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

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

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

Introduction

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

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

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

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

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

1 Scope

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

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

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

2 Principle

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

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

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

3 Reagents and materials

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

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

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

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

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

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

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

3.5 Flux.

3.5.1 General

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

3.5.2 Flux A

Flux A should be prepared by fusion of a mixture of anhydrous lithium tetraborate ($Li_2B_4O_7$) and anhydrous lithium metaborate (Li_2BO_2) by the procedure specified in Annex A. Flux should be dried at 500 °C for a minimum of 4 h and stored in a desiccator.

3.5.3 Flux B

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

4 Apparatus

4.1 General

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

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

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

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

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

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

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

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

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

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

4.5 Gas-oxygen burner.

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

4.6 Desiccator.

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

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

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

4.9 Ultrasonic bath.

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

4.10 Cooling device.

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

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

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

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

5 Sampling and samples

5.1 Laboratory sample

For analysis, use a laboratory sample of minus 100 µm particle size which has been taken and prepared in accordance with ISO 3082. In the case of ores having significant contents of combined water or oxidizable compounds, use a particle size of minus 160 µm.

5.2 Preparation of test sample

5.2.1 Preparation of pre-dried test samples

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a way that it is representative of the whole contents of the container. Dry the test sample at (105 ± 2) °C, as specified in ISO 7764.

5.2.2 Ores having significant contents of combined water or oxidizable compounds

Prepare an air-equilibrated test sample in accordance with ISO 2596 with the following types of ores:

a) processed ores containing metallic iron;

b) natural or processed ores in which the sulphur content is higher than 0,2 % (m/m);

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

6 Procedure

6.1 Preparation of discs

6.1.1 General

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

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

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

6.1.2 Weighing

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

Table 1 — Masses of specimen components

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

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

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

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

6.1.3 Mixing

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

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

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

6.1.4 Fusion

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

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

6.1.5 Casting

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

a) Casting in the crucible

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

b) Casting in a separate mould

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

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

6.1.6 Calibration discs

The synthetic set for calibration comprises six fused discs: two discs containing 100 % Fe_2O_3 only and four discs containing 100 % Fe_2O_3 “spiked” with a known amount of chlorine added using the NaCl stock solution (3.3). The mass of Fe_2O_3 and volume of stock solution is set out in Table 2, where w is the standard mass of chemical compound (referred to as “sample” in Table 2) prepared as described in Clause 3.

Addition of the stock solution is best achieved by adding the prescribed aliquot of solution to the crucible containing thoroughly mixed flux and the ignited spectroscopically pure Fe_2O_3. Once the solution is added, to minimize mechanical losses due to the spitting of wet reagents for the spiked discs, bulk moisture should be removed by drying for 2 h at 100 °C. Remaining hydrated moisture (present in the flux sample mixture) can be removed by drying at 300 °C for 10 min. Prior to fusions, samples should be mixed to ensure homogeneity.

Table 2 — Synthetic standard set

Disc ID	No	Description	Sample components	
			Mass compound, g	**Volume of NaCl solution (3.3)**, ml
Fe A Fe B	2	100 % Fe_2O_3	1,00 *w* of Fe_2O_3 (3.2)	N/A
0,6 % Cl Std A 0,6 % Cl Std B	2	0,6 % Cl: 99,4 % Fe_2O_3	0,994 *w* of Fe_2O_3 (3.2)	0,5 ml of stock solution (3.3)
1,2 % Cl Std A 1,2 % Cl Std B	2	1,2 % Cl: 98,8 % Fe_2O_3	0,988 *w* of Fe_2O_3 (3.2)	1,0 ml of stock solution (3.3)

6.1.7 Test discs

One disc from each test sample should be prepared. At least one certified reference material 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 may be high in chlorine or sodium.

6.1.8 Visual inspection

Prior to storage, discs should be inspected visually, paying particular attention to the analytical surface. The discs should not contain undissolved material and should be whole and free from crystallization, cracks and bubbles. Defective discs should be re-fused in the crucible or discarded and substitute discs prepared. The analytical surfaces of glass discs are never to be touched by hand.

6.1.9 Disc storage

As soon as possible, discs should be placed in individual polythene bags and stored in a clean desiccator so that adsorption of moisture and the possibility of contamination are minimized. To avoid contamination of the analytical surface, the specimen should be handled by its edges and the surface should not be touched by hand or treated in any way. Specifically, it should not be washed with water or other solvents, ground or polished.

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

6.1.10 Cleaning of platinum ware

Although the crucible and mould are fabricated from an alloy that is not wetted by the glass, some glass residue may adhere to the crucible and therefore they should be cleaned between each fusion. Immersion in hot citric or acetic acid (approximately 2 M) for about 1 h is usually sufficient, but the crucibles 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, which is placed in a small ultrasonic bath for about 1 min or until all residual glass is removed, rinsed in distilled water and dried 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 poured from the crucible. If a droplet adheres to the crucible, this can easily be flaked off when the crucible is cold.

