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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

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This document was prepared by Technical Committee ISO/TC 33, *Refractories*.

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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 V_2O_5 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.

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 Kα by Br Lα 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 ($Li_2B_4O_7$) 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 KNO_3, analytical grade.

6.3 $NaNO_3$, 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 Li_2CO_3, flux grade. Either dried at 220 °C or carry out a loss on drying to apply a correction factor.

6.7 V_2O_5, 99,5 % minimum.

6.8 Oxygen (O_2), 99,99 % or 99,5 %.

7 Apparatus

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 $Li_2B_4O_7$ (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 $Li_2B_4O_7$ (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 $Li_2B_4O_7$ melts. Raise the temperature to (800 ± 25) °C and add a further 4,5 g $Li_2B_4O_7$ (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.

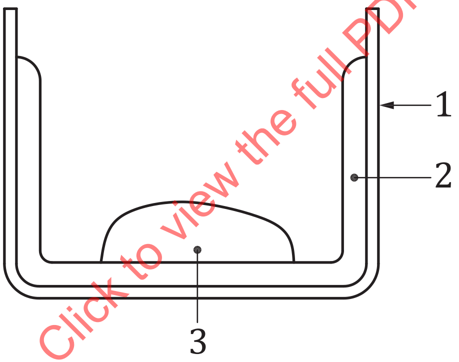
10.2.2 Method

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 ± 25) °C for (5 ± 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 SiO_2 and pure Al_2O_3 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

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

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

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

$$M_{SiO_2} = M_{SiO_2\ \text{TOTAL}} - 1{,}501\,5 \times M_{\text{SiC}}$$

where

$M_{SiO_2\ \text{TOTAL}}$ 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.

$$SiC + 2O_2 \rightarrow SiO_2 + CO_2$$

This method uses air or O_2 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 O_2 (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 CO_2. The mass change from SiC (40,10 g) to SiO_2 (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 $Li_2B_4O_7$-SiO_2 tie line shows the liquidus temperature 828 °C, but the fusion temperature of $Li_2B_4O_7$ 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 O_2 flow (see Figure 4). The temperature, which is above the CO_2 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.

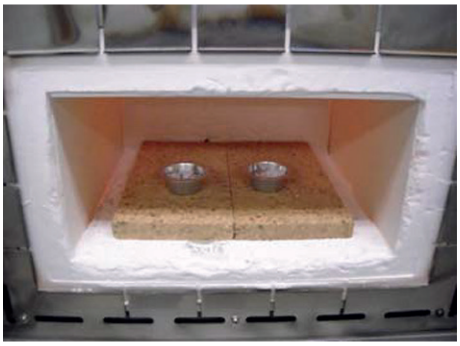


Figure 4 — Samples in place in furnace prior to fusion

Figure 5 — Sample after oxidation showing grey colouration

Figure 6 — Sample after oxidation showing white colouration

10.3.2.3 Sample fusion

After the calcination, increase the temperature to (1 150 ± 25) °C. When the electric furnace reaches 1 150 °C, remove the dish from the furnace and swirl it for 30 s in order to homogenize the melt and release bubbles, then allow it to cool. Add 100 µl of 500 g/l LiI (6.5) to the fused sample and return it to the 1 150 °C electric furnace again for 3 min. Swirl the dish well for 30 s and return it to the furnace for a further 2 min. Swirl the dish well for 30 s and return it to the furnace for a further 2 min. Swirl the dish again and allow it to cool.

The swirling and fusing times should be kept consistent to reduce the degree of vaporization of the flux.

10.3.2.4 Removal of fused cast beads

After cooling, remove the fused cast beads (see Figure 7). The bottom surface is the analysis surface.

Figure 7 — Fused bead after completion of fusion process

10.3.3 Calibration

10.3.3.1 Preparing beads for calibration curve

Weigh precisely flux (3,000 0 g) and reference material (0,300 0 g) and make the glass beads in accordance with 10.3.2.3. For reference materials containing silicon carbide, use between 0,300 0 g and 0,450 0 g of the sample. Suitable reference materials are presented in Annex B.

