PREPARATION OF REFERENCE MATERIALS OF CERAMIC RAW MATERIALS

M.F. Gazulla, M.P. Gómez, M. Orduña, E. Zumaquero, M. Rodrigo

Instituto de Tecnología Cerámica (ITC). Asociación de Investigación de las Industrias Cerámicas (AICE)
Universitat Jaume I. Castellón. Spain.

ABSTRACT

This study was undertaken in order to prepare a series of reference materials of ceramic raw materials for the calibration and/or validation of methods for determining their chemical, mineralogical and thermogravimetric composition, for use in control and research laboratories in the ceramic industry. This would allow better control of industrial processes and the development of measurement systems that enabled results to be communicated between different laboratories (raw materials suppliers, manufacturers of frits, floor, wall, and porcelain tiles, etc.) over long periods of time, thus providing measurement compatibility, in which reference materials play a critical role.

In order to prepare the reference materials of ceramic raw materials, first, the most significant raw materials used in the manufacture of red-body and white-body stoneware floor tile, porous red-body and white-body wall tile, and porcelain tile were selected. The following materials were studied: a red-firing clay for floor tiles; a red-firing clay for wall tiles, a calcium carbonate, dolomite, an imported white-firing clay, a kaolin, a silica sand, a feldspar sodium, a potassium feldspar, and a Spanish white-firing clay.

After sample preparation by crushing, quartering, and milling, a homogeneity test was conducted, this being an essential step in any reference material preparation process. Once it had been verified that the material was homogeneous, the actual characterisation was performed. Chemical characterisation was conducted with different analytical techniques: wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF) and inductively coupled plasma-optical emission spectrometry (ICP-OES), using certified reference materials for the calibration and validation of each measurement, in addition to chemical analysis in two recognised, independent laboratories. Mineralogical characterisation was done by X-ray diffraction (XRD) in which, in addition to the identification of the crystalline phases present in each sample, the phases were quantified by the Rietveld method and thermogravimetrically characterised, analysing all variations in sample weight in the temperature range from 25 to 1200°C.

Reference materials were then prepared with all the data obtained: chemical composition of each material, which included the major and minor elements, the content of each crystalline phase, and the weight loss that each material underwent in the 25–1200ºC temperature range. These reference materials can be used for the implementation, calibration, and validation of test methods in ceramic industry laboratories.

1. INTRODUCTION

The Spanish ceramic tile industry is currently internationally recognised for the competitiveness of its products, based on both their great aesthetic and technical quality. This is also the origin of the demand for a precise characterisation of the raw materials used, in order to avoid manufacturing defects, keep the production process under control, or modify the technical characteristics of the end product [1-2].

According to Kane [3] reference materials play a key role in analytical laboratories, as materials for calibrating instrumental techniques, for quality assurance, and control. However, few geological reference materials are available with analysis certificates in which the property known is accompanied by its uncertainty, as defined in the guide for the calculation of uncertainties [4], preventing appropriate traceability in the measurements made using these materials.

The importance of using reference materials lies in being able to obtain precise and comparable results, independently of where the measurements are made [5, 6].

The development of modern analytical techniques has made the availability of reference materials even more important. Certain techniques, such as wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF) and inductively coupled plasma-emission optical spectrometry (ICP-OES), can only be suitably calibrated using reference materials. This differs from the first wet methods, in which laboratories simply performed the calibrations with elementary solutions [7].

In recent years, an important technological upgrading has taken place in the control and research laboratories of Spanish ceramic sector companies, one of the most widely used methods in the chemical characterisation of solid samples being WD-XRF measurement. Most ceramic industries, particularly companies that manufacture frits, glazes, and ceramic pigments, ceramic raw materials suppliers, and even mine operators, obviously in addition to research laboratories, have WD-XRF spectrometers for quality control of their raw materials and products.

In WD-XRF measurement, the sample is customarily prepared in the form of beads and pellets. The three fundamental factors to be taken into account in this process are as follows: the matrix effect, mineralogical structure, and particle size [8], which affect each preparation procedure in a different way:

- In bead preparation, the mineralogical structure and particle size factors are fully eliminated when the sample is fused, while the matrix effect is largely cancelled owing to sample dilution as a result of the flux addition used to carry out the fusion.

- In pellet preparation, the matrix effect and the mineralogical structure can only be cancelled by using standards that have a very similar mineralogical and chemical composition to that of the materials to be tested; accurate results can only be obtained with such standards.

The foregoing highlights the importance of preparing reference materials of samples with similar characteristics to those of the materials to be tested, since in certain laboratories of the companies mentioned, where there is no bead preparation equipment, the sample is prepared in the form of pellets, and this is where the use of reference materials similar to those to be analysed is most important.

At present, there are no reference materials of ceramic raw materials with the same characteristics as those used in the ceramic sector. However, this would be of great usefulness in implementing test laboratories, whether for control or research, in ceramic industries.

