Original Paper

Preparation of reference materials for frit chemical analysis

M. Fernanda Gazulla, M. Pilar Gómez, Antonio Barba and Mónica Orduña
Instituto de Tecnologiá Cerámica, Universitat Jaume I., Castellón (Spain)

A study was undertaken on how to prepare frit reference materials in which the following elements are analysed: Si, Al, Fe, Ca, Mg, N, K, Ti, Zr, Ba, Pb, Zn, Hf, P, B and Li. The following analytical techniques were used: X-ray fluorescence spectrometry (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES), atomic absorption spectrophotometry (AAS) and titrimetry. Boron and lithium were analysed by ICP-OES, sodium and lithium by AAS, and boron by titrimetry, while the remaining frit elements and sodium were analysed by XRF.

The results found by the different methods were compared and each method was validated by means of reference materials. A procedure was established for preparing frit reference materials for calibrating and validating working methods on an industrial scale.

1. Introduction

Frits are intermediate, semi-processed products used in manufacturing glazed ceramic floor and wall tiles, to which they contribute technical and aesthetic properties.

Frits are vitreous products, made industrially by mixing different crystalline raw materials (quartz, kaolin, sodium and potassium feldspars, calcium carbonates, sodium nitrates, dolomites, zinc oxides, zirconium silicates, borates, etc.), melting these mixtures at high temperatures and then quenching them. Frit quality depends, amongst other factors, on frit chemical composition and especially on compositional consistency. Control of compositional consistency is critical to ensuring product quality.

Various instrumental techniques are available for determining the chemical composition of a given material, but they all need to be calibrated beforehand. Calibration and validation require using reference materials that ensure the traceability of the resulting data [1 and 2]. In view of the absence of any reference materials resembling the frits used in the ceramic sector, a study was undertaken on the preparation of frit reference materials.

Ceramic frits usually comprise varying concentrations of the following elements: Si, Al, Fe, Ca, Mg, Na, K, Ti, Zr, Ba, Pb, Zn, Hf, P, B and Li. Hence, all these elements need to be analysed by a technically valid method to obtain a frit reference material, whether as a certified or secondary reference material [3 to 9].

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There are different ways of preparing frit reference materials:

- Certified reference materials can be prepared by interlaboratory tests.
- Secondary reference materials can be made by mixing reference materials and producing similar compositions to the samples being studied.
- Different analytical techniques or different methods can be used for each element.

The first option is perhaps the most appropriate one, but an interlaboratory analysis cannot always be conducted. Nor does it provide an immediate response to a need. When such a need arises and a reference material is unavailable, an alternative is required. The second option for preparing frit reference materials involves mixing different reference materials similar to the raw materials making up the frits, until achiving the desired composition. The third option entails using different analytical techniques for each element, such as X-ray fluorescence spectrometry (XRF) [10 and 11], inductively coupled plasma – optical emission spectrometry (ICP-OES) [12 and 13], laser inductively coupled plasma-mass spectrometry (LA-ICP-MS) [14], atomic absorption spectrophotometry (AAS) or titrimetry [15], which yield independent analytical data. The last two options were chosen in this study as preparation methods for frit reference materials. However, the possibility of preparing such reference materials by interlaboratory tests is presently also being addressed in a parallel study.

The present paper thus sets out a methodology for calibrating and validating certain working methods usually employed in frit analysis. The validation methodology adopted uses different techniques to analyse the same element (the case of lithium, sodium and boron), while using mixtures of reference materials for the other frit elements, as well as sodium, which are analysed by XRF.

2. Experimental

2.1 Analytical techniques used

In ceramic laboratories most frit elements are analysed by X-ray fluorescence spectrometry (XRF), as this is a very fast, reproducible method. In this study, measurements were performed on a Philips, Model PW 2400, XRF spectrometer. The following elements were analysed: Si, Al, Fe, Ca, Mg, Na, K, Ti, Zr, Ba, Pb, Zn, Hf and P.

When the frit contains very low concentrations of sodium and considerable quantities of zinc, overlapping can occur between the sodium and zinc lines in XRF measurements. This is difficult to correct, as sodium lines are much less intense than the L_α and L_β zinc lines. In these cases it is advisable to verify the sodium concentration by atomic absorption spectrometry (AAS). The measurements were run on a Perkin Elmer, Model 110B, spectrophotometer. Lithium was also analysed by AAS.