10.3.3.2 Calibration curves

Carry out the calibration in accordance with ISO 12677. If the analytical tolerance is not achieved, then the application of a dilution correction is acceptable (see Annex C).

NOTE In order to discriminate between SiO_2 and SiC the latter could be measured quantitatively in accordance with ISO 21068-1.

11 Completion of the analysis

The analysis shall be completed in accordance with ISO 12677:2011, Clauses 10 to 15, with reference to ISO 12677:2011, Annexes A to I.

12 Reporting of results

Reporting of results shall be in accordance with ISO 12677:2011, Clause 15, with the inclusion of silicon carbide and free silica by calculation in accordance with ISO 21068-2 and ISO 21068-3, if required.

13 Reproducibility and repeatability of analysis

Results of round robin analysis for methods 2 and 3 are reproduced in D.2 and D.1, respectively.

Annex A
(informative)

Modification of the method for reduced material types other than silicon carbide

Table A.1 gives details of the fusion techniques to be used for reduced materials other than silicon carbide for analysis using method 2 (10.2). Similar adjustments may be made and applied to method 3 (10.3). All of these are sintered with 2,228 g of dried lithium carbonate on a protective layer of 6,6 g of fused lithium tetraborate as described in 10.2. Masses used are adjusted to give 1,5 g of material after oxidation. The masses are calculated for pure materials, so increased masses are required for less pure samples. The analyses should then match the calibrations set up for fusing 1,5 g of ignited sample with 7,5 g of a mixed flux comprising one part lithium tetraborate to four parts lithium metaborate.

Table A.1 — Fusion techniques for other materials

Material	Formula	Sample mass (g)	Comments on fusion	Analyse as
Silicon carbide	SiC	1,001	Of all these materials, this is the slowest and most difficult to oxidize in the sintering process	Silica
Boron carbide	B_4C_3	0,854	Slow to sinter	Boric oxide[a]
Boron nitride	BN	1,069	Sinters reasonably easily	Boric oxide[a]
Silicon	Si	0,701	Reactive during sintering, care should be taken to avoid the reaction breaking through the protective layer	Silica
Silicon nitride	Si_3N_4	1,167	Sinters reasonably easily	Silica
Ferrosilicon	FeSi	0,900	The reaction proceeds very quickly if a second burner is applied to the top of the Li_2CO_3 mixture during sintering	Iron silicate
Ferrosilicon	$FeSi_2$	0,840	See FeSi	Iron silicate
Aluminium	Al	0,794	Reaction is very vigorous and great care should be taken to avoid reaction with the fusion dish	Alumina
Aluminium nitride	AlN	1,206	Sinters reasonably easily	Alumina
Sialon	[b]	[b]	Sinters reasonably easily	Alumino silicate

[a] In setting up calibrations for samples containing B2O3, it is critical to make up calibration standards to determine background effects and α-corrections of B2O3 on other constituents.

[b] Sialon has the formula: Si2-zAlzN2-zO1+z (z can be 0,04 to 0,4). The z factor needs to be determined using the method in EN 12698-2[2], before the correct fusion mass can be calculated.

Annex B
(informative)

Suitable certified reference materials

B.1 General

Examples of certified reference materials for methods 1, 2 and 3 are as follows.

ECRM 781-1	Silicon Carbide Refractory
BCS-CRM 359	Nitrogen Bearing Silicon Carbide
BCS-CRM 360	Sialon Bonded Silicon Carbide
JRRM 1001	SiC 100 (ISO 21068-2:2008, Annex A)
JRRM 1002	C 5 (ISO 21068-2:2008, Annex A)
JRRM 1003	C 10 (ISO 21068-2:2008, Annex A)
JRRM 1004	C 20 (ISO 21068-2:2008, Annex A)
JRRM 1005	C 30 (ISO 21068-2:2008, Annex A)
JRRM 1006	C 50 (ISO 21068-2:2008, Annex A)
JRRM 1007	C 10 – SiC 90 (ISO 21068-2:2008, Annex A)
JRRM 1008	C 5 – SiC 30 (ISO 21068-2:2008, Annex A)
JRRM 1009	C 40 – SiC 6 (ISO 21068-2:2008, Annex A)

B.2 Specific application of Japanese reference materials

Relevant JRRM 100, 200 and 300 series. The last 10 samples exhibit a negative LOI, as shown in Table B.1.

