
**Preparation of silicon carbide and
similar materials for analysis by ISO
12677 X-ray fluorescence (XRF) —
Fused cast-bead method**

*Préparation du carbure de silicium et de matériaux similaires en vue
d'une analyse par fluorescence de rayons X (FRX) selon l'ISO 12677 —
Méthode de la perle fondue*

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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.

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Preparation of silicon carbide and similar materials for analysis by ISO 12677 X-ray fluorescence (XRF) — Fused cast-bead method

1 Scope

This document specifies requirements for the preparation of fused beads for the chemical analysis of silicon carbide containing samples using X-ray fluorescence (XRF). The test methods described in this document are for silicon carbide and silicon carbide materials; however, the principles described can be applied to other reduced materials such as boron carbide, boron nitride, ferroalloys, sialons and silicon nitride using the modifications given in [Annex A](#).

Fused cast beads of the samples prepared in accordance with this document are analysed in accordance with ISO 12677.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 12677:2011, *Chemical analysis of refractory products by X-ray fluorescence (XRF) — Fused cast-bead method*

ISO 21068-1, *Chemical analysis of silicon-carbide-containing raw materials and refractory products — Part 1: General information and sample preparation*

ISO 21068-2, *Chemical analysis of silicon-carbide-containing raw materials and refractory products — Part 2: Determination of loss on ignition, total carbon, free carbon and silicon carbide, total and free silica and total and free silicon*

ISO 8656-1, *Refractory products — Sampling of raw materials and unshaped products — Part 1: Sampling scheme*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

4 General considerations

Silicon carbides and non-oxide materials in general pose special problems in preparation and analysis.

These materials act exothermically on fusion and can easily react with the platinum alloy fusion dishes that are used to contain the reaction. In order to prevent this occurring, either some way of keeping the reaction from the dishes (using two fluxes, one to produce a protective layer and the other to react with the sample) or a different type of flux altogether is required. Sometimes a catalyst such as V₂O₅ might

be required in order to speed up the reaction. This can either be added to the flux or, in order to fit on to calibrations set up under ISO 12677, be substituted for part of the sample.

If the V_2O_5 is substituted for part of the sample in an existing calibration, additional calibration standards are required to extend the V_2O_5 calibration and to establish more accurate line interference corrections and α -corrections of V_2O_5 on other components.

Since silicon carbide samples oxidize and so gain mass on fusion, steps shall be taken to modify the amount of sample used in order to maintain the flux/reacted sample that is given for that flux chosen from ISO 12677. Otherwise mass absorption corrections are not valid.

As there is no analytical total to cross check the validity of the analysis, samples shall be prepared in duplicate at least. This may be done sequentially as the information gained in the first fusion can be used to modify the mass of sample used in the second fusion. If the results for the two fusions do not match, a further sample shall be prepared.

The samples may contain a range of non-oxide materials, so an XRD analysis (EN 12698-1 and EN 12698-2) is advisable and the data used in conjunction with the XRF analysis. Alternatively, methods in ISO 21068-2 and ISO 21068-3 can be applied.

Loss on ignition (LOI) is a complex process for these materials as it is usually very difficult to be certain of the chemical reactions taking place. It is possible that part of the sample might be oxidized during the ignition, causing difficulties in interpreting the results. The use of thermogravimetric analysis (TGA) or programmable furnaces might be required if the sample is new to the laboratory and no routine procedure has been set up.

As a different flux or split fluxes are used compared to ISO 12677, it is critical to make up blank samples to check for differences in impurities in the flux and also to check sensitivities (calibration slopes) for major constituents (usually SiO_2 and/or Al_2O_3) for the modified system.

The fusion procedure is designed to both oxidize and fuse the sample and produce a bead that can be analysed in accordance with ISO 12677.

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5 Choice of preparation procedures

Three different fusion procedures are given in [10.1](#), [10.2](#) and [10.3](#), each with its own advantages and disadvantages.

Method 1 (see [10.1](#)) has the advantage of speed. However, its disadvantage would be the loss of reproducibility due to high dilutions and a greater mass absorption of the flux. Also it is not possible to determine Na or K because of their presence in the oxidizing agents and Al because of partial overlap of Al $K\alpha$ by Br $L\alpha$ from the Br in the LiBr releasing agent. Another problem is that the matrix varies with silicon carbide (SiC) content, so alpha corrections can be variable.

