while the calculations involved in establishing the dead time from these data are shown in Table F.2.

Table F.1 — Typical measurement data

Tube current mA	Time to accumulate 10^6 counts ($N = 10^6$) s	
	Higher iron sample (T_1)	Lower iron sample (T_2)
5	84,57 84,43	257,96 258,45
8	53,16 53,15	160,85 161,27
10	42,83 42,82	129,17 129,06
14	30,90 30,87	92,06 92,19
18	21,98 22,01	64,44 64,47
24	17,88 17,86	51,51 51,62
36	13,21 13,22	36,93 36,92
50	9,71 9,68	25,82 25,85
CV of duplicates [a]	0,103 %	0,110 %

[a] See calculation given in F.3.

It can be seen from Table F.2 that when t = 1,50 µs the value of Q decreases with increasing count rate (increasing current) indicating that a higher value of t is necessary. At t = 2,00 µs this trend is absent but the coefficient of variation of Q is unacceptable. If, however, the Q values for the two highest count rates are neglected, then a trend for Q to increase with count rate is evident, indicating that the value of t needs to be reduced. At t = 1,83 µs the coefficient of variation of Q is acceptable and checking either side of this value (t = 1,81 µs and t = 1,85 µs) shows it to be a minimum. The dead time is, therefore, 1,83 µs.

Since it was necessary to delete the two highest count rates in determining the dead time, this spectrometer should be limited to count rates below that for the higher iron sample at 24 mA. This maximum count rate is, using Equation (F.2), $10^6/(17{,}87 - 1{,}83)$ or about 60 000 c/s.

Table F.2 — Calculation of result

Tube current	Average times s		$Q = (T_2 - t)/(T_1 - t)$ µs				
mA	T_1	T_2	t = 1,50	t = 2,00	t = 1,83	t = 1,81	t = 1,85
5	84,500	258,205	3,092 8	3,105 5	3,101 2	3,100 7	3,101 7
8	53,155	161,060	3,089 0	3,109 4	3,102 4	3,101 6	3,103 2
10	42,825	129,115	3,088 1	3,113 7	3,104 9	3,103 9	3,105 9
14	30,885	92,125	3,084 1	3,120 1	3,107 7	3,106 3	3,109 2
18	21,995	64,455	3,071 7	3,123 5	3,105 6	3,103 5	3,107 7
24	17,870	51,565	3,058 3	3,123 2	3,100 7	3,098 1	3,103 3
36	13,215	36,925	3,023 9	3,114 1	3,082 6	3,078 9	3,086 2
50	9,695	25,835	2,969 5	3,097 5	3,052 1	3,046 9	3,057 4
CV of Q			1,404 %	0,291 %			
CV of Q	(dropping 50 mA and 36 mA)				0,089 %	0,092 %	0,094 %

F.3 Calculation of the coefficient of variation of duplicates

For each of the two samples (higher iron, lower iron, see F.2.2.1), a number of measurements is taken in duplicate at varying currents. The coefficient of variation of duplicates for either sample is calculated as follows:

a) Coefficient of variation for 1 part of readings:

$$\mathrm{CV} = \frac{\sigma}{\bar{x}} \times 100 \qquad \text{(F.6)}$$

where

σ is the standard deviation of x_1, x_2 (see Equation F.7);

$$\bar{x} = \frac{x_1 + x_2}{2}$$

where

x_1 is the reading of sample at a given current;

x_2 is the second reading of sample at the same current.

$$\left[x_1^2 + x_2^2 - \frac{(x_1 + x_2)^2}{2} \right]^{\frac{1}{2}} \qquad \text{(F.7)}$$

b) Coefficient of variation of duplicates:

$$\text{CV (duplicates)} = \left[\frac{\sum\left(\frac{\sigma}{\bar{x}} \times 100\right)}{n}\right]^{\frac{1}{2}} \qquad \text{(F.8)}$$

where

n is the number of different current readings.

From Table F.1 and using the high iron sample, Table F.3 may be formulated.