6.2 Measurements

6.2.1 General

The analytical lines to be used and suggested conditions of measurement are given in Table 3. Other instrument parameters (collimators and detectors) should be selected according to the particular equipment.

Table 3 — Suggested analytical lines, crystals and operating conditions

Element	Line (see 6.2.2)	Voltage, Kv[a] (see 6.2.3)	Crystal[b] (see 6.2.4)	Specific line overlaps
Cl	Kα	20 to 40	Pentaerythritol (PE) or germanium (Ge)	Rh Lα

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

[b] The first crystal listed is preferred; PE is preferred over Ge.

6.2.2 Analytical lines

Line and background positions are measured.

6.2.3 XRF generator settings

The voltage (kV) is not critical and normally with a simultaneous instrument will be set in the range 20 kV to 40 kV. When using a sequential instrument, it may be advantageous to use a low kV (20 kV to 30 kV). If tube operating conditions are changed during analysis, this may result in slight instability in the spectrometer output.

Use the maximum current, mA, permissible at the chosen kV.

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 should be made under vacuum, using a proportional counter as detector, and using specimen rotation if available. A chromium, chromium/gold, scandium, scandium/molybdenum, scandium/tungsten, or rhodium target X-ray tube should be used. It is recommended that pulse height selection be used, particularly in the case where low concentrations are being determined.

6.2.4 Crystals

The crystals listed in Table 3 are those regarded as preferred for the measurement, particularly for sequential-type instruments. Other crystals could, however, be used if these are appropriate for the wavelength being measured. PE is preferred over Ge.

6.2.5 Counting times

After assembly of measurement conditions for chlorine, and prior to analysing samples, the required counting times should be determined as follows.

The sensitivity, m, as counts per second per % (c/s/%), is given by Formula (1):

$$m = \frac{I_s - I_b}{C_s} \tag{1}$$

where

I_s is the intensity, in counts per second (c/s), from the calibration standard (this is measured for 10 s);

I_b is the intensity, in counts per second (c/s), from the blank samples Fe A and Fe B (this is measured for 4 s);

C_s is the concentration of element in calibration standards, given in Table 2.

Calculate m using the data from all standards and, provided that the results agree, the average should be taken.

The required counting time, T, in seconds, is then given by Formula (2):

$$T = \frac{I_b}{m^2 \times S^2} \tag{2}$$

where S is the required standard deviation, in percentage, at low concentrations = 0,001.

6.2.6 Collimators

A collimator spacing of approximately 300 µm is recommended.

6.2.7 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 3.

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 background equivalent concentration (BEC) not exceeding 0,1 %, they may be used.

6.2.8 Sample holders

Sample holders for disc presentation should be matched in accordance with the reproducibility test specified in AS 2563.

6.2.9 Subsequent determinations

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

An entire set of blank and calibration discs should be prepared after 4 weeks or when a new batch of flux is used.

7 Calculation of results

7.1 General

Intensity measurements are performed on the Cl Kα peak position and two backgrounds positions (at ±0,5 degrees of the peak position). Calibration is established using the six discs defined in Table 2. The two blank Fe_2O_3 discs are used to correct for background and the mean value of the four Cl discs is used for calibration.

7.2 Correction for background

The mean background intensity, $\bar{I}_B$, for every sample is measured by averaging the count rates (kcps) at the background positions of ±0,5 degrees of the peak line position:

$$\bar{I}_{B,s} = \frac{I_{B1,s} + I_{B2,s}}{2} \tag{3}$$

where

s is the sample;

$I_{B1,s}$ and $I_{B2,s}$ are the background intensities at 0,5 degrees either side of the peak line position.

For each of the two Fe_2O_3 blanks, a line to background ratio (*L/B*) is established using the mean background of each blank. For example, for disc Fe A:

$$(L/B)_{\text{Fe A}} = \frac{I_{\text{Cl, Fe A}}}{\bar{I}_{\text{B, Fe A}}} \tag{4}$$

where $I_{\text{Cl, Fe A}}$ is the chlorine intensity (kcps) at the Cl line position for disc Fe A.

If the agreement between the line position intensities for the Fe_2O_3 blanks exceeds three standard deviations of counting error, then the one with the high reading should not be used for further calculation as it is indicative of contamination. In this case, just one value of *L/B* is used.

If the two Fe_2O_3 blanks show good agreement, the *L/B* ratios should be averaged.

