FLUORINE DETERMINATION IN FRITS, GLAZES, AND CERAMIC PIGMENTS BY WD-XRF

M.F. Gazulla, M. Rodrigo, M. Orduña, M.J. Ventura

Instituto de Tecnología Cerámica (ITC). Asociación de Investigación de las Industrias Cerámicas (AICE)

Universitat Jaume I. Castellón. Spain.

1. INTRODUCTION

The analysis of light elements such as fluorine by wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF) is difficult when this needs to be analysed in different matrices, owing to its low fluorescence yield, which generates a low signal/noise ratio. Some frits and glazes contain fluorine because of its opacifying properties, and in the synthesis of certain ceramic pigments, fluorine compounds such as NaF, KF, Na_2SiF_6, BaF_2, and CaF_2 are used as mineralisers. As a result, it is of particular interest to have a fast, reliable method for fluorine determination.

Fluorine can be determined in solid samples by different methods. These usually involve an extraction process (pyrohydrolysis or alkaline fusion) and subsequent fluorine measurement (titration, ion chromatography, or potentiometry), though they exhibit interferences from other elements present in the matrix (Si, Al, Fe, or P). Consequently, tedious sample preparation is required, involving lengthy analysis time.

In this study, a method was developed for fluorine analysis in frits, glazes, and ceramic pigments by WD-XRF, optimising the sample preparation method to minimise the matrix effect and optimising the measurement method to improve the signal/noise ratio. The method was validated by analysing reference materials and, in addition, comparing the results of the WD-XRF measurement of unknown samples with those obtained by the reference test (potentiometric) method.

2. EXPERIMENTAL

CERTIFICATION CENTRE	REFERENCE MATERIAL	F (%)
NATIONAL RESEARCH CENTRE FOR CERTIFIED REFERENCE MATERIALS GBW (CHINA)	GBW 07152 LITHIUM ORE GBW 07153 LITHIUM ORE GBW 07402 SOIL	0.677 ± 0.064 3.12 ± 0.18 0.2240 ± 0.0112
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY – NIST (EEUU)	SRM 1835 BORATE ORE SRM 91 OPAL GLASS POWDER SRM 120C FLORIDA PHOSPHATE ROCK	0.348 ± 0.014 5.73 3.82 ± 0.02
BUREAU OF ANALYSED SAMPLES LIMITED (UNITED KINGDOM)	BCS-CRM NO. 392 FLUORSPAR	47.35 ± 0.15
SOCIETY OF GLASS TECHNOLOGY (UNITED KINGDOM)	SGT4 FLUORIDE OPAL GLASS	4.96 ± 0.10
CANADIAN CENTER FOR MINERAL AND ENERGY TECHNOLOGY – CANMET (CANADA	SY-2 SYENITE SY-3 SYENITE	0.51 0.66
CRPG, ANRT Y GIT-IWG GEOSTANDARDS (FRANCE)	BR BASALT MICA FE BIOTITE 1.60 MICA MG PHLOGOPITE	0.10 1.60 2.85
INTERLABORATORY TEST FOR THE ANALYSIS OF GEOLOGICAL SAMPLES (GEOPT) ORGANISED BY IAG (INTERNATIONAL ASSOCIATION OF GEOANALYSTS) (UNITED KINGDOM)	OSHBO – ALKALINE GRANITE	1.13 ± 0.16

Table 1. *Reference materials used in developing the method*

To develop the method, the reference materials detailed in Table 1 were used.

The WD-XRF measurements were made using a PANalytical AXIOS spectrometer with 4 kW power and Rh tube. The beads were prepared in an automatic PHILIPS PerlX'3 fusion bead preparation machine and the pellets were pressed in a CASMON hydraulic press with a die, 40 mm in diameter. The potentiometry measurement was made with a METROHM 692pH/Ion Meter.

To develop the method, first, sample preparation in the form of beads and pellets was optimised to determine which method provided the best results.

Beads were prepared with the following sample:flux ratios: 1:2, 1:4, and 1:5. The results obtained showed that a 1:5 ratio gave rise to an appropriate homogeneous bead for measurement. Pellets were prepared mixing 9.0000 g sample with 1.0000 g stearic acid in a tungsten carbide ring mill, pressing the resulting powder at 100kN in a hydraulic press. The measurement conditions detailed in Table 2 were then optimised.

Element	Line	Crystal	Detector	V (kV)	I (mA)	2θ (º)	Back-ground 1	Back-ground 2	PHD LL	PHD UL	t (s)
F	K_α	PX1(*)	Flux	30	100	42.752	-1.7188	1.3166	23	75	100

(*) F measurement was conducted using crystal PX1 (2d=5.0234 nm).

Table 2. *Measurement conditions for the F measurement method by WD-XRF*

3. RESULTS

The calibration curve obtained for fluorine measurement in the form of beads is shown in Figure 1.

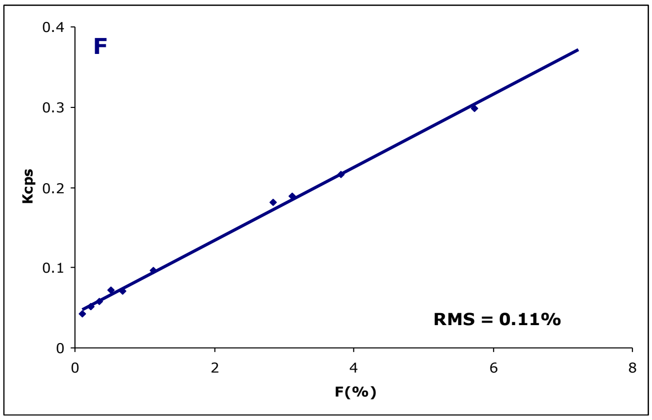

Figure 1. *Calibration curve obtained with sample preparation in the form of beads*

The calibration curve prepared with the sample in the form of beads exhibited an RMS correlation coefficient of 0.11%, though the materials used were of differing mineralogy (see Table 1). In the case of measurement using pellets, the resulting RMS was very high owing to the effects of the mineralogical structure and matrix effect. The pellet preparation method therefore requires determining sample mineralogy beforehand in order to have appropriate reference materials and preparing a calibration curve with a mineralogy similar to that of the sample.

Tables 3 and 4 detail the method validation results. Table 3 lists the results obtained in the fluorine determination in two reference materials, while Table 4 lists the analysis results of samples of frits, glazes, and pigments and compares these with those obtained by potentiometry, practically coinciding results being obtained.

Reference material	**F(%) by WD-XRF**	
	C_{cert}	$C_{measured}$
SRM 1835	0.348±0.014	0.33±0.05
SGT4	4.96±0.10	5.01±0.20

Table 5*. F (%) in the analysed reference materials*

Sample	**Frit**	**Glaze**	**Pigment 1**	**Pigment 2**
Potentiometry	1.52±0.10	0.95±0.08	0.62±0.06	0.29±0.03
WD-XRF	1.50±0.15	0.99±0.11	0.65±0.08	0.30±0.04

Table 3. *F (%) obtained using the two methods*

4. CONCLUSIONS

The methodology developed has the advantage of minimising the matrix effect and eliminating the influence of the mineralogy, obtaining acceptable uncertainties for fluorine determination in samples with F concentrations above 0.1%. In addition, shorter analysis times are required than potentiometry because little sample preparation is needed. The method is robust as it allows analysis in different types of materials and is more respectful with the environment than potentiometry because this requires using a great quantity of corrosive and/or toxic reagents.