In accordance with ISO Guide 30, in order to proceed with the preparation of a reference material it is necessary to establish a clear protocol in which all the process stages are detailed [9, 10]. The first step is the definition of the elements and types of materials to be analysed, followed by selection of these materials. The second step is to collect a considerable quantity of the material, so that once the reference material has been prepared, this will be available of a long period of time; the third step is mixing and grinding of the material to a homogeneous sample, followed by the uniformity test. In the fourth step, laboratories are chosen where chemical analysis will be performed, if possible, analysing the elements by more than one method, which are preferably independent. The material is then sent to the chosen laboratories and, finally, all the results are collected and appropriately statistically processed in order to assign every analysed element its value and uncertainty [11-13].

The study was conducted with ten representative raw materials of those used in the manufacture of red-body and white-body stoneware floor tiles, porous red-body and white-body wall tile, and porcelain tile. The following materials were studied: four clays, a calcium carbonate, a dolomite, a kaolin, a silica sand and two feldspars. These materials were chemically, mineralogically, and thermally characterised.

Chemical characterisation was conducted with different analytical techniques: WD-XRF and ICP-OES, using reference materials for calibration and measurement validation. The materials were also analysed in another, independent laboratory, the Central Geological Laboratory (CGL) of Mongolia. Mineralogical characterisation was performed by X-ray diffraction (XRD), while thermogravimetric characterisation was conducted with a thermobalance that recorded the variations in weight of the materials from 25 to 1200ºC.

2. MATERIALS AND EQUIPMENT

2.1. MATERIALS STUDIED

The materials selected for this study were geological materials that are widely used in the ceramic industry as raw materials: four clays (two red-firing clays – one for floor tile and the other for wall tile; and two white-firing clays – a Spanish and an imported clay), a calcium carbonate, a dolomite, a kaolin, a silica sand, and two feldspars (namely, a potassium and a sodium feldspar).

2.2. REFERENCE MATERIALS

In order to conduct the chemical characterisation of the materials selected at the laboratories of the Instituto de Tecnología Cerámica (ITC), these materials were divided into four groups, based on the elements they contained and their nature: Group 1: clays and kaolin; Group 2: silica sand; Group 3: sodium and potassium feldspars; and Group 4: calcium carbonate and dolomite.

The use of reference materials in the analysis of a studied sample provides measurement traceability. The reference materials used for calibration and the reference materials used for measurement validation are described below.

The following reference materials were used to prepare the calibration curves for the WD-XRF measurement:

1) Group 1 (clays and kaolin): Ceram Research England Ball Clay CAS 5, CCRMP TILL-1, GBW 03118 Graphite Ore, BCS-CRM 348 Ball Clay, GBW 07404 Soil.

2) Group 2 (silica sand): BCS-CRM 313/1 High purity silica, BCS 267 Silica brick, SRM 70a Potassium feldspar, IPT-72 Sodium feldspar.

3) Sodium and potassium group 3 (feldspars): SRM 70a Potassium feldspar, BCS-RM 201-a Nepheline syenite, BCS-CRM 375/1 Soda felspar, CCRMP SY-2 Syenite.

4) Group 4 (calcium carbonate and dolomite): BCS-CRM 393 Limestone, EURONORM-CRM 782/1 Dolomite, EURONORM-ZRM Nr 777/1 Silikastein.

The calibration curves for the ICP-OES measurement were prepared using standard solutions of 1000 mg·L^{-1} from Fluka of each analysed element.

The following certified reference materials have been used for WD-XRF measurement validation:

1) Group 1 (clays and kaolin): BCS 267 Silica Brick, Euronorm-CRM 682-1 Iron Ore, SRM 98b Plastic Clay, Euronorm-CRM 782/1 Dolomite, IPT- 53 Potassium feldspar, BCS-CRM 313/1 High purity silica, BCS-CRM 348 Ball Clay, GBW 03103 Shale and Clay, and GBW 03122 Kaolin.

2) Group 2 (silica sand): BCS 314 Silica Brick, EURONORM-ZRM Nr. 777/1 Silikastein.

3) Group 3 (sodium and potassium feldspars): IPT-72 Sodium feldspar, IPT-53 Potassium feldspar, SRM 99a Feldspar.

4) Group 4 (calcium carbonate and the dolomite): CMSI No. 1762 Dolomite, SRM 1d Limestone.

ICP-OES measurement validation was carried out using solutions of 1000 $mg \cdot L^{-1}$ from Merck of each analysed element; as well as the same standards used for WD-XRF measurement validation.

2.3. EQUIPMENT

The equipment used at the ITC laboratories is described below. To determine the chemical composition of the materials, the beads were prepared for WD-XRF measurement using a PHILIPS model PERL X'3 fusion bead preparation machine. The WD-XRF instrument used in sample measurement was a PHILIPS model PW 2400 spectrometer with Rh tube equipped with a PW 2540 VTC sample changer.

Sample preparation for the ICP-OES measurement was carried out with an ANTON PAAR model Paar Physica laboratory microwave distributed by Perkin-Elmer. The instrument used for the ICP-OES measurement was a LEEMAN LABS INC model Direct Reading Echelle inductively coupled plasma spectrometer.