XRF is not an appropriate analytical technique for lithium and boron, due to their low atomic weight. These elements can be more suitably analysed by inductively coupled plasma – optical emission spectrometry (ICP-OES). The measurements were performed on a Leeman, Model DRE (Direct Reading Echelle), spectrometer (Leeman Labs, Inc., Lowell, MA (USA)).

Boron can also be analysed by titrimetric titration based on the determination of boron in the sample in the form of dissolved boric acid. Titration takes place in three steps, using a pH meter. An NaOH standard solution is added until all the HCl in the sample (stemming from sample disaggregation) is neutralized, yielding equivalence point one, V_1. Mannitol is then added to enhance the acid character of H_3BO_3 [16], a very weak acid. Finally, the boric acid is titrated with the same NaOH standard solution used in step 1, yielding equivalence point two, V_2. The volume of the NaOH ($c_{NaOH} = 1$ mol/l) solution used ($V_2 - V_1$) serves to calculated the B_2O_3 concentration in the sample.

2.2 Sample preparation in each analytical technique

Sample preparation depends on the analytical method used. The methodology used for sample preparation in each technique is set out below [11, 17 to 19]:

a) For measurement by XRF, about 400 mg sample is weighed off to ±0.1 mg in a Pt crucible, adding the flux, consisting of a blend of lithium metaborate and tetraborate in a 1 : 15 sample/flux ratio. The mixture is homogenized and some drops of a LiBr (c = 25 mg/100 ml) solution are added as a nonsticking agent. The sample is melted in a laboratory muffle kiln at 1100 °C or in a platinum crucible fusion facility (a Philips, Model Perl X3 was used in the study), yielding a fused bead.

b) For measurement by AAS, about 500 mg sample is weighed off in a Pt crucible to ±0.1 mg, adding about 5 g flux, which is usually K_2CO_3 when analysing sodium and a blend of K_2CO_3/Na_2CO_3 in lithium analysis. The mixture is melted by holding it for a set time in a laboratory muffle kiln at 1000 °C. The fused material is subsequently dissolved in 1 : 1 HCl ($c_{HCl} \approx 6$ mol/l (1+1)) filtering and gauging the solution.

c) For measurement by ICP-OES, about 200 mg sample is weighed off in a Teflon beaker to ±0.1 mg, adding a blend of acids (HNO_3, HCl and HF). The mixture is digested in a laboratory microwave kiln by an optimized heating programme, adding $AlCl_3 \cdot 6H_2O$ (c = 100 g/l) to complex the free fluorine that could interfere in the boron measurement and attack the measuring apparatus [13], followed by filtering and gauging.

d) For measurement by titrimetry, about 500 mg sample is weighed off to ±0.1 mg in a Pt crucible, adding about 5 g flux (blend of K_2CO_3 and Na_2CO_3). The mixture is melted in a laboratory muffle kiln at 950 °C. The fused material undergoes a process designed to eliminate interferences [15], followed by filtering and gauging.

2.3 Materials

The XRF [16] measurements were run using calibration curves. The calibration curve and validation standards were prepared using blends of the reference materials listed in section 6. (Tables A1 to A3). Pure materials (ZnO, BaO, Li_2CO_3, synthetic borates such as boric, zinc, barium, acid, borax pentahydrate, etc.) were used to contribute a series of elements such as: zinc, barium, boron, lithium, etc., for which reference materials are unavailable.

The AAS measurements were performed using calibration curves. The calibration curves and validation standards were prepared using the reference materials listed in section 6 (tables A4 and A5).

The ICP-OES [12] measurements were performed using calibration curves. the calibration curves and validation standards were prepared using the reference materials listed in section 6 (tables A6 and A7).

Four synthetic standards and six solutions (for measurement validation) were made by mixing the foregoing reference materials.