Method 2 (see [10.2](#)) has the advantage of a high sample-to-flux ratio and a low mass absorption of the flux, and the only elements in the flux are Li, B and O. Its disadvantage is that it can be quite slow for samples with high SiC content, although this is less of a problem for other materials like sialon. The speed of fusion can be accelerated by adding V_2O_5 to the flux, but this means that the dilution and mass absorption of the flux is increased. Clearly, V_2O_5 cannot then be analysed. V_2O_5 is known to affect the hot strength of silicon carbides.

Method 3 (see [10.3](#)) has many of the advantages of Method 2. It has the disadvantages of higher dilution and can take up to 30 h, although this can be conducted in the absence of an operator. Additional cost of the oxygen to aid the process is minimal.

6 Reagents

The reagents shall be in accordance with ISO 12677 together with the following:

6.1 Lithium tetraborate (Li₂B₄O₇) flux grade (see ISO 12677:2011, 8.1). This requires an LOI to be determined to allow for loss during the fusion process. This gives a factor to correct the mass of un-ignited lithium tetraborate to allow for LOI. Alternatively, the flux can be pre-ignited for at least 4 h at a temperature of 650 °C to 700 °C and then stored in a desiccator.

6.2 KNO₃, analytical grade.

6.3 NaNO₃, analytical grade.

6.4 LiBr, analytical grade.

6.5 500 g/l LiI solution, weigh 25 g of LiI into a 100 ml beaker. Add 20 ml of water to dissolve it, and then transfer it to a 50 ml volumetric flask to dilute to the mark with water. The solution is stored in plastic bottles.

6.6 Li₂CO₃, flux grade. Either dried at 220 °C or carry out a loss on drying to apply a correction factor.

6.7 V₂O₅, 99,5 % minimum.

6.8 Oxygen (O₂), 99,99 % or 99,5 %.

7 Apparatus iTeh STANDARD PREVIEW

The apparatus shall be in accordance with ISO 12677 together with the following:

7.1 Laboratory furnace, for pre-oxidizing samples, capable of holding a temperature of (950 ± 50) °C.

7.2 Fusion unit or laboratory furnace, capable of the formation of borate-based beads with high homogeneity.

NOTE Several fusion units are commercially available.

7.3 Ceramic crucible, alumina or porcelain.

8 Sample

Sampling shall be carried out in accordance with ISO 8656-1. Grinding shall be according to ISO 21068-1.

9 Loss on ignition (and/or drying)

9.1 Loss on drying (LOD)

Loss on drying shall be conducted in accordance with ISO 12677 at (110 ± 5) °C.

9.2 Loss on ignition (LOI)

The objective of LOI is to combust any carbon without decomposing the silicon carbide. However, different silicon carbides react differently. Increasing temperatures for LOI can be applied until the sample gains, rather than loses, mass. The LOI at the temperature before this gain occurs can then be reported as the LOI.

DTA-TGA may be used to determine the best LOI temperature for an individual sample.

In the absence of any other data about the sample, the LOI temperature shall be in accordance with ISO 21068-2 (850 ± 25) °C.

As silicon carbide gains mass on ignition, this may be reported as a gain on ignition (GOI), as opposed to a LOI which would be a negative number.

10 Preparation procedures

10.1 Method 1 — Oxidation with alkali nitrate followed by fusion

10.1.1 Principle

The ground and homogenized sample is pre-oxidized then dissolved in $\text{Li}_2\text{B}_4\text{O}_7$ (6.1) in a liquid state at high temperature. Fusion temperature can be achieved using a laboratory furnace or a fusion device (7.2).

During dissolution, assess the homogenization of the sample flux mix by closely observing the reaction in the platinum crucible (ISO 12677:2011, 5.1).

NOTE To avoid destructive corrosion on the platinum dishes, sample pre-treatment might be necessary for materials containing other forms of carbides and metallic components.

10.1.2 Method

Ignite the platinum alloy fusion dish over a gas burner for at least 10 min and cool in a desiccator. For the oxidation procedure, mix 1,5 g KNO_3 (6.2), 1,0 g NaNO_3 (6.3), 1,5 g $\text{Li}_2\text{B}_4\text{O}_7$ (6.1) and a spatula tip of LiBr (6.4) and homogenize with 300 mg finely ground sample in a platinum crucible. Keep the sample at (500 ± 25) °C in the furnace for at least 30 min. Ensure the sample is fully oxidized before the $\text{Li}_2\text{B}_4\text{O}_7$ melts. Raise the temperature to (800 ± 25) °C and add a further 4,5 g $\text{Li}_2\text{B}_4\text{O}_7$ (6.1). Fuse the entire sample at a temperature between 950 °C and 1 150 °C. Cast the melt according to ISO 12677. Analyse in accordance with ISO 12677.

