CHEMICAL CHARACTERISATION OF CADMIUM SULPHOSELENIDE-BASED CERAMIC PIGMENTS

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1. INTRODUCTION

Pigments based on cadmium sulphoselenide ($ZrSiO_4$-CdS_xSe_{1-x}) generate a wide range of colours, from yellow to red, depending on the quantity of selenium.

These materials are difficult to analyse because they contain oxides and sulphides, which can volatilise during the sample preparation process for analysis.

Studies are reported in the literature on the synthesis methods of these pigments in which various techniques (XRD, TEM, or IR) are used to characterise the end product. However, no methodology is described for their quantitative chemical characterisation, which is very important for full pigment characterisation.

In this study, a method of characterising these pigments was established, using wavelength-dispersive X-ray fluorescence (WD-XRF) spectrometry and elemental analysis by combustion and IR detection.

2. EXPERIMENTAL PART

Four industrial cadmium sulphoselenide pigments, referenced A, B, C, and D, were selected for the study. All contained zircon ($ZrSiO_4$) as major crystalline phase, in addition to the following minor phases: cadmium sulphoselenide (Cd_2SSe), selenium sulphide (SeS_2), cadmium selenide (β-$CdSe_2$), quartz (SiO_2), and baddeleyite (ZrO_2).

The WD-XRF measurement was performed with a PANalytical AXIOS spectrometer equipped with a Rh tube and 4 kW power.

In order to characterise the samples, a semi-quantitative analysis was performed first, preparing pressed pellets, 32 mm in diameter, which were measured by WD-XRF using the UniQuant program. The calibration curves were then prepared for each of the elements in the samples, except S, which was analysed by combustion and IR detection.

As certified reference materials of this type of pigment are unavailable, in order to have calibration and validation standards, synthetic standards were prepared by mixing certified reference materials and pure oxides in appropriate proportions. The following materials were used in preparing the calibration standards:

Reference material (%)	Validation standard	
	1	2
SARM 13 Zr concent.	91.7	93.1
CdO from Fluka	3.8	1.7
SeS_2 from Alfa-Aesar	3.0	2.3
CdS from Aldrich	1.5	2.9

Table 1 Validation standards (%)

BCS-CRM 388 Zircon, BCS-RM 204a Zircon, GBW 03113 High Silica, CdS from Merck, SeS_2 from Aldrich. The composition of the validation standards is detailed in Table 1.

Sulphur was determined using a LECO CS-200 analyser. The standards used for the calibration were as follows: SRM 1886a Portland Cement, SRM 1889a Portland Cement, and SeS_2 from Alfa-Aesar.

The samples were measured in triplicate in both methods in order to be able to calculate the uncertainty properly, and the validation was performed by measuring synthetic standards 1 and 2.

3. RESULTS AND DISCUSSION

The results obtained, together with the calculated uncertainty are detailed in Table 2. To be noted are the low uncertainties obtained for all analysed elements, which confirm that the methodology developed is precise and exact.

%	A	B	C	D
ZrO_2	58.0±0.3	61.5±0.4	62.1±0.4	55.3±0.3
SiO_2	33.7±0.3	30.0±0.3	29.9±0.2	35.7±0.3
HfO_2	1.16±0.02	1.23±0.03	1.24±0.03	1.11±0.02
Al_2O_3	0.16±0.03	0.25±0.04	0.25±0.03	0.28±0.03
TiO_2	0.05±0.01	0.02±0.01	0.04±0.01	0.03±0.01
Se	1.32±0.02	1.58±0.03	0.88±0.02	1.48±0.03
Cd	4.70±0.05	4.57±0.05	4.62±0.05	5.19±0.05
S	0.99±0.05	1.05±0.04	1.00±0.05	1.18±0.05

Table 2 Results obtained for the analysed pigments

To validate the results, synthetic standards 1 and 2 were measured and the method was validated by comparing the results obtained (c_m) with the known values of the validation standards, calculating the difference between both (Δ_m) and the combined uncertainty of these values ($I_{\Delta m}$) from the following equations:

$$\Delta_m = |c_m - c_{known}| \qquad u_{\Delta m} = \sqrt{u_m^2 + u_{known}^2} \qquad I_{\Delta m} = 2 \cdot u_{\Delta m}$$

If the relationship $\Delta_m \leq I_{\Delta m}$ is obeyed, there are no significant differences between the measured value and the known value, thus validating the method.

The results obtained are detailed in Table 3. It shows that for all analysed elements, the relationship $\Delta_m \leq I_{\Delta m}$ was obeyed, which validates the developed method for both the major and the minor elements.

%	1				2			
	C_{known}	C_m	Δ_m	$I_{\Delta m}$	C_{known}	C_m	Δ_m	$I_{\Delta m}$
ZrO_2	58.7±0.1	58.9±0.3	0.3	0.6	59.6±0.1	56.5±0.3	0.3	0.6
SiO_2	35.5±0.1	35.4±0.2	0.3	0.4	30.3±0.1	30.4±0.2	0.1	0.4
Al_2O_3	0.56±0.01	0.57±0.03	0.02	0.06	0.57±0.03	0.58±0.03	0.01	0.06
HfO_2	1.18±0.08	1.16±0.02	0.01	0.17	1.17±0.08	1.21±0.02	0.01	0.17
TiO_2	0.27±0.01	0.28±0.02	0.01	0.05	0.27±0.01	0.25±0.02	0.01	0.05
Se	1.61±0.01	1.62±0.02	0.02	0.05	1.24±0.01	1.28±0.02	0.03	0.05
Cd	4.43±0.01	4.41±0.04	0.03	0.08	3.81±0.01	3.85±0.04	0.04	0.08
S	1.64±0.01	1.68±0.05	0.03	0.10	1.37±0.01	1.34±0.05	0.02	0.10

Table 3 Results obtained in measuring the validation standards

4. CONCLUSIONS

A precise and exact method has been developed for the full chemical characterisation of cadmium sulphoselenide-based ceramic pigments. WD-XRF was used, the samples being prepared in the form of pellets, for all elements except S, which was analysed with an elemental analyser by combustion and IR detection.

The absence of certified reference materials with a composition similar to that of the pigments to be analysed makes it necessary to prepare synthetic standards.

5. ACKNOWLEDGEMENTS

This study has been funded by the Valencian Institute of Business Competitiveness (IVACE) under the Research, Development, and Innovation programme, in project IMDEEA/2012/139, through the European Regional Development Fund.