Table 1. Theoretical and experimental concentrations (in % (m/m)) of each element and their uncertainty for synthetic standards 1 and 2 measured by XRF

	synthetic standard 1		synthetic standard 2	
	theoretical	experimental	theoretical	experimental
SiO_2	52.6 ± 0.2	52.7 ± 0.4	59.0 ± 0.2	58.8 ± 0.4
Al_2O_3	7.10 ± 0.14	7.2 ± 0.2	6.6 ± 0.14	6.7 ± 0.2
Fe_2O_3	0.17 ± 0.01	0.16 ± 0.02	0.24 ± 0.01	0.22 ± 0.02
CaO	9.67 ± 0.05	9.60 ± 0.15	13.0 ± 0.1	13.2 ± 0.2
MgO	3.23 ± 0.05	3.29 ± 0.08	1.34 ± 0.05	1.38 ± 0.08
Na_2O	1.36 ± 0.03	1.38 ± 0.06	0.58 ± 0.03	0.54 ± 0.06
K_2O	4.41 ± 0.02	4.41 ± 0.04	2.22 ± 0.02	2.25 ± 0.04
TiO_2	0.04 ± 0.02	0.03 ± 0.03	0.11 ± 0.02	0.13 ± 0.03
ZrO_2	7.00 ± 0.07	6.8 ± 0.2	0.30 ± 0.05	0.35 ± 0.10
BaO	0.16 ± 0.01	0.11 ± 0.05	5.11 ± 0.05	5.2 ± 0.1
PbO	0.01 ± 0.02	0.22 ± 0.04	0.15 ± 0.03	0.14 ± 0.04
ZnO	10.95 ± 0.05	10.9 ± 0.1	7.66 ± 0.05	7.6 ± 0.1
HfO_2	0.14 ± 0.02	0.12 ± 0.03	0.01 ± 0.01	0.01 ± 0.01
P_2O_5	0.31 ± 0.01	0.28 ± 0.02	0.02 ± 0.01	0.02 ± 0.01

Table 2. Theoretical and experimental concentrations (in % (m/m)) of each element and their uncertainty for synthetic standards 3 and 4 measured by XRF

	synthetic standard 1		synthetic standard 2	
	theoretical	experimental	theoretical	experimental
SiO_2	66.2 ± 0.2	66.3 ± 0.4	59.8 ± 0.2	60.3 ± 0.4
Al_2O_3	7.3 ± 0.14	7.3 ± 0.2	9.1 ± 0.14	9.1 ± 0.2
Fe_2O_3	0.17 ± 0.01	0.17 ± 0.02	0.22 ± 0.01	0.20 ± 0.02
CaO	14.2 ± 0.1	14.2 ± 0.2	9.7 ± 0.1	9.8 ± 0.2
MgO	0.33 ± 0.05	0.33 ± 0.08	1.21 ± 0.05	1.27 ± 0.08
Na_2O	3.35 ± 0.03	3.27 ± 0.06	2.26 ± 0.03	2.19 ± 0.06
K_2O	1.01 ± 0.02	1.01 ± 0.04	4.38 ± 0.02	4.41 ± 0.04
TiO_2	0.14 ± 0.02	0.14 ± 0.03	4.23 ± 0.07	4.19 ± 0.03
ZrO_2	1.90 ± 0.07	2.1 ± 0.2	4.50 ± 0.07	4.7 ± 0.2
BaO	2.29 ± 0.05	2.39 ± 0.09	1.00 ± 0.05	1.01 ± 0.09
PbO	0.20 ± 0.04	0.25 ± 0.05	1.00 ± 0.01	0.04 ± 0.03
ZnO	0.13 ± 0.02	0.15 ± 0.03	0.10 ± 0.02	0.11 ± 0.03
HfO_2	0.04 ± 0.01	0.06 ± 0.02	0.09 ± 0.01	0.09 ± 0.02
P_2O_5	0.02 ± 0.01	0.10 ± 0.02	0.03 ± 0.01	0.03 ± 0.02

Four frit compositions were also prepared to evaluate the procedure. These compositions could have been prepared by mixing the raw materials typically used in ceramic frit producing factories, but in this study they were made just as the four synthetic standards by mixing the above reference materials.

3. Results and discussion

3.1 XRF measurement validation and calculation of uncertainty

Frits are vitreous products, made industrially by mixing different crystalline raw materials (quartz, kaolin, sodium and potassium feldspars, calcium carbonates, sodium nitrates, dolomites, zinc oxides, zirconium silicates, borates, etc.), melting these mixtures at high temperatures and then quenching them. Calibration and validation standards were thus prepared by following the industrial process on a laboratory scale.