Table B.1 — Examples of reference material masses for refractories containing silicon-carbide and alumina

Beads for calibration			Component values for calibration								
Bead no.	JRRM		Mass %								
	No.	g	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	LOI[a]
1–1	101	0,300 0	88,57	8,10	0,31	0,30	1,06	0,22	1,01	0,17	0,12
1–2	103	0,300 0	80,32	18,07	0,41	0,37	0,07	0,02	0,12	0,35	0,11
1–3	105	0,300 0	70,58	24,71	0,67	2,36	0,11	0,08	0,74	0,33	0,11
1–4	107	0,300 0	55,32	37,08	2,20	1,16	0,71	0,49	0,22	2,57	0,15
1–5	109	0,300 0	54,23	41,24	0,89	1,96	0,15	0,13	0,31	0,79	0,14
1–6	110	0,300 0	49,54	46,68	0,85	1,67	0,11	0,17	0,09	0,34	0,14
1–7	202	0,300 0	85,72	7,60	3,97	0,57	0,82	0,02	1,01	0,03	0,09
1–8	204	0,300 0	89,64	4,50	2,08	0,15	1,79	0,31	0,32	0,91	0,13
1–9	206	0,300 0	92,88	1,77	3,21	0,02	1,21	0,07	0,18	0,51	0,06
1–10	208	0,300 0	94,43	0,46	0,06	0,01	4,20	0,06	0,63	0,02	0,08
1–11	210	0,300 0	97,69	0,16	0,83	0,01	0,30	0,79	0,02	0,01	0,11
1–12	303	0,300 0	36,16	59,25	1,48	0,16	1,04	0,86	0,70	0,21	0,02
2–1	102	0,420 0	112,66	19,31	5,57	0,64	0,07	0,94	0,42	0,20	−39,86
2–2	104	0,330 0	74,08	24,77	3,57	3,24	0,29	0,08	0,33	3,35	−9,98
2–3	106	0,390 0	82,69	38,88	2,50	0,88	0,19	1,27	0,78	2,36	−29,77
2–4	108	0,360 0	66,37	48,10	1,86	1,26	0,33	0,32	0,25	0,97	−19,84
2–5	203	0,360 0	104,80	6,11	2,14	0,22	4,77	0,57	0,74	0,29	−19,86
2–6	205	0,390 0	117,52	4,02	1,62	0,42	4,04	0,12	1,21	0,65	−29,87
2–7	207	0,330 0	103,46	1,87	1,07	0,09	2,77	0,18	0,05	0,23	−9,91
2–8	209	0,450 0	144,33	1,31	0,56	0,08	2,84	0,16	0,05	0,26	−49,88
2–9	210	0,450 0	146,54	0,24	1,25	0,01	0,45	1,18	0,03	0,01	−49,84
2–10	302	0,360 0	45,24	64,72	5,40	0,72	1,05	0,84	0,68	0,80	−19,77

[a] Minus value shows a mass gain (GOI).

The values should be calculated using JRRMs in ISO 12677.

Annex C
(informative)

Dilution correction for use with Method 3

C.1 General

The dilution correction covers the change of sample flux ratio caused by GOI (oxidation) in the calcination stage in 10.3.2.2 and by the vaporization at the fusion in 10.3.2.3.

C.2 Kinds of correction

Two kinds of co-existing component effects are corrected:

1) matrix correction based on SiO_2-GOI binary system;

2) dilution correction combined with GOI (oxidation) from SiC to SiO_2 and vaporization.

C.3 Calibration curves

C.3.1 General

The following formula shows the addition of vaporization correction into the formula in ISO 12677.

$$C_i = (aI_i^2 + bI_i + c)(1 + \Sigma d_j C_j + \alpha F \Delta R) + \Sigma l_j C_j$$

where

C_i	is the corrected quantitative value, in mass %, of component i;
I_i	is the standardized X-ray intensity of component i;
d_j	is the co-existing component correction coefficient of co-existing component j;
C_j	is the content percentage, in mass %, of co-existing component j;
l_j	is the overlap correction coefficient of co-existing component j on component i;
a, b and c	are the calibration coefficients;
ΔR	is the dilution correction coefficient;
αF	is the sample/flux ratio by mass (here it is 1/10).