10.2 Method 2 — Oxidation on bed of fused lithium tetraborate, followed by fusion

10.2.1 Principle

The sample is oxidized in a melt of lithium carbonate (melting point 732 °C) while an unmelted layer of lithium tetraborate (melting point 917 °C) protects the platinum crucible. Once the sample has fully oxidized, the temperature of the fusion process is increased to fully melt the lining flux to form a homogenous bead.

In the following process description it is assumed that a 35 mm diameter bead is to be used. For different sized moulds, masses used shall be scaled accordingly. When dealing with a sample of unknown purity, it is necessary to first make an estimate of the purity in terms of mineral composition and prepare a melt by weighing sufficient sample to yield approximately 1,5 g of oxidized sample in the melt. The melt shall be cooled and weighed, re-melted, cast and analysed. From the mass and the results an accurate estimate can be made of the analysis to allow a further bead(s) to be made using the correct mass of sample to produce 1,5 g of oxidized sample in the final melt.

The analyses of reduced materials shall be carried out in duplicate. Apart from the other problems, it might be difficult to ensure that all the iron has been converted to, or retained in, the ferric state and not reduced and then alloyed with the platinum. A second advantage of the use of two beads is that checks are available for all the other figures. Unless the composition of the material is known with some accuracy, it is usually best to prepare a single bead first and only prepare the duplicate when the correct mass of the sample is known.

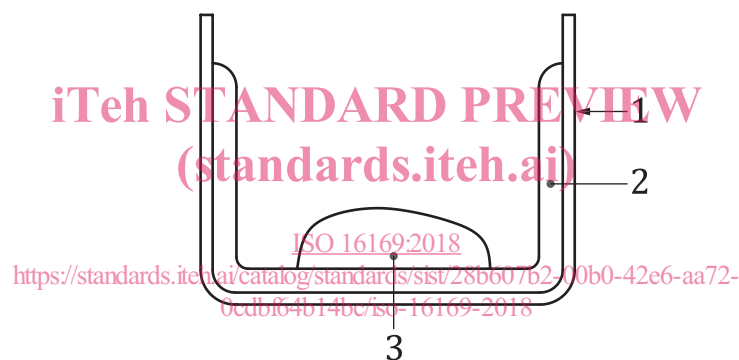
10.2.2 Method

The method is based on producing 1,5 g of sample after oxidation in 7,5 g of a flux equivalent to one part lithium tetraborate to four parts lithium metaborate, after the lithium tetraborate has reacted with the lithium carbonate and so producing a 9 g bead of approximately 35 mm diameter.

Ignite the platinum alloy fusion dish over a gas burner and cool it in a dessicator. After cooling, weigh 6,6 g of lithium tetraborate (6.1), which has been corrected for its LOI factor, into the platinum alloy fusion dish. Transfer the dish to a burner and melt the lithium tetraborate. Swirl the melt so as to run over the sides and base of the dish and then allow it to cool, forming a protective coating on the inner surface of the dish. Cool the dish to room temperature.

Weigh 1,000 g of the dried, ground sample (see Clause 8 and 9.1) on to the centre of the lithium tetraborate layer of the dish. For samples of less than 100 % silicon carbide or containing other reduced species, sufficient material is used to produce 1,500 g after oxidation (9.2). Then, on top of the sample, weigh 2,228 g of lithium carbonate (6.6) (either dried at 220 °C or corrected for its drying loss at 220 °C). The lithium carbonate and sample are intimately together and then compacted by gently pressing, ensuring none of the mixture is in contact with the unprotected part of the dish (Figure 1). If any sample remains in contact with the platinum ware, its surface will be attacked.

NOTE If V_2O_5 (6.7) is added to increase the speed of reaction, this is done together with the sample and lithium carbonate prior to the mixing stage.



Key

- 1 Pt/Au
- 2 $Li_2B_4O_7$
- 3 sample + Li_2CO_3

Figure 1 — Arrangement of lithium carbonate and sample in the fusion dish



Figure 2 — Appearance of mixture prior to sintering (left) and after successful sintering (right)

Heat the dish over a small gas burner. Start with a low flame and gradually increase the temperature until the lithium carbonate begins to react with the sample, while allowing the lithium tetraborate layer to remain solid. The reaction is very exothermic so care should be taken, particularly with samples with silicon metal present. When the reaction appears to be complete (this can take up to several hours for silicon carbide), raise the temperature of the burner to full heat and maintain for some time. Place a lid partially on the dish and transfer it to a position over a large burner, increasing the temperature slowly to the maximum heat. When the sample has fully reacted, the melt will have changed from black to an off-white colour (Figure 2). At this point, transfer the dish, lid and melt to a furnace at $(1\ 200 \pm 25)$ °C for $(5 \pm 0,5)$ min. Then transfer the dish and contents to a desiccator. When cool, weigh the dish and melt to obtain the final mass of the melt. Cast the melt in accordance with ISO 12677.