Mineralogical characterisation was conducted by X-ray diffraction (XRD) of the powder sample with a BRUKER Theta-Theta model D8 ADVANCE diffractometer with copper tube. The crystalline structures were identified using the ICDD (International Center for Diffraction Data) database of powder diffraction files (PDF-2) updated in 2004 and the EVA (Bruker) and X'Pert HighScore (Panalytical) software programs.

Thermogravimetric analysis was conducted using a METTLER TOLEDO model TGA/SDTA 851E/160 thermobalance.

Loss on ignition was determined with a LECO INSTRUMENTS model TGA-701 thermogravimetric analyser.

The particle size distribution of the materials in Group 1 was determined with a Micromeritics model Sedigraph 5100 X-ray absorption instrument, while a MALVERN MASTERSIZER laser beam diffraction instrument was used for the other materials.

3. EXPERIMENTAL DEVELOPMENT

In order to proceed with the preparation of the reference materials, the different selected materials were chemically analysed at the Central Geological Laboratory (CGL) of Mongolia and at the ITC laboratory, in addition to using two independent methods to determine the chemical composition. The protocol followed in conducting the study consisted of the stages detailed below.

3.1. SAMPLE COLLECTION

Once the materials to be studied had been defined, a considerable quantity of each selected raw material was collected, first, in order to have a sufficient quantity of sample for later when the reference material was ready, since 15-50% of the material is lost in the grinding, homogenisation, and packaging process [10]. Thus, about 100 kg of each material was collected.

3.2. GRINDING AND HOMOGENISATION OF THE SAMPLES

Geological materials are generally made up of different minerals, so that they have an intrinsically non-homogeneous composition at mineral level. The material therefore needs to be milled to a given particle size, defining the minimum quantity of sample that may be considered homogeneous [10]. Note that grinding should always be kept to a minimum, in order to cause the least possible contamination of the milling devices.

The four clay samples were subjected to grinding and homogenisation, since they had not initially been milled and were therefore not homogeneous. The red-firing clays were milled using a hammer mill until the sample particle size was below 1 mm; the white-firing clays were first comminuted in a jaw crusher and then ground in a hammer mill, because the sample consisted of large agglomerates. Once the samples had been milled, their particle size distribution was determined.

When the samples had been suitably milled, they were stored in duly labelled sealed containers. The final coding used for each studied material was as follows: red-firing clay for floor tile (MR-1) (4 containers), red-firing clay for wall tile (MR-2) (4 containers), calcium carbonate (MR-3) (4 containers), dolomite (MR-4) (4 containers), imported white-firing clay (MR-5) (5 containers), kaolin (MR-6) (10 containers), silica sand (MR-7) (5 containers), potassium feldspar (MR-8) (5 containers), sodium feldspar (MR-9) (5 containers), Spanish white-firing clay (MR-10) (4 containers).

3.3. UNIFORMITY TEST

Before proceeding with the chemical characterisation of the materials, a uniformity test was performed to determine whether the material was sufficiently homogeneous to be used as a reference material.

The value of the uniformity test depends on the accuracy of the measurement method used to carry out this test. For geological samples, the quotient between the standard deviation of the measurement, σ_{an}, and the standard deviation of the different batches, σ_p, shall be below 0.5, that is: $\sigma_{an}/\sigma_p<0.5$. The WD-XRF technique was chosen because it is a very accurate method for the major elements, which makes it an ideal method for determining the uniformity of a geological sample [14].

The literature describes various procedures for determining uniformity [10, 12-15], and details the test conditions and statistical processing of the values obtained. In this study, to carry out the uniformity test, at least one sample was taken from each container of the same material, which was then analysed three times, all sampling being random in order to eliminate any possible bias in the measurement process. The major and minor elements were analysed in the materials, and the resulting data was then processed.

The sample portion taken to carry out the uniformity test is of great importance for the future use of the reference material, since this is the minimum sample portion specified in the analysis certificate for using the reference material. In all cases, this was 0.5000 g.

The uniformity test was carried out according to ISO Guide 35 and the calculations are detailed below.

Table 1 was constructed for each analysed element in the test materials:

	Containers							
Replicate	1	2	3	4	5	…	t	Total
1								B_1
2…								B_2…
…b								…B_b
Total	T_1	T_2	T_3	T_4	T_5	…	T_t	$G=(\Sigma B_1 \ldots B_b)$
Average	t'_1	t'_2	t'_3	t'_4	t'_5		t'_t	

Table 1. Data for performance of the uniformity test

Where t is the number of containers, b the number of replicates, T the sum of the values obtained for a container, B the sum of the values obtained for a replicate for each container, t' the average of the replicates for each container and G the sum of B_1 to B_b.

S_t and S_b are then determined from the following equations:

$$S_t = \left[\left(T_1^2 + T_2^2 + \ldots + T_t^2\right)/b\right] - \left(G^2/tb\right)$$

$$S_b = \left[\left(B_1^2 + B_2^2 + \ldots + B_b^2\right)/t\right] - \left(G^2/tb\right)$$

The value of $S_{average}$ is determined from the equation:

$$S_{Average} = \left(\sum_{i=1}^{t}\right)\left(\sum_{j=1}^{b}\right) Y_{ij}^2 - \left(G^2 \big/ tb\right)$$

where Y_{ij} are all the individual values of Table 1. The value of s is then calculated from the equation:

$$s = \sqrt{\left(S_{Average} - S_b - S_t\right)/(b-1)(t-1)}$$

A 95% (α=0.05) level of probability is taken and the number of degrees of freedom (ν) is calculated from the equation: $\nu=(b-1)(t-1)$. This value and the number of replicates allow the value of q to be obtained, which is a tabulated statistical value.