C.3.2 Matrix correction

An example of the theoretical matrix correction for GOI – SiO_2 binary system is shown in Table C.1.

Table C.1 — Example of correction coefficients for GOI-SiO_2 binary system

Correction components		Analysis components							
Component	**Averaged composition**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**CaO**	**MgO**	**Na_2O**	**K_2O**
SiO_2	60,00		0,001 16	0,004 52	0,004 20	0,004 00	0,001 06	0,001 00	0,003 88
Al_2O_3	10,00	0,002 99		0,003 96	0,003 73	0,003 58	0,000 96	0,009 00	0,003 50
Fe_2O_3	1,72	0,002 60	0,002 48		0,002 11	0,002 27	0,002 38	0,002 28	0,002 33
TiO_2	0,95	0,001 70	0,001 63	0,014 96		0,001 78	0,001 59	0,001 55	0,001 66
CaO	0,81	0,001 47	0,001 43	0,015 13	0,013 16		0,001 41	0,001 38	0,002 02
MgO	0,31	0,002 79	0,002 81	0,003 64	0,003 46	0,003 34		0,000 78	0,003 27
Na_2O	0,48	0,002 59	0,002 54	0,003 19	0,003 07	0,002 99	0,002 47		0,002 94
K_2O	0,73	0,001 28	0,001 27	0,014 98	0,012 80	0,011 49	0,001 24	0,001 21	
GOI	25,00								

C.3.3 Calibration of dilution correction coefficient

C.3.3.1 General

When the oxidation during the calcination in 10.3.2.2 is complete, the sample flux ratio is different from that of beads for calibration curves. A small proportion of the flux will vaporize during fusion. To determine the coefficients of GOI at oxidation and vaporization at fusing, JRRM 1001 in ISO 21068-2, SiC (99, 58 mass %) and JRRM 210 in ISO 12677, SiO2 (97, 80 mass %) are used instead of pure materials (Figure C1).

Sample	JRRM1001 SiC 99.58%		JRRM210 SiO2 97.80%	
Supposition	Unknown sample		Sample for calibration curve	
Weigh (g)	Sample 0,300 0	Flux 3,000 0	Sample 0,300 0	Flux 3,000 0