Table F.3 — Data for determination of coefficient of variation of duplicates

Tube current mA	x_1	x_2	σ	CV	$(CV)^2$	$\Sigma(CV)^2$
5	84,57	84,43	0,099 0	0,117	$1,37 \times 10^{-2}$	0,013 7
8	53,16	53,15	0,007 1	0,013	$1,77 \times 10^{-4}$	0,013 9
10	42,83	42,82	0,007 1	0,017	$2,73 \times 10^{-4}$	0,014 2
14	30,90	30,87	0,021 2	0,069	$4,72 \times 10^{-3}$	0,018 9
18	21,98	22,01	0,021 2	0,096	$9,30 \times 10^{-3}$	0,028 2
24	17,88	17,86	0,014 1	0,079	$6,26 \times 10^{-3}$	0,034 5
36	13,21	13,22	0,007 1	0,054	$2,86 \times 10^{-3}$	0,037 4
50	9,71	9,68	0,021 2	0,219	$4,80 \times 10^{-2}$	0,085 3

Therefore, from Table F.3

$$\sum\left(\frac{\sigma}{\bar{x}} \times 100\right)^2 = 0{,}085\,3 \quad (n = 8)$$

$$\text{CV(duplicates)} = \left(\frac{0{,}085\,3}{8}\right)^{\frac{1}{2}}$$

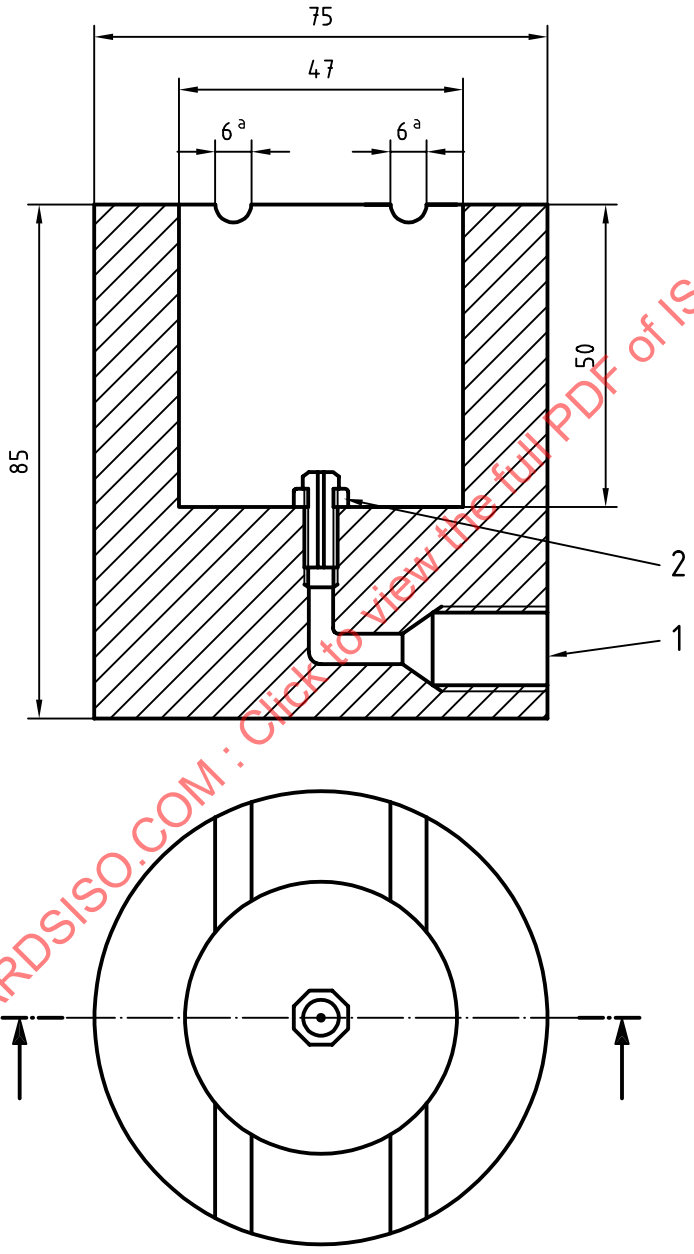
$$= (0{,}010\,7)^{\frac{1}{2}}$$

$$= 0{,}103\ \%$$

Annex G
(informative)

Air cooling block for fused discs

Dimensions in millimetres



Key

1 1/4 in gas thread connected to compressed air via a needle valve

2 3/16 in Whitworth bolt with a 1 mm diameter hole and locking nut

[a] For ceramic rods

Annex H
(informative)