Four synthetic standards were made from the reference materials to validate the XRF measurement. The validation data are set out in tables 1 and 2. The theoretical concentration of each element was found from the concentration of each reference material contained in the synthetic standard. The certificate accompanying the reference material supplied its uncertainty. The experimental concentration was found by XRF. Uncertainty was calculated as the standard deviation of the measurements of the different preparations plus the uncertainty of the standards making up the synthetic standard [20].

Analysis of the XRF data listed in tables 1 and 2 shows that the experimental values with their uncertainty lie within the range defined by the theoretical

Table 3. Theoretical and experimental concentrations (in mg/l) of sodium and lithium for the reference standards measured by AAS

	theoretical		experimental	
solution	Na	Li	Na	Li
1	10.0 ± 0.1	0.10 ± 0.01	10.1 ± 0.3	0.09 ± 0.02
2	25.0 ± 0.2	0.50 ± 0.02	25.2 ± 0.6	0.52 ± 0.05
3	50.0 ± 0.4	2.00 ± 0.08	51 ± 1	1.91 ± 0.1

Table 4. Theoretical and experimental concentrations (in mg/l) of boron and lithium for the reference standards measured by ICP-OES

	theoretical		experimental	
solution	B	Li	B	Li
4	2.50 ± 0.02	0.025 ± 0.005	2.43 ± 0.06	0.03 ± 0.01
5	5.00 ± 0.04	0.50 ± 0.02	5.07 ± 0.08	0.56 ± 0.04
6	12.50 ± 0.1	2.00 ± 0.08	12.61 ± 0.2	1.9 ± 0.1

value and its uncertainty, validating the XRF measurement method for analysing these elements in this type of material. The uncertainty accompanying the experimental value is generally slightly higher than the uncertainty of the theoretical value. However, no large rise is observed in any of the analysed elements. This indicates that the method used has low random errors, i.e., it is an accurate method. The accuracy of the method is due to the sample preparation process as well as to the actual measurement. Both analysis steps were optimized.

3.2 AAS measurement validation and calculation of uncertainty

Three solutions were prepared from the reference materials to validate the AAS measurement. Table 3 shows the validation data.

The experimental values found and their uncertainty for sodium and lithium in AAS measurement lie within the range defined by the theoretical value and its uncertainty, demonstrating the suitability of the technique for determining these elements. The sodium and lithium concentrations in the prepared dilutions were typical frit concentrations. Low deviation values were found for sodium and lithium by AAS, indicating high accuracy of the experimental values.

3.3 ICP-OES measurement validation and calculation of uncertainty

Three solutions were prepared from the reference materials to validate the ICP-OES measurement. Table 4 presents the validation data.

The boron and lithium concentrations in this series of dilutions are similar to those normally found in solutions produced by frit digestion.

The boron and lithium concentrations found by ICP-OES in the reference standard solutions show the method's suitability for measuring these elements, as the values found and their uncertainty lie within the range defined by the theoretical value and its uncertainty in every case. Unlike the uncertainty associated with the synthetic standards measured by XRF, which includes errors relating to sample preparation and measurement, the uncertainty in ICP-OES only relates to measurement error, as liquid standards are used requiring no preparation. The uncertainty associated with the ICP-OES measurement of boron and lithium exhibits low values, indicating the accuracy of the measuring method for both elements.

3.4 Evaluation of the procedure adopted

After validating all the analytical techniques used in the study for frit chemical characterization, four frit compositions (referenced A, B, C and D) were prepared using the materials indicated in section 2.3. The chemical compositions formulated resembled those of industrial frits. These mixtures of reference materials only underwent mixing and melting, analogously to the raw materials used in preparing industrial frits.

The materials used in composition preparation were reference materials and/or pure products, so that the concentration of each element was known. The mixtures were analysed by the analytical techniques validated in the study. Table 5 lists the values found in the four frit compositions. Table 6 gives the B_2O_3 concentration in each frit composition, calculated by averaging the titrimetric titration and ICP-OES data. Table 7 gives the Na_2O concentration in each frit composition, calculated by averaging the XRF and AAS data. Finally, table 8 gives the Li_2O concentration in each frit composition, calculated by averaging the AAS and ICP-OES data.

