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Review

An easy method to estimate the concentration of mineral pigments in colored mortars

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ABSTRACT

The goal of this work is to propose an easy method for the estimation of mineral pigment contents in different mortars. The accurate estimation of mineral pigment contents is very important to reduce the cost of production of the colored mortars, especially taking into account that small discrete changes in composition do not always produce noticeable color changes by the human eye. The Kubelka–Munk function in its derivative form provides a highly useful tool for characterizing pigment mixtures in mortars. It has been effective at concentration levels where XRD detection had proved to be ineffective. Calibration curves have been calculated from one mortar only. The partial overlapping of the bands, the different tinting strength and the different concentration of the pigment have been analyzed. The accuracy of the estimation of the pigment content improves when there is a slight overlap of the spectra and/or when the amount of the less tinting pigment is in greater proportion.

1. Introduction

Colored mortars and concrete have become popular among engineers and architects for such applications as facades, sidewalks, driveways, floors and other architectural uses. Nowadays and in antiquity, the number of mineral pigments is very high, for example, hematite (reddish, orange, purple, and brown), goethite (yellow), lepidocrocite (brown), calcite (white), dolomite (white), celadonite (green), malachite (green), and quartz (translucent and white). Others pigments have been produced by synthesis in the laboratory: litharge (reddish), massicot (yellow), red lead (orange), chromium oxide (green), black of coal, and Egyptian blue [1]. One very important aspect is to get permanent colors without producing adverse effects on mortars and concrete. It is imperative that the coloring agents can be used in a confident and safe manner.

Any tinting material can be of great use in many fields: dyes [2,3]; textile applications [3]; ceramic [4–7]; heterogeneous catalysis [8]; marine sediments [9]; mining in order to study and to determine the content or the identification of minerals [10–13]; farmland for studying the amount of iron oxide [14]; archaeological glass [15]; building materials [16–19] restoration and protection [18,20–23]; environmental safety [24,25]; and also in medical [26,27]; pharmaceutical [28,29] and food fields in order to detect and estimate the presence and quantity of substances [30–32].

Not all pigments have the same capacity of tinting [33,34], which means that the same amount of two different pigments will produce a different intensity of color. The quantity of pigment is inversely proportional to its tinting strength.

A diffuse reflectance spectrum of each tinted sample contains a combination of all the colors that are present in the sample. In fact, by inspecting the shape of the spectrum, one can identify the specific pigments contributing to a particular color mixture [1]. Each color mixture has a characteristic curve. This fact allows a reflectance spectrum to be used in order to quantify individual pigments [4,35–38].

The Kubelka–Munk theory [39] has been found to be useful when working with diffuse reflectance. For an infinitely thick, opaque layer the Kubelka-Munk equation may be written:

$$\frac{K}{S} = \frac{(1-R')^2}{2R'} \quad (1)$$

where R' is the absolute reflectance of the layer and K and S are the absorption and scattering coefficients, respectively. The absorption and scattering coefficients for a mixture of pigments can be

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expressed as linear combinations of those for the individual components (K_i and S_i) and their concentrations (c_i) [33–36]:

$$K = c_1K_1 + c_2K_2 + \ldots + c_nK_n$$
$$S = c_1S_1 + c_2S_2 + \ldots + c_nS_n \quad (2)$$

The relative reflectance R, which is measured against the reference standard $BaSO_4$, has been used instead of the absolute reflectanceR'. Then, the equation becomes:

$$f_{KM}(R) = \frac{(1-R)^2}{2R} \quad (3)$$

and a linear relationship should be observed between $f_{KM}(R)$ and the absorption coefficient K if S is constant [40]. This is achieved by using powders with large particle size in comparison with the wavelength used for measurement. For particle sizes larger than 5 μ, S will be independent of wavelength [40].

The Kubelka–Munk function (Eq. (3)) for a mixture M consisting of n components C_1, C_2, …, Cn will then take the form [1,40]:

$$f_{KM}(R_M) = a_1 \cdot f_{KM}(R_{C1}) + a_2 \cdot f_{KM}(R_{C2}) + \ldots + a_n \cdot f_{KM}(R_{Cn}) \quad (4)$$

where coefficients a_1, a_2, … a_n represent the intensity of color of each pigment and they will be used for calculating the concentration percentages of the pigments in the mixture.

The Kubelka–Munk function has been used successfully to describe the color as well as to carry out quantitative studies in different fields: dyes [3], ceramic tile [4], ceramic glace [5–7], oxides quantification on soils [12,14,33,41], heterogeneous catalysis [8], odontology [26,27], pharmaceutical [28,29], et cetera.

The diffuse reflectance bands, as well as the Kubelka–Munk function bands for mixtures containing small amounts of pigments are too ill defined to allow discrimination of the individual components. For this reason, the Kubelka–Munk function together with spectral derivation [12,42–44] has been used in order to accurately characterize colors in colored mortars [1]. Although some authors work even with the fourth derivative [23], most of them use the first [30,32,43] and the second derivatives of the reflectance as well as the Kubelka–Munk function [11,12,25,31,45,46]. The first derivative corrects baseline shifts [11,45], whereas second derivative is used to correct baseline offsets and sloping baselines [47].

