ANALYSIS OF MINOR ELEMENTS AND TRACES IN CERAMIC RAW MATERIALS

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1. INTRODUCTION

The emergence of new ceramic products with innovative technical characteristics and functionalities requires developing analysis methods that allow minor and trace elements to be determined, as certain elements present in very small concentrations can generate defects in the end product.

The methods customarily used for this type of analysis (GFAAS or FIAS-AAS, ICP-OES, ICP-MS, etc.) involve very tedious sample preparation as the elements to be determined need to be dissolved, requiring the performance of digestions, with a greater entailing uncertainty and corresponding increase in analysis time.

In this study, an accurate, precise analysis method was developed of minor elements and traces in different types of materials such as silica and feldspathic sands, clays, kaolins, feldspars and feldspathoids, calcites, and dolomites, by wavelength-dispersive X-ray fluorescence spectrometry (WD-XRF), using the Pro-Trace analytical program and making an extensive compilation of reference materials for the corresponding validations. The following elements were analysed: Ba, Ce, Co, Cr, Cu, Fe, La, Mn, Ni, Pb, Rb, S, Sr, Ta, Th, U, V, Y, Zn, and Zr. In addition, the developed analytical method is respectful of the environment by eliminating the sample acid digestion process.

2. EXPERIMENTAL

With a view to achieving low detection limits, the sample preparation process was optimised, on the one hand, by preparing pellets with a larger diameter and, on the other, by studying four different binders (mannitol, stearic acid, solution of n-butyl methacrylate, and mixture of polyvinylpyrrolidone (PVP) and methylcellulose (MC)) in order to obtain the best possible measurement surface for all materials. Measurements were performed using a PANalytical AXIOS spectrometer. The measurement processes used in the WD-XRF instrument to enhance the signal, using the SuperQ4 software with Pro-Trace, were as follows: determination of background noise, determination of spectral overlappings, correction of the matrix effect and SES (Smart Element Selector).

The calibration curves were prepared with a great number of reference materials of different nature: sands, kaolins, feldspars, soils, granites, basalts, syenites, sediments, etc., most of which belong to the GeoPT intercomparison programme, promoted by the International Association of Geoanalysts (IAG). The rest belonged to different certification organisations such as the National Research Centre for Certified Reference Materials GBW (China), the Bureau of Analysed Samples (BAS) (United Kingdom), the Canadian Centre for Mineral and Energy Technology (CANMET) (Canada), and the Instituto de Pesquisas Tecnologicas (Brazil). The calibration curves were then validated and the detection and quantitation limits of the method were calculated for all analysed elements.

3. RESULTS

The proposed methodology was validated by analysing different reference materials from those used in constructing the calibration curves. Table 1 details the results obtained together with the known values. No significant differences were obtained in any of the analysed elements.

Element (mg·kg^{-1})	GeoPT-9 Slate		GBW07153 Lithium ore		GBW07407 Soil	
	C_{cert}	C_{exp}	C_{cert}	C_{exp}	C_{cert}	C_{exp}
Ba	480 ± 13	474 ± 13	-	-	180 ± 27	161 ± 18
Ce	77.1 ± 2.7	75 ± 11	2.12 ± 0.24	2.5± 1.0	98 ± 1	103 ± 10
Co	29.2 ± 1.1	32 ± 5	-	-	97 ± 6	103 ± 7
Cr	70.7 ± 2.1	73 ± 2	-	-	410 ± 23	424 ± 15
Cu	40.4 ± 4.9	44 ± 6	-	-	97 ± 6	92 ± 13
Fe	-	-	2105 ± 155	2303 ± 153	-	-
La	33.2 ± 1.8	28 ± 8	1.79	2.1 ± 0.5	46 ± 5	45 ± 6
Mn	-	-	1952 ± 170	2050 ± 167	1780 ± 113	1871 ± 72
Ni	40.2 ± 1.3	39 ± 5	-	-	276 ± 15	285 ± 9
Pb	28.80 ± 0.79	27 ± 28	-	-	14 ± 3	13 ± 2
Rb	121.3 ± 3.9	116 ± 4	6718 ± 144	6880 ± 144	16 ± 3	14 ± 2
S	-	-	-	-	250 ± 36	270 ± 24
Sr	131.7 ± 2.6	126 ± 6	-	-	26 ± 4	24 ± 3
Ta	1.02 ± 0.12	2 ± 5	98 ± 10	105 ± 10	3.9 ± 0.6	5 ± 1
Th	11.3 ± 1.0	11 ± 2	-	-	9.1 ± 0.7	9 ± 1
U	1.92 ± 0.09	2 ± 1	-	-	2.2 ± 0.4	2 ± 2
V	129.8 ± 5.1	129 ± 5	-	-	245 ± 21	243 ± 14
Y	27.75 ± 0.74	27 ± 4	13.3 ± 0.4	11.1 ± 1.3	27 ± 4	27 ± 2
Zn	111.4 ± 3.4	112 ± 4	-	-	142 ± 11	144 ± 7
Zr	174.2 ± 5.7	181 ± 8	-	-	318 ± 37	319 ± 22

***Table 1** Results of the analysis method validation*

The detection limits (DL) and quantitation limits (QL) were then calculated, which are shown in Table 2.

Element	DL (mg·kg^{-1})	QL (mg·kg^{-1})	Element	DL (mg·kg^{-1})	QL (mg·kg^{-1})
Ba	14	47	**Rb**	0.5	1.7
Ce	19	64	**S**	16	50
Co	2.4	8.0	**Sr**	0.7	2.4
Cr	4	14	**Ta**	2.3	7.7
Cu	10	32	**Th**	0.6	2.1
Fe	14	45	**U**	1.0	3.3
La	16	54	**V**	4	13
Mn	2.5	8.2	**Y**	0.5	1.7
Ni	2.4	7.9	**Zn**	1.4	4.6
Pb	1.4	4.8	**Zr**	0.6	1.9

***Table 2** Detection and quantitation limits for all elements analysed by WD-XRF*

4. CONCLUSIONS

The developed method is a reliable, robust method for analysing minor elements and traces in practically any type of ceramic raw material in a relatively short time. A great number of standards were used, which allowed a very wide range of concentrations for all the analysed elements to be obtained. The optimisation of sample preparation, in the form of pressed pellets, and of the measurement conditions, together with the use of the Pro-Trace software and of a WD-XRF instrument that could operate at 4kW power, enabled very low detection limits to be obtained for all analysed elements. In addition, the method is more respectful of the environment than other methodologies because no acids are needed, as no sample digestion process is required.

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