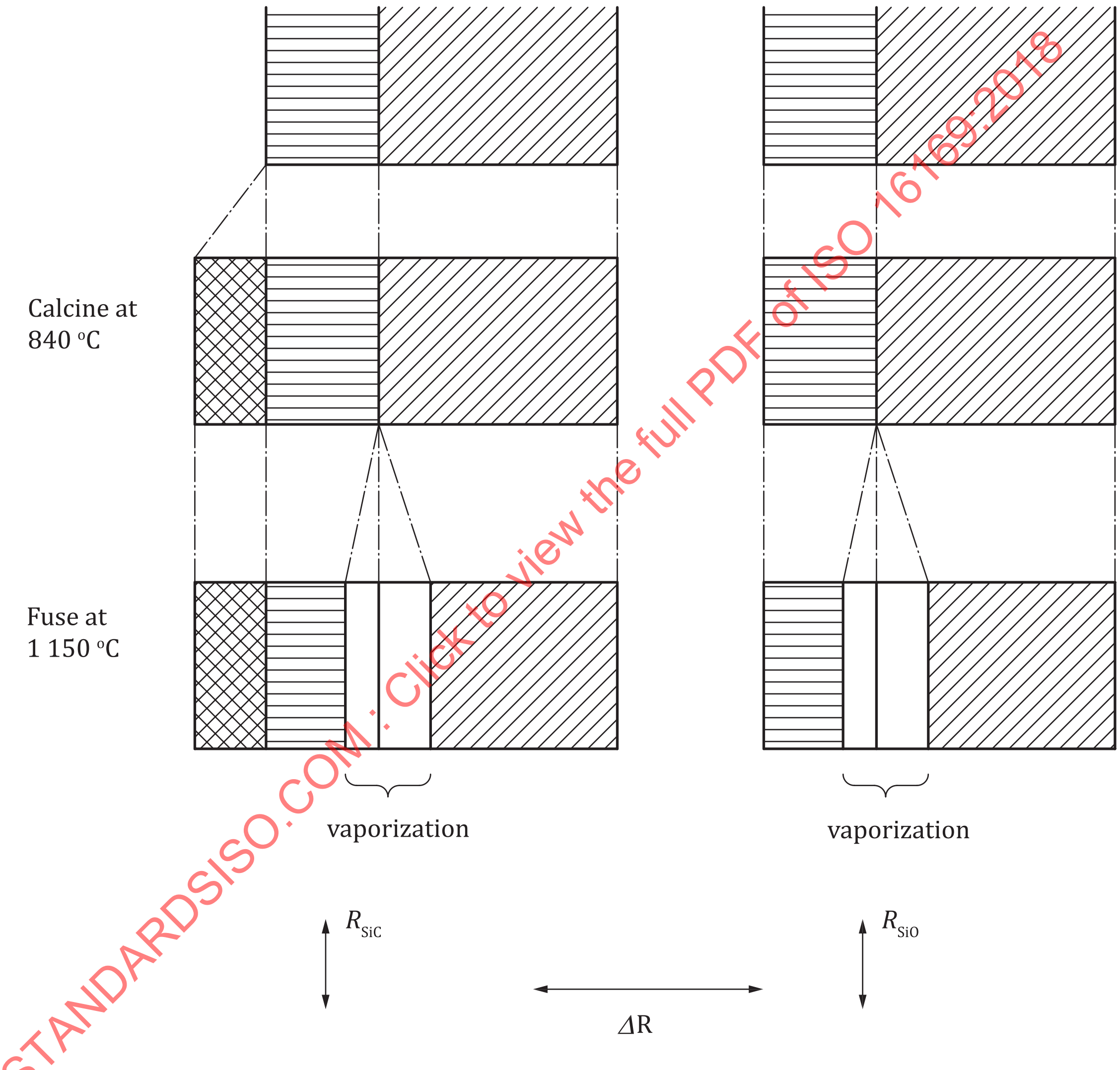


Figure C.1 — Concept of GOI and vaporization at fusing

C.3.3.2 Measurement of GOI at the oxidation for SiC in 10.3.2.3

Fuse 0,300 0 g of JRRM 1001 and 3,000 0 g of flux in accordance with 10.3.2.2 and measure the mass difference between before fusion and after fusion. Calculate the vaporization from the increase of mass as follows:

$$R_{\mathrm{SiC}} = 0{,}148\,9 - [m_2 - (m_1 + 3{,}300\,0)]$$

where

R_{SiC}	is the amount vaporized, in grams, for silicon carbide;
0,148 9	is the theoretical value of GOI when 0,300 0 g of JRRM 1001 (SiC, 99, 58 mass %) is fully oxidized;
m_1	is the mass, in grams, of Pt fusion dish;
m_2	is the total mass, in grams, of fused cast bead and Pt fusion dish.

C.3.3.3 Measurement of vaporization at fusing for SiO_2 in 10.3.2.3

Fuse 0,300 0 g of JRRM 210 and 3,000 0 g of flux in accordance with 10.3.2.3 and measure the mass difference between before fusion and after fusion. Calculate the increase of mass as follows:

$$R_{\mathrm{SiO}} = m_2 - (m_1 + 3{,}300\,0)$$

where

R_{SiO}	is the amount vaporized, in grams, for silica;
m_1	is the mass, in grams, of Pt fusion dish;
m_2	is the total mass, in grams, of fused cast bead and Pt fusion dish.

C.3.3.4 Calculation of dilution correction coefficient

Dilution correction coefficient (ΔR) is calculated as follows

$$\Delta R = (R_{\mathrm{SiC}} - R_{\mathrm{SiO}} / 3{,}300\,0)$$

where

ΔR	is the dilution correction coefficient;
R_{SiC}	is the amount vaporized, in grams, for silicon carbide;
R_{SiO}	is the amount vaporized, in grams, for silica.