Computer program for calculation of results

A computer program for calculating the results is to be found on the following pages.

```
REM PROGRAM FOR CALCULATING COMPOSITION OF IRON ORE. : NA NOT MEASURED.
PRG$ = "WG27BISO.15-7-98"  ' (MONITOR CALIBRATION EXCEPT FOR FE. FE USING 30,66 AND 100. ALPHA AND BETA and GAMMA) MOD, TO FILE 20-4-96"
REM WRITTEN BY K.NORRISH ,CSIRO DIVISION OF SOILS
REM WRITTEN IN MICROSOFT BASIC
REM STANDARDS NUMBER 9516 IRON ORE WG27B5
REM CATCH WEIGHTS ARE USED. WEIGHTS OF FLUX, NANO3, SAMPLE ARE STORED IN FILE "DATASET.WT"
REM INTENSITY DATA IS IN FILE "DATASET.INT"
REM MATRIX COEFFICIENTS ARE IN FILE "ALPHAS.MAT"
REM OXIDE CONCENTRATIONS ARE USED FOR CALCULATIONS. THESE ARE CONVERTED TO ELEMENTS PRIOR TO FINAL OUTPUT.
REM LOSS ON IGNITION IS NOT REQUIRED AS LOSS CORRECTED ALPHAS ARE USED
WIDTH LPRINT 160: PRINT CHR$(27); "!"; CHR$(5);
DEFDBL B, D-E, L, Q-S
REM*****************************************************************
REM INPUT RUNNING CONDITIONS
 INPUT "DATASET NAME "; LBN$      ' INPUT NAME OF DATA SET IE NAME USED IN THE .WT and .INT files
10 LB2$ = LBN$ + ".WT"
LB3$ = LBN$ + ".INT"
 OPEN LB2$ FOR INPUT AS #2
 INPUT #2, NOS                    ' NUMBER OF SAMPLES
 INPUT #2, NME                    ' NUMBER OF MEASURED ELEMENTS
 INPUT #2, FLUXWT                   '  FLUX MASS
 INPUT #2, SAMPWT                   '  SAMPLE MASS
 LB5$ = LBN$ + ".RES"
 INPUT "DEADTIME IN MICRO-SECONDS "; DTIM: DTIM = DTIM * .000001
OPEN LB5$ FOR OUTPUT AS #5
REM*****************************************************************
 DIM R(60, 22), ALPHA(22, 22), TITLE$(NOS), CS(NOS, 22), SWG(NOS), K(22), CERR(22), DRIFT(NME)
 DIM OXI(22), TG(22), B(22), S(22), OVLP(22, 22), EI(22), CORR(22), CORB(24), MAT(34, 22), STD(23), MON(10, NME), CHECK(NME)

REM  R() FOR INTENSITIES; ALPHA() FOR ALPHAS; TITLE$() FOR SAMPLE NAMES; CS() % OF OXIDES IN CALIBRATION SAMPLES;
REM SWG() MASS OF SAMPLE RELATIVE TO THE NOMINAL MASS FOR THE NOMINAL FLUX MASS; K() CONSTANTS IN DRIFT CORRECTION;
REM CERR() COUNTING ERROR AT VERY LOW CONCENTRATIONS;

REM OXI() MASS FRACTIONS OF ELEMENTS IN OXIDES; B() BACKGROUND CONCENTRATIONS, %; S() KC/S/% FOR EACH ELEMENT;
REM OVLP() OVERLAP FACTORS; EI() ELEMENT CONCENTRATIONS; CORR() AND CORB() OVERLAP CORRECTIONS FOR STANDARDS;
REM MAT() MATRIX CORRECTIONS FOR SAMPLES;
REM STD() SYNTHETIC STANDARD CONCENTRATIONS, %; MON() MONITOR INTENSITIES
REM *****************************************************************
REM  ELEMENT SYMBOLS IN SYSTEM ORDER
DATA FE,SI,CA,MN,AL,TI,MG,P ,S ,K ,SN,V ,CR,CO,NI,CU,ZN,AS,PB,BA,CL,NA
DIM EL(22) AS STRING * 2, ER(22), T(22), P(22)
FOR J = 1 TO 22
      READ EL(J)          ' ELEMENT NAME
NEXT J
DATA FE2O3,SIO2 ,CAO  ,MN3O4,AL2O3,TIO2 ,MGO  ,P2O5 ,SO3  ,K2O  ,SNO2 ,V2O5 ,CR2O3,CO3O4,NIO  ,CUO  ,ZNO  ,AS2O3,PBO ,BAO ,CL   ,NA2O
DIM OX(22) AS STRING * 5
FOR J = 1 TO 22
      READ OX(J)          ' OXIDE FORMULA
NEXT J