Finally, ω is calculated from the equation: $\omega = qs\sqrt{b}$ This parameter is used to determine the degree of uniformity of each batch of material.

The calculated value of ω is compared with all the absolute values of $\Delta t'_t$, which are the differences between batches (containers), so that for the sample to be homogeneous $|\Delta t'_t| < \omega$ always needs to be obeyed.

3.4. CHEMICAL CHARACTERISATION

Chemical characterisation was conducted at the ITC laboratories by means of two analytical techniques: WD-XRF and ICP-OES. In addition, the materials were also analysed in another laboratory with recognised experience in the field of chemical analysis of geological materials

3.4.1. Chemical characterisation by WD-XRF

In order to carry out the WD-XRF chemical characterisation, the samples and standards were prepared in the form of beads, as described elsewhere[16]; the calibration curves were constructed from the reference materials detailed in section 2.2.

Different activities were undertaken to validate the measurements:

1) The chemical analysis laboratory participated in different interlaboratory tests, these being principally:

- The International Proficiency Test for Analytical Geochemistry Laboratories organised by the International Association of Geoanalysts (IAG).
- A certification program organised by the U.S. Geological Survey of the University of Denver, aimed at certifying a set of geological materials: G-3, RGM-2, and STM-2.

2) Samples were analysed by two recognised, independent methods [17]: WD-FRX and ICP-OES.

3) The reference materials detailed in section 2.2 were used to validate the measurements.

4) Analysis of the same materials in two different laboratories of proven quality, which had previously participated in intercomparison exercises. In addition, preliminary studies were conducted with the CGL laboratory, which led to preparation of the following reference materials: USZ 3-85, GSO 3319-85, STSEV 5748-86 ("CuMo" Copper-molybdenum ore), USZ 24-99 (Serpentinite GAS), USZ 26-99 (Tungsten molybdenum ore "WMo"), USZ 36-2002 (Chromium Ore "XXX"), YC 3 37-2003 (Magnesite), and ST SEV 3530-82 (Phosphorite "HF").

3.4.2. Chemical characterisation by ICP-OES

In order to carry out the ICP-OES determination, acid digestion of the samples was performed in a laboratory microwave kiln, described elsewhere [18], and the measurement was made on the resulting solution.

The ICP-OES measurements were validated in the same way as the validation of the WD-XRF method.

3.4.3. Determination of loss on ignition

Loss on ignition of the samples was determined by two methods: by the traditional method in a muffle kiln, calcining the sample to a temperature of 1000ºC for two hours, and with a thermogravimetric analyser, in which the sample was subjected to a peak temperature of 1000ºC to constant weight.

3.5. MINERALOGICAL CHARACTERISATION [19-23]

Mineralogical characterisation was carried out by XRD, using the random powder method to avoid preferential orientations; the structures were identified by comparing the diffractograms obtained with those of pure crystalline structures compiled in databases (JDCPS files).

The crystalline structures were quantified by the Rietveld method, which is a multi-parameter fitting method. The refinement of a crystalline structure by the Rietveld method consists of minimising the difference between an experimental diffractogram and a calculated one, using an approximate structural model and certain parameters that allow the intensities of the different reflections of the diffractogram to be distributed.

3.6. THERMOGRAVIMETRIC ANALYSIS [22-24]

Thermogravimetry is a technique that measures the mass of a substance as a function of temperature when this substance is subjected to a controlled temperature cycle. This analysis method complements other types of analysis, since it serves to distinguish between the reactions that cause weight loss in each range of temperatures, and allows them to be associated with compounds of different nature, such as organic compounds, carbonates, clay minerals, etc.

4. RESULTS AND DATA PROCESSING

4.1. RESULTS OF THE UNIFORMITY TEST

Parameters ω and $\Delta t'_t$, described in section 3.3, were determined for all analysed elements, and the uniformity condition ($|\Delta t'_t| < \omega$) was met for every batch of each material. Therefore, the test indicates that the materials display appropriate uniformity for them to be used as reference materials of geological samples.

4.2. RESULTS OF THE CHEMICAL CHARACTERISATION

Measurement validation was conducted, on the one hand, by analysing reference materials similar to the samples being studied and, on the other, by participating in the International Proficiency Test for Analytical Geochemistry Laboratories organised by the International Association of Geoanalysts (IAG) since 2000, involving interlaboratory tests in which about 90 laboratories worldwide participate. ITC has participated in the following tests: GeoPT 7: GBPG-1 Garnet-biotite plagiogneiss, GeoPT 8: OU-4 Penmaenmawr microdiorite, GeoPT 9: OU-6 Penrhyn slate, GeoPT 10: CH-1 Marine sediment, GeoPT 11: Ou-5 Leaton Dolerite, GeoPT 12: GAS Serpentinite, GeoPT 13: Loess, GeoPT 14: OShBO Alkaline granite, GeoPT 15: MSAN Ocean floor sediment, GeoPT 16: BNV-1 Nevada Basalt, GeoPT 17: OU-8 Calcareous sandstone, GeoPT 18: KPT-1 Quartz diorite, GeoPT 19: MGR-N Garbo, GeoPT 20: OPY-1 Ultramafic rock and GeoPT 21: MGT-1 Granite.