Analyse the bead in accordance with ISO 12677, using the normal calibration and the analytical data obtained to calculate the optimum mass to be used for the second bead to ensure an apparent analytical total of 100 % and a bead mass of approximately 9 g.

Analyse the second bead along with the first bead. If the analyses differ significantly, according to ISO 12677:2011, Annex G, prepare a further bead.

In calculating the final results, first correct the analysis for any slope or background factors obtained by fusing duplicate samples of pure SiO₂ and pure Al₂O₃ fused in the same manner, but using 1,5 g of ignited sample or a mass corrected for their 1 200 °C LOI. Then calculate the analyses of the oxidized sample by applying the following correction to the results:

$$\% \text{ corrected} = \% \text{ after blank and slope correction} \times (m_{\text{melt}} / 9) \times (1,5/m_{\text{sample}})$$

where

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m_{melt} is the mass in g of the melt after fusion;

m_{sample} is the mass in g of the sample taken.

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The results shall then be corrected for tungsten carbide (WC) content from contamination by grinding media and LOI as in ISO 12677:2011, Annex B.

A good approximation of SiC content (M_{SiC}) can be obtained by the following formula:

$$M_{\text{SiC}} = 1,993\ 9 \times (\text{analytical total} - 100 \%)$$

The actual silica (SiO₂) content (M_{SiO_2}) of the sample can then be calculated as:

$$M_{\text{SiO}_2} = M_{\text{SiO}_2 \text{ TOTAL}} - 1,501\ 5 \times M_{\text{SiC}}$$

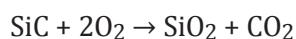
where

$M_{\text{SiO}_2 \text{ TOTAL}}$ is the total silica content.

10.3 Method 3 — Oxidation on bed of lithium tetraborate at 840 °C in oxygen, followed by fusion

10.3.1 Principle

To avoid the silicon carbide attacking the platinum fusion dish as the fused beads are made, the following oxidization is performed by calcination prior to fusion.



This method uses air or O₂ instead of reagents to create the oxidation condition.

The sample powder and flux shall be kept in a platinum fusion dish at 840 °C under air or O₂ (6.8) flow, and then fused at 1 150 °C when the calcination is completed. 840 °C is below the fusing temperature but above the reaction temperature of releasing CO₂. The mass change from SiC (40,10 g) to SiO₂ (60,09 g) in the dish causes a change in the sample flux ratio as compared with the ratio of standard beads for the calibration curves, matrix correction coefficients and line overlap corrections. The correction procedures take account of the change of sample-to-flux ratio cause by oxidation (GOI) and volatilization, see [Annex C](#).

NOTE The procedure was devised with a study of the phase diagram in Reference [9]. The Li₂B₄O₇-SiO₂ tie line shows the liquidus temperature 828 °C, but the fusion temperature of Li₂B₄O₇ occurs at 850 °C, so 840 °C was selected as the optimum temperature for oxidation.

10.3.2 Method

10.3.2.1 Weighing of the sample and flux

Ignite 1 g of sample to approximately 850 °C in a ceramic crucible (7.3) in accordance with ISO 21068-1 and allow to cool. Weigh 1 g of lithium tetraborate flux (6.1) to the nearest 0,1 mg and transfer it to the pre-ignited platinum fusion dish for making glass bead (Figure 3). Flatten it in order to protect the surface of the fusion dish. Weigh 0,3 g of sample to the nearest 0,1 mg of the residue after ignition at approximately 850 °C. Mix 2 g of lithium tetraborate flux to the nearest 0,1 mg into the sample and transfer it onto the flux already in the dish.



Figure 3 — Sample in crucible prior to ignition

10.3.2.2 Calcination

Heat the mixed sample and flux in the platinum fusion dish for preparing fused cast beads at approximately (840 ± 5) °C in an electric furnace under air or O₂ flow (see Figure 4). The temperature, which is above the CO₂ degassing temperature and below the fusing temperature, promotes the oxidation process. When the sample colour changes to between grey (see Figure 5) and perfectly white (see Figure 6), the oxidation is complete.

NOTE 1 Even high silicon carbide bearing CRM, JRRM 1001 (SiC 99,58 mass %, reference value) in ISO 21068-2:2008, B.1, can be oxidized within 30 h.

NOTE 2 Running oxygen or air at 100 ml/min is effective at fully oxidising the sample under these conditions.