```

```
REM*************************************************************************
REM SYN ORE CONCENTRATIONS :- FE2O3,SIO2,CA0,MN3O4,AL2O3,TIO2,MGO,P2O5,SO3,K2O,SNO2,V2O5,CR2O3,CO3O4,NIO,CUO,ZN0,AS2O3,PBO,BAO,CL,NA2O
5  DATA 64, 9.5, 4.2914, 1.888, 5, 1.5, 5, 2.65, 2.3, 1.759,0.2, 0.2, 0.2, 0.2, 0.2, 0.2, 0.2, 0.1118, 0.2, 0.2, 0.0,.070
RESTORE 5
FOR J = 1 TO 22
        READ STD(J)          'SYN ORE CONCENTRATION ARRAY
NEXT J
 REM*************************************************************************
REM FACTORS TO CONVERT FROM OXIDES TO ELEMENTS
2  DATA  0.6994,0.4674,0.7147,0.7203,0.5293,0.5995,0.6031,0.4364,0.4005,0.8302,0.7877,0.5602,0.6842,0.7342,0.7858,0.7989,0.8034,0.7574,0.9283,0.8957,1.0,0.7419
FOR I = 1 TO 22
         READ OXI(I)   ' MASS FRACTION OF ELEMENT IN OXIDE
NEXT I
REM*************************************************************************
REM INPUT WEIGHTS OF FLUX,NANO3, SAMPLE, AND SIO2
    Q = 100 * FLUXWT / SAMPWT
 LINE INPUT #2, DUM$
 FOR N = 1 TO NOS
       TITLE$(N) = INPUT$(12, #2)   ' SAMPLE NAME

1      INPUT #2, W1, W2, W3, W4      ' MASSES OF FLUX, NANO3,SAMPLE, SIO2
       IF N > 20 THEN GOTO 60       ' TEST SAMPLES
       IF N < 4 GOTO 60             ' MONITOR AND SYNTHETIC STANDARDS
       IF N = 4 THEN CS(4, 2) = Q * W3 / W1: GOTO 60                        ' SIO2
       IF N = 5 THEN CS(5, 2) = Q * W3 / W1: GOTO 60                       'SIO2
       IF N = 6 THEN CS(6, 1) = Q * W3 / W1: GOTO 60                        'FE2O3
       IF N = 7 THEN CS(7, 1) = Q * W3 / W1: GOTO 60                        'FE2O3
       IF N = 8 THEN CS(8, 1) = Q * W3 / W1: CS(8, 2) = Q * W4 / W1: GOTO 60    'FE2O3 AND SIO2
       IF N = 9 THEN CS(9, 1) = Q * W3 / W1: CS(9, 2) = Q * W4 / W1: GOTO 60    'FE2O3 AND SIO2
       IF N = 10 THEN CS(10, 1) = Q * W3 / W1: CS(10, 2) = Q * W4 / W1: GOTO 60  'FE2O3 AND SIO2
       IF N = 11 THEN CS(11, 1) = Q * W3 / W1: CS(11, 2) = Q * W4 / W1: GOTO 60  'FE2O3 AND SIO2
       IF N = 12 THEN CS(N, 3) = Q * W3 / W1: CS(N, 2) = Q * W4 / W1: GOTO 60    'CAO AND SIO2
       IF N = 13 THEN CS(N, 6) = Q * W3 / W1: CS(N, 2) = Q * W4 / W1: GOTO 60    ' TIO2 AND SIO2
       IF N = 14 THEN CS(N, 12) = Q * W3 / W1: CS(N, 2) = Q * W4 / W1: GOTO 60   ' V2O5 AND SIO2
       IF N = 15 THEN CS(N, 13) = Q * W3 / W1: CS(N, 2) = Q * W4 / W1: GOTO 60   ' CR2O3 AND SIO2
       IF N = 16 THEN CS(N, 4) = Q * W3 / W1: CS(N, 2) = Q * W4 / W1: GOTO 60    ' MN3O4 AND SIO2
       IF N = 17 THEN CS(N, 14) = Q * W3 / W1: CS(N, 2) = Q * W4 / W1: GOTO 60   ' COO AND SIO2
       IF N = 18 THEN CS(N, 19) = Q * W3 / W1: CS(N, 2) = Q * W4 / W1: GOTO 60   'PBO AND SIO2
       IF N = 19 THEN CS(N, 17) = Q * W3 / W1: CS(N, 2) = Q * W4 / W1: GOTO 60   ' ZNO AND SIO2
       IF N = 20 THEN CS(N, 20) = Q * W3 / W1: CS(N, 2) = Q * W4 / W1: GOTO 60   ' BAO AND SIO2
60
       IF N < 21 THEN CS(N, 22) = R(N, 22)
        SWG(N) = .01 * Q * (W3 + W4) / W1