The results of the evaluation show that:

a) Frit Na_2O concentration can be determined by both XRF and AAS, as the outcomes are the same. It will normally be measured by XRF together with the other frit elements. When it is deemed necessary to verify the value found, owing to the characteristics of the sample, the Na_2O concentration will also be measured by AAS.

b) Li_2O concentration can be determined by ICP-OES or AAS, as both methods yield good results and no interferences are found in the measuring process.

c) B_2O_3 concentration can be measured by ICP-OES and titrimetry. However the latter method exhibits a lower uncertainty. This is due to the difference in sample preparation in these methods and because ICP-OES requires sample dilution, whereas in the volumetric

Table 5. Frits A, B, C and D composition data (in % (m/m))

	frit A		frit B		frit C		frit D	
	theoretical	experimental	theoretical	experimental	theoretical	experimental	theoretical	experimental
SiO_2	56.7 ± 0.2	57.1 ± 0.4	57.3 ± 0.2	57.6 ± 0.4	59.5 ± 0.2	59.1 ± 0.4	53.6 ± 0.2	54.0 ± 0.5
Al_2O_3	5.80 ± 0.14	5.9 ± 0.2	16.70 ± 0.15	16.8 ± 0.2	7.20 ± 0.15	7.2 ± 0.2	7.60 ± 0.15	7.8 ± 0.2
B_2O_3 1)	4.50 ± 0.07	4.55 ± 0.15	3.80 ± 0.07	3.74 ± 0.15	2.10 ± 0.07	2.08 ± 0.15	1.59 ± 0.08	1.70 ± 0.15
Fe_2O_3	0.14 ± 0.01	0.14 ± 0.02	0.23 ± 0.01	0.23 ± 0.02	0.19 ± 0.01	0.18 ± 0.02	0.15 ± 0.01	0.15 ± 0.02
CaO	7.50 ± 0.05	7.50 ± 0.15	0.96 ± 0.04	0.89 ± 0.09	13.80 ± 0.06	13.8 ± 0.1	7.50 ± 0.07	7.40 ± 0.10
MgO	2.43 ± 0.05	2.5 ± 0.1	0.43 ± 0.05	0.46 ± 0.08	0.33 ± 0.05	0.35 ± 0.08	2.78 ± 0.05	2.83 ± 0.09
Na_2O 2)	0.92 ± 0.03	0.93 ± 0.05	3.70 ± 0.03	3.76 ± 0.07	1.15 ± 0.03	1.10 ± 0.06	1.43 ± 0.03	1.33 ± 0.07
K_2O	3.62 ± 0.02	3.61 ± 0.04	1.54 ± 0.02	1.49 ± 0.04	4.52 ± 0.02	4.54 ± 0.04	4.75 ± 0.02	4.72 ± 0.04
TiO_2	0.04 ± 0.02	<0.03 ± 0.03	0.26 ± 0.02	0.25 ± 0.03	0.02 ± 0.01	0.02 ± 0.02	0.04 ± 0.01	0.03 ± 0.02
ZrO_2	6.3 ± 0.1	6.0 ± 0.2	12.8 ± 0.1	12.8 ± 0.2	–	<0.1 ± 0.1	7.30 ± 0.07	7.1 ± 0.2
BaO	0.15 ± 0.01	<0.09 ± 0.09	0.30 ± 0.05	0.33 ± 0.08	–	<0.1 ± 0.1	–	<0.1 ± 0.1
Li_2O 3)	0.09 ± 0.01	0.10 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.50 ± 0.02	0.49 ± 0.04	–	<0.01 ± 0.01
PbO	0.43 ± 0.01	0.35 ± 0.08	0.30 ± 0.01	0.24 ± 0.08	–	<0.03 ± 0.03	–	0.03 ± 0.02
ZnO	11.20 ± 0.07	11.3 ± 0.1	0.50 ± 0.04	0.51 ± 0.05	10.70 ± 0.07	10.5 ± 0.1	12.2 ± 0.08	12.2 ± 0.1
HfO_2	0.13 ± 0.02	0.11 ± 0.03	0.26 ± 0.02	0.25 ± 0.03	–	0.04 ± 0.03	0.15 ± 0.02	0.12 ± 0.04
P_2O_5	0.03 ± 0.01	0.03 ± 0.02	0.36 ± 0.01	0.36 ± 0.02	0.02 ± 0.01	<0.02 ± 0.02	0.29 ± 0.01	0.24 ± 0.05

1) Calculated by titration and ICP-OES.
2) Calculated by XRF and AAS.
3) Calculated by AAS and ICP-OES.