In these interlaboratory tests, the value assigned to each analysed element is obtained by rigorous statistical data analysis. The value of z is calculated from the equation:

$$z = X - X_a / H_a$$

where: X is the value given by each participating laboratory, X_a is the assigned value, and H_a is the standard deviation given by the Horwitz equation: $H_a = k \cdot [X_a]^{0.8495}$ where k takes on values from 0.01 of 0.02 depending on the quality demanded by each laboratory [3].

The results are considered satisfactory if the values of z lie between -2 and 2. In the exercises in which ITC participated, values of z below 2 were obtained in all tests, for all elements.

According to Pauwels et al. [11, 15, 25-27], the precision and traceability of a value can be calculated in several ways, for example by carrying out a number of independent repetitions using a primary analysis method, comparing the results obtained by a series of standard methods and/or comparing the results obtained by several independent methods in different laboratories. In order to calculate the uncertainty of a certified reference material, these authors advise considering the following sources of error: the own measurement process and the lack of uniformity and stability in the short and long term, so that the uncertainty is given by the equation:

$$U = k\sqrt{U_{char}^2 + U_{bb}^2 + U_{lts}^2 + U_{sts}^2}$$

where:

- k: cover factor that usually has a value of 2 or 3.
- U_{char}: the uncertainty value of the measurement, in which three constituents are considered: the uncertainty associated with the reference material (U_r), the uncertainty associated with the measurement procedure (U_R), and the uncertainty associated with the sample measurement (U_{sample}).

$$U_{char} = k\sqrt{U_r^2 + U_R^2 + U_{media}^2}$$

- U_{bb}: uncertainty due to non-uniformity: $U_{bb}^2 = s_{meas}^2 + s_{bb}^2$, where s_{meas}^2 lis the repeatability of the measurement and s^2_{bb} the standard deviation between batches.
- U_{lts}: uncertainty associated with long-term stability.
- U_{sts}: uncertainty associated with short-term stability.

When the material is homogeneous the non-uniformity contribution (U_{bb}) may be considered negligible, and in geological materials, the terms U_{lts}^2 and U_{sts}^2 may also be considered negligible, so that the uncertainty of the value is given by the equation:

$$U = k\sqrt{U_{char}^2}$$

Tables 2 to 4 present the results obtained for each analysed material together with their uncertainty.

In regard to the results obtained in the chemical analysis, to be noted is the good agreement between the values found by the two independent methods, WD-XRF and ICP-OES, used at the ITC laboratory, for both the major and minor elements. In addition, there are no significant differences between the values obtained at the CGL and the ITC laboratories, since the differences lie within the calculated uncertainty.

	MR-1			MR-2			MR-3	
	ITC		CGL	ITC		CGL	ITC	CGL
	WD-FRX C (%)	ICP-OES C (%)	WD-XRF C (%)	WD-XRF C (%)	ICP-OES C (%)	WD-XRF C (%)	WD-XRF C (%)	Wet Method C (%)
SiO_2 (%)	64,7±0,4	-	64,51	56,1±0,3	-	55,72	0,45±0.05	0,425
Al_2O_3 (%)	17,0±0,2	17,1±0,4	16,85	14,9±0,3	15,2±0,4	14,58	0,79±0.04	-
Fe_2O_3 (%)	5,65±0,10	5,57±0,15	5,56	5,26±0,09	5,24±0,15	5,19	0,063±0.003	-
CaO (%)	1,21±0,05	1,22±0,08	1,2	7,80±0,09	7,75±0,15	7,86	55,1±0.2	55,24
MgO (%)	1,33±0,06	1,28±0,09	1,27	1,60±0,05	1,63±0,09	1,59	0,12±0.02	<0,3
Na_2O (%)	0,22±0,02	0,21±0,03	0,17	0,20±0,02	0,19±0,04	0,17	-	-
K_2O (%)	3,15±0,04	3,12±0,06	3,1	3,06±0,04	3,03±0,07	3,02	0,025±0.005	-
TiO_2 (%)	0,79±0,03	0,77±0,04	0,82	0,71±0,03	0,75±0,05	0,73	0,01±0.01	<0,05
P_2O_5 (%)	0,08±0,01	0,08±0,02	0,09	0,12±0,01	0,11±0,02	0,12	<0,01±0.01	<0,05
ppc (1000°C)	5,82±0,05	-	6,04	10,3±0,1	-	10,45	43,5±0,4	43,2

Table 2. Results obtained by the two laboratories in the chemical analysis of the materials MR-1, MR-2, and MR-3 by different methods