        R(N, 22) = 375.6 * W2 / W1     ' NANO3 ADDED
        R(N, 22) = R(N, 22) + CS(N, 22)
        CS(N, 22) = R(N, 22)
NEXT N
FOR J = 1 TO 22
      CS(3, J) = STD(J) * SWG(3)
      CS(2, J) = STD(J) * SWG(2)
NEXT J
R(2, 22) = R(2, 22) + CS(2, 22)
```

```
R(3, 22) = R(3, 22) + CS(3, 22)
CS(2, 22) = R(2, 22)
CS(3, 22) = R(3, 22)
CLOSE #2
REM*****************************************************************
REM INTENSITY ENTRIES
62 OPEN LB3$ FOR INPUT AS #3
   LINE INPUT #3, DUM$
   LINE INPUT #3, DUM$
   DUM$ = INPUT$(12, #3)
   FOR I = 1 TO NME
            INPUT #3, R(0, I)    ' 0 IS FOR COUNTING TIME
66  NEXT I
DUM$ = INPUT$(12, #3)
FOR I = 1 TO NME
              INPUT #3, MON(0, I)    ' FIRST SAMPLE IS MONITOR
              MON(2, I) = MON(0, I)
 NEXT I

FOR N = 2 TO NOS
            DUM$ = INPUT$(12, #3)
IF DUM$ = "MONITOR     " THEN
            NOS = NOS - 1
        N1 = N2: N2 = N: GOSUB CORRECT
            GOTO 63
            END IF
            FOR I = 1 TO NME
                  INPUT #3, R(N, I)
                  R(N, I) = 1000 * R(N, I)
         NEXT I
63   NEXT N
GOTO 67
REM ***************************************
FOR I = 1 TO NME
      IF I = 1 THEN DRIFT(1) = .2 ELSE DRIFT(I) = 2!    ' DRIFT FOR FE SET TO <0.2%, 2.0% FOR OTHER ELEMENTS
      NEXT I
REM CORRECT FOR DRIFT

CORRECT:
FOR I = 1 TO NME
      IF I = 1 THEN CHECK(I) = .4 ELSE CHECK(I) = 3
      NEXT I
      FOR I = 1 TO NME
            MON(1, I) = MON(2, I)
            INPUT #3, MON(2, I)
            NEXT I
      FOR I = 1 TO NME
            K(I) = (MON(2, I) - MON(1, I)) / (N2 - N1)
      DRIFT(I) = ABS(100 * (MON(2, I) - MON(1, I)) / MON(1, I))   'CHECK MAGNITUDE OF DRIFT
            IF DRIFT(I) > CHECK(I) THEN
            PRINT #5, "EXCESSIVE ("; DRIFT(I); ") MONITOR DRIFT FOR "; EL(I); " AND ERRORS MAY RESULT"
                  PRINT "WARNING! EXCESSIVE ("; DRIFT(I); ") MONITOR DRIFT FOR "; EL(I); " AND ERRORS MAY RESULT"
```

```
        SLEEP 3
      END IF
    NEXT I
  FOR N = N1 + 1 TO N2 - 1
    M = M + 1
    FOR I = 1 TO NME
      R(M, I) = R(N, I) * MON(0, I) / (MON(1, I) + (N - N1) * K(I))
      IF R(0, I) = 0 THEN R(M, I) = 0
    NEXT I
  NEXT N
  RETURN
REM*****************************************************************
REM APPLY DEAD TIME CORRECTION TO ALL READINGS
67  FOR I = 1 TO NME      ' ELEMENT COUNT
    FOR N = 1 TO NOS  'SAMPLE COUNT
        IF R(N, I) = 0# GOTO 80       ' ELEMENT NOT MEASURED
        R(N, I) = R(N, I) / (1 - R(N, I) * DTIM)
80  NEXT N
  NEXT I
REM *****************************************************************
REM GET MATRIX COEFFICIENTS
OPEN "ALPHA.MAT" FOR INPUT AS #4
LINE INPUT #4, DUM$
  LINE INPUT #4, DUM$
DUM$ = INPUT$(16, #4)
INPUT #4, NCOMP
DUM$ = INPUT$(16, #4)
INPUT #4, NLINES
FOR I = 1 TO 12
    LINE INPUT #4, DUM$
NEXT I
FOR J = 1 TO NCOMP
    DUM$ = INPUT$(9, #4)
    INPUT #4, DUM
    FOR I = 1 TO NLINES
        INPUT #4, ALPHA(I, J)
    NEXT I
NEXT J
```