For each subsequent disc measured (the Cl blanks and the test samples), the mean background intensity $\bar{I}_B$ should be multiplied by the ratio (*L/B*) derived from the Fe_2O_3 blanks to give the corrected background intensity (CORR-I_B):

$$\text{CORR-}I_B = \bar{I}_{B,s} \times (L/B) \tag{5}$$

This is subtracted from the gross chlorine line intensity to give the net chlorine line intensity, I_{Net}:

$$I_{\text{Net s}} = I_{\text{Cl,s}} - \text{CORR-}I_{\text{B,s}} \tag{6}$$

7.3 Calibration

Calibration is based on the net line intensity divided by the mass of Cl added. For the 1,2 % Cl blanks, a 1 ml solution containing 0,013 2 g NaCl is added. This is equivalent to 0,008 007 g Cl. Therefore, for the 1,2 % Cl samples, calibration is based on the net line intensity of the 1,2 % calibration standard divided by 0,008 007, as follows:

$$\text{CALIB}_{1,2} = \frac{I_{\text{Net }1,2}}{0{,}008\,007} \tag{7}$$

where

$\text{CALIB}_{1,2}$ is the calibration factor for the 1,2 % Cl calibration standard;

$I_{\text{Net }1,2}$ is the net line intensity of the 1,2 % Cl calibration standard.

For the 0,6 % Cl samples, calibration is based on the net line intensity of the 0,6 % calibration standard divided by 0,004 004:

$$\text{CALIB}_{0,6} = \frac{I_{\text{Net } 0,6}}{0{,}004\,004} \qquad (8)$$

where

$\text{CALIB}_{0,6}$ is the calibration factor for the 0,6 % Cl calibration standard;

$I_{\text{Net } 0,6}$ is the net line intensity of the 0,6 % Cl calibration standard.

The calibration values of the four Cl discs are averaged to give an overall calibration factor (*CALIB*). Then, the Cl concentration in subsequent test samples (*X*, in %) is determined by:

$$X = \frac{I_{\text{Net,s}}}{\text{CALIB}} \times 100 \Big/ mass \qquad (9)$$

where mass is the weight of the sample, in grams.

8 General treatment of results

8.1 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 should, therefore, be checked for acceptability.

BECs should not exceed 0,1 %. If the BEC is too high, it indicates contamination of the flux or an instrument operating well below optimum. In such cases, the cause should be determined and rectified.

8.2 Repeatability and permissible tolerances

The precision of this analytical method is expressed by the following regression formulae:

$$R_d = 0{,}003\,28 + 0{,}086\,57\,X \qquad (10)$$

$$P = 0{,}004\,10 + 0{,}079\,57\,X \qquad (11)$$

$$\sigma_d = 0{,}001\,16 + 0{,}030\,59\,X \qquad (12)$$

$$\sigma_L = 0{,}001\,23 + 0{,}034\,74\,X \qquad (13)$$

$$\sigma_R = 0{,}001\,52 + 0{,}045\,54\,X \qquad (14)$$

where

X is the chlorine content of the sample;

R_d is the independent duplicate limit;

P is the permissible tolerance between laboratories;

σ_d is the independent duplicate standard deviation;

σ_L is the between-laboratories standard deviation;

σ_R is the reproducibility standard deviation.

8.3 Determination of analytical result

8.3.1 Mean of duplicates

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

8.3.2 Between-laboratories precision

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 described in Clause 6.

Compute the following quantity:

$$\mu_{12} = \frac{\mu_1 + \mu_2}{2} \qquad (15)$$

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 in Formula (11) and calculate P.

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

8.4 Check for trueness

The trueness of the analytical method should be checked by applying it to a certified reference material (CRM) or a reference material (RM) (see 6.1.7). Calculate the analytical result (μ) for the CRM/RM using the procedures in Clause 7 and compare it with the reference or certified value A_c. There are two possibilities:

a) $|\mu_c - A_C| \leq C$ in which case the difference between the reported result and the 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.

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

C should be calculated as follows:

$$C = 2\sqrt{\sigma_L^2 + \frac{\sigma_d^2}{n} + \frac{s_c^2}{N_c}} \tag{16}$$

where

s_c is the standard deviation of laboratory means (each value for calculating the standard deviation is the average value in each certifying laboratory) of the CRM/RM;

N_c is the number of certifying laboratories;

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

A CRM certified by only one laboratory should be avoided.

8.5 Calculation of final result

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.

8.6 Oxide factor

Chlorine should be reported as total chlorine.

9 Test report

The test report should include the following information:

a) the name and address of the testing laboratory;

b) the date of issue of the test report;

c) a reference to this Technical Report, i.e. ISO/TR 16043;

d) the details necessary for the identification of the sample;

e) the result of the analysis;

f) the reference number of the result;

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

Annex A
(informative)

Preparation of flux A

A.1 General

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

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

Table A.1 — Reagent masses for flux A

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

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

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

b) Fuse at 1 100 °C. Swirl when molten.

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

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

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

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

If a graphite crucible was used, the glass surface 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. Overnight usually is sufficient.

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

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