	MR-4		MR-5		MR-6		MR-7	
	ITC	CGL	ITC	CGL	ITC	CGL	ITC	CGL
	WD-XRF C (%)	Wet Method C(%)	WD-XRF C (%)	WD-XRF C (%)	WD-XRF C (%)	Wet Method C(%)	WD-XRF C (%)	Wet Method C(%)
SiO_2 (%)	<0,1±0,1	0,09	58,5±0,3	58,21	54,4±0,3	54,20	99,0±0,4	99,24
Al_2O_3 (%)	<0,05±0,05	0,09	27,4±0,2	27,1	32,2±0,2	32,42	0,52±0,04	0,50
Fe_2O_3 (%)	0,03±0,01	0,03	0,88±0,02	0,87	0,58±0,01	-	0,052±0,004	-
CaO (%)	30,7±0,2	30,9	0,33±0,02	0,35	0,19±0,01	<0,3	0,09±0,01	<0,3
MgO (%)	21,6±0,2	21,32	0,47±0,04	0,51	0,12±0,02	<0,3	<0,01±0,01	<0,3
Na_2O (%)	0,06±0,01	0,03	0,39±0,02	0,39	0,07±0,01	0,08	<0,01±0,01	<0,03
K_2O (%)	<0,01±0,01	0,01	2,00±0,04	2,11	0,77±0,03	0,79	0,10±0,01	0,09
TiO_2 (%)	<0,01±0,01	<0,05	1,32±0,05	1,4	0,23±0,01	0,22	0,04±0,01	0,045
P_2O_5 (%)	<0,01±0,01	<0,05	0,06±0,01	0,07	0,05±0,01	0,041	<0,01±0,01	<0,05
ppc (1000ºC)	47,5±0,4	47,3	-	-	11,2±0,1	11,21	0,24±0,01	0,22

Table 3. Results obtained by the two laboratories in the chemical analysis of the materials MR-5, MR-6, and MR-7

	MR-8		MR-9		MR-10	
	ITC	CGL	ITC	CGL	ITC	CGL
	WD-XRF C (%)	Wet Method C(%)	WD-XRF C (%)	Wet Method C(%)	WD-XRF C (%)	WD-XRF C (%)
SiO_2 (%)	69,0±0,4	68,63	71,4±0,4	71,55	66,0±0,4	65,68
Al_2O_3 (%)	16,9±0,2	16,87	16,9±0,3	16,62	20,2±0,2	20,04
Fe_2O_3 (%)	0,13±0,02	0,125	0,10±0,01	0,095	2,63±0,07	2,65
CaO (%)	0,44±0,02	0,36	0,62±0,03	-	0,25±0,02	0,25
MgO (%)	0,04±0,01	<0,3	0,06±0,01	<0,3	0,36±0,03	0,39
Na_2O (%)	2,16±0,04	2,18	9,55±0,12	9,62	0,15±0,02	0,14
K_2O (%)	10,9±0,1	-	0,39±0,02	0,42	2,25±0,04	2,24
TiO_2 (%)	0,04±0,01	0,043	0,10±0,01	0,11	1,05±0,04	1,07
ppc (1000ºC)	0,52±0,01	0,51	0,38±0,02	0,43	6,75±0,10	6,85

Table 4. Results obtained by the two laboratories in the chemical analysis of the materials MR-8, MR-9, and MR-10

4.3. RESULTS OF THE MINERALOGICAL AND THERMOGRAVIMETRIC CHARACTERISATION

Table 5 presents the mineralogical composition together with the uncertainty of each analysed material. This information complements the chemical analysis.

Table 6 presents the results obtained in the thermogravimetric analysis, which show good agreement with the results obtained by gravimetry.

Material analysed	Identified crystalline phases	(%) by weight
MR-1	Quartz (SiO_2) Kaolinite ($Al_2Si_2O_5(OH)_4$) Illite/MuscoviteM.($KAl_2(Si_3Al)O_{10}(OH,F)_2$) Microcline ($KAlSi_3O_8$) Hematites ($Fe_2O_3$) Calcite ($CaCO_3$) Dolomite ($CaMg(CO_3)_2$) Albite ($NaAlSi_3O_8$)	40 ±2 21 ±3 17 ±2 9 ±0.5 3 ±0.25 3 ±0.25 3 ±0.25 2 ±0.5
MR-2	Quartz (SiO_2) Kaolinite ($Al_2Si_2O_5(OH)_4$) Illite/MuscoviteM.($KAl_2(Si_3Al)O_{10}(OH,F)_2$) Microcline ($KAlSi_3O_8$) Calcite ($CaCO_3$) Hematites ($Fe_2O_3$) Albite ($NaAlSi_3O_8$)	32 ±2 23 ±3 14 ±2 13 ±0.5 12 ±0.25 3 ±0.25 1 ±0.5
MR-3	Calcite ($CaCO_3$) Dolomite ($CaMg(CO_3)_2$)	97 ±2 1 ±0.5
MR-4	Dolomite ($CaMg(CO_3)_2$) Calcite ($CaCO_3$)	99 ±1 1 ±0.5
MR-5[1]	Kaolinite ($Al_2Si_2O_5(OH)_4$) Quartz (SiO_2) Illite/MuscoviteM.($KAl_2(Si_3Al)O_{10}(OH,F)_2$) Microcline ($KAlSi_3O_8$)	52 ±3 22 ±3 14 ±2 4 ±1
MR-6	Kaolinite ($Al_2Si_2O_5(OH)_4$) Quartz (SiO_2) Illite/MuscoviteM.($KAl_2(Si_3Al)O_{10}(OH,F)_2$)	67 ±3 19 ±3 11 ±2
MR-7	Quartz (SiO_2)	99 ±1
MR-8[1]	Microcline ($KAlSi_3O_8$) Albite ($NaAlSi_3O_8$) Quartz (SiO_2) Illite/MuscoviteM.($KAl_2(Si_3Al)O_{10}(OH,F)_2$) Kaolinite ($Al_2Si_2O_5(OH)_4$)	57 ±3 18 ±2 14 ±2 2 ±1 <1
MR-9[1]	Albite ($NaAlSi_3O_8$) Quartz (SiO_2) Illite/MuscoviteM.($KAl_2(Si_3Al)O_{10}(OH,F)_2$)	73 ±4 16 ±2 4 ±2
MR-10[1]	Quartz (SiO_2) Kaolinite ($Al_2Si_2O_5(OH)_4$) Illite/MuscoviteM.($KAl_2(Si_3Al)O_{10}(OH,F)_2$) Microcline ($KAlSi_3O_8$)	22 ±2 35 ±3 14 ±2 3 ±1

