ANALYSIS OF VERY SMALL-SIZED CERAMIC SAMPLES BY WD-XRF

Gazulla, M.F.; Vicente, S.; Orduña, M.; Ventura, M.J.

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

1. INTRODUCTION

The chemical analysis of very small-sized ceramic samples is of particular interest in the analysis of impurities in raw materials, product defects, contaminations or simply when only a very small quantity of sample is available. Chemical analysis of such samples often allows the origin of a given defect to be determined. To date, very small-sized samples have been analysed by techniques such as scanning electron microscopy (SEM), X-ray microfluorescence (μ-XRF), laser ablation inductively coupled plasma optical emission spectrometry (laser-ICP-OES), etc., in which qualitative or semi-quantitative analyses are generally performed. As a result, the information obtained is not very accurate, partly because in these methods it is difficult to use reference materials that assure the measurements.

This study was undertaken with a view to fine-tuning a series of sample preparation and measurement methods that would allow precise and accurate quantitative analysis of very small-sized samples by wavelength-dispersive X-ray fluorescence (WD-XRF) spectrometry. This would enable samples to be characterised that, owing to their small size, could otherwise only be analysed by SEM, μ-XRF, laser-ICP-OES, etc., in order to obtain precise and accurate results and to extend the possibilities of chemically characterising such materials for laboratories that only have WD-XRF facilities.

2. EXPERIMENTAL PART

The study was conducted using the following different types of materials: powder samples (impurities found in clays, feldspars, limestone, silica sands, frits and ceramic glazes), as well as ceramic pieces with visible surface defects.

The study was performed by analysing the analysis steps involved, i.e. sample preparation and the measurement process, and determining the optimum conditions.

In order to prepare the beads, a Pt/Au dish (A - Figure 1), 6 mm in diameter, was designed so that the beads could be measured with the device shown in Figure 1 (B).

Figure 1: Dishes designed for bead preparation (A), 6 mm in diameter, and sample holder for the WD-XRF measurement (B)

The following variables were studied in preparing the samples as beads: sample quantity, sample/flux ratio, quantity of bead releasing agent, and fusion conditions (time and temperature).

Samples were prepared for surface analysis by using a drill bit, 6 mm in diameter (Figure 2), such that areas without and with a defect of the same piece could be isolated.

Figure 2. Samples and 6 mm drill bit for obtaining ceramic surface samples

Measurement conditions (analytical line, crystal, detector, tube power (voltage and intensity) and measuring time) were optimised for each analysed element: Si, Al, Fe, Ca, Mg, Na, K, Ti, Mn, P, Zr, Ba, Pb, Pr, Zn, Hf, Sr, Pr, Co, Ni, Sn, Cr, V, and La.

Three measurement methods were fine-tuned: two for powder samples (one for raw materials and another for frits and glazes) and a third method for surface analysis. The first two were established by constructing calibration curves using reference materials and surface analysis by means of a method through fundamental parameters using the UniQuant program.

In order to carry out the calibration and validation of the developed methods, reference materials were used from the following suppliers: National Institute of Standards and Technology – NIST (USA), Bureau of Analysed Samples – BAS (UK), National Research Centre for Certified Reference Materials GBW (China), Instituto de Pesquisas Tecnologicas (Brazil), CRPG, ANRT, and GIT-IWG Geostandards (France), Canadian Center for Mineral and Energy Technology – CANMET (Canada), SA Bureau of Standards – SABS (Republic of South Africa), Bundesanstalt für Materialprüfung – BAM (Germany), Merck, Alfa-Aesar, and Sigma-Aldrich.

3. RESULTS

The optimum conditions determined for bead preparation are detailed in Table 1.

Type of material	Sample quantity (g)	Sample/ flux ratio	Quantity of bead releasing agent (mL)	Fusion conditions		Result
				t (min)	T (ºC)	
Raw materials	0.0600	1:10	0.25	10	1100	√
	0.0300	1:10	0.25	10	1100	√
	0.0250	1:10	0.20	5	1100	√
	0.0150	1:10	0.20	5	1100	√
	0.0150	**1:10**	**0.20**	**3**	**1100**	√
	0.0100	1:10	0.20	3	1100	X
Frits and glazes	0.0200	1:15	0.20	5	1100	√
	0.0150	1:15	0.20	3	1100	√
	0.0100	**1:15**	**0.20**	**3**	**1100**	√
	0.0085	1:15	0.20	3	1100	x

Table 1. Optimum conditions for preparation of beads, 6 mm in diameter

The new sample preparation approach provided low detection and quantification limits, with a more than thirty-fold reduction in sample quantity, since instead of weighing 0.5000–0.4000 g sample to prepare beads 27 mm in diameter, it sufficed to weigh 0.0150–0.0100 g sample for beads 6 mm in diameter.