Several authors [1,12,44] have demonstrated that the best results in the determination of the amount of the tinting species in several supports are achieved when the second derivative of the Kubelka–Munk is used. Scheinost et al. [44] get good results for the determination of the relative content of Goethithe and Hematite in soils, but in the case of Magnetite the results were poor. Da Costa et al. [48] and Van San et al. [49] determined the amount of Al substituted in various materials. Fernández-Rodríguez and Fernández-Fernández [1] have demonstrated the presence of Goethite in some pigments by using derivative techniques in combination with the Kubelka–Munk function in cases where XRD detection had proved to be ineffective. The detection limit seems to be at least one order of magnitude smaller than that of ordinary XRD [44].

Knowing the proportion of pigment needed to achieve the desired color in a more accurate manner, will permit a reduction of the amount of tinting pigment and thus to minimize the cost. Nowadays, the procedure in order to quantify the required amount of pigment consists in consulting a color card [16], but it would be better to have a mathematical function for each color that relates the amount of pigment with the intensity of color [1]. This would enable the computer control of the tinting pigment formulations and facilitate the identification of the amount of pigments that were used in a mortar/concrete.

The aim of this study is to propose an easy method to quantify the amount of a pigment present in a mixture that works well from

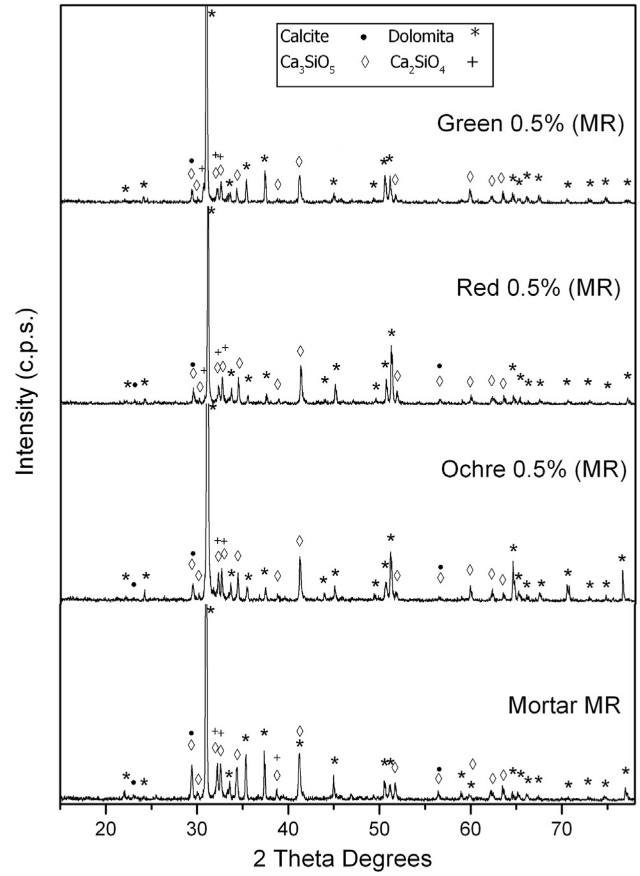

Fig. 1. XRD patterns for mortar MR and for pigments Ochre, Red and Green at 0.5% (in weight) in mortar MR.

low to high concentrations of pigment. In order to achieve this goal, it has been established a relationship between the amounts of pigment mixed with a mortar and the height of the peak in the second derivative of the Kubelka–Munk function obtained from the diffuse reflectance spectrum, for different mixtures of mortars and pigments that are widely used in industry.

In the present study, in order to enhance the sensitivity of the diffuse reflectance spectra by means of their second derivatives, the second derivative of a mixture have been expressed as a linear combination of the second derivatives of the pigments in the mixture. Therefore, the following assumption has been made:

$$f''_{KM}(R_M) = b_1 \cdot f''_{KM}(R_{C1}) + b_2 \cdot f''_{KM}(R_{C2}) + \ldots + b_n \cdot f''_{KM}(R_{Cn}) \quad (5)$$

2. Materials and methods

In the present survey, three mineral pigments and two different mortars have been used for the study. The mineral pigments are namely: Bayferrox Ochre 920 C (Ochre), Bayferrox Red 130 C (Red) and Green Chromium Oxide GN (Green), all from Lanzes Energizing Chemistry and supplied by Grupo Puma, Cemkosa (Córdoba, Spain). The studied mortars were a single-layer type mortar commercially available under the name Morcendur-R (MR) and a coating type mortar commercially available under the name Morcen Sec thin coat (MS), both from Grupo Puma.

The two mortars used are a mixture of calcite ($CaCO_3$, 05-0586 [50]), dolomite ($CaMg(CO_3)_2$, 36-0426 [50]) and Portland cement (mainly calcium silicate, Ca_2SiO_4, 23-1043 [50] and Ca_3SiO_5,