Table 5. Mineralogical composition of the materials.

Material analysed	Thermal processes	LOI (%) thermograv.
MR-1	Loss of moisture and/or adsorbed water Hydroxide decomposition Clay mineral dehydroxylation Carbonate decomposition Loss of volatiles	5.7 ±0.1
MR-2	Loss of moisture and/or adsorbed water Hydroxide decomposition Clay mineral dehydroxylation Carbonate decomposition Loss of volatiles	9.9 ±0.1
MR-3	Carbonate decomposition	43.5 ±0.2
MR-4	Carbonate decomposition	47.4 ±0.2
MR-5	Loss of moisture and/or adsorbed water Hydroxide decomposition Clay mineral dehydroxylation Carbonate decomposition Loss of volatiles	7.7 ±0.1
MR-6	Loss of moisture and/or adsorbed water Clay mineral dehydroxylation	10.9 ±0.2
MR-7	Loss of moisture and/or adsorbed water Loss of volatiles (OH^-)	0.3 ±0.1
MR-8	Loss of moisture and/or adsorbed water Loss of volatiles	0.5 ±0.1
MR-9	Loss of moisture and/or adsorbed water Loss of volatiles	0.4 ±0.1
MR-10	Loss of moisture and/or adsorbed water Hydroxide decomposition Clay mineral dehydroxylation Carbonate decomposition Loss of volatiles	6.3 ±0.1

(1) Some of the analysed materials have a considerable quantity of material of low crystallinity, which does not diffract X-rays. These materials usually have a clayey nature (kaolinite or mica) or certain hydrated compounds of iron and aluminium.

Table 6. Thermogravimetric analysis of the materials analysed

5. CONCLUSIONS

1. Ten ceramic raw materials were selected: four clays, a calcium carbonate, a dolomite, a kaolin, a silica sand and two feldspars, since these raw materials are among the most widely used in the manufacture of stoneware floor tile, porous wall tile, and porcelain tile.
2. Ten homogeneous materials were obtained after a crushing, quartering, and grinding process; i.e. which passed the uniformity test, since the values of the statistical parameter that defines the degree of uniformity (ω) were smaller than the differences between batches of the same material (Δt_i). As a result, they can be used as geological reference materials; the minimum sample quantity to be taken is 0.5000 g in order to assure that the sample portion will be sufficiently homogeneous, since this was the quantity of sample used to carry out this test.
3. The measurements were validated as follows:
   a) analysis of the elements at the ITC laboratory by two methods: WD-XRF and ICP-OES; the results obtained displayed no significant differences, thus validating both measurement methods;
   b) analysis of reference materials similar to the samples being analysed;
   c) analysis at two independent qualified laboratories; the values found for the studied materials at the two laboratories displayed no significant differences, thus providing two series of independent data for the obtainment of the reference values.
4. In addition to the chemical analysis, a mineralogical characterisation has been carried out, in which the quantity of each crystalline phase has been analysed by the Rietveld method, as well as a thermogravimetric characterisation, which was used to corroborate the loss on ignition values found by the traditional method, and to associate the losses with the different physico-chemical processes that unfold during the thermal treatment of these materials.
5. The study conducted has led to the obtainment of the following series of reference materials of ceramic raw materials: four clays referenced MR-1, MR-2, MR-5, and MR-10; a calcium carbonate, MR-3; a dolomite, MR-4; a kaolin, MR-6; a silica sand, MR-7; and two feldspars, MR-8 and MR-9. These reference materials can be used to implement, calibrate, and validate test methods.

6. ACKNOWLEDGEMENTS

This study has been funded by the Valencian Institute for Medium and Small-sized Enterprise (IMPIVA) within the framework of the Research, Development and Innovation programme of the plan for company services centres, reference IMIDIC/2005/11.