The results obtained on measuring the surface of a piece, in which the part with a defect and the part without a defect were measured, are detailed in Table 2.

Oxides (%)	Piece A Part without a defect	Piece A Part with a defect
SiO_2	59.9	58.5
Al_2O_3	8.8	8.6
Fe_2O_3	0.10	2.33
CaO	8.26	7.80
MgO	2.46	2.41
Na_2O	2.98	2.83
K_2O	2.69	2.43
TiO_2	<0.01	<0.01
ZrO_2	6.53	6.27
BaO	<0.01	<0.01
PbO	<0.01	<0.01
ZnO	6.03	6.22
HfO_2	0.12	0.10
P_2O_5	0.16	0.16
SrO	0.05	0.04
SnO_2	1.87	1.75
Cr_2O_3	0.01	0.32

Table 2. Analysis of Piece A

The results obtained in the chemical analysis of the part without a defect and the part with a defect of Piece A show that the defect consisted of a Fe and Cr compound, suggesting that this was a type of steel stuck to the surface of the piece.

The results obtained in the chemical analysis of four pieces corresponding to two formulations of the same glaze, two of which displayed different surface finishes (Pieces 1 and 2), while the other two exhibited a notable difference in tone (Pieces 3 and 4), are listed in Table 3.

Oxides	PIECE 1 Surface with 'good' glaze	PIECE 2 Surface with 'bad' glaze	PIECE 3 Blue piece Tone 1	PIECE 4 Blue piece Tone 2
SiO_2	54.6	55.7	54.1	53.6
Al_2O_3	7.4	6.5	7.0	8.0
Fe_2O_3	0.11	0.09	0.09	0.10
CaO	9.3	9.4	9.3	9.0
MgO	2.35	2.35	2.35	2.1
Na_2O	0.49	0.55	0.49	0.50
K_2O	3.4	3.9	3.4	3.4
ZrO_2	6.35	6.30	6.32	6.25
ZnO	11.2	11.1	11.1	11.4
HfO_2	0.13	0.13	0.13	0.13
P_2O_5	0.18	0.22	0.18	0.17
Co_3O_4	<0.01	<0.01	1.2	1.8

Table 3: Results obtained in ceramic surface analysis

The results obtained in Pieces 1 and 2 exhibited a considerable difference in the values of Al_2O_3 and K_2O: it was later found that potassium feldspar had been used in the formulation of the Piece 2 glaze composition, instead of kaolin.

The results obtained for Pieces 3 and 4 displayed differences in the concentrations of Al_2O_3, Co_3O_4, and ZnO, which might have been due to a difference in the pigment addition. Indeed, since the ratio between the surplus of Al_2O_3, Co_3O_4, and ZnO matched the formula of the pigment $(Co,Zn)Al_2O_4$, it was verified that there had indeed been a mistake in the added quantity of pigment.

4. CONCLUSIONS

A series of methods were fine-tuned to carry out the chemical analysis by WD-XRF of a very small quantity of sample of ceramic materials. In the case of powder samples, in which samples were prepared as beads, the necessary sample quantity for the samples of ceramic raw materials was 0.0150 g, and a sample:flux ratio of 1:10 was used. For the analysis of frits and glazes the necessary sample quantity was 0.0100 g, and the sample:flux ratio used was 1:15. A thirty- to forty-fold reduction was thus achieved in the sample size needed to perform chemical analysis by WD-XRF.

The values obtained for the detection limit, the quantification limit, and the measurement uncertainties were low and similar to the values obtained by the usual method that requires a greater quantity of sample, thus extending the field of application of WD-XRF.

A method was also established for the analysis of certain surface defects when these are clearly visible, such as those produced by an error in formulating a glaze composition, inappropriate proportioning, a mistaken raw material, or a defect produced by a given impurity.

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