Table 6. B_2O_3 concentration values (in % (m/m)) found by ICP-OES and titrimetry in frits A, B, C and D

frit	ICP-OES	titrimetry	average
A	4.47 ± 0.15	4.63 ± 0.10	4.55 ± 0.15
B	3.66 ± 0.15	3.82 ± 0.10	3.74 ± 0.15
C	2.17 ± 0.15	1.98 ± 0.10	2.08 ± 0.15
D	1.60 ± 0.15	1.79 ± 0.10	1.70 ± 0.15

Table 7. Na_2O concentration values (in % (m/m)) found by AAS and XRF in frits A, B, C and D

frit	AAS	XRF	average
A	0.90 ± 0.02	0.96 ± 0.05	0.93 ± 0.05
B	3.77 ± 0.07	3.75 ± 0.07	3.76 ± 0.07
C	1.16 ± 0.03	1.04 ± 0.05	1.10 ± 0.06
D	1.39 ± 0.07	1.27 ± 0.06	1.33 ± 0.07

Table 8. Li_2O concentration values (in % (m/m)) found by AAS and ICP-OES in frits A, B, C and D

frit	AAS	ICP-OES	average
A	0.11 ± 0.01	0.089 ± 0.008	0.10 ± 0.01
B	0.030 ± 0.005	0.050 ± 0.005	0.04 ± 0.01
C	0.46 ± 0.03	0.51 ± 0.03	0.49 ± 0.04
D	0.010 ± 0.005	0.008 ± 0.003	0.01 ± 0.01

method, a much larger quantity of sample can be used without dilution.

d) The remaining frit elements are determined by XRF. This is the fastest reproducible method, demonstrated by the low uncertainty accompanying the experimental value.

4. Conclusions

A technologically valid methodology has been developed in this study for determining the chemical composition of all the elements usually found in ceramic frits. The procedure combines the use of different analytical techniques (AAS, ICP-OES and XRF) to determine the same element, together with the use of mixtures of reference materials (synthetic standards).

The methodology developed in this study allows preparing reference materials for chemical analysis of ceramic frits. This is of great importance, as such materials are not available on the market.

Frits can therefore be analysed for use as reference materials which can serve as standards for calibrating and/or validating industrial working methods in factories, where methods need to be fast and easy to perform.

The XRF technique was shown to enable analysing precisely and accurately, the largest number of elements typically found in ceramic frits.

5. References

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6. Appendix

Table A1. Chemical composition (in % (m/m)) of siliceous sands, kaolins, related materials and zirconium silicates

	N° 267 silica brick	N° 313/1 high purity silica	N° 314 silica brick	Nr. 777-1 (silica stone)	N° 348 ball clay	CAS 5 ball clay	GBW 03122 kaolin	N° 388 zircon	SARM 13 zirconium concentrate
SiO_2	95.9	99.78	96.2	95.06	51.13	56.13	44.53	32.7	32.56
Al_2O_3	0.85	0.036	0.77	0.793	31.59	29.06	38.62	0.33	0.61
Fe_2O_3	0.79	0.012	0.53	0.329	1.04	1.12	0.72	0.049	0.187
CaO	1.75	0.006	1.81	2.83	0.173	0.21	0.16	(0.04)	(0.14)
MgO	0.06	0.0013	0.05	0.071	0.305	0.36	0.068	(0.03)	(0.04)
Na_2O	0.06	0.003	0.05	0.027	0.344	0.40	0.069	(0.02)	–
K_2O	0.14	0.005	0.09	0.157	2.23	2.37	0.049	(0.02)	–
TiO_2	0.17	0.017	0.19	0.45	1.08	1.48	0.39	0.25	0.295
MnO	0.15	–	<0.01	–	–	–	0.21	–	–
P_2O_5	–	–	–	–	0.071	–	–	0.12	0.23
ZrO_2	–	–	–	–	–	–	–	66.2	64.01
HfO_2	–	–	–	–	–	–	–	1.30	1.29