REFERENCES

[1] SÁNCHEZ, E.; GARCÍA-TEN, J.; REGUEIRO, M. Materias primas para la industria cerámica española. Situación actual y perspectivas. Bol. Soc. Esp. Ceram. Vid., 45(1), 1-12, 2006.

[2] REGUEIRO, M. Cerámica y vidrio en España. [en línea]. [Consulta: 2006-10-18] <http://www.ucm.es/info/crismine/Ceramica_vidrio.pdf>

[3] KANE, J.S. Report of the International Association of Geoanalysts on the Certification of Penrhyn Slate, OU-6. Geostand. Geoanal. Res. 28(1), 53-80, 2004.

[4] ELLISON, S.L.R.; ROSSLEIN, M.; WILLIAMS, A. (eds.) Quantifying uncertainty in analytical measurement (Guide to the expression of uncertainty measurement). 2ª. [s.l.]: Eurachem, 2000.

[5] ISO GUIDE 33: 1989. Uses of certified reference materials.

[6] URIANO, G.A.; GRAVATT, C.C. The role of reference materials and reference methods in chemical analysis. CRC Crit. Rev. Anal. Chem., 6, 363-411, 1997.

[7] POTTS, P.J. Handbook of Rock Analysis. United Kingdom: Viridian Publishing, 2003.

[8] BENNETT, H.; OLIVER, G.J. XRF analysis of ceramics, minerals and allied materials. Chichester: John Wiley, 1992.

[9] ISO GUIDE 30. Terms and definitions used in connection with reference materials.

[10] KANE, J.S.; POTTS, P.J.; WIEDENBECK, M.; CARIGNAN, J.; WILSON, S. International Association of Geoanalysts' protocol for the certification of geological and environment reference materials. Geostand. Newsl., 27(3), 227-244, 2003.

[11] PAUWELS, J.; VEEN, A. van der; LAMBERTY, A.; SCHIMMEL, H. Evaluation of uncertainty of reference materials. Accred. Qual. Assur., 5, 95-99, 2000.

[12] ISO GUIDE 35: 1989. Certification of reference materials. General and statistical principles.

[13] ASTM E 826-85: 1996. Standard practice for testing homogeneity of materials for the development of reference materials.

[14] FERN, T.; THOMPSON, M. A new test for 'sufficient homogeneity'. Analyst, 126, 1414-1417, 2001.

[15] VEEN, A. van der; LINSINGER, T.; PAUWELS, J. Uncertainty calculations in the certification of reference materials. 2. Homogeneity study. Accred. Qual. Assur., 6, 26-30, 2001.

[16] GAZULLA, M.F.; GÓMEZ, M.P.; BARBA, A.; ORDUÑA, M. Chemical characterisation of geological raw materials used in traditional ceramics. Geostand. Newsl., 28(2), 203-212, 2004.

[17] EPSTEIN M.S. The independent method concept for certifying chemical-composition reference materials. Spectrochim. Acta B., 46(12), 1583-1591, 1991.

[18] BARBA, A.; GAZULLA, M.F.; GÓMEZ, M.P.; JARQUE, J.C.; MESTRE, S. Microwave-assisted digestion of ceramic frits for boron and lithium determination by inductively coupled plasma spectrometry (ICP-OES). Glass Sci. Technol., 75(5), 254-258, 2002.

[19] BRINDLEY, G.W.; BROWN, G. Crystal structures of clay minerals and their X-ray identification. London: Mineralogical Society, 1984.

[20] KLEIN, C.; HURLBUT, C.S. Manual de mineralogía II: basado en la obra de J. Dana. 4ª ed. reimp. Barcelona: Reverté, 2001.

[21] GAZULLA, M.F.; GÓMEZ, M.P.; BARBA, A.; ORDUÑA, M. Chemical and phase characterisation of ceramic pigments. X-Ray Spectrom., 36(2), 82-91, 2007.

[22] SMOTHERS, W.J.; CHIANG, Y. Handbook of differential thermal analysis. New York: Chemical Publishing, 1966.

[23] STUCKI, J.W.; BISH, D.L.; MUMPTON F.A. (eds.) Thermal analysis in clay science. Boulder, CO: The Clay Minerals Society, 1990.

[24] HATAKEYAMA, T. AND ZHENHAI LIU (EDS.) Handbook of thermal analysis. Reimp. Chichester: John Wiley & sons, 2000.

[25] PAUWELS, J.; LAMBERTY, A.; SCHIMMEL, H. The determination of uncertainty of reference materials certified by laboratory intercomparison. Accred. Qual. Assur., 3, 180-184, 1998.

[26] VEEN, A. van der; PAUWELS, J. Uncertainty calculations in the certification of reference materials. 1. Principles of analysis of variance. Accred. Qual. Assur., 5, 464-469, 2000.

[27] VEEN, A. van der; LINSINGER, T.; LAMBERTY, A.; PAUWELS, J. Uncertainty calculations in the certification of reference materials. 3. Stability study. Accred. Qual. Assur., 6, 257-263, 2001.