Table A2. Chemical composition (in % (mm)) of calcium and magnesium carbonates, dolomites, talcs, wollastonites and borates

	N° 393 limestone	N° 1762 dolomite	N° 389 high-purity magnesite	GBW 03123 kaolin	N° 203a talc	1835 borate ore
SiO_2	0.70	0.96	0.89	50.50	59.7	18.41
Al_2O_3	0.12	0.295	0.23	0.39	0.30	3.47
Fe_2O_3	0.045	0.375	0.29	0.41	0.22	1.14
CaO	55.4	30.60	1.66	40.39	0.25	21.62
MgO	0.15	20.73	96.7	0.95	32.08	3.41
Na_2O	(0.017)	–	0.03	0.052	0.02	3.484
K_2O	0.02	–	0.01	0.14	0.005	1.26
TiO_2	0.009	–	0.01	0.022	<0.01	0.13
MnO	–	–	–	0.096	–	–
P_2O_5	(0.005)	0.003	–	–	0.13	–
B_2O_3	–	–	–	–	–	18.74
L.O.I.	43.4	46.30	–	6.93	6.78	25.72

Note: L.O.I. stands for: loss on ignition.

Table A3. Chemical composition of calcium phosphates, feldspars and related materials and rutile (in % (m/m))

	120c florida phosphate rock	N° 375 soda feldspar	N° 376 potash feldspar	99a feldspar	FK-N potash feldspar	70a potassium feldspar	N° 201a nepheline syenite	670 rutile
SiO_2	5.5	67.10	67.10	65.20	65.02	67.1	57.30	0.51
Al_2O_3	1.30	19.80	17.70	20.50	18.61	17.9	23.54	–
Fe_2O_3	1.08	0.12	0.10	0.06	0.09	0.07	0.12	0.86
CaO	48.02	0.89	0.54	2.14	0.11	0.11	1.07	–
MgO	0.32	(0.04)	(0.03)	0.02	0.01	–	0.025	–
Na_2O	0.52	10.40	2.83	6.20	2.58	2.5	7.53	–
K_2O	0.147	0.79	11.20	5.20	12.81	11.8	8.90	–
TiO_2	0.103	0.380	<0.02	0.007	0.02	0.01	0.05	96.16
MnO	3.16	–	–	–	–	–	–	–
P_2O_5	15.7	–	–	–	–	–	–	–
ZrO_2	–	–	–	–	–	–	–	0.84
Cr_2O_3	–	–	–	–	–	–	–	0.23
V_2O_5	–	–	–	–	–	–	–	0.66

Table A4. Sodium and lithium concentration (in % (m/m)) in the reference materials used to prepare the AAS measurement calibration curves

	Li	Na
lithium carbonate (Merck)	18.74 ± 0.14	–
NaCl (Merck)	–	39.35 ± 0.20

Table A5. Sodium and lithium concentration (in mg/l) in the standard reference materials used to validate the AAS measurement calibration curves

	Li	Na
RM 3171 A	–	100.0 ± 0.5
RM 3179-I	–	100.0 ± 0.5
multielemental atomic absorption standard solution	50 ± 0.5	–

Table A6. Lithium and boron concentration (in % (m/m)) in the reference materials used to prepare the ICP-OES measurement calibration curves

	Li	B
lithium carbonate (Merck)	18.74 ± 0.14	–
boric acid (Merck)	–	20.86 ± 0.10

Table A7. Lithium and boron concentration (in mg/l) in the standard materials used to validate the ICP-OES measurement calibration curves

	Li	B
RM 3107	–	5000 ± 30
RM 3179-II	100.0 ± 0.5	–

Contact:
Mr M. Jesús José Ferrandis
Instituto de Tecnología Cerámica
Centro de Documentación
Campus Universitario Riu Sec
12006 Castellón
Spain
E-mail: mjose@itc.uji.es